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

Stefan Zumbühl[a,*], Balthazar Soulier[a,b], Christophe Zindel[c]

[a] *Bern University of Applied Sciences, Art Technological Laboratory HKB, Fellerstrasse 11, 3027 Bern, Switzerland*
[b] *Atelier Cels, Rue Cels 7, Paris 75014, Île-de-France, France*
[c] *Independent Historian of Art Technology, Switzerland*

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ABSTRACT

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 in the technological background, i.e. the relationship between the material and the processing method. This study has specifically focused on the use of pumice stone 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 siccativation of oil-based varnishes with pumice stone and bone ash 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 of young films and showed a stabilizing effect on the long-term degradation during aging.

1. Introduction

The topic of varnishes is given considerable weight in many historical recipe books on painting techniques. These recipes are mainly the basis for today's ideas on historical craft traditions. Due to the great variety of manufacturing instructions, however, the practical implementation of such recipes is often inconclusive. Complementary support can, nevertheless, be drawn by means of material analysis of original coatings. Yet, a major difficulty lies in the availability of preserved genuine varnishes especially on objects before 1800. One of the sole category of historical artefacts on which the original transparent coatings has been preserved over the centuries are stringed instrument varnishes. Very early on, original varnishes on lutes, viols and violins were held in high esteem and were considered an integral part of the authenticity of the instrument [1]. This is one of the reasons why historical varnishes have been preserved here, while on other objects like furniture and paintings, varnishes were often considered as renewable wear layers [2]. Written sources from the 16th to the 18th century attest that the composition and function of coatings on stringed instruments were fundamentally no different from varnishes on other objects [1,3]. The examination of stringed instruments varnishes is therefore decisive to better understand the technology and behaviour of historical varnishes in general. In recent years, numerous studies have been published with the aim of better understanding the composition of violin coatings [4–17]. Although the analytical results were often comparable, they were interpreted in different ways [12]. While a lot of information has been gained on historic material combinations, many side parameters referring to the manufacturing processes are still in the dark, despite their possibly decisive role. In particular historical practices to increase the siccativity of oil-based transparent coatings has not been thoroughly considered so far. The focus of the study presented here was not primarily set on material analyses per se, but rather on the exploration of the system properties as a whole, i.e. the physicochemical interactions characterising the varnish technology of the 16th–18th century, especially the nature and function of drying agents.

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[*] Corresponding author at: Bern University of Applied Sciences, Art Technological Laboratory, Fellerstrasse 11, CH-3027 Bern, Switzerland.
E-mail address: stefan.zumbuehl@hkb.bfh.ch (S. Zumbühl).

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2. Research aim

In order to better understand the varnish tradition of the 16^{th}–18^{th} century, the original coatings of stringed musical instruments manufactured by various lute and violin makers based in different Italian cities were examined. Both, the main organic and inorganic components were characterised, using micro-samples. These data were the starting point for the study of some technological aspects of historical varnish production in general. In a first step, the material information was verified against historical written sources which form the basis for the following investigations. For this purpose, a comprehensive research on historical varnish recipes was carried out and the genealogy of reliable recipes was traced. The overall focus of this research is to unravel essential principles that are involved in the formulation of historical oil-based varnishes, i.e. the function and system-relevant significance of individual components. First results have shown that the use of solid siccative materials in oil-based varnishes plays an important technological role and should be devoted a specific focus.

3. Experimental

Analysis of historical samples: Micro-samples (c. 10–20 μm) from stringed instruments which are clearly considered as authentic with well-preserved original coatings were collected over the last 10 years and constitute the material resource of this study. Each instrument was comprehensively examined using multispectral (VIS/UV) light sources and a stereomicroscope. The varnish samples were taken at representative and protected locations. In order to exclude contamination as far as possible, micro-samples were taken at several places and sorted out under the light microscope (with epifluorescence contrast). Infrared spectroscopy μ-FTIR was used for the chemical determination of the distinctive organic components. As this study focus on the functional role of the main components, by favouring a statistical approach over the in-depth characterisation of single samples. To increase the spectral selectivity of μ-FTIR, a derivatisation method with sulfur tetrafluoride SF_4 was used, which makes it possible to reliably detect the various terpeneous components on microsamples (less than 20 μm), even in very aged varnishes [19]. However, since the mechanical properties of a varnish material strongly depend on the intermolecular interactions, the segment mobility of the molecules and the degree of cross-linking, it is also of relevance to characterise the oxidation and ageing state. One focus of attention here was the detection of carboxylic acid groups and in particular the carboxylates. The analytical procedure is described in Refs. [18,19]. The FTIR measurements were performed on a Bruker® Hyperion 3000/Tensor 27 infrared spectrometer before and immediately after derivatisation. The micro-samples were analysed in transmission mode at 4 cm^{-1} spectral resolution and 64 scans. At least two samples of each instrument were measured. Following the FTIR measurements, the same samples were transferred to a carbon adhesive for elemental analysis on a Zeiss EVO MA10 scanning electron microscope, equipped with a Thermo NORAN System 7 EDS system. The analyses were performed at 20 KeV and 1 nA excitation in high vacuum mode. Approximately 10 window and point measurements were made in total per sample.

Experimental reconstruction: For the reconstruction, an oil varnish containing solid dryers was produced. Detailed information on historical raw materials can only be derived to a limited extent. Many historical recipes mention different kind of thickened oils, often produced by photooxidative pre-drying. From the different descriptions a honey-like consistency can be assumed. The viscosity is probably a decisive factor, because otherwise the solid additives will settle down. Therefore, a Linseed oil stand oil Kremer (73201) was used for the following experiments. Two parts oil and one part powdered pine colophony (material collection BFH) were heated to c.220 °C for 6 h on a magnetic stirrer. The pumice stone (Kremer 599913) and the bone ash (Kremer 58920) were ground in a mortar, sieved with a 50 μm sieve and added in different amounts (0.125 g, 0.25 g, 0.5 g and 1 g) under continuous stirring to 5 g of hot varnish. The various varnish mixtures were then applied at a film thickness of 50 μm and a width of 13 mm using a Film Applicator Model 360 (Erichsen) on 5 cm long glass slides and a wood panel. The sample weight was c.17+/−1 mg. The samples were aged under light conditions generated by light fluorescence tubes True Lite 5500 K and Philips UV-20W/08 F20 T12 BLB of ≈2100 lm/m^2 and 557 mW $l\,m^{-1}$ at ≈40 °C and atmospheric oxygen content over 10 days. Gravimetric measurements were performed on a Mettler MT5 scale (accuracy: 0.001 mg). The increase in weight was calculated based on the amount of binder (without solids). For cross-sectional analyses, samples of the applied varnishes were embedded in Araldit 2020 epoxy resin and subsequently ground and polished with Micro-Mesh® polishing cloths. The SEM-SE images of the powder particles were made with an excitation voltage of 5 KeV and 100pA, the SEM-BSE Images of the cross-section with an excitation voltage of 20KeV and 200pA. The Wolff-Wilborn scratch hardness test was carried out on four- week old films with pins of hardness 6B, 4B, 2B, B, HB and H.

