

EXPERIMENTAL CHARACTERIZATION OF OIL-COLOPHONY VARNISHES: A PRELIMINARY STUDY

Maduka L. WETHTHIMUNI^{1*}, Claudio CANEVARI², Arianna LEGNANI¹,
Maurizio LICHELLI^{1,3}, Marco MALAGODI^{3,4}, Michela RICCA⁵, Alberto ZEFFIRO¹

¹ University of Pavia, Department of Chemistry, via Taramelli 12, 27100 Pavia (Italy)

² Civica Scuola di Liuteria, via Noto 4, 20141 Milano (Italy)

³ University of Pavia, Arvedi Laboratory of Non-Invasive Diagnostics, via Bell'Aspa 3, 26100 Cremona (Italy)

⁴ University of Pavia, Department of Musicology and Cultural Heritage, corso Garibaldi 178, 26100 Cremona (Italy)

⁵ University of Calabria, Department DIMEG, via Pietro Bucci, Arcavacata di Rende, 87036 Cosenza (Italy)

Abstract

Historically, the varnishes had the aim to protect the bowed musical instruments by the external agents and to confer them an aesthetic value. During the 17th and 18th century, in Italy, the bowed instruments, especially violins, were generally covered by a layer of varnish made with several natural materials such resins, oil or hide glue: i.e., instruments by the great violin maker Antonio Stradivari were covered often with a layer of varnish made of linseed oil and colophony in the ratio 3:1, respectively. The main aim of this work was to study the modifications that occur in those kinds of varnishes, after exposing them to some factors of degradation. In order to study the different properties of organic coatings and their suitable compositions, different mixtures of linseed oil and colophony were recreated in the laboratory following an ancient recipe: linseed oil and colophony were mixed together with different ratios (50/50 and 75/25, respectively) and then, they were applied on Maple wood samples and on glass slides for experimental purposes. In order to investigate the different external factors which cause the varnish layer degradation, samples were analyzed by different techniques before and after different ageing processes (thermo-hygrometric cycles, exposition to UV lamp and to acid vapors). Out of strong experimental evaluation, all the results suggested that the composition of 75/25 (oil: colophony) is much better as a varnish for musical instruments.

Keywords: Antonio Stradivari; Varnish; Linseed oil; Colophony; micro FTIR; Hardness; SEM; TGA

Introduction

It is generally known that artworks are covered by varnishes made from different organic compounds. In the past, those organic compounds were generally natural products such as drying oils, essential oils, tree resins and gums, insect resins, dyes, various proteins or polysaccharides, which were used alone or mixed together, possibly purified, pre-treated or diluted in a volatile solvent [1]. Those materials were used on several artworks, even stone ones [2, 3], with the main aim to protect the surfaces. On musical instruments, and especially in bowed ones, the varnishes were applied by the violin-makers to protect the instruments from humidity, dust, mechanical damage, and climate changes, and to enhance its appearance [4]. At

* Corresponding author: madukalankani.weththimuni@unipv.it

the same time, those organic compounds applied on wood could increase the degradation phenomena, especially biological ones [5].

Since the 16th century, the principal binders for the varnishes have been the siccativ vegetable oils, because of their ability to confer to the varnishes a higher gloss and transparence [1]. The siccativ oils most often used for oil varnishes were linseed and walnut oils. These materials contain mainly triglycerides of saturated and unsaturated fatty acids and differentiate from each other only in the relative proportion of fatty acids. Moreover, unsaturated fatty acids undergo a chemical reaction known as auto-oxidation. The process requires oxygen (air) and it is accelerated by the presence of trace metals. Mixtures of siccativ oils and diterpenic resins, especially *Pinaceae* ones, have been the most used for musical instrument since the 17th century, even by the great violin maker Antonio Stradivari for his violins [6]. In fact, the analyses performed on several violins made by the Stradivari highlighted the presence of natural components like linseed oil hardened by natural resins, such as colophony derivatives [7]. Colophony has been used in many coating applications such as adhesives, varnishes and inks, because of fast drying properties, excellent solubility and compatibility with other resins and oils, and ready availability. The principal components of colophony are resin acids, which are mono-carboxylic acids of alkyl hydro-phenanthrene [8]. The resin acids can be divided into two subgroups: the pimaric- type acids and the abietic-type acids [8]. The basic difference between the two groups lies in the substituent at the C-13 position, which is isopropyl in abietanes and vinyl or methyl in primaranes [8, 9]. Several scientific researches showed as, in the varnishes used by Stradivari, the ratio between linseed oil and colophony is 3:1, with the probable addition of colorants [7].

Thanks to those results, today the violin makers are rediscovering this kind of natural, historical varnishes, even with different linseed oil/colophony ratios. In fact, the violin makers are now utilizing varnishes with an increase of the colophony component, even with 1:1 ratio, basically with the aim to confer a higher elasticity to the varnish. It's important to consider that often the violins are played by violinists and this can modify the superficial layers. It's known that the playing routine of the musical instrument can cause different changes to the violin structure [10] and particularly on the varnishes, due to the contact with the player. In fact, it's easy to observe a strong degradation of the organic films on the musical instruments and a consequent widespread worn-out of the varnishes. The principal causes of this degradation are (i) the contact with the acid pH of the skin of violinist, (ii) the combined effect of humidity of sweat and human temperature, and (iii) the exposure to light, especially to its UV component.

