A Recreation of the Particulate Ground Varnish Layer Used on Many Violins Made before 1750

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Abstract

The results of research by a number of writers are summarized and additional research by the authors is presented. The acoustic function of the ground varnish is discussed. A case is made that the ground varnish should have the lowest possible penetration into the wood. Emulsion varnishes have lower penetration than solvent-based varnishes. It is proposed that the ground varnish layer widely used before 1750 consisted of an oil-resin mix, emulsified with glue and stabilized by the addition of clay particles. This was applied directly to the wood and acted as both sealer and ground. The method of making and applying such a varnish is described. The physical and chemical properties of this varnish are similar to those measured on classical instruments.

String instruments made throughout Europe from the earliest times were varnished in a way that violinmakers in modern times have been unable to reproduce. These varnishes were not all the same everywhere, but they show certain common features that suggest that they were made broadly in the same way. After 1700 the use of these varnishes began to die out, surviving longer in some places than others, and by about 1750 their use had all but disappeared. Despite persistent efforts since about 1800, no recreation of this classical varnish, especially the ground layer, has been attained.

There was always a ground varnish and this was probably overlaid with a finishing varnish that was clear for many makers, while for others it was colored. Where the top layer is colored, its loss by wear exposes the ground varnish, often with a very attractive appearance. Photographs taken with an electron microscope reveal that the ground layer varnish is distinctly different from the top layer varnish. Some of these photographs show a ground varnish with no top varnish, but the absence of the top layer is very probably due to it having worn off. This paper is only concerned with the ground layer varnish, which is considered by many to have the greatest influence on the tonal quality of the instrument.¹

Several researchers have discovered useful facts about the nature of the ground layer of classical violin varnishes. This paper begins with an examination of this knowledge, to which we add some of our observations about the acoustic requirements of violin varnish. Assembling all this information points to the varnish being a pre-polymerized oil-resin mix, emulsified with glue, stabilized by the addition of clay particles, and diluted with water until it can be spread onto the instrument with the thumb. An emulsion is a stable combination of oily and aqueous ingredients whose close integration is maintained by emulsifying and stabilizing agents. In an emulsion, fine droplets of the aqueous medium can disperse into the oily medium to form a water-in-oil emulsion, or fine droplets of oil can disperse into the aqueous (water) medium to form an oil-in-water emulsion.

WHAT DO WE KNOW ABOUT THE GROUND VARNISH?

What does it look like?

Classical ground layers come in a variety of colors and these can all be reproduced by the traditional methods of pre-polymerizing an oil-resin mix. When pre-polymerization is achieved by low-temperature cooking or sun thickening, it appears to have a pale yellow color. This color is seen in the Amati varnish and in the ground layer used by Stradivari, Guarneri *del Gesù*, and the Cremonese school in general. Cooking at higher temperatures produces the darker colors seen on some old instruments.

Many writers have described the ground varnish used by classical makers as having exceptional transparency. While we agree that the ground has distinctive visual characteristics, we do not consider the transparency to be exceptional. Fry [1] describes the ground used by the Cremonese makers as being dichroic: appearing yellowish in thin areas and reddish-amber in thick areas, depending on the method of wood preparation and the viewing angle. This has been said to result from the varnish being birefringent, which means it has two refractive indices. Condax [2, 3] used the term "dichroism," but he demurred from saying the varnish is birefringent. We consider this still to be a matter of uncertainty, although again we do not deny that the varnish is very attractive.

What does it look like microscopically?

Barlow and Woodhouse [4] have published several electron microscope pictures of cross sections through the varnish films. In Fig. 1, the wood is split along the grain. Figure 1a, an example from P. Rombouts of Amsterdam, shows that two different types of varnish have been applied. Figure 1b shows a cross section through the ground varnish on a Stradivari. The appearance of these ground layers is typical of instruments made in Italy and northern Europe from 1550 to 1750. Not all the samples tested had the particulate layer, but significantly, the three Stradivari samples tested did have it. Others may have lost it by wear. The thin upper layer (on the Rombouts sample) has a cross section rather like a piece of broken glass or toffee. All conventional oil or spirit varnishes break, exposing a fracture surface similar to this. Figure 2 shows a cross section through a solvent-borne varnish film, i.e., a solvent-thinned oil varnish or a spirit varnish film.