4. Analytical results

4.1. The organic components of varnishes

To understand the materiality of varnishes, micro-samples were investigated using Infrared spectroscopy μ-FTIR prior to and after derivatisation with SF_4 [18,19]. The obtained spectra show that all samples dated before 1750 are oil-based varnishes. After derivatisation with SF_4, it was possible to assign the main resin component to exudate from the Pinacea family (Fig. 1). In contrast to other diterpene resins, the fairly stable α,β-unsaturated ketones showing νC=O IR-band ≈ 1685 cm^{-1} will form over time in these resins [20]. In combination with the weak νC=C signal of the conjugated diene at ≈1610 cm^{-1}, it is a characteristic markers for the Pinacea resins (pine, larch, fir colophony or terpentine). Other resinous components could not be unambiguously detected in any sample. These results are consistent with previous pyGC-MS examinations by Echard et al. [9]. Drying oil and resins from the Pinaceae family were identified throughout and, in only in few cases any more components were detected [9]. It can be concluded that the instrument makers employed common and readily available oils and resins and that they likely did not employ an unusual or “secret” ingredient, as concluded by Echard et al. for the Stradivari varnish [21]. An overview of the current results unveil (Table 1) that the coatings of instruments from various violin making centres and the different workshops show only minor differences. The same IR pattern indicate the same raw materials which are present in similar relative proportions and showing a comparable oxidation state (Fig. 1D). From a technological point of view it is noticeable that most of the varnishes examined are very strongly saponified and show dominant $\nu_a COO^-$ carboxylate bands (Fig. 1C, Table 1). In general, the degree of saponification can vary significantly. The dominant band lies in the range between 1560–1590 cm^{-1}, with the absorption maximum shifting to higher wave numbers as the degree of saponification increases. It can be assumed that these are primarily organic calcium salts.

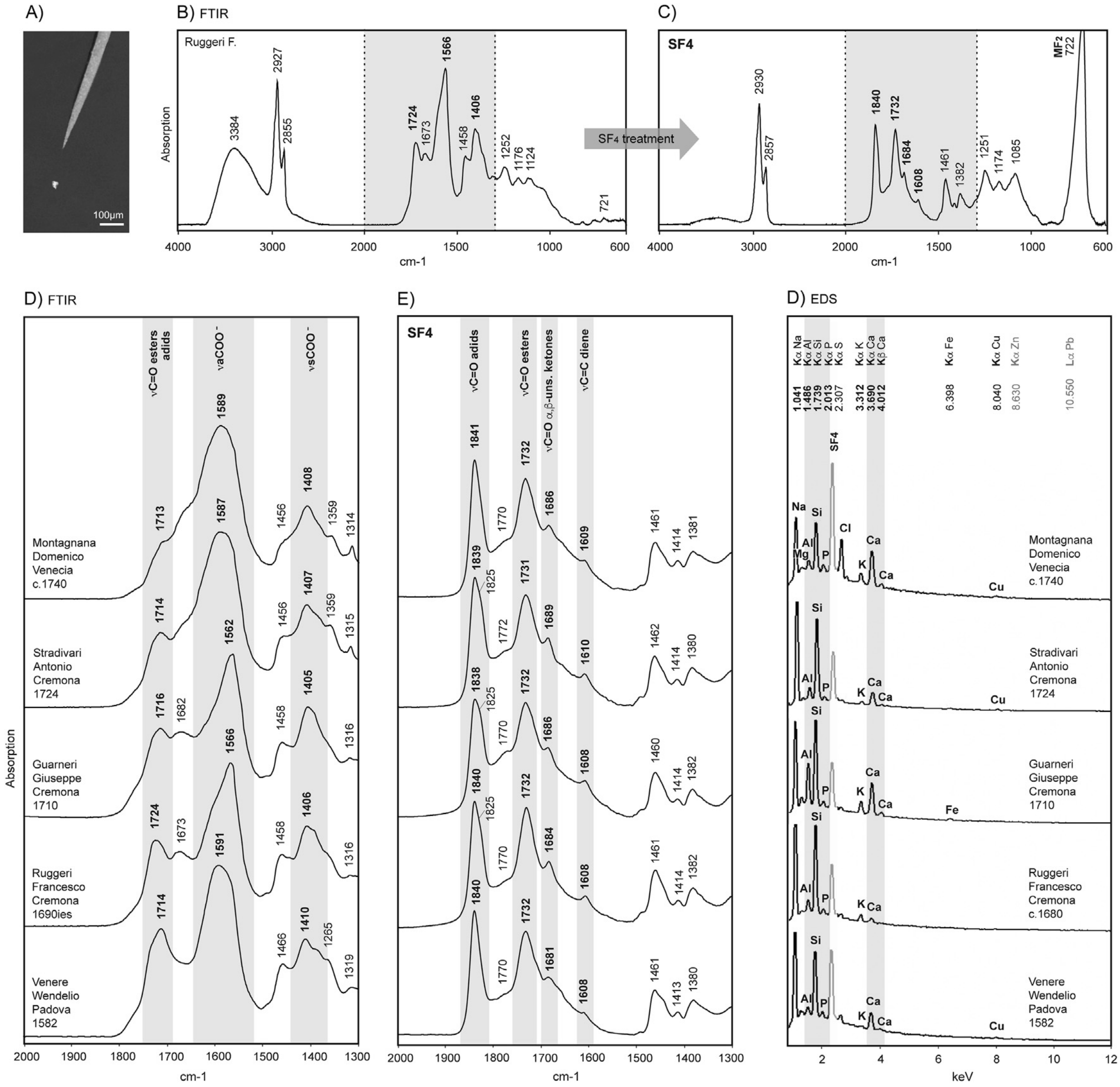


Fig. 1. Infrared spectra of varnishes from different instrument makers, time periods and cities. (A) Typical sample size, (B) FTIR spectrum of a sample prior to derivatisation, (C) after derivatisation with sulfur tetrafluoride (SF_4). (D) FTIR spectra of music instruments: The samples show high saponification. (E) After derivatisation, the samples show a similar pattern, indicating comparable composition and aging products. (D) EDS window spectra.

