All that glitters is not bronze

Diving into the intricacies of so-called “bronze paints” on gilded wood

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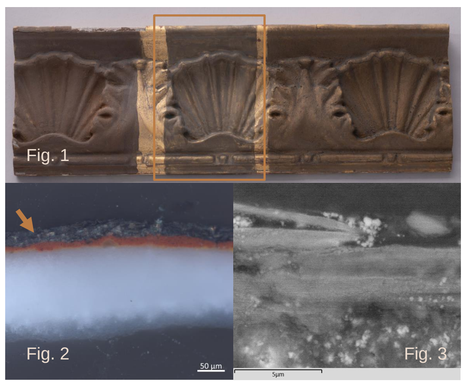

Fig.1: Mock-up with mica in shellac. Fig. 2: Cross-section photomicrograph (VIS), mica in shellac (top layer). Fig. 3: SEM backscatter electron image of mica in shellac.

The Getty Conservation Institute (GCI) Cleaning of Wooden Gilded Surfaces project aims to address the challenges presented by the cleaning of wooden gilded surfaces and to identify and disseminate appropriate treatment options. Part of this project’s broad scope is the study of “Bronze paints,” which were used on wooden gilded surfaces to retouch or overpaint gilding or as an original “gilding” medium. As representatives of those surfaces, project-specific mock-ups and European picture frames from various time periods were used to study and document different bronze paints, examining both binding media and bronze paint particle morphology. Cross-sections of samples were examined with optical microscopy and elemental composition of the particles was determined by XRF and SEM-EDX, while binding media was identified via FTIR in ATR and transmission modes and GC-MS. Historic and contemporary sources were consulted on materials, production, and application of bronze paints.

The project can be found here: https://www.getty.edu/conservation/our_projects/education/cleaning_wooden_gilded/

TERMINOLOGY

Bronze paint, often used to designate any gold-colored paint, is a misleading term, as it contains no bronze. However, other terms like “brass-based paint” do not encompass the whole range of materials used. Hence, the term bronze paint is used as an umbrella term, despite its terminological inaccuracy.

PARTICLE MATERIALS

In the past, most metal-based materials included copper, copper alloys (fig. 4-9), tin (fig. 10), and, since the late 19th century, aluminium (fig. 4, 5). Prior to the increasing use of automated processes of the 19th c., metal particles were made by grinding/milling metal leaf or rolling metal filings. Color was manipulated by alloying, annealing, mixing particles of different materials(fig. 4, 5), and, by the late 19th c., by applying aniline dyes. While the mineral mica (sheet silicate, fig.1-3) was used on altarpieces or architectural elements in the 17th and 18th c., its use in bronze paints drastically increased in the 20th and 21st c. SEM-EDX analysis on the studied frames identified copper-zinc-alloys, a tin-zinc alloy, and aluminium as particles in the bronze paint.

MORPHOLOGY

The morphology of the individual particles influences appearance: the flatter, bigger, and more horizontally aligned the particles, the higher the gloss and opacity. Particle morphology and distribution can be indicative of material, production processes and application method (see image captions). However, it might also influence response to cleaning systems. Thus, cross-sections of samples from mock-ups and original frames were studied with optical microscopy and SEM in preparation for upcoming cleaning tests.