The aim of this study is to evaluate whether the current varnishes are better than historical ones, to find out what are the external factors that can cause more degradation to those materials, and to understand which composition of varnish is more useful for conservation. For this purpose, two varnishes were prepared with different ratios between oil and colophony: 50/50 (linseed oil/colophony) mixture, to simulate the varnish used today by violin makers and 75/25 (linseed oil/colophony) mixture, to reproduce the Stradivari's one [9-10]. In order to investigate the degradation processes, the two kinds of varnishes were applied on both Maple wood samples and glass slides and exposed to three different ageing processes for 14 days: (i) humidity (RH) /temperature (T) cycles, (ii) exposition to acid vapor, (iii) exposition to UV lamp. All the ageing processes are in agreement with several standard conditions mentioned in the literature [11, 12]. Finally, properties and performances of varnishes before and after ageing processes were evaluated by colour, contact angle measurements, micro- Fourier transform infrared spectroscopy (FTIR), optical microscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and hardness measurements.

Experimental

Materials

Pure linseed oil (n73054 Kremer) was purchased from Kremer-Pigmente and used without any further purification. Colophony was purchased from Cremona-tools and was used without any further purification. $\text{Mg}(\text{NO}_3)_2$ and HCl (ACS reagent, 37%) were supplied by Sigma Aldrich.

In this work, Maple was used as wood substrate. Maple wood is a hard wood material which carries brighter sound waves well. Hence, it is mainly using for preparing important parts of the musical instruments. Wood specimens (5x5x0.5 cm) were kindly provided by Civica Scuola di Liuteria (Milan, Italy).

Methods

Preparation and application of varnishes

Varnishes were prepared following an ancient recipe [13, 14]. Pure linseed oil was heated temperature until 270°C and was maintained for 3 hours, then, it was cooled to 150°C. At this stage ($T = 150^\circ\text{C}$), milled colophony was added into the cooked linseed oil according to the envisaged oil/resin weight ratio. This mixture was heated again until 250°C for a half an hour. Two kinds of varnishes with different ratios were prepared: 50/50 and 72/25 (linseed oil/colophony). After preparing the varnishes, they were applied on Maple wood specimens and on glass slides (microscope slides) using flat brushes made from boar hair, because these kinds of varnishes are self-levelling. Ultimately, all the samples were dried under UV light for 2 days in order to accelerate the siccative process.

Artificial ageing of samples

All the samples were exposed to three different kinds of ageing processes: acid, thermal and UV ageing. Acid ageing was performed by exposing samples to acid vapour (HCl) for 2 weeks. Here, the samples were kept in a desiccator with 54% of RH obtained by $\text{Mg}(\text{NO}_3)_2$ [15]. Thermal ageing was carried out in a climate chamber at 45°C with 70% of RH for 14 days [16]. In the last case, samples were exposed to UV light for 14 days (halogen lamp power 1000W/m², wavelength (λ): <295nm, and $710 \pm 20\text{W/m}^2$ of average irradiation). During the exposition to UV lamp T was kept at about 45°C and RH at about 28% [17].

Analysing properties of considered varnishes

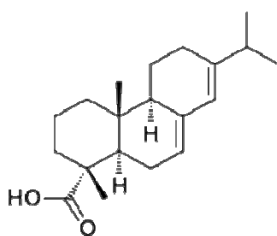
In order to evaluate the properties of varnishes before and after ageing, different experimental techniques were used. Chromatic variations of the wood surface were measured by Konica Minolta CM-2600d spectrophotometer, determining the L^* , a^* and b^* coordinates of the CIELAB space, and the global chromatic variations ΔE^* , according to the UNI EN 15886 protocol [18]. Water contact angle measurements on the wood specimens were carried out by a CAM 200 apparatus (KSV Instruments). Infrared spectra were collected by a Nicolet iN10 Thermo Fischer $\mu\text{FT-IR}$ spectrometer in ATR mode (Germanium crystal). Optical microscope observations of the wood specimens and of the films deposited on glass supports were done using a light polarized microscope Olympus BX51TF, equipped with the Olympus TH4-200 lamp (visible light) and the Olympus U-RFL-T (UV light). Scanning electron microscopy (SEM) images (backscattered electron, BSE) were collected by using a Tescan FE-SEM, operating in both low and high vacuum, samples were platinum-palladium (about 20nm of Pt-Pd) sputtered using a Cressington sputter coater 208HR. Thermogravimetric analyses was acquired with the instrument TGA 1 Star System of Mettler Toledo, in N_2 atmosphere. Hardness was determined by pencil test according to the ISO standard (ISO 15184:1998).

Results and Discussion

Properties of films on glass

The morphological differences of the films before and after ageing cycles were observed by optical microscope and chemical changes due to ageing were studied by micro FTIR analyses. Moreover, a thermo gravimetric analysis was performed in order to evaluate the degradation temperatures of different components present in the varnishes.

In the samples of 50/50 unaged varnish, optical microscope observations show some aggregated materials, probably particles, inside the varnish layer as highlighted in figure 1a, which can be due to either unreacted or undissolved colophony. These particles were found even in the varnish films exposed to acid, thermal and UV ageing (Fig. 1c, e, and g). In thermal aged samples, most area of varnish layer became dark yellow (Fig. 1e). Particles in the UV aged varnish layer turned to black colour may be due to the photo-oxidation of undissolved colophony (Fig. 1g).