4.2. Mineral additives in varnishes

The inorganic components were investigated with energy dispersive X-ray spectroscopy. The investigation of the colouring agents which can occur in several instrument varnishes was not attended here. The results (Table 2) correspond to the information from the literature [3,4,6–8,10,12,13]. Alkali silicates in combination with calcium phosphate were detected as the main components in all samples. Bone ash can be determined on the basis of the inter-dependent signal intensities of Ca and P. In general, a heterogeneous distribution of Si, Al, Na, K was found in the examined varnishes. In addition, further minor components and trace elements such as Mg, Fe, Ti, Mn, Cl, and Ba can be detected, which is consistent with other studies [6,8,13]. The mineral components are very finely ground and can have variable morphology [4,10]. These measurements show that in all samples the typical elements and trace elements of ground pumice are present [22–24] (except Cu, which probably is originated from the cooking process, and sometimes NaCl presumably from the use of the instrument) (Table 2). Pumice is a Rhyolite glass froth [23,24] but often contains microcrystalline iron-magnesium silicates. It is thus composed essentially of alkali feldspar and quartz, but much of these silicates may be present as their high-temperature modification [22]. The paragenetic origin of pumice rock is a melt of amphiboles (group of rock-forming, ferromagnesian inosilicates), clinopyroxene (Ca, Fe, Mn-containing inosilicates), various alkali feldspars (such as the Ba, Ca, Na, K-containing plagioclase, tectosilicate), phlogopite (K, Mg-alumo-silicate, phyllosilicate), hauyne (Na, Ca-alumo-silicate with sulfate and chloride anions, tectosilicate of the sodalite group) and titanite (Ca, Ti-silicate, nesosilicate). Titanium is an important indicator for this kind of volcanic products and is typically present in concentrations of around 0.5–3%. Volcanic rock silicates generally have a characteristically fine-grained or aphanitic to glassy texture [22]. Echard et al. [15] observed that the elements of the alumino-silicates and the other minerals in violin varnishes could be detected well, whereas these could not be identified with XRD, which would be consistent with an amorphous, glass-like material.

5. Reconstruction

In order to understand the significance of these analytical results in a wider context, they were compared to historical information. Lead-containing solids like massicot/litharge (PbO) or white

Table 1
FTIR results. The table shows the relevant absorption bands, which are relevant to the identification of the components.

Instrument maker	Place	Date	Typus	Provenance	$\nu C=O$	$\nu_a COO^-$	pinacea resin		MF_2
Instruments from the 16th century									
Maler Laux	Bologna	c.1540	Lute	M. de la musique Paris	Multi-layered system with different composition				
Frei Hans II	Bologna	c. 1570	Lute	KHM Vienna	1710	**1568**	1687	1609	**719**
Frei Hans II	Bologna	c. 1580	Lute	KHM Vienna	1715	**1573**	1685	1608	**722**
Venere Vendelio	Padova	1582	Lute	KHM Vienna	**1714**	**1591**	1681	1608	**721**
Instruments from the 17th and 18th century									
Amati Niccolo	Cremona	1668	Violin	Private collection	**1712**	–	1668	1609	735
Guarneri Andrea	Cremona	1674	Cello	Private collection	**1716**	–	1684	1608	740
Guarneri A. & G.	Cremona	1695	Cello	Private collection	**1716**	–	1685	1608	741
Guarneri Giuseppe	Cremona	c.1700	Cello	Private collection	**1716**	–	1685	1608	731
Guarneri Giuseppe	Cremona	c.1710	Violin	Private collection	1712	**1575**	1685	1610	**723**
Guarneri Giuseppe	Cremona	1710	Violin	Private collection	1716	**1562**	1686	1608	**740**
Guarneri Giuseppe	Cremona	1725	Violin	Private collection	**1716**	**1570**	1686	1607	**741**
Ruggeri Francesco	Cremona	c.1680	Violin	Private collection	1724	**1566**	1684	1608	**722**
Ruggeri Francesco	Cremona	1694	Violin	Private collection	**1712**	–	1685	1608	(734)
Stradivari Antonio	Cremona	1701	Violin	Private collection	1713	**1568**	1686	1609	**741**
Stradivari Antonio	Cremona	1703	Violin	Private collection	**1715**	–	1686	1609	(728)
Stradivari Antonio	Cremona	1710	Violin	Private collection	1710	–	1686	1608	734
Stradivari Antonio	Cremona	1714	Violin	Private collection	1713	**1572**	Protein*		**722**
Stradivari Antonio	Cremona	1720	Violin	Private collection	1709	**1561**	1685	1608	**728**
Stradivari Antonio	Cremona	1721	Violin	Private collection	**1716**	**1566**	1685	1609	**727**
Stradivari Antonio	Cremona	1722	Violin	Private collection	**1713**	**1568**	1684	1609	**736**
Stradivari Antonio	Cremona	1724	Violin	Private collection	1714	**1587**	1689	1610	**720**
Stradivari Antonio	Cremona	1729	Violin	Private collection	**1717**	–	1686	1607	733
Stradivari Francesco	Cremona	1742	Violin	Private collection	**1716**	–	1685	1609	**736**
Stradivari Omobono	Cremona	1740	Violin	Private collection	**1714**	–	1685	1608	734
Rogeri Giovanni Battista	Brescia	1697	Violin	Private collection	1716	–	1686	1609	**729**
Rogeri Giovanni Battista	Brescia	c.1680	Violin	Private collection	1710	**1561**	1684	1607	**734**
Gagliano Allessandro	Napoli	c.1705	Violin	Private collection	**1717**	**1566**	1685	1608	**739**
Cappa Gioffredo	Torino	1696	Cello	Private collection	**1710**	**1567**	1685	1608	**738**
Cappa Gioffredo	Torino	c.1700	Violin	Private collection	**1710**	1562	Protein*		**732**
Bellosio Anselmo	Venezia	c.1770	Cello	Private collection	1711	**1570**	Protein*		**719**
Goffriller Matteo	Venezia	c.1700	Cello	Private collection	1714	**1571**	1688	1610	**719**
Goffriller Matteo	Venezia	c.1725	Cello	Private collection	**1716**	–	1685	1608	(739)
Montagnana Domenico	Venezia	1734	Violin	Private collection	**1714**	**1570**	1686	1609	**719**
Montagnana Domenico	Venezia	c.1740	Cello	Private collection	(1710)	**1589**	1686	1609	**720**
Serafin Santo	Venezia	1752	Cello	Private collection	**1715**	–	1685	1609	734

zinc vitriol ($ZnSO_4$) are often assumed to be present as catalytic components in order to increase the drying rate of oils [25]. Analytical results derived from this substantial series of historical violins revealed, however, that neither lead nor zinc could be detected in any of the samples, meaning that these elements may, if at all, only be present in traces below the detection limit of the method applied (0.1−0.02 wt%, depending on settings). In this context it is interesting to note that many historical sources recommend the addition of bone ash and ground pumice to the oil-resin mixture to improve the drying property. It is therefore of particular interest to look at these historical varnish recipes in more detail.