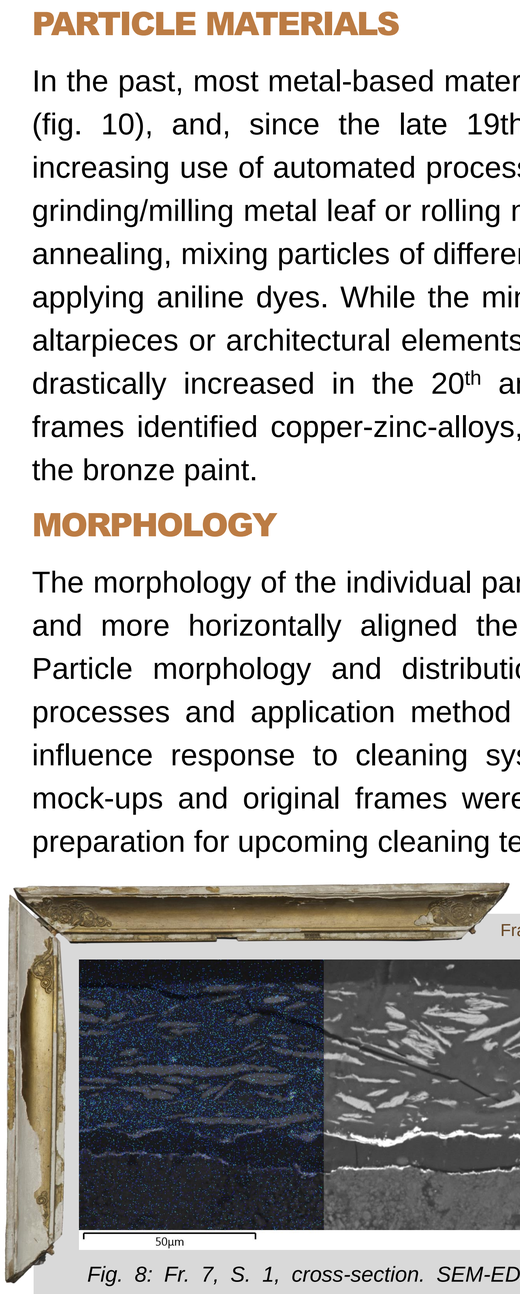

Fig. 8: Fr. 7, S. 1, cross-section. SEM-EDX elemental mapping of lead (left) identified its presence in the binder. BEI (right): The flat copper-zinc alloy particles also show some repeated folds but are shorter than the ones seen on frame 6 (see fig. 4 and 5).

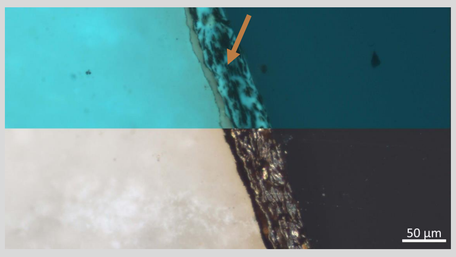

Fig. 9: Fr. 7, S. 1, cross-section photomicrographs, UV 430 nm (above), VIS (below). The “floating” metal particles are less horizontally aligned in the white fluorescing binder than the ones in frame 6 (fig. 4 and 5). The high ratio of binder to particles suggests potentially increased sensitivity to cleaning systems.

Fig. 10: Fr. 2, S. 4, cross-section, BEI. Particles consist of mostly tin and some zinc (SEM-EDX). The layer was burnished after application, as evidenced by the tight arrangement of the particles as well as the surface gloss of the frame in high points. The difference in appearance of the particles in the backscatter electron image is due to metallic versus corroded areas, not differences in flake composition.