Formula of abietic acid

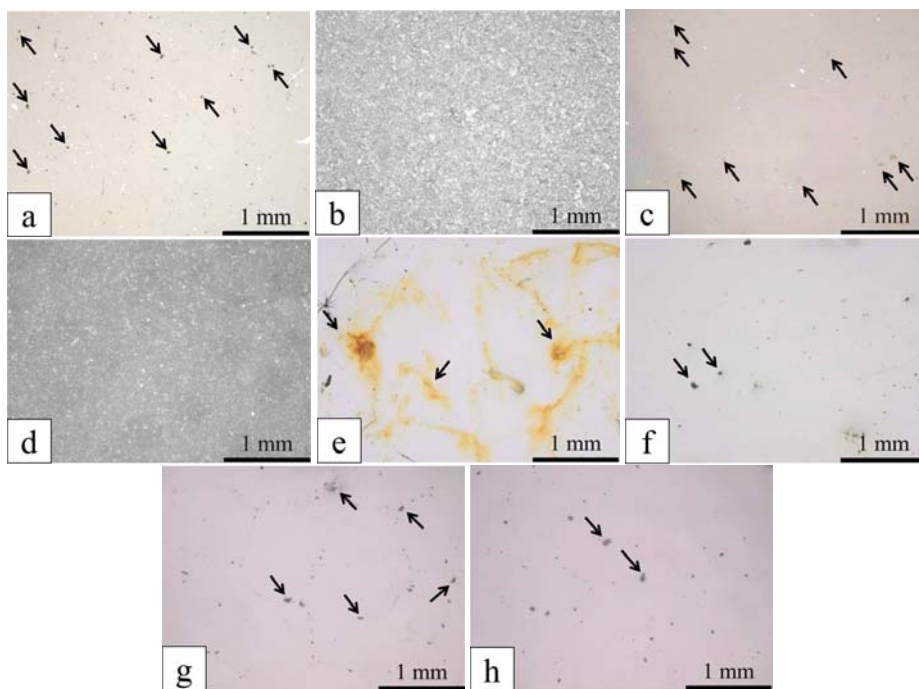


Fig. 1. Optical microscope images of films of both 50/50 and 75/25 varnishes: (a) and (b) unaged, (c) and (d) acid aged, (e) and (f) thermal aged, and (g) and (h) UV aged, respectively

As reported in the literature, when pure abietic acid is exposed to air, temperature, and ultraviolet light, the disappearance of the double-bond chromophore and saturation of the conjugated double-bond system by oxygen can be observed. This first result seems to suggest as the increasing of the colophony in the contemporary varnish induce a lower homogeneity in those film, with the consequent production of areas where the resin tends to settle and, after ageing, to modify the chromaticity of the varnish.

On the contrary, the 75/25 varnish shows a higher homogeneity of the film under the microscope magnifications, with a very few amount of particles of undissolved colophony before and after ageing (Fig. 1b, d, f, and h). All the samples are similar to each other and after thermal ageing, the surfaces of the films appear unaltered and without any dark yellow areas (Fig. 1f). In this case, it's possible to hypothesize that the low amount of colophony in the varnish could facilitate a correct polymerization of the film, in the cross linking process, with the consequence of a stronger layer, more homogeneous and resistant to the ageing cycles.

In order to investigate the chemical changes of varnishes due to the different ageing processes, micro FTIR (ATR mode) analyses were performed. In the 50/50 films, just small differences among all the spectra can be observed, particularly in the fingerprint region (1850cm^{-1} - 675cm^{-1}). For instance, the shape of the broad peak in between 1100 - 1200cm^{-1} due to the overlapping of C-O stretching absorptions of linseed oil and colophony (1164cm^{-1} and 1179cm^{-1} , respectively) [19], becomes less symmetric after thermal and UV ageing (Fig. 2b). These differences could be due to the oxidation process which occurred during different ageing. Moreover, after the UV ageing, more changes can be observed in the varnish layer, particularly, the peak at around 969cm^{-1} which corresponds to C=C bending and the peak at around 745cm^{-1} due to vibrations of carbon skeleton (Fig. 2a and b) [20].

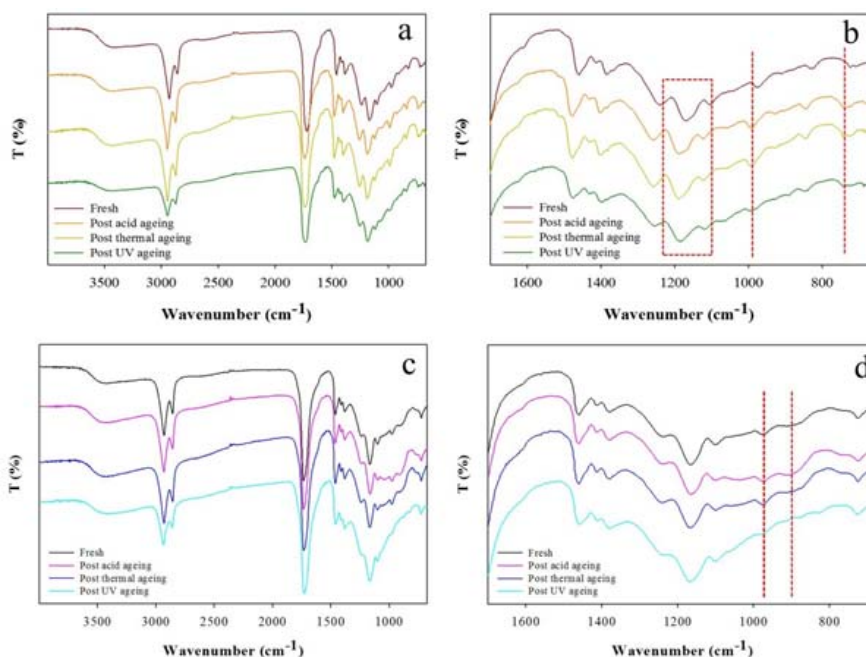


Fig. 2. Micro FT-IR spectra of varnish films before and after ageing in a two different ranges, 4000 - 800cm^{-1} , and 1700 - 675cm^{-1} , respectively: (a) and (b) 50/50 and (c) and (d) 75/25

The FTIR spectra of 75/25 films, before and after ageing, did not highlight strong differences, expect some small absorption shift and shape variations (Fig. 2c and d). Taking into consideration the fingerprint zone, only the UV ageing seems to cause some modification to the varnish, contrary to what is observed for acid and thermal ageing (Fig. 2d). In particular, there is a significant difference in the peak of C=C bending at around 969cm^{-1} .

