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A Technical Note on the Treatment of Tin Plate: The Five Percent Solution

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The treatment of a collection of tin-plated iron objects is described. Rust was removed from the surface of patinated tin plate using 5% citric acid thickened with gelatine. The thirty-six objects were treated in the context of a redevelopment project at Green Gables, a historical house in Prince Edward Island National Park.

Le traitement d'une collection d'objets en fer-blanc est décrit. La rouille a été enlevée de la surface étamée patinée à l'aide d'une solution à 5 % d'acide citrique épaissie avec de la gélatine. Les 36 objets ont été traités dans le cadre du projet de réaménagement de Green Gables, une maison historique du Parc national de l'Île-du-Prince-Édouard.

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Introduction

The backdrop to this discussion of the treatment of tin-plated artifacts is the Webb Farm on Prince Edward Island, which Lucy Maud Montgomery used as the setting for her story *Anne of Green Gables*.[1] The site, which is now called "Green Gables House," is within Prince Edward Island National Park but is not in itself a historic site. It is furnished as an authentic nineteenth-century farm house. The site is visited in the summer months by over 300,000 visitors, up to 5,700 a day, with an average of 3,000 per day. This tourist traffic puts a considerable strain on the small house.

Many visitors expect to see Green Gables as described in the book, with some evidence of the fictional characters. Parks Canada curators, in their interpretation of the site, have been influenced by the expectations of the public. For example, the porch gable bedroom is furnished as that of a young girl of Anne's age in the book. The artifacts are real, but they are used to perpetuate this literary illusion.

In 1993, it was decided to furnish several rooms at Green Gables that had not previously been open to the public. The "redevelopment" consisted of outfitting two small rooms, one as a dairy porch, the other as a pantry. Many of the items to be used in furnishing these two rooms were made from unpainted tin-plated iron. The items purchased for the pantry and the dairy porch included milk pails, strainers, measuring cups, moulds, and cookie cutters. At the time of acquisition, some of these artifacts were heavily corroded.

In the Montgomery "Anne" book series, the kitchen, pantry, and dairy porch are the domain of Marilla Cuthbert, and it is evident from the stories that Marilla was a fearsome housekeeper. There are many references in the books to household articles being polished or scoured to "the highest possible perfection of gloss and glitter."[2] If the tin-plated artifacts were going to be part of a representation of that time and place, the corrosion would have to be removed.

Tin plate was the nineteenth century choice for utilitarian items.[3] Iron was cheap and strong, but prone to rusting. Tin was expensive and weak but resistant to corrosion. The combination of tin over iron combined the best of both metals. Items made from this material were light weight and silvery in colour when new. This was an appealing substitute for cast iron. For conservators in the twentieth century such artifacts provide excellent examples of inherent vice.

Manufacture of Tin Plate

Until modern electroplating methods came into use, tin plate was made by soaking an iron plate in a bath of molten tin, and then after cooling, dipping it in a second tin bath for the finishing coat. The two baths were made with different sources of tin and were commonly slightly different alloys. The exterior grade, usually "London Tin" from Australia, was chosen for its better colour.[4] The resulting tin plate was then either steam pressed over an iron mould, or formed with a hammer. Edges were often rolled over an iron wire.[5]

The coating procedure was the critical step in the manufacture of tin plate. An iron-tin alloy forms at the interface between the iron and the tin coating. The corrosion resistance of the finished article is dependent on the continuity of the iron-tin alloy.[6] The long term stability of tin plate artifacts is affected by manufacturing methods as well as by use and storage conditions. Rust spots start at points where the iron-tin alloy is not continuous, and then grow quickly because of the electrochemical potential of iron with respect to tin.

Corrosion of Tin

Another form of corrosion of tin-plated iron occurs through a process of patination with the result being a thin, stable, protective layer on the tin plate. The tin-plated items eventually acquire a smooth grey layer of stannic oxide (SnO_2). When the freshly solidified tin is exposed to air an oxide film forms quickly. This coating thickens slowly, being controlled by the rate at which anions can diffuse through the film. This oxide is usually alpha stannous oxide (SnO). The stannous oxide converts slowly to stannic oxide (SnO_2) to develop a crystalline oxide film.[7] Tin is amphoteric, which makes it difficult to treat with chemical methods because it is adversely affected by both acids and bases.[7] It is also quite soft in its unpatinated form and is easily scratched or abraded during use, thereby exposing the iron to the air and allowing it to rust. During treatment the softness of the tin limits the methods available to remove the rust. Once tin has acquired a thick patina of the oxide it is less susceptible to scratching, and is more resistant to acids and bases.

