Article

Let's pretend – conservation of an early imitation tortoiseshell.

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Abstract: Tortoiseshell has been used as a decorative material in the arts since the beginning of recorded history. It has always been scarce and is therefore often imitated. Het Loo Palace in Apeldoorn, The Netherlands, has a cabinet from the 1840's in its collection with a rare imitation finish: it is not horn, nor is it one of the semi-synthetic plastics that were developed in the nineteenth century. Over time the finish had become dull, cracked, distorted and fragments have chipped off. In order to develop an appropriate method of treatment, it was necessary to study its composition and material properties. It proved to be a rare imitation material, made out of animal glue.

Keywords: Het Loo Palace, Frederik Koster, silverware cabinet, craquelure, faux tortoiseshell, imitation, animal glue, gelatine, glutin, conservation.,

1. Introduction

Het Loo Palace in Apeldoorn was a residence of the Dutch royal family from the last decades of the seventeenth century until the death of Queen Wilhelmina in 1962. In the 1980's it was turned into a state museum showcasing the history of the House of Orange-Nassau.

One of the most extraordinary pieces in the collection is a silverware cabinet that is likely to have been bought by King William II, and was brought to Het Loo after his death by his son King William III.^[1] The cabinet was made in the 1840's in the

historicist (revival) style, combining elements of the Gothic and Baroque periods; most noticeable in the use of pinnacles, pierced columns and ripple mouldings (cf. figure 1).

The upper part of the cabinet is fitted with plate-glass windows with red silk curtains and mirror glass on the inside. The lower part has mirror glass on the front and sides. The imitation tortoiseshell is applied to the top gallery (now partly missing), the front, the sides and top of the lower part.

The cabinet is ascribed to Frederik Koster, a cabinetmaker from Utrecht. It is a showpiece, demonstrating the skills of a craftsman. It is known from an inventory that King William II bought a "silverware cabinet, decorated with tortoiseshell and plate-glass" at an exhibition in 1847. [2]

And it was in this period that Koster acquired the title 'Royal Purveyor of tortoiseshell furniture'.



Figure 1 The silverware cabinet (Photo: Het Loo Palace).

Only a few cabinetmakers in The Netherlands were able to work with this material at the time. [3] Paul Rem, curator of furniture at Het Loo Palace further suggests that Koster used this particular imitation tortoiseshell to demonstrate his knowledge of the latest materials, as he could have also used horn: an already known faux tortoiseshell. [4]

2. Object inventory

The imitation tortoiseshell is in bad condition. It is dull, cracked, distorted and fragments have chipped off (cf. figure 2).

Moreover, the material is brittle and therefore extremely vulnerable in the distorted areas. The damage has been caused by the interplay of the material properties of the imitation material, the construction of the cabinet and the conditions of storage. The imitation material is sensitive to fluctuations in relative humidity: it expands and contracts. It is glued to a wooden substrate that is also water sensitive, but expands and contracts at a different rate and in a different direction. The imitation is thus restricted in its dimensional change, which tension and, consequently, causes cracking.

most common pattern craquelure starts at the edges. The finest cracks are visible to the eye only as dullness, but as the material deteriorates further, repeatedly going through cycles of shrinkage and expansion, small cracks appear. These are visible along all the edges and can, at their worst, run through the whole surface to the opposite edge. This process is accelerated by moisture acting on the increased surface area of the distorted areas. Especially when brittle, these areas can easily chip off, making the substrate visible. In areas where the substrate cannot expand and contract because of underlying joints, there is hardly any damage visible.



Figure 2 The pattern of craquelure (Photo: Author).

Another pattern of craquelure is the result of conservation treatment in the 1990's. In 1993 the Cultural Heritage Agency of The Netherlands performed FTIR analysis on a sample and stated that it was composed of casein, starch and a natural resin. It was 'possibly casein formaldehyde', but the research was 'not conclusive'.[5] At the time, the conservation of (semi-)synthetic materials was still in its infancy, and it was therefore not possible to obtain advice on a methodology of treatment. An experiment was made to reconstruct the original appearance of the finish, but this resulted in new craquelure after a couple of weeks. It was then decided to place the cabinet back in storage, in anticipation of advances in conservation science.