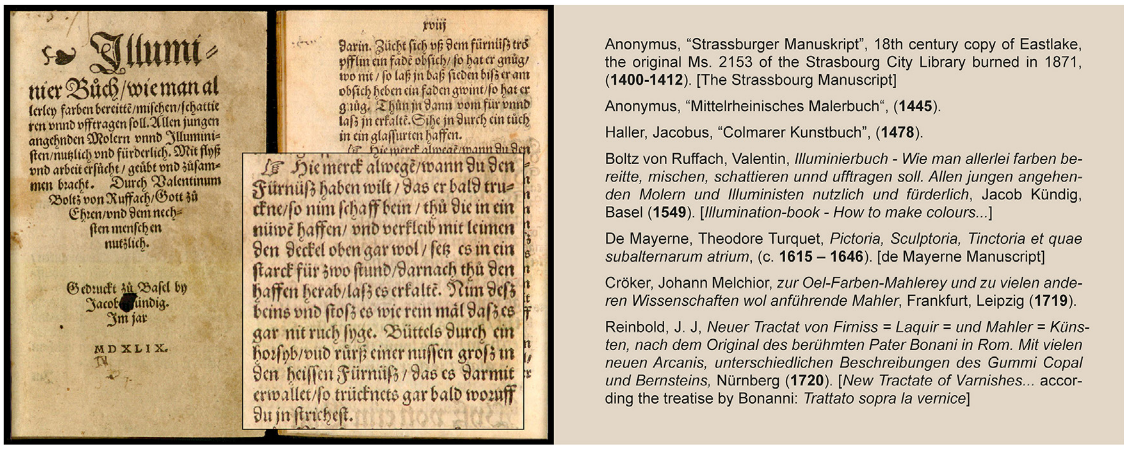
5.1. Historical written sources on the use of mineral siccatives for oil varnishes

The reference to using pumice and bone ash as drying agents for oils occur from the 15th to the 19th century. The genealogy of these recipes can be traced back to the Strasbourg manuscript (1400–1412). In there one learns about the preparation of painting oils: «*Take linseed oil or hemp seed oil or nut oil as much as you want and add burnt bone white and a lot of pumice and let the oil boil*» [26,27]. In the "Mittelrheinischen Malerbuch" (1445) and the "Colmarer Kunstbuch" (1478) [28], this special technique is explicitly mentioned for the formulation of varnishes. In general, these siccatives are used for different oil/resin mixtures. In most cases the driers remain in the varnish. In some cases, such as the Solothurn manuscript (c.1500), the siccative is filtered out after cooking [30]. In the "Illumination Book of Boltz von Ruffach" (1549), both, the production of the raw materials and their use are explained in detail: «*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 it as much as a walnut into the hot varnish* [...] *so it dries quickly on whatever you spread it on*» (Fig. 2) [29,32]. Another recipe is based on both substances: «*Take white pumice stone and burned sheep bones* [...]» [31]. Cröker (1719) also describes this kind of varnish preparation in detail [32], what shows that this method of siccativation had not changed significantly from the 16th to the 18th century. Several other sources of this time go back to the description of Boltz von Ruffach. It is somewhat astonishing that these driers were very common north of the Alps while there is no mention of them in Italian recipe books [33]. This is an interesting point for the understanding of the specific varnish of violin makers. One possible hypothesis is that these recipes may have originally spread to Italy through the migration of the German lute makers starting from beginning of the 16th century. But this historical aspect of music instruments is out of the scope of this paper and will be discussed elsewhere.

An important aspect concern the nature of solids and their admixture. It is apparently important that the solid must be ground very finely. DeMayerne (1615-1646) explicitly writes that these additives must be "as fine as dust powder" [25,34]. This has optical as well as technical reasons. Since the trace elements of pumice

Table 2
Result overview of the element analysis EDS by components. Bold: high concentration, normal: medium concentration, in brackets: low concentration /traces. (*Cu*): The traces of copper are possibly due to the cooking process (pans made from copper). Other compontens: Elements, which were detected in individual particles, not assigned to a specific component.

Instrument maker	Place	Date	Typus	Bone	Pumice		Other components
Instruments from the 16th century							
Maler Laux	Bologna	1540	Lute	Multi-layered system with different composition			
Frei Hans II	Bologna	1570	Lute	Ca	**Si**, Al, **Na**, K,	(Mg), Fe, (Cl)	
Frei Hans II	Bologna	1580	Lute	Ca, ((P))	**Si**, Al, **Na**, K,	(Mg), Fe, (Cl), Ti	**Fe**,Cr
Venere Vendelio	Padova	1582	Lute	Ca, (P)	**Si**, Al, **Na**, K,	(Mg), **Fe**, (Cl), (Mn), (Ti), (Zn), (*Cu*)	**Fe**,Cr
Instruments from the 17th and 18th century							
Amati Niccolo	Cremona	1668	Violin	**Ca,** (P)	**Si**, Al, Na, K	Mg, (Fe), (Cl)	
Guarneri Andrea	Cremona	1674	Cello	Ca, (P)	**Si**, **Al,** Na, K	Mg, (Cl), Ti, (*Cu*)	**Cr**
Guarneri A. & G.	Cremona	1795	Cello	**Ca,** (P)	Si, Al, Na, K	(Mg), (Fe), (Cl), *(Cu)*	
Guarneri Giuseppe	Cremona	c.1700	Cello	**Ca,** P	**Si**, **Al**, **Na**, K	(Mg), (Fe), (Cl), *(Cu)*	**Fe,**Cr
Guarneri Giuseppe	Cremona	c.1710	Violin	Ca, P	**Si**, **Al**, **Na**, K	(Mg), (Fe) (Cl), (Mn), (Ti), Ni,	**Fe**,Cr
Guarneri Giuseppe	Cremona	1710	Violin	Ca, P	**Si**, Al, **Na**, K	(Mg), (Fe), (Cl), (Ti)	
Guarneri Giuseppe	Cremona	1725	Violin	Ca, P	**Si**, Al, **Na**, K	(Mg), (Fe), (Cl), (Ti), (*Cu*)	
Ruggeri Franceso	Cremona	c.1680	Violin	Ca, (P)	**Si**, Al, **Na**, K	(Mg), (Fe), (Cl)	
Ruggeri Franceso	Cremona	1694	Violin	Ca, (P)	**Si**, **Al**, Na, K	Mg, (Cl), (Cu)	
Stradivari Antonio	Cremona	1701	Violin	Ca, P	**Si**, Al, **Na**, (K)	(Mg), Fe, (Cl), (Ti)	
Stradivari Antonio	Cremona	1703	Violin	**Ca,** P	Si, Al, Na, K	Mg, (Fe), (Cl), (*Cu*)	
Stradivari Antonio	Cremona	1710	Violin	Ca, P	**Si**, Al, **Na**, K,	(Mg), (Fe), **Cl,** (Ti)	
Stradivari Antonio	Cremona	1714	Violin	Ca, P	**Si**, Al, Na, K	(Cl), (Ti)	(Au), (Se)
Stradivari Antonio	Cremona	1720	Violin	Ca, P	**Si**, Al, **Na**, K,	Mg, (Cl), (Ni), (Ti)	(Fe,Cr)
Stradivari Antonio	Cremona	1721	Violin	Ca, P	**Si**, Al, **Na**, K	(Mg), (Fe), **Cl,** (Mn), (Ti)	(Fe,Cr), (Au)
Stradivari Antonio	Cremona	1722	Violin	Ca, P	**Si**, Al, **Na**, K	(Mg), **Fe**, (Cl), (Ti), Ba	Cr
Stradivari Antonio	Cremona	1724	Violin	Ca, P	**Si**, Al, **Na**, K	(Mg), (Fe), (Cl), (Mn), (Ti), (*Cu*)	**Fe**,Cr
Stradivari Antonio	Cremona	1729	Violin	Ca, P	**Si**, Al, Na, K	(Mg), (Fe), (Cl), Ni	**Fe**,**Cr**
Stradivari Francesco	Cremona	1742	Violin	Ca, P	**Si**, Al, **Na**, (K)	(Mg), (Fe), (Cl), *(Cu)*, (Ba)	**Fe**,Cr
Stradivari Omobono	Cremona	1740	Violin	Ca, P	**Si**, Al, **Na**, K	(Mg), (Fe), Cl, (*Cu*)	
Rogeri Giovanni Battista	Brescia	1697	Violin	Ca, P	**Si**, Al, **Na**, K	Mg, (Fe), (Cl), (Ti), (*Cu*)	
Rogeri Giovanni Battista	Brescia	c.1680	Violin	Ca, P	**Si**, Al, **Na**, (K)	(Mg), (Fe)	
Gagliano Allessandro	Napoli	c.1705	Violin	Ca, (P)	Si, Al, **Na**, K	(Mg), (Fe), (Cl), (*Cu*)	**Fe**,**Cr**
Cappa Gioffredo	Torino	1696	Cello	Ca, P	**Si**, Al, **Na**, K	(Mg), Fe, (Cl), (Mn), (Ti)	**Fe**,Cr
Cappa Gioffredo	Torino	c.1700	Violin	Ca, P	Si, Al, **Na**, K	(Mg), (Fe), (Cl), (*Cu*)	**Fe**,Cr, Au
Bellosio Anselmo	Venezia	1770	Cello	**Ca,** P	**Si**, Al, **Na**, K	(Mg), **Fe**, (Cl), (Ti)	
Goffriller Matteo	Venezia	c.1700	Cello	**Ca,** P	**Si**, **Al**, **Na**, (K)	(Mg), Fe, (Cl), ***Cu***	
Goffriller Matteo	Venezia	c.1725	Cello	**Ca,** P	**Si**, Al, **Na**, K	(Mg), (Fe), Cl, (Ti)	
Montagnana Domenico	Venezia	1734	Violin	**Ca,** P	**Si**, Al, **Na**, K	(Mg), **Fe**, /**Cl,** (Mn)	**Fe**,Cr
Montagnana Domenico	Venezia	c.1740	Cello	Ca, P	**Si**, Al, **Na**, K	(Mg), (Fe), (Cl)	
Serafin Santo	Venezia	1752	Cello	Ca, P	**Si**, Al, **Na**, K	Mg, (Fe), (Cl), (Ti), (*Cu*)	



