Propolis (bee glue): an unusual mordant for gilding in Italian renaissance paintings?

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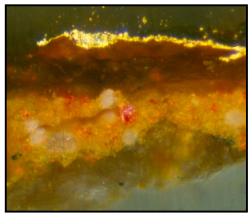
During the recent conservation treatment of a group of three *spalliere* panels painted around 1494 by the anonymous painter known as the Master of the Story of Griselda, we had the opportunity to study these panels in detail and an unusual thick, yellowish, unpigmented mordant was noticed in areas of mordant gilding in all three panels. An extremely similar mordant was found in another work thought to be by the Master of the Story of Griselda, a painting of *Alexander the Great*, from the Barber Institute in Birmingham. It was also found in a work by the Perugian artist Giannicola di Paolo, and in two, slightly earlier, Northern Italian works by Giambono and Vivarini.



Cross-section taken from area of mordant gilding from the Master of the Story of Griselda, *The Story of Patient Griselda, Part III Reunion* (NG 914), c. 1493-1500

Gold leaf was used by Renaissance artists in a variety of ways. Where a highly burnished, reflective finish was required water gilding was used, with a bole layer (a soft iron-containing clay in Italy or an iron oxide mixture in Northern Europe) bound with size (glue). The bole layer imparts a warm colour to the thin gold leaf and provides a smooth, slightly yielding cushion against which to burnish the gold, or to add punched or incised detail.

However for fine details mordant gilding was used which involves applying small pieces of gold leaf on to an adhesive or mordant previously applied to the areas to be decorated. Various materials have been used as mordants, but they are usually yellowish in colour and should dry quickly to allow the mordant to become sufficiently tacky for the gold to adhere. Most documentary sources, including Cennino Cennini, gives recipes for an oil-based mordant based on thickened and pre-polymerised linseed oil mixed with a variety of pigments, of which several are always good driers. The addition of a little varnish is sometimes mentioned also. Mordantgilding has a yellower, more matt surface than water gilding. Other possible adhesives for gold are described in the sources (although some perhaps describe methods for manuscript illumination rather than panel painting) including egg white, gum, size (or glue) or garlic juice mixed with a little bole and lead white (described by Cennino and others).

In some areas in the National Gallery panels the yellowish unpigmented mordant was applied over an orange-brown base paint (composed of orange earth pigment, vermilion and lead white in oil), while in other areas it was applied directly onto the azurite paint layer or onto the gesso. When the mordant was examined by EDX analysis, no inorganic material was detected in the region of the mordant. When examined by FTIR microscopy, a very unexpected spectrum was obtained which did not correspond to any of the oil, proteinaceous or carbohydrate-based materials mentioned in the sources. The IR spectra instead suggest that the mordant is composed of esters of aromatic acids and polyphenolic compounds.

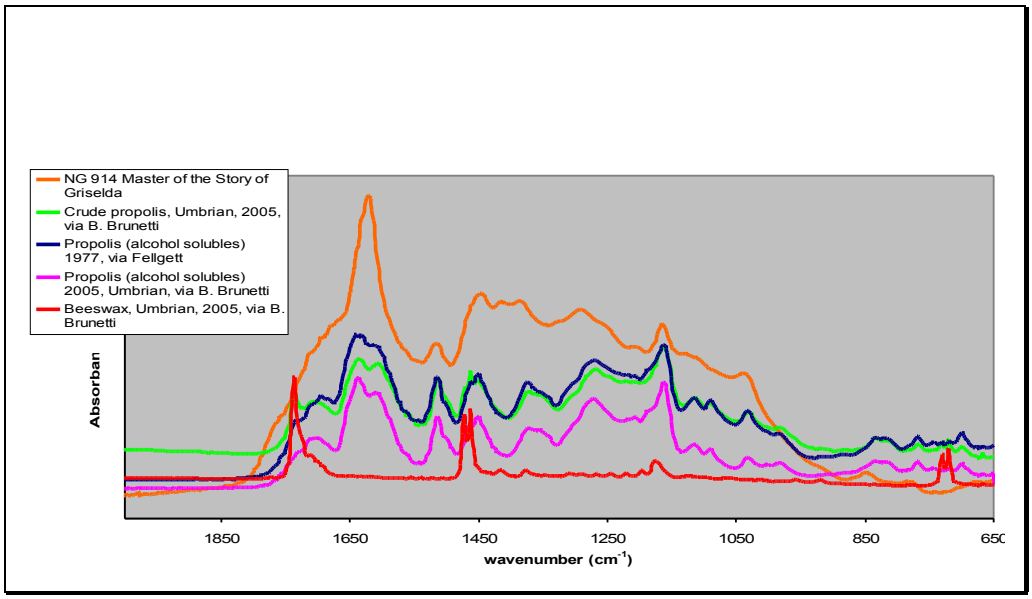
The mordant contained little or no fatty acids, no wax components and no di- or triterpenoid resin components when examined by GC-MS analysis (after derivatisation with TMTFTH). However, a

number of compounds were detected based on hydroxy or methoxy benzoic acids.

Mass spectral data: (TMTFTH derivatisation)

Retention time/mins	B^+, M^+	Component
24.7, 25.2, 25.4	360, 165	Benzoate ester of substituted aromatic alcohol?
23.6, 23.7	358, 165	Dehydrogenated benzoate ester of substituted aromatic alcohol?
15.8	196, 165	Dimethoxybenzoic acid methyl ester
14.1	150, 182	Methyl 4-methoxysalicylate
12.7	135, 166	Methoxybenzoic acid, methyl ester

One material which is rich in polyphenolic components, is sticky and would have been available to artists is propolis (although there appear to be no documentary reference to it use in artworks). Propolis, which is also known as bee glue, is a chemically complex sticky, dark-coloured resinous hive product containing material collected by bees from buds or other plant exudates, volatile substances and beeswax. It is used by bees as a sealant and to protect the nest against micro-organisms. Both Aristotle and Pliny give accounts of propolis – mentioning its medicinal properties. Interest in the material has revived for medical use and much work has been done on the chemical composition because it has been shown to exhibit antibacterial, antiviral, anti-inflammatory,anti-oxidant etc properties. The studies have shown that propolis is a very complex mixture of components – mainly polyphenols including flavonoids, phenolic acids and esters of aromatic alcohols, but also fatty acids, hydrocarbons and terpenes.



Propolis samples give IR spectra that are close to that for the mordant samples, although there are some minor differences. The composition as determined by GC-MS analysis is more divergent however. What is striking is that propolis samples tend to show a parallel series of benzoic and phenylpropenoic (cinnamic) acids and esters with hydroxy and methoxy substituents but only benzoic acid derivatives were found in the mordant samples.

These differences could result from the highly variable nature of propolis, or may be linked to changes that occur on ageing. It is possible that the phenylpropenoic acids and esters could cross-link. If cross-linking occurs then this might explain why only benzoic acid derivatives were detected in the mordant samples.

Of course an alternative explanation is that the mordant is not proplis. Other materials that are also rich in esters of benzoic and cinnamic acids (with corresponding aromatic alcohols) include various

balsamic resins (such as gum benzoin and storax resin). Again these materials were introduced early into Europe, but probably as medicines or as cosmetics or perfumes and have also not been encountered before as mordants. The IR spectra of the mordant samples show similarities to those of various balsamic resins, but the match is not exact.

Further work is required to fully identify this unusual mordant material, including a study of the changes that occur when propolis and balsamic resins age. If suitable mordant samples from paintings become available, it is also intended to try further GC-MS analysis (using silylation but avoiding sample hydrolysis) and to try py-GC-MS analysis.

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