3. Identification

Optical and instrumental analysis

The faux tortoiseshell material on the silverware cabinet has a thickness of 1 mm and is glued to the cabinet in sheets of equal size. The different sheets are butted against one another at regular intervals.

A small sample of the imitation tortoiseshell was analysed under an optical microscope and showed a layered structure: two transparent layers, each one topped with a much thinner colored band (cf. figure 3).



Figure 3 Sample of the imitation tortoiseshell under an optical microscope (Photo: Author).

These characteristics seem to suggest a laborious process in which a plastic material was cast and dyed in different stages, resulting in relatively small sheets of imitation tortoiseshell.

The FTIR analysis in 1993 stated that the imitation material was made out of casein and was possibly even casein formaldehyde. However, in FTIR one can observe the vibration band of amide or amino groups of proteinaceous material, but not distinguish between e.g. casein and animal glue.

Furthermore, the presence of casein formaldehyde material can be excluded, since it was available on an industrial (commercial) scale only after 1896 ^[6], while the cabinet dates from the 1840's.

Indeed, the first patents for casein formaldehyde plastic material only appear after 1900.^[7,8]

The other semi-synthetic plastic from the nineteenth century, cellulose nitrate, was only commercially available after the 1860's and would have been detected with FTIR.

It cannot be a material like horn, let alone tortoiseshell, because the imitation is water sensitive and has a different pattern of craquelure.

These characteristics seem to suggest a proteinaceous material such as casein or gelatin.

New pyrolysis-GCMS analysis concluded that the imitation material was made out of gelatin and starch.[5] A resin was not found in the second analysis, or in the cross section or solubility tests. The sample for the earlier FTIR analysis was probably taken from a section that had once been varnished to restore the level of gloss. The pyrolysis-GCMS analysis also excludes the presence of the organic curing agent tannin. The inorganic curing agent alum can be detected with FTIR, but unfortunately budget constraints meant it was not possible to investigate this further. For the same reason, it was not possible to again use pyrolysis-GCMS to determine whether the animal glue was derived from either hide, bone or fish bladder (isinglass). The precise determination of the proteinaceous material, whether it is hide, bone or fish bladder glue, could be conducted in future by e.g. ELISA (Enzyme-linked Immuno-sorbent Assay).[9]

The imitation material is made out of gelatin (glutin) and starch with the likely addition of alum as a curing agent.

Historical source analysis

The author found hardly any literature on proteinaceous plastic materials published before the beginning of the twentieth century. A rare exception on plastic materials is a French trade magazine from 1799 that describes the

process of wire netting, in which a sheet material is made by repeatedly dipping a wire mesh in gelatin, building it up layer by layer. [10] Other publications on casein or gelatin as binding media or glues were only found dating back to the end of the nineteenth century. [11,12]

Meanwhile, the only nineteenth century publication on proteinaceous plastics the author has found is Die Imitationen. Eine Anleitung zur Nachahmung von Natur- und Kunstproducten... by the German chemist Sigmund Lehner. This title is part of the comprehensive Die Chemisch-Technische Bibliothek (volume 101), a practical series of books on the latest developments in science and industry of the time, published by A. Hartleben's Verlag in Vienna from 1875 to 1949. In Die Imitationen, a process is described to imitate exotic materials like ivory, mother of pearl and tortoiseshell, using casein or gelatin.[13] This process was already outdated at the time of its first publication in 1883 (translated): "In recent times, tortoiseshell imitations made of glue have lost their use, because they can be made far more durable from Celluloid".[14] The same applies to a casein preparation not yet hardened by formaldehyde, described in 1898 by Johannes Höfer in Die Fabrikation künstlicher plastischer Massen.[15]

The casting process described in Die Imitationen might have well been applied in the 1840's. Three components are needed for the imitation tortoiseshell: a binding medium, filler and pigment.[16] The binding medium, either casein or animal glue, has to be soluble in hot water, transparent and colorless. A mixture of binding medium and filler is cast out on a glass plate which is fitted to a table with screws, allowing the plate to be levelled (cf. figure 4). Rulers have been placed on the sides and at one end to control the thickness of the casting. The surface is then evened out with a spatula, allowing excess material to flow out on one side. When the plastic material has set, the

mottled pattern of tortoiseshell is painted in with a brush. This process can be repeated to gain more depth. Afterwards the glass plate with the faux tortoiseshell is placed in a warm room to dry and then placed in an oven to further reduce the moisture content.

