

COMPARATIVE STUDY OF RUST CONVERTERS FOR HISTORIC OUTDOOR METALWORK

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Abstract

The degradation and subsequent treatment of iron is an important consideration for conservators. Rust is of particular concern as it weakens the underlying layers of metal, and unlike the protective patina that other metals develop, iron oxide causes weakening and further corrosion.

This paper aims to provide the reader with the knowledge required to make an informed decision when selecting a rust converter. All the chemicals trialled are commercially available in small quantities, with the exception of the 'CCI recipe'. The 'CCI Recipe' was added to the study after a survey of chemicals used was sent out to metals conservators and the results were found that a majority of the conservators polled used this recipe as opposed to a commercially available product. This study did not want to invent a new treatment, but simply evaluate those readily available to find the chemical class that performed best over time.

Project Aims:

The main goal of this study is to provide the user, either home owner or museum conservator, with the knowledge needed to make an informed decision when selecting a rust converter. With the exception of the 'CCI Recipe', all of the chemicals in this study are commercially available in quantities small enough for the average home preservation practitioner to obtain. The 'CCI Recipe' was added to the study after a survey of chemicals used was sent out to metals conservators and the results showed that the majority of the conservators polled used this recipe as opposed to a commercially available product. This study did not intend to invent a new treatment but simply to evaluate those readily used in order to find the chemical class that performed best over time.

Introduction

The degradation and subsequent treatment of iron is an important consideration for conservators. Architectural structures, artistic elements and historic tools serve as simple examples of the ways in which iron is used as a significant component of important cultural artefacts. These objects are often exposed to outdoor conditions without protection; when exposed to precipitation and oxygen in the atmosphere, iron undergoes oxidation to form iron oxide (commonly known as rust). Rust is of particular concern to conservators, as it weakens the object and allows damage to underlying layers of metal. Unlike the protective patina that some metals develop, iron oxide causes weakening and further corrosion to occur. Treatment methods and protective measures are therefore of particular interest to those caring for objects susceptible to iron oxide corrosion.

In 1995, the Canadian Conservation Institute (CCI) published an article in the *Journal of the International Institute for Conservation* focusing on methods of protecting outdoor iron artefacts (Binnie et al., 1995). In particular, the CCI study investigates how commercial rust converting products perform as rust converters and corrosion inhibitors. Samples were treated with a variety of commercially available rust converters, and then exposed to

either outdoor conditions or artificial weathering. Due to the inclusion of natural weathering, the study spanned almost eight years. The study conclusively rated the performance and durability of ten rust converting products; however, fifteen years later almost none of the tested rust converters are still accessible through local or online retail. Wanting to test currently available rust converters and use modern analytical techniques, the National Center for Preservation Technology and Training (NCPTT) Materials Research Program undertook a comparative study of rust converters. Unlike the CCI study, NCPTT's study did not naturally weather the samples but solely used artificial weathering.

In this study, naturally rusted samples were treated with five rust converters that were chosen for accessibility and chemical variance. To evaluate which commercially available rust converters function best over an extended period of time, NCPTT used several analytical techniques. Condition was assessed before treatment, after treatment and at several points during artificial weathering. Photography was used to document physical appearance throughout the experiment. Colorimetry, magnetic induction thickness measurements, gloss measurements and laser profilometry together charted changes in the surface and coating of the samples. Finally, Fourier Transform Infrared Spectroscopy helped to characterise the primary chemical compounds present on the surface of the treated metal during the study.

In this laboratory study, NCPTT's research team sought answers to the following questions:

- Which rust converters most effectively react with rust to treat corrosion?
- Which rust converters will best prevent future corrosion when exposed to weathering?
- Which commercially available rust converting products will best treat objects of historic and cultural value?

Materials and Methods

Sample Materials

As noted, two main considerations in choosing the rust converting products were: (1) commercial availability, and (2) chemical variance. Commercial products were selected either by recommendation from practising conservators or through sales ranking on Amazon.com. All rust converters tested were purchased through local hardware stores or online retail. The only exception was the 10% tannic acid solution: this was prepared in NCPTT's lab, but all ingredients are commercially available from chemical companies.