Treatment

The condition of the thirty-six tin-plated iron pieces varied greatly. Some objects were shiny, with no discernible patina. Others exhibited a smooth, dark grey patina with little or no damage to the tin layer. The majority, however, showed signs of manufacturing flaws in the tin coating, with scratches or losses exhibiting rusting of the exposed iron. A review of the literature revealed no established strategies for the treatment of unpainted tin plate. There seemed to be few options other than the usual painstaking, mechanical methods for rust removal.[8] Many of the treatments applied to unplated iron are unsuitable for tin-plated objects. Tin is too soft for abrasives that are hard enough to remove rust, and spot electrolysis can cause tin to replate onto the bare iron areas in an uncontrollable way.

This laboratory has been using 6H pencils as a mild abrasive on bare iron for some time. This method proved to be effective on the tin-plated items where large patches of the tin coating were missing. The resulting graphite residues were carefully removed with denatured alcohol because of concerns about possible interactions between the carbon of the graphite and tin and iron components. The pencils were easy to keep away from softer tin surfaces adjacent to losses, but could not be used in cases where the rust was sitting on top of the tin.

Many items showed an overall orange discolouration that was caused by iron corrosion on top of the tin plate. The problem was to find a method that would remove the iron corrosion without affecting the tin corrosion that formed the patina. Mechanical methods were tried, using scalpels, soft glass bristle brushes, walnut shell in an air abrasive unit, and dental tools. All of these methods marked the tin, so experimentation with chemical methods of removal was begun.

A number of solutions were tested on both bright (unpatinated) and patinated areas of the tin. All chemicals tested affected the bright areas, therefore rust removal on these pieces had to be limited to mechanical methods. Given the softness of the unpatinated areas, even mechanical methods involved some degree of risk.

Phosphoric acid and citric acid solutions have been used to remove rust in a variety of circumstances and were therefore tested on patinated areas of the tin-plate. Phosphoric acid was prepared using a purchased 85% phosphoric acid solution in distilled water, at dilutions of 5%, 7%, and 10% v/v.

Phosphoric acid proved to be unsuitable for the treatment of these tin-plated surfaces. At all concentrations and on all test pieces it changed the colour of the patina to a blue grey that is unlike the natural colour of tin. After treatment with phosphoric acid the surface seemed rough, as one would expect if the patina had been dissolved and then redeposited by the solution, or the surface was unevenly etched.

Citric acid was tested at 5%, 7%, and 10% w/v prepared from powder in distilled water. The first test used citric acid buffered to neutral pH with ammonium hydroxide. The buffered solution proved safe for the patinated tin, but even with 10% w/v citric acid it was not particularly effective in removing rust. The application of the solution proved difficult to control, especially on curved surfaces. When tested, unbuffered citric acid lightened the colour of the patina at all three concentrations but did not alter the tone or texture of the surface. A search of the literature brought to light the abstract of an article by Desai *et al.* on the effect of various protective colloids in protecting brass from citric acid.[9] If a colloid could offer similar protection to tin plate, it might make treatment of these problematic artifacts possible.

Thickening of the citric acid solution solved two problems, making it easier to use on curved surfaces and providing a buffering effect. Agar agar gel was considered as a thickening agent as it has been used successfully in enzyme treatments to control delivery of the enzyme. However, Desai *et al.* rated the various colloids in order of decreasing effectiveness in inhibiting attack as gum arabic > egg albumin > gelatine > agar agar > dextrin> potato starch.[9] Gelatine was selected for testing as it was more readily available. The finished gel was 5% citric acid and at least 2.5% gelatine, w/v. This gel was stiff enough that it could be cut to the shape of the rust spot. The gel could be applied and left for several hours on the surface of most of the pieces without adversely affecting the tin-plate. This treatment softened the rust, which could then be removed with swabs. On most pieces this treatment had to be repeated several times to remove most of the rust. A convenient side effect of the stiff gelatine was that it absorbed the metal citrate complex like a poultice, turning yellow in the process.

Individual testing of each artifact suggested that the citric acid gel technique would be useful for rust removal on many of the pieces, although results on the tin plate proved to be unpredictable. For each artifact it was important to start testing in an inconspicuous area and with a short contact time. Occasionally the tin plate in contact with the gel showed a lightening in colour similar to the effect observed when the ungelled citric acid solution was tested. When a change was noticed, the treatment was halted. This work suggests that, as a general rule, the darker the patina the greater the likelihood of success with this treatment.