The classical ground varnishes have a very different appearance at the broken faces than do solvent-borne varnishes. The surface looks more like a broken biscuit and appears to contain a lot of discrete particulate material. These particles appear to be held together with some sort of binder.

Another characteristic of the ground layer, which is not clearly demonstrated in these pictures but which was noted by Barlow and Woodhouse [4] after studying many examples, is the lack of penetration of the varnish into the wood. It has been suggested that the penetration of solvent-borne oil varnish into unsealed wood varies with the formulation of the varnish, but from our observation of electron microscope pictures, this penetration is comparatively enormous.

It is not possible to see any evidence of the presence of a sealer under the ground in any of these pictures. Had a sealer been used, one would expect to see some discrete layer of it somewhere, albeit very thin. None of these pictures shows any such layer.

What is the particulate material?

By using Energy Dispersive Analysis by X-rays (EDAX), Barlow and Woodhouse [4] determined that the particles contained elements consistent with them being mineral material. The elemental composition of this mineral material varied widely from one sample to another, even within samples of varnish by the same maker. Barlow et al. [5] reported that most of the particles have diameters less than $4 \,\mu m$ and are rough in shape, some being nearly spherical. From our observation of the pictures made by Barlow and Woodhouse [4] and the accompanying EDAX analysis, we suspect that the particles are of soiltype minerals that have undergone weathering, possibly various clays and siliceous material. Although clay particles, particularly kaolinite, generally have a flat, plate-like morphology, weathering tends to blunt the corners of the plates. The wide variation in the mineral content of the particulate matter suggests that its function is not likely to be a chemical one.

Mayer [6] noted that emulsions can be stabilized by the addition of finely divided particulate material. It is, for example, commonly known that ground pepper will help stabilize a dressing made as an emulsion of olive oil and vinegar. If the components of the ground layer were bound together by an emulsion, the presence of the particulate material might be an effective stabilizer.

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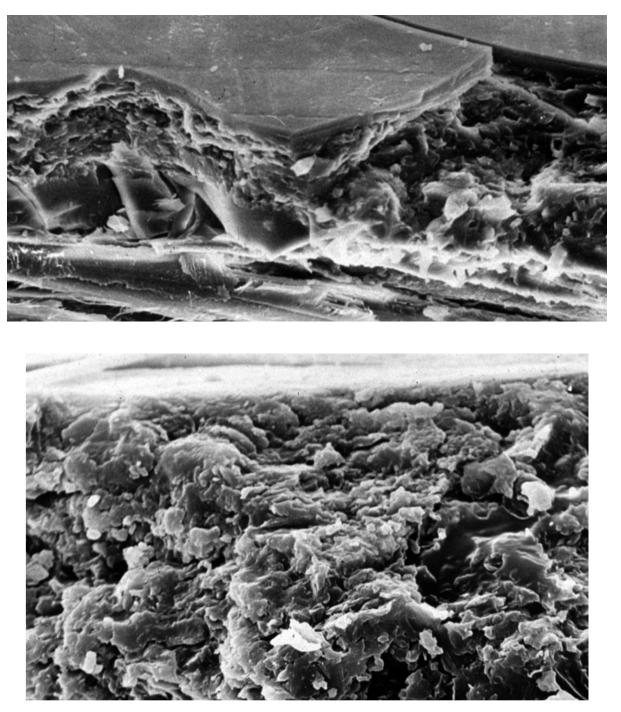


Figure 1. Cross sections through classical varnish treatments measured with an electron microscope: P. Rombouts, Amsterdam, width of photo: 160 μ m (top); and A. Stradivari, Cremona, width of photo: 80 μ m (bottom). (Photographs supplied by Dr. C. Barlow, University of Cambridge, UK.)

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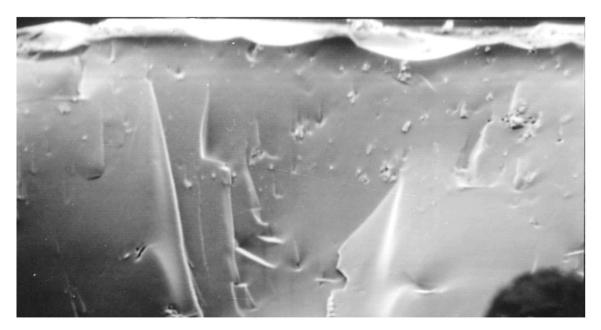


Figure 2. Cross section through a solvent-borne varnish film. Width of photo: 80 µm.

