

THE “PERFECT” FILL FOR THE MAGNIFICANT TINTYPE

Juan-juan Chen, Thomas Edmondson, John McElhone, and Irene Brückle

ABSTRACT

This paper discusses the treatment of filling the emulsion loss of a tintype at Heugh-Edmondson Conservation Services and the follow-up experiments to look into the issues concerning the possible effect of the added material to the iron support at the National Gallery of Canada. The emulsion loss was filled with cast gelatin film that was toned with watercolor and varnished with Paraloid B-72 to match the appearance of the original. Follow-up experiments showed that if the iron support was not properly protected, rust might occur after the gelatin film was attached. The iron support treated with tannic acid, however, appeared to be stable in an enclosed chamber of high relative humidity for three weeks after the gelatin film was attached. The final results of these tests will be presented in the next *Topics*.

PART I: TREATMENT

The Object and Its Condition

Many new conservation treatments are developed because the conservator is faced with a problem that has not been solved yet. Such is the case with the tintype in Figure 1. It is a particularly interesting image that shows seven young men wearing all sorts of different hats. The scene conveys a sense of their close friendship and the fun it must have been for them to have their picture taken at a photo studio.

The plate was in good condition except the loss of emulsion and the black lacquer at both upper corners. This damage was caused by the iron support having been bent, which caused the emulsion and lacquer to release. Though stripped bare and exposed to the environment, the iron support of the damaged areas did not exhibit visible rust. It indicates that the damage happened fairly recently. This alone would probably not present a problem, since it is unlikely that the iron corrosion will continue if the tintype is kept in a well-controlled environment. Of concern to us was, however, the visual distraction of the two losses in viewing the image. In order to re-integrate the appearance of the photograph, we decided to perform a cosmetic treatment after we had obtained permission from the owner.

Looking for a Solution for a “Perfect” Fill.

While thinking over this treatment, we first had to consider the quality of the fill materials to be used. They had to be stable, chemically compatible with original materials, and they were not to interfere with any future treatment or scientific analysis of the original substrate. In addition to these considerations, we were challenged to find a way of making an inconspicuous and aesthetically compatible fill for this tintype. This meant that: First, the fill needed to match the thickness of the loss. Second, the surface texture and gloss needed to be similar to that of the varnished collodion emulsion. Third, the inpainting that was to be applied to the fill needed to match the continuous tone of the image. We felt that just building up the thickness of the loss with acrylic colors or pigments mixed with different binders would not give a satisfactory result.

While considering our alternatives, it occurred to us that to obtain a fill with an even and smooth surface, it might be advantageous to cast a film. Allowing the liquid film material to flow across a perfectly horizontal plane with a smooth surface, it would first level and then dry evenly. A wooden tripod with a smooth platform used to hold a 4x5 camera served very well for our purpose. It provided a means of establishing a level surface for the casting. (One can also use Play-doh underneath the center of a piece of glass to achieve a leveled plane.) Photographic grade gelatin was chosen as the fill material because its working properties were perfect for our task: gelatin is a viscous liquid while warm; and we found that it can be easily tinted if watercolor is incorporated in the liquid.

The emulsion loss on the tintype was measured with a micrometer, using a piece of silicone release Mylar[®] to protect both sides of the tintype. The thickness of the loss was calculated by subtracting the thickness of the bare metal from the thickness of the undamaged tintype.

A five percent solution of photographic grade gelatin in de-ionized water was used to cast the films. We were able to make dry gelatin films of different thickness by applying different quantities of liquid gelatin in a defined area on a piece of 5 mil Mylar[®]. (Silicone release Mylar[®] was tried and found to have too much surface tension to spread the gelatin solution to a uniform thickness, and the samples lifted and curled, making them useless for fills.) A piece of graph paper was placed underneath the Mylar[®] to guide the delivery of the gelatin solution to the 4x4 cm square area that we had mapped out to create a fill material for our treatment. The Mylar[®] and graph paper assembly was secured with masking tape onto the leveled tripod platform. The tape had to cover all around the edges of the Mylar[®] in order to prevent the Mylar[®] from curling while the gelatin was drying. There was just enough surface tension between the warm gelatin and the uncoated Mylar[®] to keep the solution from spreading too far. A bamboo skewer was very helpful to guide the liquid gelatin to fill the 4 x 4 cm square.

The initial trials were aimed at finding the right thickness of the film. Five films were cast with 30, 35, 40, 45, and 50 drops of warm gelatin respectively, each dried in a 4 x 4 cm square. It took about one day for the solution to dry. The gelatin films dried with a beautiful gloss and could be released from the Mylar[®] easily. The thickness of the films was measured with a micrometer at the center of the films. We found that a film dried from 35 drops of 5% gelatin solution produced a film just slightly thinner than the loss, which was 5/1000 inch, the same thickness as 5 mil Mylar[®].