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gnůg. Thůn jn dann vom für vnnd
laß jn erkaltẽ. Sihe jn durch ein tůch
in ein glaſſurten haffen.

☞ Hie merck alwegẽ/wann du den
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ckne/ſo nim ſchaff bein / thů die in ein
nüwẽ haffen/ vnd verkleib mit leimen
den deckel oben gar wol / ſetz es in ein
ſtarck für zwo ſtund/darnach thů den
haffen herab/laß es erkaltẽ. Nim deß
beins vnd ſtoß es wie rein mål daß es
gar nit ruch ſyge. Büttels durch ein
horſyb/vnd rürß einer nuſſen groß in
den heiſſen Fürnüß / das es darmit
erwallet/ſo trücknets gar bald woruff
du jn ſtricheſt.

Anonymus, “Strassburger Manuskript”, 18th century copy of Eastlake, the original Ms. 2153 of the Strasbourg City Library burned in 1871, (**1400-1412**). [The Strassbourg Manuscript]

Anonymus, “Mittelrheinisches Malerbuch“, (**1445**).

Haller, Jacobus, “Colmarer Kunstbuch”, (**1478**).

Boltz von Ruffach, Valentin, *Illuminierbuch - Wie man allerlei farben bereitte, mischen, schattieren unnd ufftragen soll. Allen jungen angehenden Molern und Illuministen nutzlich und fürderlich*, Jacob Kündig, Basel (**1549**). [*Illumination-book - How to make colours...*]

De Mayerne, Theodore Turquet, *Pictoria, Sculptoria, Tinctoria et quae subalternarum atrium*, (c. **1615 – 1646**). [de Mayerne Manuscript]

Cröker, Johann Melchior, *zur Oel-Farben-Mahlerey und zu vielen anderen Wissenschaften wol anführende Mahler*, Frankfurt, Leipzig (**1719**).

Reinbold, J. J, *Neuer Tractat von Firniss = Laquir = und Mahler = Künsten, nach dem Original des berühmten Pater Bonani in Rom. Mit vielen neuen Arcanis, unterschiedlichen Beschreibungen des Gummi Copal und Bernsteins,* Nürnberg (**1720**). [*New Tractate of Varnishes...* according the treatise by Bonanni: *Trattato sopra la vernice*]

Fig. 2. Left: Detail of a varnish recipe from Bolz von Ruffach (1549) describing the use of bone ash as a dryiers for varnishes. The book is available in the library of the University of Basel [https://www.e-rara.ch/bau_1/content/zoom/1711022]. Right: Selection of historical recipe books from the 15 to 18th century describing the production and the use of bone ash as a drier for oil-based varnishes. The list contains only the early most important publications, which were copied in the following time period.

minerals are responsible for the catalytic effect, a large surface area and homogeneous distribution is of relevance. However, the amount to be used is not clearly defined anywhere. The Strasbourg manuscript (1400–1412) it simply mentioned "a lot of pumice", while the "Illumination book" by Boltz von Ruffach (1549) states the quantity of a walnut is added to 4 pounds of varnish (c.1.4 kg) [31]. Cröker (1719), on the other hand, suggests equivalent amounts of pumice and resin [32]. Analytical results indicate that the quantity must have been substantial in any case. Such high amounts of additives are not unusual. It is also well-known from the use of glass powder in paints [32,35], which also achieved a certain popularity during the same time period [36–39]. In conclusion it seems, however, that the relative amount of bone ash and pumice stone was an empirical value. Reinbold (1720) [40] wrote: «*You can add as much you like to the hot varnish, but the more you add, the sooner it dries*».