Condax [2, 3] had earlier found a lot of inorganic material in the varnish. He also identified the presence of cellulose (perhaps from sanding dust), filaments of cotton (perhaps from application by a cotton pad), plant spores (perhaps from outside drying), starch grains (the use of which is discussed below), and a great deal of epithelia (flakes of skin, suggesting application by the hand).

What is the binder?

The EDAX analysis by Barlow et al. [5] was not capable of identifying the presence of elements of low atomic weight, particularly those lighter than sodium; hence, it could not be used to measure the carbon, nitrogen, and oxygen content of the organic components. This was unfortunate because the common varnish ingredients of resins and oils are all made from such elements with low atomic weight. Had there been a recurring pattern of elements with higher atomic weight, it might have suggested the presence of an inorganic binder such as waterglass (sodium silicate), but there was none. The likely conclusion is that the binder comprised the low atomic weight elements-carbon, nitrogen, and oxygen-found in common drying oils and resins.

The normally cautious Hill brothers [7] said without reservation that the ground layer was

basically an oil varnish. This is a view that has been fairly generally accepted by British makers, although many Italian makers have maintained that it was a spirit varnish. White [8] tested varnish samples from a Serafin violin top, a Zanetto viola top, and a Tononi cello rib. The samples were collected by scraping, and if there were topcoat varnishes they would have been included. The Serafin varnish had a resin component mainly from a *pinus* source with small amounts of copal and sandarac. The oil was walnut, but only enough was used to plasticize the varnish. The Zanetto varnish consisted of pine resin and walnut oil, and the Tononi varnish contained mainly pine resin with a little mastic, some beeswax, and some form of dammar with walnut oil. In a subsequent article, Dilworth [9] reported the results of White's examination of the varnishes on a violin by Giuseppe Guarneri filius Andrea and a Montagnana cello. The Guarneri varnish was found to be mainly linseed oil with small proportions of (copal) resin and mastic added. The Montagnana sample was similar, with the copal being replaced by pine resin.

White's tests for proteinaceous material, such as glue or albumen, all proved positive, but only in small amounts. Not enough was found to support the possibility of egg tempera as a binder. The Montagnana sample had the great-

est quantity of glue. When considering the Serafin, White concluded that there was a hydrophilic (water-based) ground with a hydrophobic (oil- or spirit-based) top layer varnish. Condax [2, 3] examined samples from 60 classical instruments. He also identified the presence of small percentages of the colloid, glue (as distinct from other proteinaceous non-colloidal material like epithelia), in the samples, which he believed indicated that the varnish was applied as an emulsion. White was unenthusiastic about it being an oil-glue emulsion because of the lack of a precedent for it. If there had been an obvious precedent for this ground layer, it would have not eluded rediscovery for over 200 years.

At one point in Fig. 1a there appears to have been a leak from the mixture of what Barlow et al. [5] believed was an oil or oil-like material that had penetrated the wood. On some violins by some makers, this leaking was not uncommon; on others it was not observed. This suggests that the oily material was a component of the binder that was able to escape from the varnish into the wood, perhaps from an unstable emulsion.

Penetration into the wood

Photographs using an electron microscope do not reveal any sealer film below the ground. As noted above, Barlow and Woodhouse [4] found that, in general, the penetration of the ground into the wood was very low. Greater penetration can occur at isolated points due to the leaking of the oily phase from unstable emulsions. This could only have occurred if there was no sealer under the varnish. It is possible that the ground layer sometimes did not seal all the pores. For example, if one examines carefully the backs of violins by Stradivari and Guarneri del Gesù, one occasionally observes that where the pores in the maple are large, the ground did not bridge over the holes and the colored top varnish passed through the holes in the ground into the wood, showing up as distinct colored dots. The poster of the Kreisler Guarneri del Gesù published by The Strad demonstrates this. Where the top varnish has worn off, the ground has holes in it that are filled with red topcoat varnish. The sinking of the topcoat varnish into these holes has left holes in the top coat, which have filled with dirt. These holes occur on the line of the flames in the maple. This suggests that the ground acted as a sealer and has bridged over all but the largest wood pore holes. It also suggests that there is no sealer under the ground. Had there been a sealer, the colored varnish would not penetrate the wood at the holes in the ground. *The Strad* poster of the *Heifetz* Guarneri *del Gesù* shows complete sealing of the pore holes, and where the ground has been worn off, dirt has entered the wood. Below, we show that, with correct formulation of the emulsion, all pore holes can be bridged.