Rust converters

Rustoleum® Rust Reformer® is a tannic acid-based rust converting product. It also has an acrylic vinylidene chloride copolymer additive. Tannic acid acts as a chelating agent while the copolymer creates a protective coating. The product has a pH of 2.13, falling in the mid-range pH of this study's converters. Rust Reformer® has a relatively thick consistency, and is bluish-white in appearance. While available online, Rust Reformer® is also available through local hardware stores.

OSPHO®, manufactured by the Skybryte Company, is a phosphoric acid based rust converting product balanced with dichromate and wetting agents. OSPHO® is by far the most acidic rust converter of those tested. The product's pH is 0.08, and it is a thin, translucent green liquid.

Corroseal® is a rust converting product based on gallic acid. This converter is composed of gallic acid, ethylene glycol and acetate. It is relatively acidic, both generally and in comparison to other tested converters, with a pH of 1.50. Corroseal® is creamy white and has a thick consistency.

RCx427 is a product of Enviro-Safe Services, Inc. that uses oxalic acid as the rust converting compound. Like Corroseal®, it also incorporates ethylene glycol in the chemical composition. The active ingredient, oxalic acid, exhibits physical properties after conversion that are different from other common converters: instead of causing the iron oxide layer to darken, it instead turns it a light grey. Of the tested rust converters, this product is the least acidic with a pH of 3.11. RCx427 has a thick consistency and is a blue-grey colour.

The 10% Tannic Acid solution stands out from the other rust converters in that the solution is not commercially available but must be prepared. However, a survey of metal conservators, carried out by conservation graduate student Rose Daly, indicated that the 'CCI Recipe' for tannic acid solution was used more often than commercially available rust converting products. As such, it was deemed important to include it in the study. The preparation method outlined in the CCI note 'Tannic Acid Treatment' was followed (1989). As directed, 2.75 ml of phosphoric acid was added to lower pH to 2.39, and fell into the mid-range of acidity in this study's converters. The solution is thin and appears a translucent, orange-red colour.

Primary chemical converters

Among the five chosen rust converting products, there are four active compounds that act as rust converters: tannic acid, gallic acid, oxalic acid and phosphoric acid.

Tannic acid is a tannin naturally found in many woods (mahogany, oak, walnut), but is also synthetically manufactured. While the chemical formula can vary, especially in naturally derived samples, commercial tannic acid has the molecular formula of $C_{76}H_{52}O_{46}$. It has the highest molecular weight of the active rust converting compounds investigated in this study, with a molecular weight of 1701.2 g/mol. Tannic acid acts as both a reducing agent and chelating agent for metal cations. The acid reacts with rust to form a layer of iron tannate.

Gallic acid can be found naturally in barks and plants such as sumac and witch hazel, and is found both free and as parts of plant polyphenols. The molecular formula of this organic acid is $C_7H_6O_5$, and at 170.12 g/mol it has a significantly lower molecular weight than tannic acid. Gallic acid will act as a reducing agent when exposed to iron oxides. When applied to iron oxide, gallic acid complexes with the metal ions to create a layer of iron gallate.

Oxalic acid is a dicarboxylic acid whose conjugate base functions as a reducing agent and chelating agent for metal cations. Even smaller than gallic acid, oxalic acid has a molecular formula $C_2H_2O_4$ and has a molecular weight of 90.03 g/mol. However, gallic acid is found most often in its dihydrate form ($C_2O_4H_2 \cdot 2H_2O$). Oxalic acid occurs naturally in plants such as rhubarb, but is also found in animal and bacterial processes.

Phosphoric acid is a relatively harsh inorganic acid. This triprotic acid has the chemical formula H_3PO_4 and a molecular weight of 98.00 g/mol. Phosphoric acid is a known treatment for rust and is a major component of naval jelly and other rust dissolvers. When applied to rust, a dark ferric phosphate layer forms that can be removed to expose a clean surface or can remain on the object to prevent further corrosion.