5.2. Reconstruction of historical recipes

In order 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 (Fig. 3B). The fine powder was simply stirred into the hot varnish as described by Boltz von Ruffach [29]. Due to the fineness of the solid and the high viscosity of the varnish, the components can be mixed to a stable suspension. Even after several days, only small amounts of solid material had settled. Varnishes with ground pumice remain quite transparent, since the thin silicate structures transmit light very well [24] and the mean refractive index of pumice powder (n_D c.1.50) is very close to that of oil (n_D c.1.48–1.49) and colophony (n_D c.1.52–1.55). Depending on the concentration of solids, however, they may show an inherent brownish colour (Fig. 3C). The colour depends on the type of pumice and the transparency given by degree of vitrification of the volcanic material (Fig. 4). On the other hand, varnishes with bone ash appear milky, since the refractive index of calcium phosphate (n_D c.1.65) is somewhat higher than that of the organic medium. But of particular importance is the fact that the particles remain evenly dispersed upon drying. Local accumulation of solids on the wood surface was observed in strongly absorbent areas only (Fig. 5A). Although the resulting varnishes have different optical properties (Fig. 3D), they form clear, transparent coatings on wood (Fig. 3E).

5.3. Influence of the resin and siccatives on the varnish properties

It is well known, that the oil/resin ratio and the preparation process have an influence of the processing capability [40,41], but also on the final film properties. Two aspects were thus investigated here, the siccative effect of pumice and bone ash on oil-based varnishes and the change of material properties due to the addition of solids. The drying properties were determined gravimetrically. The catalytic effect of the driers and the resulting increase in weight during oxidation was tested with 50 μm thick varnish films on glass slides (Fig. 6). 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 substantially increased once again. However, since only the trace elements are responsible for the catalytic effect, larger quantities of 10–20% by weight are required for suitable drying properties. The drying time is effectively reduced from six to four days, which corresponds to a classical activation with organic lead salts (Fig. 6).

Since larger quantities of additives are necessary for a good drying effect, this aspect also influences other system properties since this type of solid driers also has filler characteristics. From polymer science [42–44] it is well established that even relatively small amounts of filler particles do have a strong influence on the mechanical properties of elastomers and other polymers [45,46]. The modulus increases with increasing volume percentage of filler up to approximately 20–40 volume percent [47,48]. Especially the particle dimension and the interfacial polymer/solid interactions have a pronounced influence on composite behaviour [48,49]. Thus, in order to qualify this effect, the mechanical strength of the surface was tested with the scratch hardness test according to Wolff-Wilborn. The results showing a clear relationship between a significant increase in resistance of a four week old varnish with growing solid content (Fig. 7). These studies prove that the addition of pumice and bone ashes do influence various relevant properties of the young varnishes. The change in mechanical properties during aging could not be further investigated here. However, these are likely to be significantly influenced by the degree of saponification of the varnishes during ageing. Thus, it can be assumed that the elastic capacity is reduced over decades or centuries. In order to understand the different dependencies it is essential to explore the different aspects more closely in the general context.

6. Discussion

Our current understanding of historical varnishing technology is primarily derived from written recipe collections. With a growing research interest, this knowledge is continuously being supplemented by data from chemical analysis of preserved transparent coatings. While a lot of information has been gained on historic material combinations used for vanishes, while the use of specific processing aids and the related preparation techniques are little studied. It is undisputed that a certain basic knowledge of craftsmanship is required to understand such formulations. This also applies, among other aspects, to the use of driers. While in historical recipe collections, the use of siccatives is usually demonstrated by means of exemplary recipes, this remains unmentioned in many other recipe sources. It is thus assumed that the application is transferable to comparable systems. With this in mind, the varnishes of historical stringed instruments were examined to gain a deeper insight into the varnish tradition of the 16th–18th century.

6.1. Influence of the resin on the drying rate

Analytical data collected suggests that, in principle, that the varnish formulations used for violins are derived from a general varnish tradition. This is not surprising, since the varnish recipes in historical recipe collections are often conceived for a wide variety of applications. Two aspects are to be emphasized with regard to the production of these oil-based varnishes. The analytical data on Italian stringed instruments from different workshops and a wide range of time periods indicates that from the 16th century to the middle of the 18th century an interrelated varnishing technique has remained. The FTIR data suggest that in all cases oil and Pinacea resins were used as the main ingredients in comparable proportions (Fig. 1, Table 1). The resin content is important to increase the glass transition temperture of the varnish and modify optical properties. But up from the 15th century, the resins were also explicitly admixed as a drying accelerator. This means that the photosensitivity and oxidisability of the terpene were of central technological importance. This drying technique for oil paint was first indicated in the Strasbourg Manuscript [50]. In the 16th century it can also be found in Italian sources, as described for example by Armenini [51]. This technique is relevant since the use of many other drying agents was unsuitable to achieve transparent coatings. The widespread opinion that varnishes containing Pinacea resins such as the ẅernice communeӓre to be regarded of lower quality coatings for handcrafts [52] is short-sighted from technological point of view. Thus, the popularity of colophony and Pinacea balsams for varnishes was therefore not only a question of the price and availability, but was probably largely based on technical criteria. Since abietic acid is very susceptible to oxidation [19], these diterpenes show a significantly better drying effect than other resins like Mastic. Gravimetric data shows (Fig. 6), that the resin content has a great influence on the drying behaviour of the oil. The fact that Pinacea resins were important resin raw materials at that time, can also be deduced from the inventory of the Venetian pharmacist and trader of paint materials Jacopo de'Benedetti from 1594. This gives an insight into material trading from the early period of the