If a ground that does not penetrate the wood completely wears off the surface, the pores would be open to penetration. In areas that are in contact with musicians' hands, such as the scroll and the neck, finger grease and oils will have penetrated and fill the grain in a fairly colorless way. In areas like the lower back, there may be less grease and more scope for dirt. This will undoubtedly vary also depending on how often a violin has had polish applied to it.

The floor varnishes in use today are in most cases emulsions of acrylic and other resins. In the recent past, floors were commonly varnished with oil-based varnishes or polyurethane. Floors with oil varnish take a coat or two to seal the wood and have the effect of accentuating the grain of the wood and strengthening its color. When the varnish wears off, there is no tendency for dirt to penetrate the wood. The emulsion varnish, on the other hand, seals the wood on the first coat and begins to build up varnish on the outside of the wood. The color of the wood is less affected, and when the varnish wears off, the wood gets dirty. The message is that emulsion varnishes have much lower penetration into the wood than solvent-based varnishes.

In London in 1998 there was a very good exhibition of British violin making through the ages [10]. It was clear that the early English makers used a varnish that, like the emulsion floor varnish, did not accentuate the grain or color of the wood. Within a year or two of 1715 these varnishes completely disappeared (at least in the examples on display) and varnishes that accentuated the wood grain and color were used. We have no idea why this change was so sudden and universal, but it is consistent with a change from an emulsion to a solvent-borne ground varnish.

We have investigated the tonal effect of vary-

ing the degree of penetration. We found that solvent-borne varnishes applied to unsealed wood dulled the tone of the bowed violin by effectively cutting off the high-frequency harmonics in the sound spectrum. Some people may like this sound (for much the same reason as turning down the treble control on an amplifier can give an illusion of increased bass), but there is no question that the projection and carrying power of the instrument will be reduced significantly. This is described in greater detail in a paper by Harris [11]. Audio spectral analysis tests by Rodgers [12] indicated that good modern violins show a high-frequency cutoff at ~4,500 Hz, while the Stradivari violin he tested did not cut off until 9,000 Hz. This high-frequency difference between modern violins and fine old Cremonese instruments was also reported by Buen [13].

Other treatments, such as oiling the wood with linseed oil or giving it a coat of sodium silicate as advocated by Sacconi [14], were found to be equally damaging to the carrying power. This led us to try some of the sealers. We tried egg white, Sacconi's White Varnish [14], dilute gelatin, and casein. These help to reduce penetration and improve the carrying power, but further experience led us to conclude that since these sealers all penetrate the wood to some extent themselves, they are still not good enough. Eventually we began sealing the wood with a modern polymer. This hydrophilic material placed a very thin film on the surface. It has very low penetration, apparently unlimited bridging power over pore holes, and a modulus of elasticity the same as the wood itself. We reached the conclusion that the coating was acoustically invisible. The usual varnishes were applied over this sealer. The brilliance and projection of the violins were remarkable. Acoustic analysis showed that the frequency response function of the radiated sound of the bowed instrument dropped off at a much lower rate with rising frequency than was found with all other varnish treatments we tried. We were well aware that this coating had nothing to do with the historical varnishes pre-1750, but it did convince us that the varnish should not be allowed to penetrate the wood.

In an early effort to minimize penetration, we applied a layer of amorphous silica, which

had high oil absorbency, directly onto the wood surface. This was then followed by the varnish. We expected that the amorphous silica would absorb the varnish at the wood interface and prevent penetration into the wood. However, as the silica was hydrophilic in nature and possessed a high density of surface silanol groups, it was able to chemically bind closely to the wood surface. This had the effect of engendering a close association of the varnish with the wood surface rather than providing a barrier, and thus resulted in poor projection of the sound. The net result reinforced our developing understanding that nothing must be allowed into the wood.