Experimental Methods

Sample Preparation

All testing was done on coupons of three inch (76.2 mm) by six inch (152.4 mm) by 11 gauge (3.0607 mm) naturally rusted A36 carbon steel. All pieces were cut from the same piece of metal, which was naturally, uniformly weathered. The samples were cut by pneumatic shear to minimise impact to the corrosion layer. Thirty-one samples were chosen that showed relatively even corrosion and colour.

In preparation for testing, all samples were hand brushed with a stainless steel wire brush to remove any loose corrosion products on the surface. This is the same procedure that an outdoor artefact would receive before being treated. When performing evaluation methods (other than photography), samples were placed in a holder so that the tested portion of the sample would be the same portion as exposed to artificial weathering.

Sample Treatment

All samples were treated according to application methods indicated by the manufacturer (or indicated in the article as in the case of the tannic acid solution). All rust converters were applied in one coat with a three-inch natural bristle brush. The CCI notes for the tannic acid method specified that brushing should continue as the coating dries, so the tannic acid samples were treated accordingly (CCI, 1989). Application instructions for all commercial converters

assume application of a top coat following the converter; however, since converters are often used independently in conservation treatments and because the focus of this study was specifically the performance of the rust converters, no top coat of paint was applied.

The purpose of artificial weathering in this study was to simulate the long-term durability and efficacy of the five selected rust converters on rusted metalwork. In a laboratory accelerated weathering experiment, factors such as humidity and light/dark exposures could be controlled. Thus, the samples and converters were compared under the same controlled conditions. Additionally, it shortened the study duration in comparison to natural weathering.

All accelerated weathering studies used a Q- Panel Lab Products model QUV/ Spray Accelerated Weather Tester (weatherometer). This instrument uses panels of UVA-340 lamps to control a programmable cycle of light and dark. The bulbs' irradiance is calibrated to a constant level of 0.77 W/m². The weatherometer was programmed for a continuing cycle of UV exposure for 4 hours at 60 degrees C followed by 4 hours of condensation at 50 degrees C. Note that this step was in the dark (no UV light) to mimic the natural cycle of night and day, and the temperature drop encourages condensation from the surrounding humid air inside the weatherometer. The water that condenses inside the weatherometer initially comes from a lower holding pan, supplied from a filtered water system. These cycles were repeated for a total of 1032 hours, with condition evaluations being performed approximately every 250 hours.

Throughout the course of treatment and weathering, multiple evaluation methods were used to chart the physical and chemical condition of the samples. Samples were evaluated before treatment, after treatment and at multiple points during the weathering process. Together, the methods reveal the efficacy of rust conversion as well as the durability of the rust converter coatings when exposed to weathering. Photography offers visual documentation of colour, condition and rust formation; colorimetry and gloss measurements quantitatively measure visual elements of the surface layer; magnetic induction measures the thickness of coatings on the surface (whether the coating is iron oxide or a protective layer formed after treatment); laser profilometry maps surface texture; and Fourier Transform Infrared Spectroscopy helps to characterise the primary chemical compounds present on the surface of the samples. All measurements were taken six times: before treatment, after treatment before weathering, and after approximately each 250 hours of weathering.

Sample colour was measured in five repeatable spots and averaged. Samples were measured before treatment, after treatment but before weathering, and after each 250 hours of weather. Colour measurements were taken using the Minolta CR-400 colorimeter and SpectraMagic NX Pro-USB version 1.52 software. Data were collected and recorded in the L*a*b system.

NCPTT uses a Solarius LaserScan, 3-D non-contact laser profilometer to characterize sample surfaces. The instrument uses a class II diode laser (670 nm wavelength) and a 2 µm spot size. The vertical resolution of this instrument is 0.1 µm. The laser is scanned over an area

of 20 mm (x-axis) by 14 mm (y-axis) at a scan speed of 5 mm/s and a resolution of 25 µm. A sample holder was constructed to ensure that sample orientation was consistent and that the same portion of the sample was examined to allow for comparative evaluation.

Visual appearance was documented using a Nikon D5000 digital camera with Nikon DX 35 mm lens. The camera was mounted to a Polaroid copy stand and placed 18.5 inches above the samples. A Kodak grey card was used as the background for the samples. Samples were illuminated at 90 deg. from the right and left with four Tungsten 500 watt photo lamps.