Toning

As already mentioned, liquid gelatin can be easily toned with watercolor. The addition of the watercolor (in this case, Chinese white, lamp black, and yellow ochre) turned the gelatin film opaque, making it look surprisingly similar to the collodion emulsion. The two sides of the gelatin film exhibit different shades and degrees of gloss: the side dried against the Mylar[®] exhibits higher gloss and a cooler tonality than that exposed to the air. For this tintype, the air-dried side of the film had a better match in color than the other side.

There were design elements in the loss area that needed to be recreated in order to make the insert less noticeable. Because of the slick surface and nonporous surface, gelatin film does not receive brush stroke as agreeably as paper fill does. An airbrush was used to create the general image that was missing in the loss area. There was no record of the photograph to show what was present in the missing section. We decided to make a gradual transition from the original image to the fill by continuing the column seen in the original image into the fill area. Our intention was not to create a new design but to create an insert that would recede visually into the background and not draw the viewers' attention away from the original image.

To be able to use toned liquid gelatin with the airbrush, the dilute gelatin solution was kept warm over a pot of hot water. We did run into difficulty with the gelatin cooling and clogging the airbrush nozzle. It would have been advantageous to keep the airbrush nozzle in warm water when it was not in use. The dilute gelatin solution was toned slightly with lamp black. Mylar templates were made to block certain areas during airbrushing in order to create the shapes and shades of the design for the fill.

Attaching the Fill

Because the gelatin film was quite rigid, trimming it and cutting it to match the loss area proved to be a difficult task. Unlike a sheet of paper, the gelatin film cannot be shaped to produce a very neatly fitting joint. Though the gelatin film can be manipulated with a small amount of water to soften the edges to make fitting easier, it is nonetheless important to cut the edge as exact as possible. Photocopies of this tintype were used as guides to cut the fill. Two photocopies were aligned with the fill that was placed in the middle, like a sandwich package. The bottom copy was used to align the design between the fill and the original. The other copy set on top of the fill as a guide for cutting. The non-joining edge of the fill was left untrimmed for easy handling during attaching.

In preparing the tintype for inserting the fill, the bare metal in the loss area was coated twice with 15% Paraloid B-72 in toluene with a brush. The plate was left in the fume hood to dry overnight. Taking advantage of gelatin's ability to be softened with moisture, synthetic emulsion adhesive Beva D-8 was used to adhere the fill to the metal plate. A one-to-one dilution of Beva D-8 with deionized water was brushed onto the back of the fill, and, sparingly, along the edge to be joined with the original. The water in the diluted adhesive emulsion swelled and softened the gelatin just enough to conform the film to the bent metal support. The excess non-joining edge was trimmed after the fill was secured.

Final Retouching and Rehousing

There were still tiny gaps at the joint, which were carefully filled with the same toned gelatin solution used for casting by applying with a brush. Some retouching could be carefully done with a fine brush with toned gelatin solution, applied while warm, in the fashion of dots. To prevent the gelatin from reacting with moisture in the air and to match the gloss of the original, the fill was lightly sprayed with 10% B-72 solution in toluene. The original was protected with a piece of Mylar[®] during this step. Finally, the treated tintype (Figure 2) was housed in a sink mat, glazed, and sealed with Filmoplast[®] P90 along the edges (Figure 3).

PART II: FOLLOW-UP EXPERIMENTS

Visually, the infill integrates with the original image very well. The distraction caused by the loss is eliminated. Gelatin is a fairly stable material if it is treated well. Yet, whether its hygroscopic nature and the little moisture introduced with the emulsion adhesive could affect the iron support was not known to the authors. Are there better alternatives than gelatin for making the fill? Will the materials added to the tintype affect the stability of the object, especially the iron support? If the support is already corroded, what measures should be taken before a fill is adhered on top of the damaged area? Does the iron support need to be treated before adhering a fill regardless of whether it is corroding or not? Can Paraloid B-72 coating prevent or retard iron corrosion? If not, what measures should be taken before adhering the fill? The following experiments were based on these questions.

Object conservators have used a variety of methods to treat rust. We investigated tannic acid, which has been used successfully in the conservation of archaeological iron and outdoor steel (Bennie, Selwyn, Schlichting, & Rennie-Bisaillon, 1995; Carlin & Keith, 1996; Pelikan, 1966; Smith, 1990). Tannic acid can be extracted from different plant sources, such as oak gall, or bark of the sumac tree. The composition of tannic acid is complex and varies. Listed in this paper is one of the varieties, called corilagin, which has the empirical formula $C_{27}H_{24}O_{18}$ (figure 4). Regardless of its variation in molecular size, tannic acid is a polygalloyl glucose. Key to the use of tannic acid in the treatment of metal corrosion is the many hydroxyl groups that give the tannic acid its metal chelating ability. Through the hydroxyl groups, tannic acid chelates the ferric ions and renders them insoluble in the form of a blue-black ferric tannate. Acting as a passivating layer, ferric tannate may also inhibit the diffusion of dissolved oxygen to the underlying metal surface.