The measurements of thermogravimetric analysis suggested that pure components (cooked linseed oil and colophony) decomposed at 428°C and 310°C , respectively (Table 1). For instance, the 50/50 mixture presents two different degradation temperatures, ascribable to (i) the heterogeneous film production, (ii) undissolved colophony, presence in the oil matrix (Table 1). The both melting points are caused by the degradation temperatures of colophony and linseed oil, respectively. In thermal aged samples (50/50 varnish), it was possible to see a third temperature degradation at 126°C , that may be due to the loss of deeply absorbed water [21-23]. On the contrary, the varnish of 75/25 shows only two degradation temperatures. It suggested that there is no any water absorbed into this varnish matrix. It may be due to the absence of undissolved colophony in 75/25 varnish. According to this experiment, the samples after UV ageing show the lowest degradation temperature, when compared to other ageing processes (329°C). On the contrary, in the 75/25 varnish, it's evident only one degradation temperature, suggesting a higher homogeneity of the mixture (Table 1). Moreover, even in this case, the strong decrease of temperature is caused more by UV ageing than acid and thermal ageing.

Table 1. Degradation temperatures of pure components and two different varnishes

Films	T/ $^\circ\text{C}$ (50/50 varnish)	T/ $^\circ\text{C}$ (75/25 varnish)
Cooked linseed oil	428	
Colophony	310	
Unaged	374 – 435	431
After acid ageing	340 – 417	421
After thermal ageing	126 – 371 – 426	101 – 419
After UV ageing	329 – 413	417

Properties of treated wood specimens

Chemical properties and morphological aspects of varnishes applied on Maple wood samples were investigated through colorimetric assay, contact angle measurements, optical microscopy, SEM, micro FTIR and pencil hardness test, before and after the ageing cycles. The aim of this section is to investigate the interaction of the varnishes with the wood and to reproduce a real case of study. For instance, the appropriate varnishes are going to introduce to real musical instruments.

First of all, chromatic variations were measured: the first results before the ageing processes seem to confirm that the 75/25 varnish, if compared to the 50/50 one, produces a more homogeneous film displaying a lower interference with the natural colour of the wood (here, the colour difference between treated and untreated wood was calculated: $\Delta E^* = 7 \pm 2$ and 19 ± 9 , respectively) (Fig. 3a). The chromatic coordinates of the varnish film on the wood specimens are affected to a different extent by the accelerated ageing processes. The overall colour changes were evaluated by ΔE^* between aged samples and the corresponding treated unaged samples. The lowest chromatic variation was induced by acid aged samples ($\Delta E^* < 1$), while the highest chromatic variation was registered after exposing to the thermal ageing ($\Delta E^* > 27$) for both varnishes (Fig. 3b). The chromatic coordinates indicate that the b^* component changes more than L^* and a^* , with a visible variation to the yellow-dark colour (Fig. 3b). This tendency has to be considered an important result, if compared with the written sources

contemporary to the making of musical instruments, where the original colour of the surfaces of the historical violins, especially those made by Stradivari, is described to be yellow, transparent and with a gold effect [24]. However, it is important to remember that the varnish is a complex system that comprises mainly different organic compounds, occasionally admixed with inorganic components, altogether interacting, ageing and degrading, with sometimes a very strong inhomogeneity: this system can produce several chromatic variations on the violin surfaces [25].

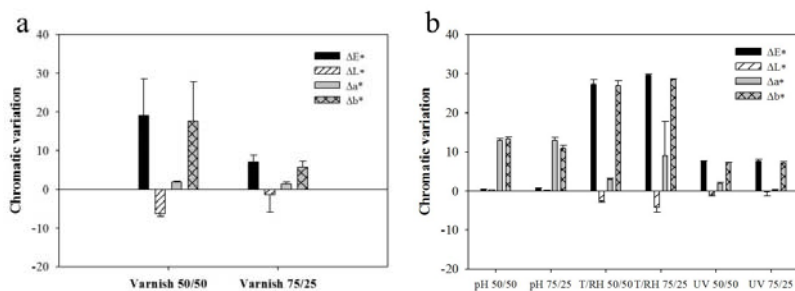


Fig. 3. Chromatic variation of both varnishes after treatments (a) and ageing processes (b)

Contact angle measurements of both 50/50 and 75/25 varnishes were measured in order to study the hydrophobic properties of the varnishes (Table 2). Unexpectedly, no significant changes were observed after ageing of both types of coatings. There is only a stable difference between the two varnishes, with a higher hydrophobic tendency of the 75/25 varnish if compared to 50/50 one. It is because of more linseed oil present in the 75/25 varnish than the 50/50 one. In a common sense, oil is a nonpolar material and it is not making any hydrogen bond with water molecules. So, they have repulsion in between each other. Therefore, oil is a hydrophobic material.

Table 2. Contact angle measurements α ($^\circ$) of wood samples after treatments and ageing

Wood samples	α ($^\circ$) of 50/50 varnish	α ($^\circ$) of 75/25 varnish
Unaged	90 ± 4	116 ± 12
After acid ageing	94 ± 6	111 ± 16
After thermal ageing	98 ± 25	115 ± 22
After UV ageing	90 ± 5	110 ± 17

However, some interesting result comes from the FTIR spectra, where it's possible to suggest that linseed oil has an activating role in the oxidation reactions occurring in colophony compounds, and that conservation state of varnish could be closely related to the composition of the oil/resin mixture. In fact, the concentration of colophony affects the oxidation of the oil, and vice-versa.