Further evidence of this emerged accidentally. We had performed many acoustic tests on three violins in the white. When these tests were finished we carefully dusted off the rosin on the violins and washed them with isopropyl alcohol to remove other slightly grubby marks. Any microscopic traces of rosin remaining on the surface would be washed into the wood by this process. When varnished and finished, these violins all lacked the clarity and brilliance of our usual work. One test violin was used more than the others in the white and would have accumulated more rosin dust. It was the most affected tonally. Fry [1] quoted Vidal, Vuillaume, Savart, and Lupot as all contending that if a violin is not varnished, the tone is alright for a while but gradually it loses clarity and brilliance, becoming steadily duller. This is probably caused by the wood pores becoming filled with dirt, grease, and rosin.

On three occasions we have found it necessary to remove very poor over-varnish from a violin. We first removed the varnish from the sides, then played it and found no tonal difference. We then removed the back varnish and again noticed no tonal difference. We then removed the varnish on both sides of the fingerboard, bridge, and tailpiece line, and again, no difference was noticed. But when the varnish was removed from the area between the soundholes and between the end of the fingerboard and the tailpiece, the tone was clearly different! We reached the conclusion that the varnish only in the area between the soundholes really affects the tone.

Wang and Burroughs [15] noted that very high-frequency sound beams are radiated from

the motions of the belly in the general region of the bridge and *f*-holes. The effect of varnish penetration is to cut the high frequencies. We have been unable to find a convincing reason why the penetration of varnish should have this effect, but we are certain that it does.

When the varnish wears off of a violin and dirt gets into the wood, there is probably little effect on the sound unless it happens in the area between the *f*-holes. Fortunately, this is an area where it seldom does happen because of the sheltering effect of the strings, etc. Classical violins were often finished with scrapers and the surface was slightly rough, particularly in the curls of the maple. When the varnish wears off, it is inevitable that traces remain in the troughs of the rough surface and are detectable with UV light. The observation of these need not be an indication that the varnish has actually penetrated the wood surface.

Summary of research studies

The classical ground-layer varnish contains a drying oil, a resin, glue, and comparatively large quantities of clay-sized mineral particles. It was very possibly an emulsion and may have been applied while in a fairly viscous state by spreading with the hand. The tonal benefit that it offers is consistent with its very low penetration into the wood.

OUR EXPERIMENTS WITH EMULSION VARNISHES

Classical ground layers appear to have used a binder made from an oil and a resin. (Available evidence indicates as unlikely that there was any rigid or routine formulation.) We decided to begin by cooking together linseed oil and rosin until the firm pill stage is reached. The cooking pre-polymerizes the oil and makes it more siccative. The resulting material was used in all the varnish formulations that follow.

Formulation 1: A simple oil-in-water emulsion

The first experiment was to try emulsifying the oil-rosin mix with ordinary violinmakers' glue. It was easy to form the emulsion, but there was the obvious disadvantage that the mixture had to be kept hot, and applied hot, to keep the glue liquid. The exact formulation was adjusted to give the least penetration into the wood. During the development of the emulsion, a small drop of the emulsion was put on paper and spread out a little with the finger. By holding the paper up to the light and viewing its transparency, we could easily assess the amount of penetration into the paper, both immediately and after a day. The lower the penetration, the more opaque the paper remained. Later, we tested samples on diaphanously thin plane shavings of spruce. Finally, we arrived at a formulation that had excellent "hold out." Some of this was applied to wood and examined under an electron microscope. Figure 3 shows a view of this.

Figure 3 shows no evidence of penetration. Also, the cut surface of the emulsion varnish has a coarser appearance than that of the solventborne varnish shown in Fig. 2. It also has a slightly particulate appearance, although it did not contain added particulate material.

Formulation 2: A water-in-oil emulsion

To overcome the problem of having to apply the mixture hot, we consulted old recipe books to find traditional methods of making glue liquid at room temperature. The most common method was to add nitric acid. Nitric acid was used to separate gold and silver, according to an early work on assaying published in 1510. We even found a contemporary woodcut illustration (published in 1574) of a nitric acid production plant in Venice, showing it being manufactured on an industrial scale [16]. The addition of nitric acid does tend to make the glue, and hence the emulsion, hygroscopic. Fry [1] contended that the action of nitric acid on the resin in varnish promoted the dichroism he observed.