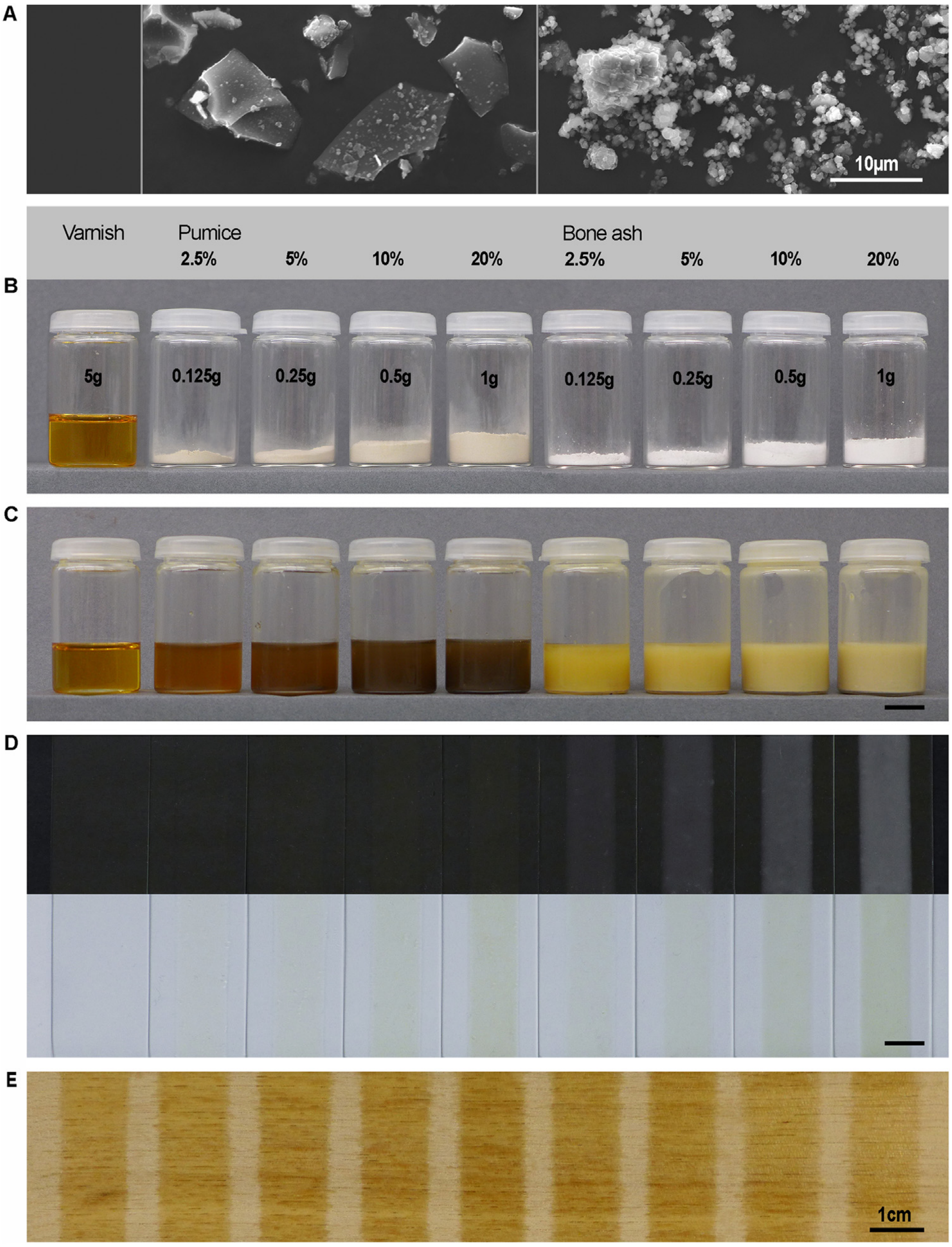

Fig. 3. (A) Scanning electron microscope images (REM-SE) of the powdered pumice stone (left) and bone ash (right). (B,C) Different amounts of the ground solid were added to the varnish. (D) 50 µm thick films on glass, and (E) varnish films on wood.

time window under investigation. The majority of the organic raw materials in his inventory were conifer resins and trading products obtained thereof (including ready-made varnish). Several hundred kilograms of these materials were in stock, while other resins were only available in small quantities or not at all [53].

6.2. Influence of the solid siccatives on the drying rate

A uniformity was also observed with regard to the use siccative. Pumice in combination with calcium phosphate were detected in all varnish samples investigated (Table 2). Contrary to expectations, no elements were found that could indicate the presence of siccatives such as zinc vitriol or lead compounds. Especially the use of pumice makes sense for transparent coatings because its refractive index is close to that of the organic medium and therefore the mixture appears transparent (Fig. 3). This makes evident why this drier is often recommended in in relation to varnishes. It is important to note that the solid must be ground to a very fine powder. This is important to increases the active surface area and allows a homogeneous dispersion throughout the varnish (Fig. 5A). No clear information can be derived from the written sources regarding the amount of additive. Nevertheless, some information could be obtained from the reconstructions. The effect of pumice was much better than that of bone ash. Concluding we may derive that whenever historical recipes refer to use ä lot of pumice, it is probably right to assume that at least 10–20% by weight of drying aids were added.

6.3. Use of solid additives as stabilisers

So far it has been shown that all components have a characteristic function in the varnish system except for bone ash. Calcium compounds are generally poor driers for oil-based systems [54], since calcium exists only in one stable oxidation state.

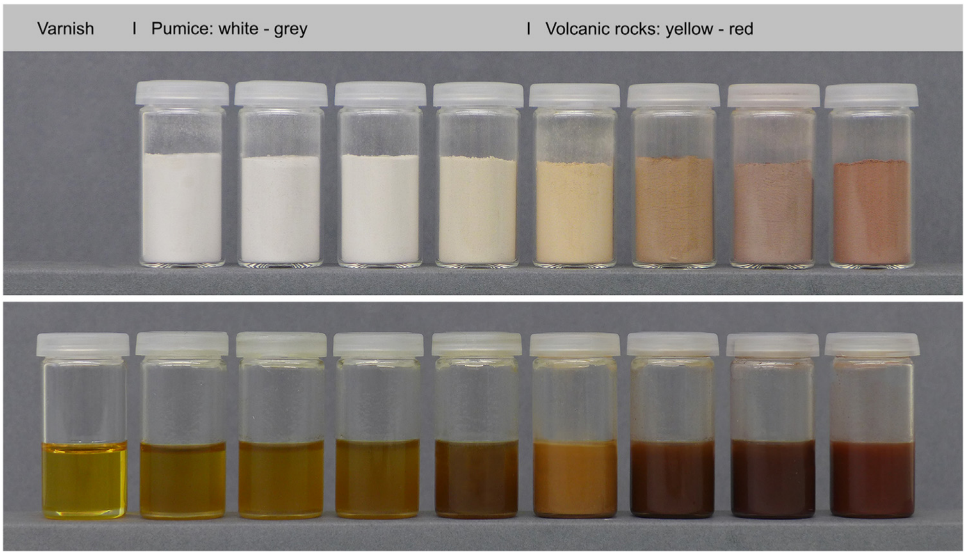

Fig. 4. Varnishes containing 10% of different pumice and coloured volcanic rocks like pozzolanes.

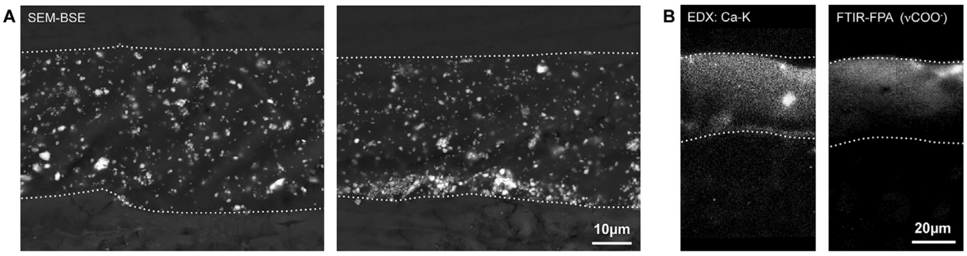

Fig. 5. (A) The SEM-BSE images of cross-sections shows the particle distribution within the varnish. The bone ash quantity is 20%. The particles are evenly distributed within the varnish even after drying (left). Only in highly absorbent areas agglomeration of the particles occur at the interface to the wood. (B) Calcium distribution (Ca-K) and the localisation of the calcium carboxylates (COO^-) in the varnish of lute by Hans Frei c.1540–1565.