From literature, it's well known that the carbonyl absorption peaks of linseed oil and colophony are at around 1741cm^{-1} and 1696cm^{-1} , respectively [26-28]. After ageing some variations in FTIR spectra can be observed both in the C=O stretching region and in the fingerprint zone (see Fig. 4a, b c and d). In particular, it was possible to observe a small shifting ($1717\text{-}1714\text{cm}^{-1}$), different shapes (symmetric shape peaks in both fresh and acid aged samples and in the other cases asymmetric shape peaks) and also broadening of the carbonyl peaks in the 50/50 varnish due to the oxidation of linseed oil (Fig. 4a). On the other hand, the 75/25 varnish acted quite different way in the degradation cycles. Particularly, the oxidation of linseed oil can be noted in the UV ageing (mainly those significant differences can be seen: C=C bending peak

at round 969cm^{-1} ; peak around 818cm^{-1} which is representing the CH stretching; only one peak around 714cm^{-1} with respect to the other graphs; and different shape of carbonyl bands), while in the both thermal and acid ageing, it wasn't possible to observe the degradation of either colophony or linseed oil (see Fig. 4d).

The morphological differences of the treated surfaces were observed by optical microscope and SEM observations. As reported in Figure 5, the two varnishes confer different morphological characteristics to the samples, with an inhomogeneous film in the 50/50 one, before and after ageing processes. In fact, the optical microscopic examination highlighted on the surface a widespread roughness and a lot of deposits of material that are probably ascribable to the colophony not dissolved in the oil. On the contrary, the 75/25 varnish showed a homogeneous coating layer, without precipitates in the film. That confirms again that the 75/25 ratio can produce a more compact and unvarying varnish film (Fig. 5b, d, f, and h). The specimens treated with 50/50 varnish after acid ageing appear to be shinier and reddish (Fig. 5c). The surface of specimens that underwent thermal ageing displays dark brown spots under the varnish layer and different areas dried and melted (Fig. 5e). UV aged samples were morphologically quite similar to the unaged one (Fig. 5g). On the other hand, in the case of the 75/25 varnish after acid ageing, the samples appeared without any superficial modification (Fig. 5d). Even for this varnish after thermal ageing, some significant differences on the surface can be noticed (Fig. 5f), while the layers of varnish 75/25 after UV ageing are still homogeneous (Fig. 5h).

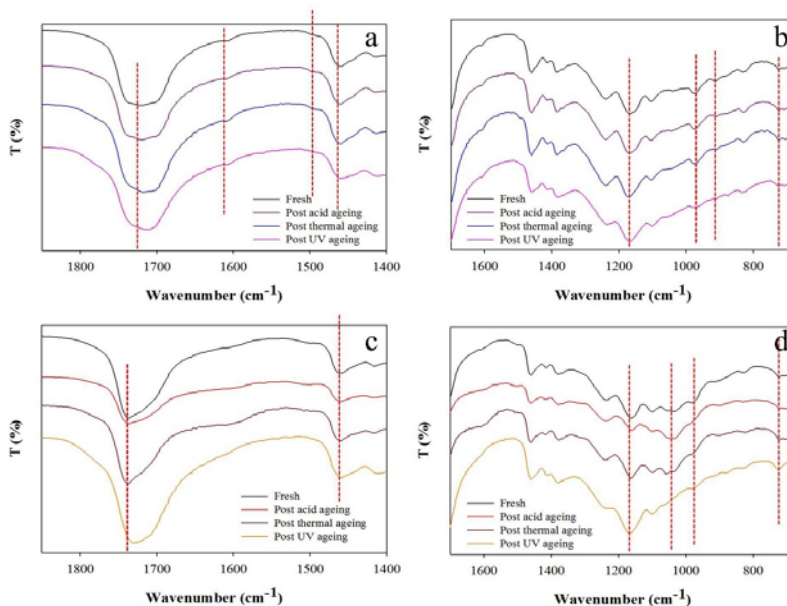


Fig. 4. Micro FTIR spectra of treated wood specimens by varnishes before and after ageing processes in different ranges, $1850 - 1400\text{cm}^{-1}$ and $1700 - 675\text{cm}^{-1}$: (a) and (b) 50/50 and (c) and (d) 75/25

The microscopic morphology of the surface was studied by SEM investigations and the obtained results were compared to those observed by optical microscope. In the case of 50/50 varnish before ageing, a spread layer of the varnish covering the wood surface can be observed which does not allow observing the wood surface (by fiber or cells). The coating is characterized by the presence of white colour particles, ascribable to the un-linked colophony

particles (Fig. 6a). On the contrary, 75/25 varnish seems to interact mainly with the wood surface, possibly due to a deeper penetration in the samples, and the surface appears very similar to the untreated one (Fig. 6b).

The effect of the acid exposition can be well highlighted in the loosing of the covering uniformity of the 50/50 varnish: in fact, differently from the not aged, in this case it's possible to observe the fibers of the wood. The white particles are still spread out present (Fig. 6c).

On the contrary, after the acid interaction, the 75/25 coating seems to be unaltered, compared to the unaged samples, without evidences of corrosion processes of the wood fibers, even at higher magnifications (Fig. 6d). This result seems to confirm the stronger resistance of the varnish with a higher amount of oil to the corrosion processes due to the acidity.