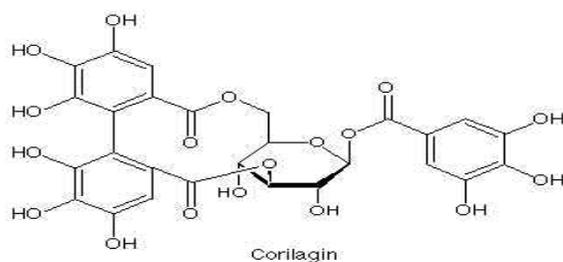


Figure 4

EXPERIMENTAL

A. Casting different film-forming materials

Some common film-forming materials were cast on silicone release Mylar to observe their working property and their physical properties as possible fill for tintypes. They are listed in the following table.

Table 1. Film-forming materials tested

PVA	PVA emulsion	Acrylic	Acrylic emulsion	Gelatin, 275 bloom	Others
20% AYAA in toluene	Jade 403, no dilution	20% Paraloid B-72 in toluene	Rhoplex N580, no dilution	10%	2% Klucel G/ethanol
20% AYAF in toluene	Jade 403, 1:1 dilution	20% Paraloid B-72 in acetone	Rhoplex N580, 1:1 dilution	7.5%	2% Methyl cellulose
20% AYAT in toluene	CM Bond M-4, no dilution	-	Lauscaux 486, no dilution	5%	-
-	CM Bond M-4, 1:1 dilution	-	Lauscaux 480, 1:1 dilution	3%	-
-	-	-	Lauscaux 360, no dilution	1%	-
-	-	-	Lauscaux 360, 1:1 dilution	-	-
-	-	-	Mixture of Lauscaux 486 and 360, 1:1 dilution	-	-

B. Tannic Acid Treatment and High Humidity Accelerated Aging

To complete the experiment, three tintypes, A, B, C, were selected from the study collection of the conservation and Restoration Laboratory at the National Gallery of Canada. Tintype A has severe corrosion on the back and underneath the collodion layer. It was faced with Japanese paper and 15% B-72/toluene. The back was sanded down to bare metal. In some area, the formation of rust was encouraged through the repeated application of water while keeping the tintypes in the open air for several days. Then the plate was designed to accommodate different combination of treatments listed in Table 1. The entire plate was exposed to high humidity for three weeks. The humidity was kept constant with in an enclosed chamber with saturated salt solution of sodium chloride, which gave 75.5% RH at 20°C.

Due to inclusive results, another tintype (tintype B) was treated with the same method as Tintype A except four coats of B-72 to avoid incomplete coating. The plate was designed to have the combinations listed in Table 2.

Table 1. Different Combination of Treatments on the back of Tintype A

- A-1. bare iron
- A-2. bare iron, B-72/toluene
- A-3. bare iron, Rhoplex N580, gelatin film
- A-4. bare iron, Rhoplex N580, gelatin film (hardened)
- A-5. bare iron, B-72/toluene, Rhoplex N580, gelatin film
- A-6. bare iron, B-72/toluene, Rhoplex N580, gelatin film, B-72/toluene
- A-7. rusted iron, B-72/toluene
- A-8. rusted iron, treated with tannic acid, B-72/toluene
- A-9. rusted iron, treated with tannic acid, B-72/toluene, Rhoplex N580, gelatin film
- A-10. rusted iron, treated with tannic acid, B-72/toluene, Rhoplex N580, gelatin film, B-72/toluene

Note: The material listed after was applied on top of the previous one.

Table 2. Different Combination of Treatments on the back of Tintype B

- B-1. bare iron
- B-2. bare iron, B-72/toluene
- B-3. bare iron, Rhoplex N580, gelatin film
- B-4. bare iron, B-72/toluene, Rhoplex N580, gelatin film
- B-5. bare iron, treated with tannic acid, B-72/toluene

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- B-6. bare iron, treated with tannic acid, Rhoplex N580, gelatin film
 - B-7. bare iron, B-72/toluene, Rhoplex N580, gelatin film
 - B-8. rusted iron, B-72/toluene
 - B-9. rusted iron, treated with tannic acid, B-72/toluene
 - B-10. rusted iron, treated with tannic acid, B-72/toluene, Rhoplex N580, gelatin film
 - B-11. rusted iron, treated with tannic acid, B-72/toluene, Rhoplex N580, gelatin film, B-72/toluene
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Note: The material listed after was applied on top of the previous one.