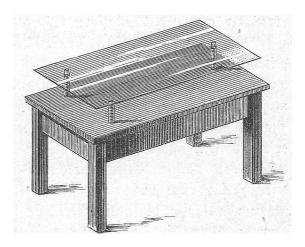


Figure 4 Table with horizontal glass plate. [15]

In the last phase of the production process the imitation tortoiseshell is assumed to be 'hardened' or cured, making the product less water sensitive. [17] A curing agent causes crosslinking to the protein. The degree of crosslinking largely determines the durability of the final product.

A solution of formaldehyde in water is also mentioned in the 1884 edition of *Die Imitationen* as a curing agent, but in the 1840's only solutions of either tannin or alum, applied in the production of leather for centuries, could have been used as hardening (crosslinking) agents. In volume 22 (1781) of the famous, and at that time by far the largest encyclopaedia published by Krünitz (242 volumes between 1773 to 1858), the use of alum was already described for hardening layers of isinglass glue for 'Flemish images' ("images de Flandre", i.e. small transparent images of saints). [18]

A curing solution may not be too high (not higher than 4-5% for formaldehyde), as too fast surface curing will prevent the curing agent's diffusion to the core.^[19] If the curing rate is too low, curing is incomplete or takes too much time (up to months). This might well also be the problem with both tannin and alum. However, time constraints in the research did not permit comparative testing.

3. Conservation

The silverware cabinet is one of the most extraordinary pieces in the collection of Het Loo Palace. However, the faux tortoiseshell is a challenging material. The craquelure is part of its natural ageing, i.e. is a kind of 'patina', being not durable. The new treatment will therefore differ from that in the 1990's in that it will not try to restore the original appearance. The aim of the treatment is rather to prevent further deterioration and give back to the cabinet its historical aesthetics, by cleaning, consolidating and reconstructing the finish with the conservation of craquelure.

Conservation literature

Ever since the early 1990's there has been little progress in the conservation of proteinaceous plastics, in contrast to the other 19th century plastics, such as vulcanized rubber, cellulose nitrate and cellulose acetate. Some studies have been conducted on casein formaldehyde, but not resulted in any treatment methodology. [20-22] Kaner (2010) suggests that water can be used as a plasticiser to parts.[23] treat distorted Α further comparison of various fields of conservation on the treatment craquelure showed that apart from water (with or without a thickening agent), heat is often used as a plasticizing method. [24,25] Furthermore, some valuable studies on the reconstruction of tortoiseshell were identified, most notably by Williams (2002). [26] He suggests various methods for obtaining imitations made of animal glue with a curing agent to obtain specific patterns or properties. Another method is

using faux tortoiseshell made of cellulose acetate.

Cleaning

The imitation tortoiseshell was gently cleaned with a microfiber cloth and, where necessary, with cotton swabs dampened with Shellsol® D40, as an aliphatic mineral spirit does not affect gelatin and was sufficient to remove accretions of dirt.

Consolidation

the The craquelure caused by conservation treatment in the 1990's had been transferred onto a sheet of Melinex® (PET film) and showed that the surface had, after the initial damage, remained stable over a period of about twenty years. It was supposed that the problem might not be the plasticizer itself, but the amount of added water. This would determine whether or not new damage would occur. The water could be reduced considerably. since it was only needed to treat distorted areas; not to swell the gelatin and restore the original appearance. After some tests on gelatin casts, a new attempt was done in a discrete area.