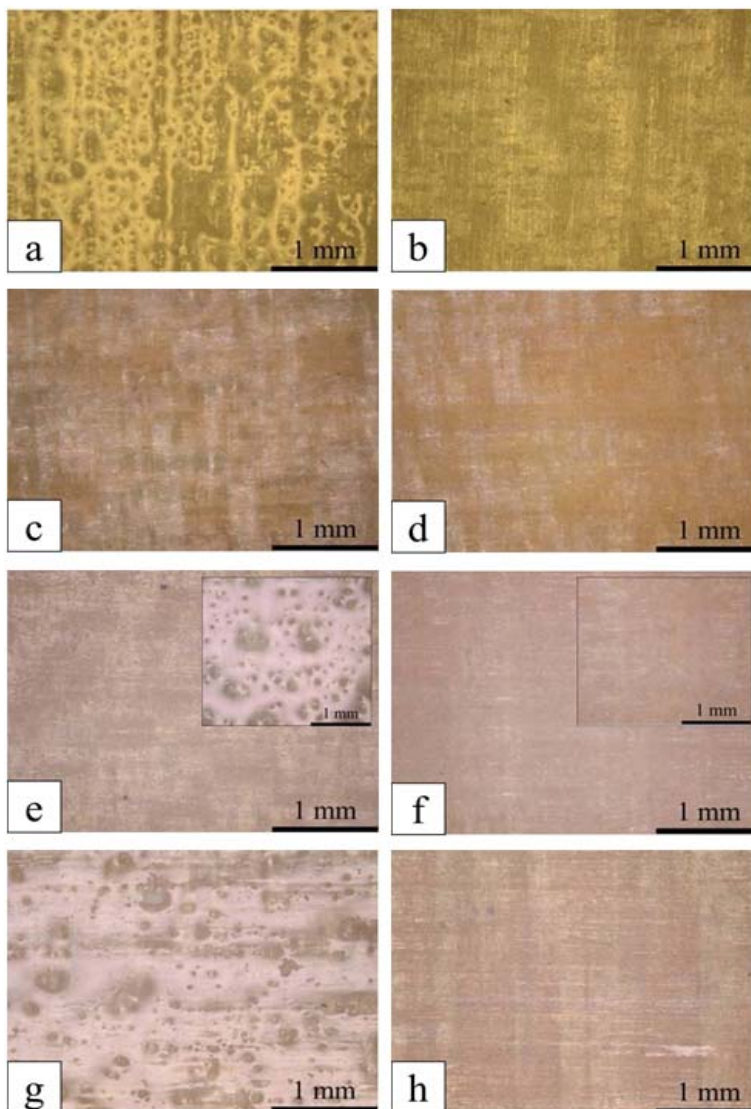


Fig. 5. Optical microscope images of treated wood samples by both 50/50 and 75/25 varnishes: (a) and (b) unaged, (c) and (d) acid aged, (e) and (f) thermal aged (unmelted and melted area in the inset), and (g) and (h) UV aged, respectively

An interesting effect of the 50/50 coating deterioration is due to the thermal ageing, especially if compared with the 75/25 sample. In fact, after the ageing cycles, the surface has totally lost the aspect of the not aged one, with the fibers exposed and evident signs of corrosion (Fig. 6e). The 75/25 surfaces appear with a stronger roughness after the thermal ageing, but in general, there are no significant differences if compared with the not aged one, even at higher magnifications; once again, the varnish with a higher amount of oil seems to produce a good coating and to perform a stronger protection to the hygro-thermal gradients (Fig. 6f).

No significant modifications are disclosed after UV ageing, for both the varnishes (Fig. 6g-h).

The pencil hardness test (*ISO 15184:1998*) was done in order to evaluate the mechanical properties of varnishes. In fact, the main parameters for selecting good varnish are (i) durability of varnish layer on the wood surface, (ii) resistance to the abrasion. Those characteristics are particularly important for this kind of varnishes that historically were applied to musical instruments and that are exposed to mechanical abrasion due to the player. According to the considered standard, the hardness changes from 9H (harder) to 9B (softer) and there is an intermediate level (F) exactly in between those two values (the scale like this: 9B-8B-7B-6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H-7H-8H-9H).

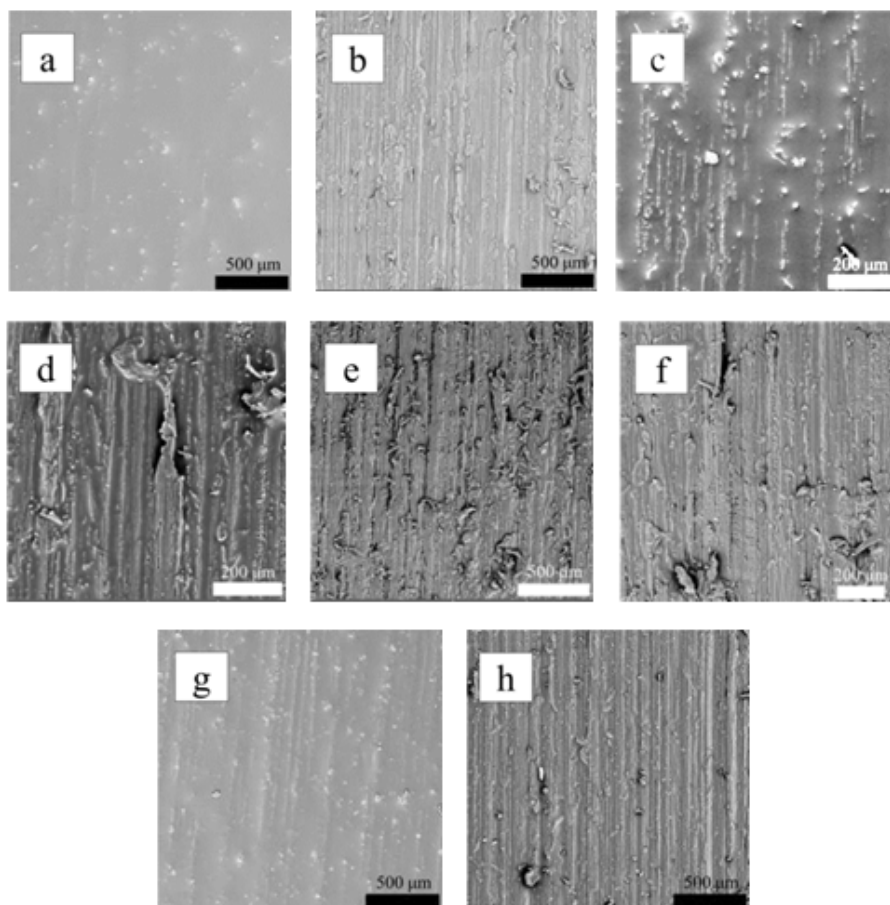


Fig. 6. SEM images of treated wood by both 50/50 and 75/25 varnishes: (a) and (b) unaged, (c) and (d) acid aged, (e) and (f) thermal aged, and (g) and (h) UV aged