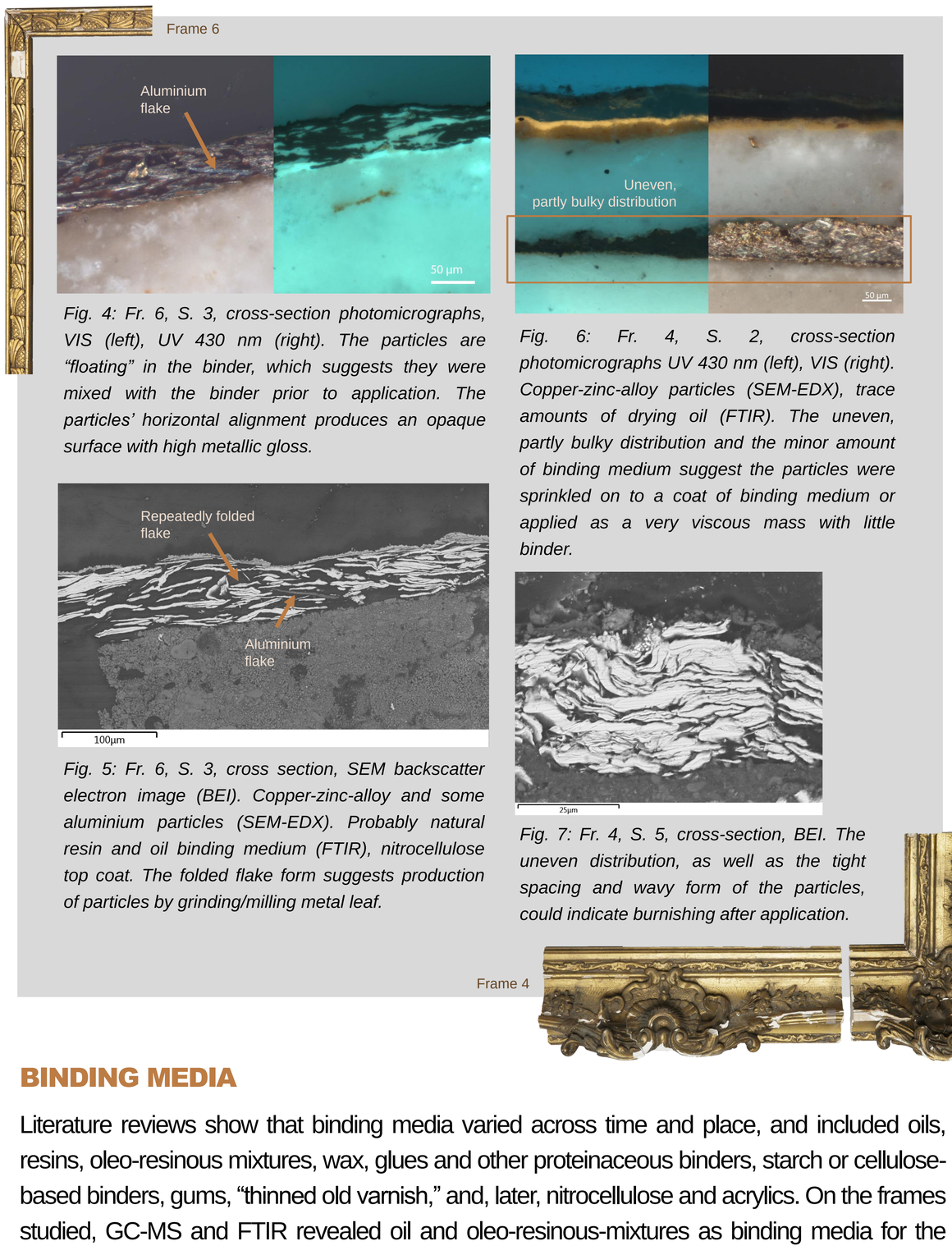

Fig. 4: Fr. 6, S. 3, cross-section photomicrographs, VIS (left), UV 430 nm (right). The particles are “floating” in the binder, which suggests they were mixed with the binder prior to application. The particles’ horizontal alignment produces an opaque surface with high metallic gloss.

Fig. 5: Fr. 6, S. 3, cross section, SEM backscatter electron image (BEI). Copper-zinc-alloy and some aluminium particles (SEM-EDX). Probably natural resin and oil binding medium (FTIR), nitrocellulose top coat. The folded flake form suggests production of particles by grinding/milling metal leaf.

Fig. 6: Fr. 4, S. 2, cross-section photomicrographs UV 430 nm (left), VIS (right). Copper-zinc-alloy particles (SEM-EDX), trace amounts of drying oil (FTIR). The uneven, partly bulky distribution and the minor amount of binding medium suggest the particles were sprinkled on to a coat of binding medium or applied as a very viscous mass with little binder.

Fig. 7: Fr. 4, S. 5, cross-section, BEI. The uneven distribution, as well as the tight spacing and wavy form of the particles, could indicate burnishing after application.

BINDING MEDIA

Literature reviews show that binding media varied across time and place, and included oils, resins, oleo-resinous mixtures, wax, glues and other proteinaceous binders, starch or cellulose-based binders, gums, “thinned old varnish,” and, later, nitrocellulose and acrylics. On the frames studied, GC-MS and FTIR revealed oil and oleo-resinous-mixtures as binding media for the bronze paint. Nitrocellulose was found as an additional coating on frame 6. SEM elemental mapping on frame 7 identified lead in the binding medium, most likely as a siccative (fig. 8).

PRELIMINARY CONCLUSION & FURTHER RESEARCH

The cross-sections revealed distinctive visual differences in the material and morphology of particles as well as their distribution. The instrumental analysis identified both particle and binder materials on select historic frames, providing a basis for evaluating the outcome of future cleaning tests. It may also help in characterizing production and application techniques that can be linked to treatises and manuals. Several metal soaps were identified in multiple instances on the samples, which could warrant additional study of additives and corrosion phenomena. Incidentally, some historic treatises have previously described the corrosive properties of certain binding media in relation to metal particles. Ongoing research will use mock-ups to examine the individual influence of flake morphology, binders, and bronze paint application techniques on cleaning methods.

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ABBREVIATIONS

ATR: Attenuated total reflectance
BEI: Backscatter electron image
C: Century
EDX: Energy-dispersive X-ray spectroscopy
FTIR: Fourier-transform infrared spectroscopy
GC-MS: Gas chromatography-mass spectrometry
SEM: Scanning electron microscope
UV: Ultraviolet light
VIS: Visible light
XRF: X-ray fluorescence

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