A mixture of demineralised water and ethanol (1:1) was applied with a syringe. The ethanol was added to lower the surface tension, enabling the water to flow in between the finish and the substrate. After five minutes, the plasticity was tested with light finger pressure and the material had lost most of its tension. This however did not work in more heavily distorted areas. During further testing, depending on the degree of distortion, either a cotton swab moistened with the mixture of water and ethanol was placed underneath the flake, or a thin layer of fish glue was brushed on its reverse side. This seemed to work. Afterwards the swabs were removed with a tweezer and the glue with a slightly dampened microfiber cloth. The treated area was transferred onto a a sheet of Melinex®. After one month it showed no further deterioration.

Then testing was carried out to choose the best consolidant. The consolidant had to have a low viscosity for easy penetration, good adhesion, some elasticity to allow for dimensional change and had to be reversible. As a first test the dissolved acrylic resins Paraloid® B67 (25 % in Shellsol® D40 / A 25%) and B72 (25% in ethanol) proved inadequate because of their long curing time and poor adhesion. It further seemed that the consolidant needed some water too, to plasticise the distorted areas. Further testing showed a mixture of fish and hide glue (1:1) worked best. It is a thin glue that is liquid at room temperature, flexible, and contains a relatively low percentage of water.

The distorted parts of the imitation tortoiseshell were plasticized with a mixture of water and ethanol and consolidated with a mixture of fish and hide glue. Then the surface was clamped with acrylic sheets. The clamps were temporarily removed in order to wipe off the excess glue with a slightly dampened microfiber cloth. The surface was then clamped for 24 hours and cleaned again (cf. figure 4).



Figure 5 The left part of the top is consolidated (Photo: Author).



Figure 6 Detail of top with reconstructions. Photo: Author



Figure 7 The top is saturated (Photo: Author).

Reconstruction

The appearance of the original imitation tortoiseshell had to be approximated in colour, transparency and gloss. Research commercially available into tortoiseshell showed that the matching patterns and colors weren't available. Tests were done with animal glue casts, but their long-term stability was unknown. Epoxy resin was chosen as a casting material, because it is durable, not sensitive to moisture and it dries quickly without the inclusion of air bubbles. A commercial epoxy glue (Polypox THV 500) was used, which will, as do most epoxies, yellow over time.[27] But the original tortoiseshell is yellow in color too. Moreover, the new inserts can be removed since they are cast separately from the object and held in place with a reversible glue. The inserts have been documented.

The film was cast on a glass plate that was lightly powdered with talc and the mottled pattern was painted in with epoxy pigments that were thinned down with epoxy resin. The result was an imitation with a general match in color and pattern, allowing for further adjustment in specific areas. Then the film was scraped, sanded and sawn to match the missing areas. In

addition, small cuts were made with a fretsaw to imitate craquelure. Then, if needed, the color was adjusted by staining the adherent with Orasol® water dyes and the pattern by brushing Golden® acrylic paint on the back of the inserts. A mixture of fish and hide glue was used to put the inserts in place (cf. figure 6).

An even gloss was obtained by saturating dull areas and small craquelure with a low molecular varnish. The low molecular varnishes have relatively short polymer chains, allowing for deep penetration. A solution of the urea-aldehyde resin Laropal A81 (20%) was used in a mixture of the hydrocarbon solvents Shellsol T (aliphatic) and Shellsol A (aromatic) in a 2:1 ratio. It was brushed on and applied again once. Then a stronger solution (40%) was used to fill the remaining craquelure, since the substrate was saturated but the cracks were not (cf. figure 7).

4. Conclusion

The cabinet is finished with a rare imitation tortoiseshell, of which no other examples are currently known. The material is part of an early phase of the development of relatively durable proteinaceous material,

which would lead to the semi-synthetic casein formaldehyde. It is a natural glue that is probably treated with the hardening agent alum. The imitation material is hygroscopic by nature, which imparts to the craquelure an aging characteristic.

5. Experimental

Golden[®] (acrylic paints, Golden Artists Colors, Inc.)
Laropal[®] A81 (Aldehyde resin, BASF)
Melinex[®] (PET film, Teijin DuPont Films)
Orasol[®] (Dyes, BASF)
Paraloid[®] B67 and B72 (Acrylic resins, Rohm and Haas/Dow)
Polypox[®] THV 500 (Epoxy, Poly-service)
Shellsol[®] A, D40, T (Solvents, Shell Chemicals)

Acknowledgments

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