The results obtained from the test before ageing process (Table 3) indicate a better performance for 75/25 varnish (hardness is 2H). Moreover, hardness of the varnish layer considerably changed due to the ageing processes. In particular, a lower hardness decrease (softening) was observed after thermal ageing (melted part) in both types of varnishes. The result totally agrees with the results obtained from other analyses, as reported earlier. This behavior seems to be the disappearance of double bonds as well as other changes of both linseed oil and colophony due to oxidation induced by thermal ageing. It means that the varnish layer became softer due to bond breaking and changing the C- skeleton. On the contrary, UV ageing doesn't affect the hardness of 75/25 varnish (the value of hardness remains as before ageing), while it induced a decrease of the hardness of 50/50 varnish. Ultimately, it is worth to indicate that the 75/25 varnish performs way better than the 50/50 varnish.

Table 3. The results of pencil hardness test of treated wood samples by 50/50 and 75/25 varnishes

Wood samples	Hardness of the layer of varnish	
	50/50	75/25
Unaged	H – 2H	2H
After acid ageing	B – HB	H
After thermal ageing – melted area	2B – B	F – H
After thermal ageing – unmelted area	F – H	F – H
After UV ageing	HB – F	2H

Conclusions

A strong experimental evaluation was performed in order to investigate the chemical-physical characteristics of two varnishes with different compositions. The two varnishes were prepared following an ancient recipe: 50/50 (linseed oil/colophony) varnish, just in order to simulate a product used today by violin makers, and 75/25 (linseed oil/colophony) varnish, to reproduce a kind of coating that was spread out utilized during the 16th and 17th century. The varnishes were applied to both Maple wood specimens and glass slides and several analyses were carried out before and after different ageing cycles (UV, thermal and acid expositions).

First of all, colour measurements have shown that the 75/25 composition can produce a varnish with a higher resistance to the chromatic variations. In fact, there were not significant changes in the physical properties of the 75/25 samples after exposure to acid vapors and UV rays; only a drastic chromatic variation happened after thermal ageing, with the consequence of an increasing of the b* component and a dark/yellowish colour.

The results of optical microscopes observations, SEM and TGA experiments are all in good agreement with each other indicating that 75/25 varnish shows a very good homogeneity of the film, both onto the wood surface and glass specimens. These results let us to suppose that this ratio in the varnish can facilitate the polymerization of the film, in comparison with the 50/50 one. In fact, this film appears not homogeneous, with several melted areas and a lot of precipitates and particles spread out in all the varnish, probably ascribable to undissolved colophony. However, TGA results revealed as the UV ageing seems to be the most affecting ageing process for both the varnishes.

Concerning micro FT-IR analyses, the results indicate that both varnishes show some chemical differences in the principal absorption peak after ageing processes, especially in the fingerprint region. Generally, the results are in agreement with the TGA analysis, suggesting as

the UV ageing would be unexpectedly the more aggressive ageing process, even for the 75/25 varnish, followed by acid and thermal ageing processes.

Hardness measurements suggested that the hardest films were obtained by 75/25 mixture before ageing processes. Furthermore, hardness of the varnish layer significantly changed due to ageing processes, indicating that the worst damage was due to thermal ageing in both types of varnishes.

Results obtained confirm that linseed oil performs an activating role in the oxidation reactions occurring in colophony compounds, but just in the 75/25 varnish, and that the performance of films regarding the resistance to the main degradation causes could be closely related to the proportion of resin in the mixture. Questions regarding the contemporary use of 50/50 oil/resin mixtures are still open, but it seems quite clear as a lower amount of resin in the mixture could confer a higher quality and durability to the varnish, especially in the case of the ancient musical instruments that are still played.

Acknowledgements

The authors gratefully acknowledge Dr. Marco Gargano, University of Milano, for his assistance in some analyses. We would like to thank the Civica Scuola di Liuteria, Milan, Italy for supplying wood samples.

References

- [1] J.D.J. van den Berg, *Analytical chemical studies on traditional linseed oil paints*, **PhD Thesis**, University of Amsterdam, 2002.
- [2] D. Miriello, M. Malagodi, S.A. Ruffolo, M.F. La Russa, G.M. Crisci, A. Pezzino, R. Galluccio, D. Barca, E. Marasco, *Diagnostics, deterioration and provenance of stone materials from the Jefferson Page tomb (Non-Catholic Cemetery of Rome, Italy)*, **Environmental Earth Sciences**, **60**, 2010, pp. 829-836.
- [3] M.F. La Russa, S.A. Ruffolo, M. Malagodi, D. Barca, R. Cirrincione, A. Pezzino, G.M. Crisci, D. Miriello, *Petrographic, biological, and chemical techniques used to characterize two tombs in the Protestant Cemetery of Rome (Italy)*, **Applied Physics A: Materials Science and Processing**, **100**, 2010, pp. 865-872.
- [4] A. Lattuati-Derieux, S. Gomes, S. Tirat, S. Thao-Hey, J.-P. Echard, *New insights into molecular evolution of oil/colophony varnishes: towards pyrolysis-gas chromatography/mass spectrometry based quantitation*, **e-Preservation Science**, **11**, 2014, pp. 53-63.
- [5] M. Clausi, G.M. Crisci, M.F. La Russa, M. Malagodi, A. Palermo, S.A. Ruffolo, *Protective action against fungal growth of two consolidating products applied to wood*, **Journal of Cultural Heritage**, **12**(1), 2011, pp. 28-33.
- [6] M. Malagodi, C. Canevari, L. Bonizzoni, A. Galli, F. Maspero, M. Martini, *A multi-technique chemical characterization of a Stradivari decorated violin top plate*, **Applied Physics A: Materials Science and Processing**, **112**(2), 2013, pp. 225-234.
- [7] B. Brandmair, S. P. Greiner (editors), **Stradivari Varnish: Scientific analysis of his finishing technique on selected instruments**, London and Munich, 2010.
- [8] J.P. Echard, L. Bertrand, A. von Bohlen, A.-S. Le Hô, C. Paris, L. Bellot-Gurlet, B. Soulier, A. Lattuati-Derieux, S. Thao, L. Robinet, B. Lavédrine, S. Vaiedelich, *The nature of the*