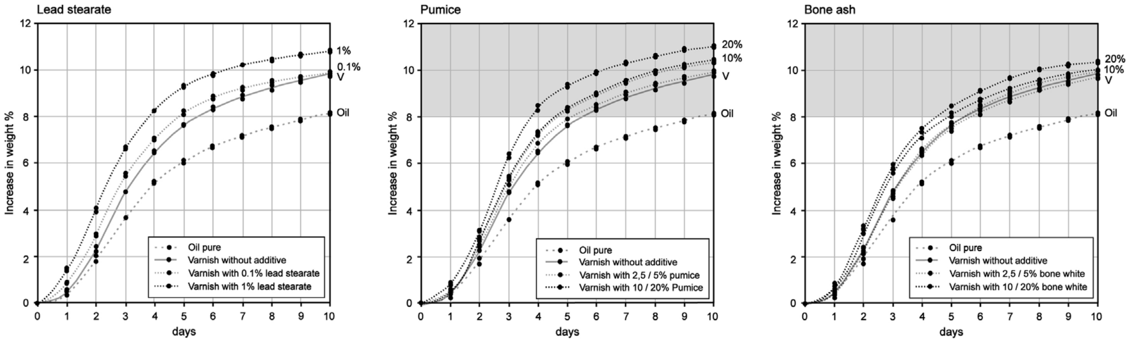

Fig. 6. Increase in weight of varnishes with different concentration of driers (related to the amount of organics). The measurements were carried out over 10 days after application. Oil: Pure oil without resin and additives, oil, V: varnish from oil and colophony, %: Amount of siccative. Each trend curve was determined with two samples. At a weight increase of c.8% the surfaces were no longer sticky and the samples were solid.

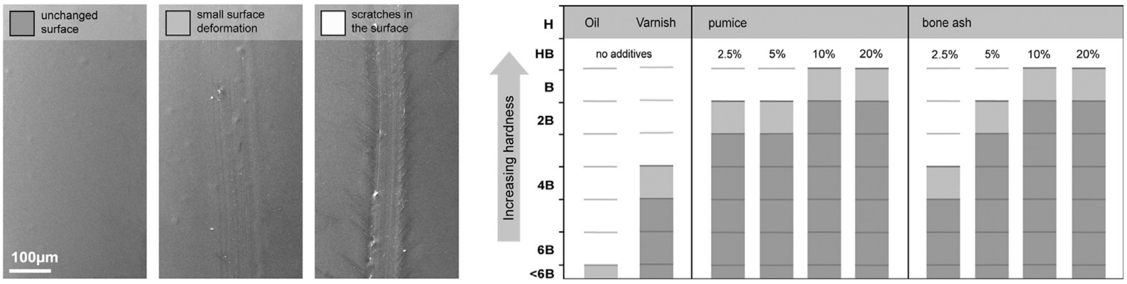

Fig. 7. Scratch hardness test according to Wolff-Wilborn. The surface resistance was determined optically under a stereo microscope.

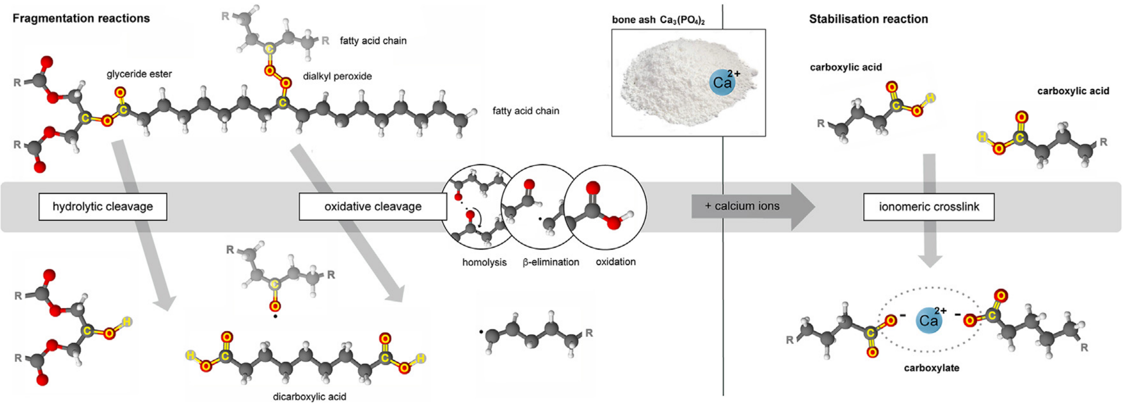

Fig. 8. Characteristic ageing reactions of drying oils (left) and stabilising of degradation products by forming an ionomeric network (right).

As a secondary drier, bone ash can only be used in combination with another drying aid. Furthermore, it has less favourable optical properties than pumice. So, it is even more remarkable why the combination of these two materials is propagated in almost all recipes. Although pumice is generally the main component of solid aggregates, the most analysed also contained calcium phosphate. Thus, the question arises as to what function this component must be assigned. It is noteworthy that many varnish samples were highly saponified (Fig. 1, Table 1). In historical instruments this chemical reaction products were identified as calcium carboxylates (Fig. 5B). Today we are well aware of the fact that ions have a major influence on the mechanical stability of aged oils. In addition to the desired cross-linking, oils and resins are also subject to oxidation and fragmentation reactions during ageing (Fig. 8). Over time, this results in an increased acidity of the system and the formation of low-molecular weight degradation products. These ageing products can only be stabilized by the formation of ionomeric cross-links whereby a stable network is formed in the presence of multivalent cations. (Fig. 8) [55]. Thus, bone ash as a calcium source has a persistent effect on the long-term stability of a varnish. The extent to which craftsmen were familiar with this effect on an empirical basis is speculative, of course. But in any case, from a technological point of view the addition of bone ash as a kind of chemical stabilizer makes perfect sense. Furthermore, it has been shown that these additives also represent a physical stabilization due to their filler characteristics (Fig. 7). It is difficult to state if this increase in mechanical resistance is only a positive side effect of the siccativation or if it even is an intentional optimization of the varnish system, since the studied documents give no information on this aspect. But it is undisputed, however, that craftsmen of the time generally possessed extensive empirical knowledge and probably were well aware with this kind of technological interrelationship.

7. Conclusion

While a lot of information has been gained on historic material combinations used for varnishes, the production process itself is barely studied. The FTIR and EDS data of Italian stringed instruments from different workshops and a wide range of time periods allow an insight into the oil/resin-based coating technique from the 16th to the 18th century. The comparison with historical recipes shows, that these varnishes can be regarded as part of a general manufacturing tradition of different craft trades. The special feature of these systems lies not as much in their materiality itself, but rather in the specific and coordinated interdependency of the individual components. The most samples contained a considerable amount of pumice and bone ash. As we can see from historical written sources, this kind of solids were popular siccatives and additives at that time, as they are almost transparent in oil. The results of the reconstruction confirm that the materiality of instrument varnishes is 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 the various components have a specific function. Fine grained pumice stone acts as a catalyst and showed a good drying accelerating effect, whereas bone ash as a calcium ion source have a stabilizing effect on the long-term degradation due to the formation of ionomeric cross-links during aging. The complex dependency of the individual components could explain why the historical recipes do not change fundamentally during this time period.

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