Emulsions require an emulsifying agent (in our case, the protein-based glue), but in addition, stabilizers may be needed to hold the emulsion together for the full drying time of the film. The stability of an emulsion is dependent on its environment and the nature of the substrate to which it is applied. For example, an emulsion that is stable enough to dry on paper can come apart on spruce. When an unstable emulsion comes apart, the separate phases can leak into the wood, as may have been observed by Barlow

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Figure 3. An oil-in-water emulsion of cooked oil-rosin, emulsified with hot glue with no added stabilizer, applied to spruce cut across the grain. Width of photo: 80 µm.

and Woodhouse [4]. In this formulation we used starch as the stabilizer and found it to be effective. The motivation to try starch came from Condax's report [3] that starch was present in some varnishes. The resulting emulsion was a water-in-oil emulsion, and its ability to hold out was very sensitive to changes in the recipe.

Figure 4a shows the excellent cell bridging. The structure showed fine holes like meringue. The varnish contained no particulate material. It had a lava-like appearance and looked even more particulate than formulation 1, but it still lacked the visual effect of the particulate material present in the old ground varnishes. The varnish was applied to a cello using the hand, probably adding epithelia to the brew. Tonally, the result was indistinguishable from the instruments varnished by our standard method using our polymer sealer. The varnish film was, however, slightly hygroscopic, although it was certainly not water soluble. Somehow, we still needed to reduce the glue content.

Formulation 3: An improved oil-in-water emulsion

We were reluctant simply to throw in clay particles just to make it look right under an electron microscope and give an EDAX analysis that agreed with that of the classical varnishes. We had to know why we were adding it and what its function was. Since particulate material is reputed to aid in the formation of emulsions [6], we decided to add some to the emulsion to see if we could reduce the amount of glue and hence reduce its hygroscopicity. We believed that the chemistry of the particulate material was unimportant, so we had a free choice. We chose kaolin (China clay) because its refractive index most closely matches that of a dried linseed oilresin varnish film and would therefore result in the least loss of transparency. The kaolin was ground into the rosin-oil mix before the emulsification. Initially, a nitric-glue medium was added and worked into the oily medium. A water-in-oil emulsion was formed, but on further manipulation it flipped over to an oil-in-

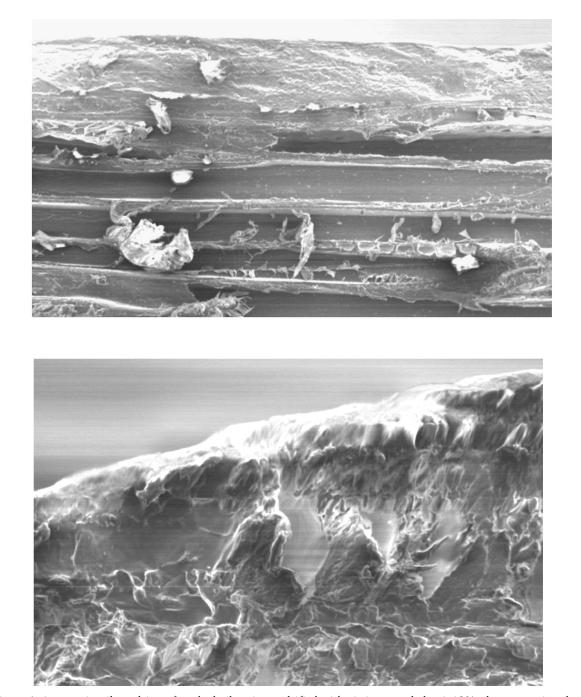


Figure 4. A water-in-oil emulsion of cooked oil-rosin emulsified with nitric-treated glue (~18% glue content) and stabilized with starch. Applied to spruce and split along the grain. Width of photos: $160 \mu m$ (top) and $25 \mu m$ (bottom). Note the particulate appearance even though there is no added particulate material.

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water emulsion. This emulsion required substantially less glue than an emulsion without the kaolin. Also, we discovered that, as the proportion of kaolin was increased and the glue content reduced, it was no longer necessary to make the glue liquid at room temperature. So we later changed to using normal violinmakers' glue as the emulsifying agent at room temperature with no nitric acid. The addition of the kaolin and the removal of the nitric acid together made possible a big reduction in the amount of glue. The kaolin clay behaved as an effective stabilizer. This resulting oil-in-water emulsion was more robust in its nature, and the resulting film showed no sign of being hygroscopic.