The initial formulation of 5% citric acid and 2.5% gelatine in distilled water worked well on many artifacts. Later, more systematic testing of thickened phosphoric acid (5%,7%, and 10% v/v) and citric acid (5%, 7%, and 10% w/v) was carried out. At 10% both acids made the gel unstable and runny. At 7% it was softer, but could be stiffened by using more gelatine. At all tested concentrations in the gel, the phosphoric acid still caused undesirable changes in the colour of the patina. The 5% citric acid proved to be the most convenient concentration. For subsequent treatments the gel was thickened with 5% or twice as much gelatine as used in the original formulation. During this testing an attempt was made to determine the pH of the solutions. The results with both pH metres and indicator strips were variable, probably due to the colloidal nature of the mixture.

The preferred citric acid gel treatment technique was as follows:

- determine the volume of liquid required to make a 2 cm thick layer in a flat bottomed dish;
- weigh out 5 g of citric acid for every 100 mL of finished solution;
- dissolve the citric acid in less than half of the finished volume of water;
- weigh out 2.5 - 5 g of gelatine for every 100 mL of finished solution;
- soften the gelatine in a small quantity of water for 10 minutes;
- dissolve the softened gelatine with less than half of the finished volume of boiling water;
- add the citric acid solution to the dissolved gelatine, then add water to make up the final solution volume;
- allow the solution to cool slightly;
- when the solution has cooled, pour it into a flat dish and chill (lining the dish with wax paper will make the finished gel easier to handle as it will have paper stuck to one side; it is possible to cut gel and paper together with scissors into the appropriate shape);
- leave the gel on the surface of the artifact for 20 minutes to an hour, and then swab off the rust;
- the used gel can be returned to the refrigerator and replaced with a chilled one (the gels can be re-used until they are bright yellow with reaction products);
- after treatment the area is rinsed with distilled water and air dried (de-watering with acetone has been suggested, but no problems with re-rusting were noticed during the air drying).

This technique provided an efficient and controllable method of treatment. It should be emphasized that this is a slow method that works only on thin layers of rust. Thicker layers were reduced using mechanical methods until only a thin layer remained, and there was a chance that the soft tin plate layer would be exposed and possibly scratched in the process. The citric acid gel was then used to remove the remainder of the rust. This set of artifacts was then coated with microcrystalline wax to protect them from possible contact with ungloved fingers.

Conclusions

Treatment of all of the artifacts for Green Gables was completed on schedule, and the tin plate objects now form part of the interpretation of a nineteenth-century pantry and dairy porch. Tourists travelling to Prince Edward Island in search of the fictional setting from the Montgomery book will find the reality of a working farmhouse, enhanced by this collection of tin plate.

The research done to arrive at this treatment protocol was not rigorous. As is often the case when working to meet a deadline, enough work was done to provide a solution that was suitable for the needs of the artifacts and the curator, and stayed within conservation standards. The empirical data generated by this work was promising enough to merit more investigation. Experiments should be carried out to gain a greater understanding of the action of the colloid in moderating the effect of the organic acid and to have a detailed look at the effect of this treatment on the microstructure of the tin-plated surface. However, this type of technical study, for example, documenting the surface before and after treatment using scanning electron microscopy, would require more sophisticated equipment than was available to the author. An investigation of other active agents in the gel and other gelling agents could also be performed. Since this work was completed many other chemicals have been suggested, or experimented with, by others. A comparative study of their effects on a variety of patinated metals might increase the options available for future treatments.

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Afterword

In the summer of 1997 there was a fire in Green Gables House, and the entire contents of the house were subjected to extensive heat, smoke, and water damage. The fire started in an area adjacent to the room where the artifacts discussed in this paper were displayed, making these items some of the most damaged. The tin-plated items were particularly difficult to clean, possibly because of changes in the tin caused by exposure to heat, ash, and smoke. The effects of soot and heat on the wax coating, applied during the conservation of the artifacts, made it extremely difficult to remove. The items have been cleaned and temporarily returned to display. However, the damage is permanent, and the curator for the site will gradually replace these tin plate artifacts.

Materials

Citric acid, USP grade: Bebbington Chemicals, 20 Wright Avenue, Dartmouth, Nova Scotia, B3B 1G6, Canada.

Gelatine: Knox unflavoured gelatine from grocery stores.

Phosphoric acid: Anachemia AC-7439 ortho 85%: Anachemia Canada Inc., P.O. Box 147, Lachine, Montreal, Quebec, H8S 4A7, Canada.

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9. Desai, M.N., Talati, J.D., and Trivedi, A.M., "The effect of various protective colloids on the corrosion of brass," *Werkstoffe u. Korrosion*, vol. 10, no. 1, 1959, pp. 26-29.