A Fischer FMP30 Deltascopie measured coating thickness on all tested samples. The Deltascopie uses a magnetic induction probe to determine the coating thickness on steel and iron base metals. The axial probe allows measurement of coatings between 0 – 2000 µm. Due to the high sensitivity of the instrument and natural irregularities that occur in outdoor weathering, it was determined that averaging between a higher number of measurements (10) was needed to gather reliable data for comparison.

Measurements of gloss were made using a BYK Gardner micro-TRI-gloss glossimeter. The glossimeter measures gloss level by directing light at a defined angle and measuring the reflected light with a reflectometer. A gloss unit is defined by ASTM standards D523 and D2457. In this study, surfaces were low gloss and measurements were taken at 85° (all 60° readings were less than 10 gloss units).

Results

All samples were removed from artificial weathering at 1032 hours and the final evaluations were done. The original experimental design for this study was to run for 3000 hours of weathering and evaluate the samples every 500 hours. However, the rust converters failed at a faster rate than originally thought and so 1000 hours seemed adequate. By this time all coatings, with the exception of the Rustoleum® Rust Reformer®, were showing significant signs of corrosion.

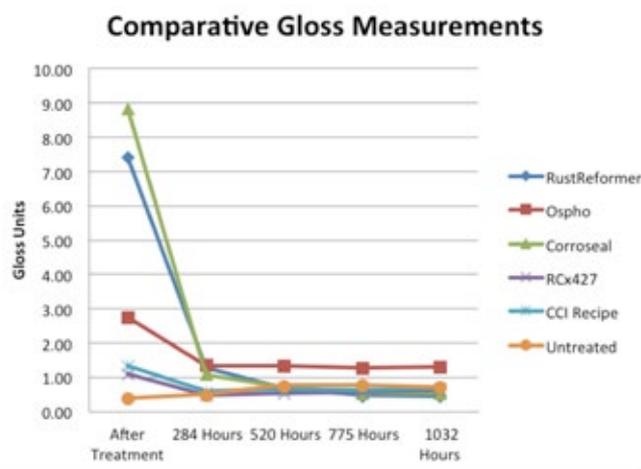


Figure 1. Change in gloss measurements throughout the accelerated weathering.

Figure 1 shows the change in gloss throughout the testing. It is evident that both the Rust Reformer® and Corroseal products contain polymer additives that give the converter an initial gloss appearance. This glossy sheen is not always desirable to the conservator, but as can be seen in Figure 1 the gloss is quickly lost to weathering. After the first 284 hours most converters drop down to a similar gloss rating.

The second line of testing can be seen in Figure 2 with the change in coating thickness throughout the accelerated weathering. The DeltaScope measures the thickness of coating from the surface of the steel coupon and so the average starting thickness of 1.67 mm in the untreated sample is the corrosion layer on the coupon's surface. All of the samples have a fairly even corrosion layer of around 1.50 mm to 1.70 mm. The measurement over the original corrosion layer gives the converter's coating thickness. On the samples treated with Ospho and the CCI Recipe there is a decline in thickness; it is believed that the converter coating weathered thin or was lost before a new corrosion layer began to form. That most samples increase in thickness is confirmed by the active corrosion seen in the visual ranking of the coupons. The only exception to this is the Rust Reformer®; this group of samples showed no active corrosion but had the highest increase in coating thickness.

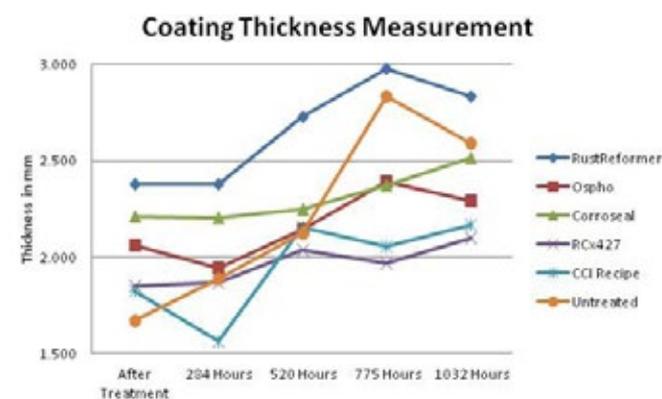


Figure 2
Change in coating thickness throughout the accelerated weathering.