The emulsions presented in Figures 5 and 6 show the effect on the appearance (under the electron microscope) of reducing the glue content and increasing the clay content. With increasing kaolin content, the glue content can be reduced to the point where there is no need to add nitric acid. The coating images of Fig. 6 show closer agreement with the varnish samples from classical violins that Barlow and Woodhouse [4] examined. It should be remembered, while making this comparison, that we used a pure form of unweathered kaolin, whereas the violinmakers of the classical era were likely to have used quite a mixture of weathered clay particulates and siliceous material.

The particles in our emulsion were examined from many angles and were found to be particles of the oil-rosin mix that had formed around the China clay particles. They varied in size and shape depending on the nature and size of the agglomerates of the clay particles in the mix. It seems likely that grinding the clay into the oil-rosin mix more thoroughly could break up some of the agglomerates, reduce the effective particle size, and increase dispersion accordingly. These emulsions were all formulated for "holdout" and "pore bridging." This is well demonstrated in Fig. 5 (top), where it can be seen to be "reluctant" to come through the open pore. There is a visible crack at the cutoff point between the varnish and the wood. It is probable that this crack was caused by the stress of breaking the sample for microscopy, but it only occurred in the samples of virtually zero penetration. It is not apparent in all the pictures above because of the viewing angle. The samples using our polymer sealer showed the same crack. Claire Barlow has mentioned, in both papers and lectures, that she observed this apparent crack at the interface between the wood and ground varnish on some of the classical samples.

While any emulsion, regardless of how carelessly it is formulated, will have low penetration, it is possible by careful formulation and testing to reduce the penetration to almost zero. It is quite possible that the Cremonese makers, realizing the tonal importance of very low penetration, did formulate their ground emulsions carefully. Conversely, some of the old varnish grounds may well have been simply unemulsified mixtures of resin-oil with a handful of clay added. We have experimented with such unemulsified mixtures to investigate the effect of adding particulate material.

Figure 7 demonstrates how increasing the particulate content of an emulsion formula (with a fixed quantity of glue) affects the holdout on paper. The paper shown here is of poor quality, being thin and poorly coated (or uncoated), which places a more demanding test on the emulsion than would be the case with high-quality coated paper. The paper is shown against back lighting: where the penetration is greatest, the color is lightest. The top row of samples had not been emulsified and was a simple oil-resinparticulate mix. The second row of samples had been emulsified. The percentage of particulates increases from left to right. In comparing the two rows, it is evident that the penetration was much greater for the unemulsified samples than for the emulsified samples. But also going from left to right in both rows, as the particulate content increased, the penetration was reduced. So there would be some benefit from throwing a handful of particulates into an unemulsified oilresin mix, but there would be greater benefit from emulsifying the brew.

The formulation of the Harris & Sheldon emulsion ground varnish

We suggest that emulsion varnishes made of a siccative oil-resin mix, emulsified with glue (without nitric acid treatment) and stabilized by the addition of clay-sized mineral particles, as presented above, have similar properties as the ground layers widely used by violinmakers

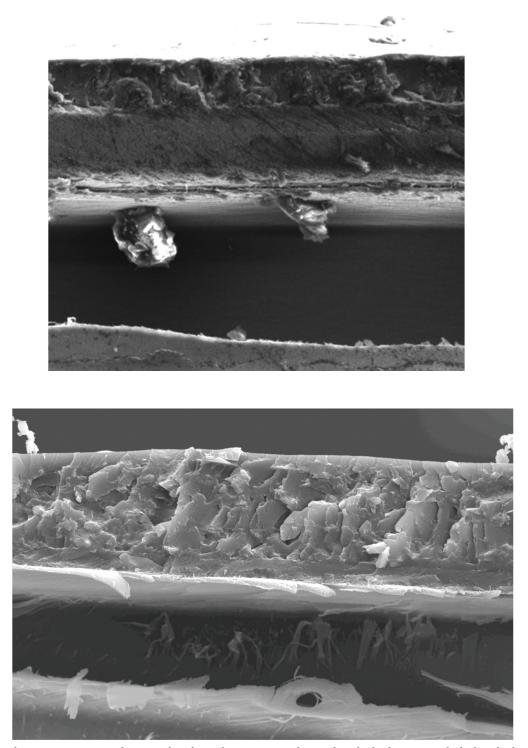


Figure 5. Electron microscope photographs of an oil-in-water emulsion of cooked oil-rosin emulsified with glue and stabilized with kaolin clay, applied to spruce and split along the grain. Kaolin and glue content: 12.6% and 9.2% plus nitric acid (top); 17.5% and 2.9% (bottom).