Following a recipe published by CCI, a 2.5% aqueous solution of tannic acid was prepared and applied in warm condition to the designated areas, including the un-corroded metal and the pre-rusted areas (Logan, 1995). Continuous brushing was necessary to introduce oxygen for the formation of ferric tannate.

Gelatin films were cast film of 10% 275 bloom gelatin solution approximately 5/1000 inches. They were not toned in order for observation of any corrosion activities underneath the film. Rhoplex N580 was used as the adhesive in this experiment instead of Beva D-8 as used in the

Based on CCI's research on adhesive in 1994, Rhoplex N580 appears to have good dark and light aging property and not releasing any acid that will accelerate the corrosion of the iron support (Down, MacDonald, Tétreault, Williams, 1992). It remains neutral in both three-year light aging and four-year dark aging. In this experiment, therefore, Rhoplex N580 was used instead of Beva D-8.

Each layer was left in the open air to dry or let solvent evaporate before proceeding to the next layer.

One tintype (tintype C) had heavy rust along the front edges was also tested with tannic acid on the front. Tannic acid was slowly brushed on rust repeatedly after previous coat was dry.

RESULT AND DISCUSSION

A. Cast films

Evaluating the working properties, drying speed, film flexibility and toughness, gelatin is still a more appealing material than all others tested. The strength of a gelatin film is dependent on the Bloom number of the gelatin. Films made from Fisher "Type A pure gelatin" with the Bloom strength of 275 all appeared to have good flexibility. The film cast from 10% solution, however, could build up the thickness easier for the thickness of 5/1000 inches.

B. Accelerated Aging in Humidity Chamber

After three weeks, the first plate (Tintype A) had developed new rust almost throughout the entire plate except areas treated with tannic acid (A-8, A-9, A-10). All areas treated with tannic acid appeared to be fine except some spots on the margin, where the tannic acid treatment was not complete. Two forms of rust were observed on this plate. Dot-like corrosion grew out the B-72 coating and a bit of corrosion grew along the margins of the tannic acid-treated area. Filliform corrosion was visible underneath B-72 coating and or Rhoplex N-580 adhesive. The area that pre-rusted and coated with B-72 (A-7) had developed more rust than the area of B-72 coated bare iron (A-2) and bare iron (A-1).

There was no visible difference in the amount of rust formed on the areas with gelatin films attached (A-3, A-4, A-5, A-6) regardless coated with B-72 or not.

Object conservators have noticed the fact that a coating with B-72 does not always protect metal from corroding, but instead can accelerate corrosion (Day, 2001). They noticed that incomplete coatings could accelerate reactions because the pits became small reservoirs of moisture to drive forward the corrosion process. The rust formation that occurred underneath the B-72 layer indicated that moisture was probably trapped underneath the coating.

Second plate, Tintype B, which had thorough coating of B-72, showed different result from Tintype A. It was interesting to observe that the area treated with tannic acid appeared to be stable. None of the areas protected with B-72 showed any sign of new rust forming, regardless of the pre-treatment. In other words, the bare iron area, the pre-rusted area, the tannic-acid treated area, and the area to which a gelatin film had been adhered all were adequately protected during this experiment by the thorough coating with B-72.

After more than ten applications of the 2.5% tannic acid on Tintype C, the rust is still present underneath the tannate layer. Therefore, it will be more efficient to mechanically remove as much as loose rust as possible before tannic acid is applied. This decreases the working time and maximizes the efficiency of the tannate. The excess tannate on the surface of the varnished tintype could be removed with damp cotton swabs. No staining of tannate was observed on the tintype.

CONCLUSION

The technique developed in this treatment for filling emulsion loss on tintypes has several advantages in addition to the satisfying visual resemblance. The gelatin fill can be removed just by peeling the fill out of the plate. The photographic grade gelatin should be very pure and stable in normal circumstances. It differs from collodion binder in many ways, providing no obstacle for future scientific analysis.

It should be noted that this technique might not be applicable when the losses are small. Cutting small fills from a gelatin film can be difficult due to its toughness. If the design of the image in the loss is complex, it will be possible but time-consuming for air-brushing.

The results of the experiments indicated that incomplete B-72 coating accelerated the corrosion whereas thorough coating could prevent corrosion after the fill was attached with emulsion adhesive. Therefore, care should be taken to ensure a good coating is applied. One can also eliminate as much moisture on the surface of the area to be treated as possible before coating, so no or little moisture is trapped underneath the coating.

We found that it is a promising treatment to stabilize the surface of the iron support with tannic acid. Tannic acid converts rust, and iron metal, into a passivating layer of ferric tannate, protecting the surface from corrosion. In addition, the blue black color of the ferric tannate is more sympathetic for viewing than the brown or orange rust.

The duration that the samples exposed to the high humidity environment was three weeks.

Further investigation is needed in order to understand the long-term stability of the ferric tannate, and thus how long it can remain as a passivating layer.

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