Laser profilometry measures a wide variety of surface parameters; for this study Sk was chosen to reflect the total change in core roughness of each sample. The rust converter treatment smoothes the total roughness of the samples; as the coating fails the roughness of the sample increases. The Sk values for the samples tested are shown in Figure 3. All measurements are in μm ; no sample changed more than 10 μm . These measurements are not an average of multiple samples, as was the case for all the other tests in this study. Laser profilometry can only effectively be compared to changes on the same sample. The roughness of most samples increased at approximately the same rate, with a few exceptions. The CCI Recipe had the least overall change but the greatest roughness overall. The Ospho sample decreased in roughness this could be due to the white film that formed on the sample's surface. This white hazy film is typical of phosphoric acid interacting with moisture.

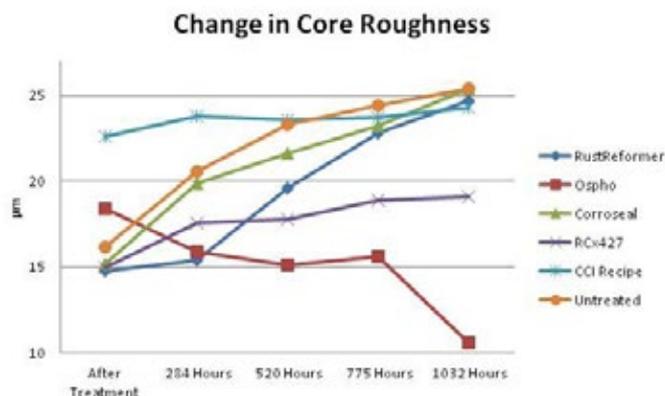


Figure 3.
Laser Profilometer measures core roughness as Sk.

FTIR was run in % transmittance in a range of 400 cm^{-1} to 4000 cm^{-1} using a Perkin Elmer Spectrum One with Harrick Upward-Facing Cricket attachment. Unfortunately, very little information was gathered from this phase of the testing. Both tannates and the polymer additives are detected around 2900 cm^{-1} and 1700 cm^{-1} making it difficult to distinguish if one was deteriorating during the weathering process.

All of the samples had a significant colour shift from the treated sample through the accelerated weathering process. Most samples shifted intensity and $+a^*$ measurements toward the red spectrum. The Rust Reformer® samples darkened after the first weathering; this is likely due to the copolymer additive further polymerising under the QUV's UV light.

The final evaluation, and one of the most telling evaluations done during this comparative study of rust converters, is the visual appearance. Not only does photography of the samples support all other testing but it adds a very important aesthetic element into the study. Table 1 shows the coupons as they weathered. The Rust Reformer® sample shows a uniform look with no visibly active corrosion.

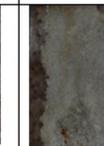
	Treated	After 284 Hours	After 520 Hours	After 775 Hours	After 1032 Hours
Rust reformer					
Ospho					
Corroseal					
RC x 427					
CCI recipe					
Untreated					

Table 1. Photography of the treated and weathered coupons.

Conclusion

After each of the tests were performed and the 1032 hours of accelerated weathering completed, many questions were answered and many were raised. Overall, the Rustoleum® Rust Reformer® performed the best, with no active corrosion evident and a nice even surface finish intact. The main active ingredient in the Rust Reformer® is tannic acid. However, the additive acrylic vinylidene chloride copolymer may have been just as important in sealing the metal's surface. The combination of the two outlasted all other converters in this study. This product is readily available online and in most large hardware stores.

This study gives the end user information to make a more educated choice when looking to treat their historic ironwork. Whether the end user is the owner of a historic home or a technician at a museum, this research will help them in future treatments.

Future work on this study includes natural weathering of samples under the same testing regime and further testing of rust converters while exposed to a salt environment.

References

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