- extraordinary finish of Stradivari's instruments*, **Angewandte Chemie International Edition**, **49**, 2010, pp. 197-201.
- [9] G.F. Chen, *Developments in the field of rosin chemistry and its implications in coatings*, **Progress in Organic Coatings**, **20**, 1992, pp. 139-167.
- [10] J.R.-Noguera, F.C.B.-Galiano, J.M.R.-López, M.A. F.-Vivas, I.M.-Sánchez, *Study of biodegradation of diterpenic varnishes used in art painting: Colophony and Venetian turpentine*, **International Biodeterioration and Biodegradation**, **62**, 2008, pp. 427-433.
- [11] J.P. Echard, C. Benoit, J. Peris-Vicente, V. Malecki, J.V. Gimeno-Adelantado, S. Vaiedelich, *Gas chromatography/mass spectrometry characterization of historical varnishes of ancient Italian lutes and violin*, **Analytica Chimica Acta**, **584**(1), 2007, pp. 172-180.
- [12] M. Fioravanti, G. Goli, B. Carlson, *Viscoelastic and mechano-sorptive studies applied to the conservation of historical violins: A case study of the Guarneri "del Gesù" violin (1743) known as the "Cannone"*, **Journal of Cultural Heritage**, **14**, 2013, pp. 297-303.
- [13] P. Baraldi, **Manoscritto Bolognese 2861 (XV secolo)**, Biblioteca Universitaria di Bologna.
- [14] F.Frezzato, C. Seccaroni, **Segreti di arti diverse nel Regno di Napoli – Manoscritto It. III 10 della Biblioteca Marciana di Venezia**, Il Prato, Saonara (PD), 2010.
- [15] L.T. Gibson, C.M. Watt, *Acetic and formic acids emitted from wood samples and their effect on selected materials in museum environments*, **Corrosion Science**, **52**(1), 2010, pp. 172-178.
- [16] M. Lazzari, O. Chiantore, *Drying and oxidative degradation of linseed oil*, **Polymer Degradation and Stability**, **65**(2), 1999, pp. 303-313.
- [17] D. Scalarone, M. Lazzari, O. Chiantore, *Ageing behaviour and pyrolytic characterization of diterpenic resins used as art materials: colophony and Venice turpentine*, **Journal of Analytical and Applied Pyrolysis**, **64**(2), 2002, pp. 345-361.
- [18] * * *, **Conservazione dei Beni Culturali - Metodi di prova - Misura del colore delle superfici**, UNI EN 15886:2010.
- [19] C. Daher, V. Pimenta, L. Bellot-Gurlet, *Towards a non-invasive quantitative analysis of the organic components in museum objects varnishes by vibrational spectroscopies: Methodological approach*, **Talanta**, **129**, 2014, pp. 336-345.
- [20] C. Daher, C. Paris, A.S. Le Hô, L. Bellot-Gurlet, J.P. Echard, *A joint use of Raman and infrared spectroscopies for the identification of natural organic media used in ancient varnishes*, **Journal of Raman Spectroscopy**, **41**(11), 2010, pp. 1494-1499.
- [21] E.P. Favvas, E.P. Kouvelos, S.K. Papageorgiou, C.G. Tsanaktsidis, A.C. Mitropoulos, *Characterization of natural resin materials using water adsorption and various advanced techniques*, **Applied Physic A**, **119**(2), 2015, pp. 735-743.
- [22] S. Boyatzis, E. Ioakimoglou, P. Argiti, *UV Exposure and Temperature Effects on Curing Mechanisms in Thin Linseed Oil Films: Spectroscopic and Chromatographic Studies*, **Journal of Applied Polymer Science**, **84**(5), 2002, pp. 936-949.
- [23] M.K. Dubey, S. Pang, J. Walker, *Oil uptake by wood during heat-treatment and post-treatment cooling, and effects on wood dimensional stability*, **European Journal of Wood and Wood Product**, **70**(1), 2012, pp. 183-190.
- [24] S.F. Sacconi, **The "Secrets" of Stradivari**, Libreria del Convegno, Cremona (CR), 1979.
- [25] L. Bertrand, L. Robinet, S.X. Cohen, C. Sandt, A.S. Le Hô, B. Soulier, A. Lattuati-Derieux, J.P. Echar, *Identification of the finishing technique of an early eighteenth*

- century musical instrument using FTIR spectromicroscopy*, **Analytical and Bioanalytical Chemistry**, **399**, 2011, pp. 3025-3032.
- [26] J. Mallégo, J.L. Gardette, L. Jacques, *Long-term behaviour of oil-based varnishes and paints I. Spectroscopic analysis of curing drying oils*, **Journal of the American Oil Chemistry Society**, **76**(8), 1999, pp. 967- 976.
- [27] J. Mallégo, J.L. Gardette, L. Jacques, *Long-term behaviour of oil-based varnishes and paints. Photo- and thermooxidation of cured linseed oil*. **Journal of the American Oil Chemistry Society**, **77**(3), 1999, pp. 257-263.
- [28] V. Beltran, N. Salvadó, S. Butí, G. Cinque, *Micro infrared spectroscopy discrimination capability of compounds in complex matrices of thin layers in real sample coatings from artworks*, **Microchemical Journal**, **118**, 2015, pp. 115-123.
-

Received: August, 10, 2016

Accepted: September, 25, 2016