

Varnish technology during the 16th - 18th century: The use of pumice and bone ash as solid driers

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Analytical investigation

In order to better understand the varnish tradition of the 16th-18th century, the original coatings of stringed musical instruments manufactured by various lute and violin makers based in different Italian cities were examined and compared to historic sources. The analytical data unveiled, that the varnishes were made from drying oil and resins from the Pinaceae family, with the addition of pumice and bone ash (Fig. 1). First mentions on the use of these additives as drying agents date back to the time well before violin making.

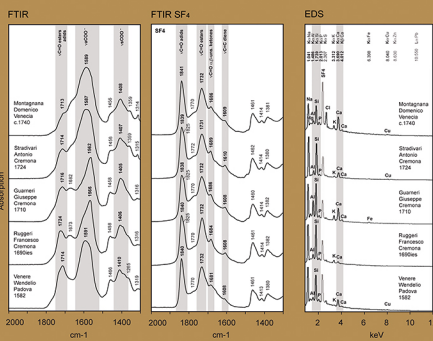


Fig. 1 Analytical data of varnishes. FTIR: spectra of instrument varnish samples. These show very high saponification of the oil/resin varnish. FTIR SF4: After derivatisation with sulfur tetra fluoride, all samples show a similar pattern, indicating comparable composition and aging products. EDS: Energy dispersive spectra with element combinations that support the presence of pumice [Al, Si, Na, K, Ca, Ba, Fe, Mn, Ti] and bone ash [Ca, P] in all samples.

Historical written sources

The genealogy of varnish recipes containing pumice and bone ash as drying aids can be traced back to the Strasbourg manuscript (1400-1412). The "Illumination Book of Boltz von Ruffach" (1549) states: «So notice here, if you want to have a varnish that dries quickly, take sheep bones [...] take the burnt ones and crush it as fine as flour so that it is no longer coarse. Sieve it through a hair sieve and stir the volume of a walnut into the hot varnish [...] so it dries quickly on whatever you spread it on» (Fig. 2). Another recipe refers: «Take white pumice stone and burned sheep bones [...]».

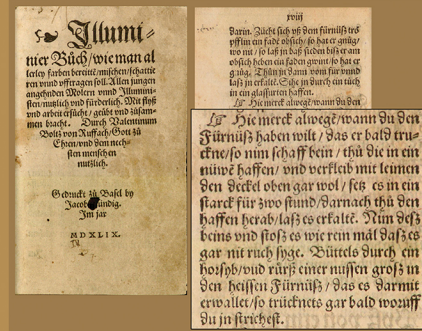


Fig. 2 Detail of a varnish recipe from Boltz von Ruffach (1549) describing the use of bone ash as a drier for varnishes. Similar recipes containing pumice and bone ash can be also found in: „The Strassbourg Manuscript“ (1400-1450), „Mittelheinisches Malerbuch“ (1445), „Colmarer Kunstbuch“ (1478), „de Mayerne Manuscript“ (c. 1615 - 1646), Cröker (1719), and Reinbold (1720), etc.

Reconstruction of historical recipes

To evaluate the effect of pumice and bone ash as drying agents, oil/colophony varnishes containing different amounts of pumice and bone ash (2.5-20% by weight) were produced. The fine powder was simply stirred into the hot varnish as described by Boltz von Ruffach. Due to the fineness of the solid and the high viscosity of the varnish, the components can be mixed to a stable suspension. Varnishes with ground pumice remain quite transparent, since the refractive index of pumice powder (no c.1.50) is very close to that of oil (no c.1.48-1.49) and colophony (no c.1.52-1.55). Depending on the concentration of solids, however, they may show an inherent brownish colour (Fig. 3).

The drying properties were determined gravimetrically. The data show that the raw materials and the composition of the varnish have a great influence on the drying rate. The resin content leads to a considerable acceleration of the drying time. With the addition of finely ground pumice, the drying rate of such varnishes can be increased once again (Fig. 4). However, since only the trace elements of pumice are responsible for the catalytic effect, larger quantities of 10-20% by weight are required for suitable drying.

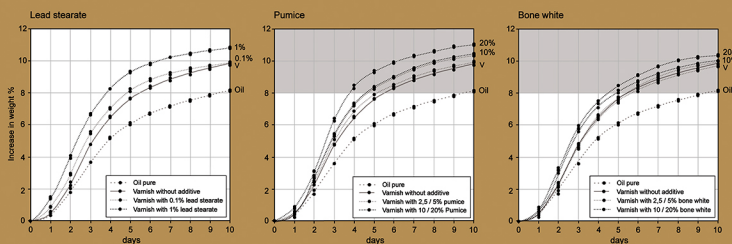


Fig. 4 Increase in weight of varnishes with varying concentration of driers. The measurements were carried out over 10 days after application. At a weight increase of ~8% the surfaces were no longer sticky and the samples were solid (grey area).



Fig. 3 Reconstructions of historical recipes. A) Scanning electron microscope images (SEM-SE) of the pumice stone (glass shards, left) and bone ash (calcium phosphate, right). B,C) Different amounts of the ground solid were added to the varnish. D) 50 µm thick films on glass, and E) varnish films on wood.

Conclusion

The historical varnish technology is of interest to various fields in cultural heritage. To understand the material properties of these historic surface coatings it is important to get insight into the technological background, i.e. the relationship between the material and the processing method. This study has specifically focused on the use of pumice and bone ash often mentioned in historical sources as driers for oil-based coating systems. For this purpose lute and Italian violins from the period between the 16th to the mid 18th century were examined. Both, the main organic composition of the varnish and the addition of mineral additives were considered. Based on the analytical data and the corresponding information from historical written sources, the historical method of siccation of oil-based varnishes was simulated experimentally. The results of these reconstructions confirm that the technological know-how behind these varnishes is far more complex than it may appear at first glance and that the organic and inorganic components must be regarded as a balanced technological system where each of the various components has a specific function. In this context, these inorganic additives effectively induced accelerated drying, improved the mechanical film properties and showed a stabilizing effect on the long-term degradation during aging due to the calcium soap formation [Zumbühl et al. 2020].