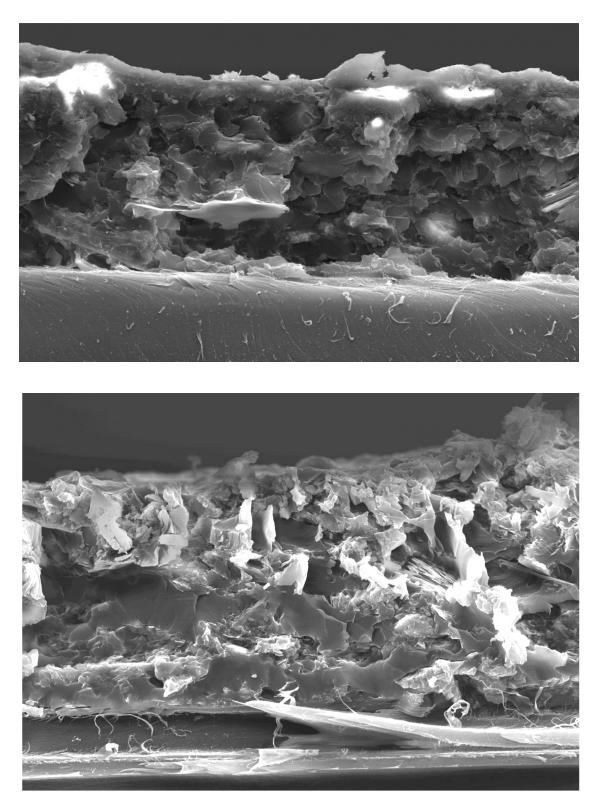


Figure 6 Electron microscope photographs of oil-in-water emulsions of cooked oil-rosin emulsified with glue and stabilized with kaolin clay, applied to spruce and split along the grain. Kaolin and glue content: 24.2% and 2.6% (top); 29.8% and 2.4% (bottom). Width of photos: 80 µm.

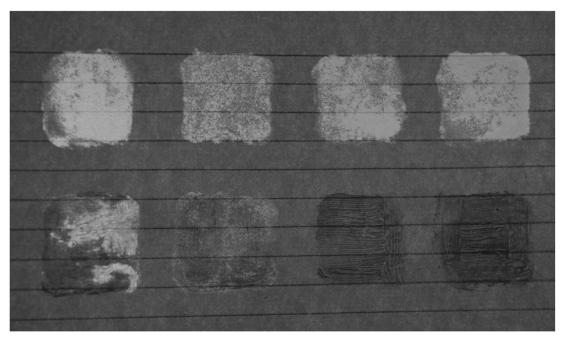


Figure 7. Samples of unemulsified (top row) and emulsified (bottom row) varnish, with increasing content (left to right) of particulate material, laid on paper to demonstrate penetration. The samples were lit from behind. The darker the color, the less penetration there is (the lines are the usual lines printed on writing paper). The added clay reduced the penetration, but emulsification had an even greater effect.

before 1750. In this paper, we refer to this family of varnishes as the "Harris & Sheldon emulsion ground varnish." Within this family of varnishes it is possible to give a more specific formulation that optimizes the acoustic and visual qualities.

The basic criterion in the formulation of this emulsion is its ability to hold out from penetrating a very thin sample of belly wood. But, as Figures 5 and 6 show, this can be achieved with a lot of glue and little or no particulate material right up to very little glue and a lot of particulate material. The high-glue option may require addition of nitric acid to achieve room temperature workability, and this could lead to problems of hygroscopicity. The low-glue/high-particulate option may cause a loss of transparency and lead also to poor bridging over pore holes in the maple backs of some instruments. (This may have happened to the Kreisler Guarneri del Gesù violin.) The option we most prefer has a glue content of 2.6% and a particulate content of 25%. Examination of the few pictures of Cremonese varnish films available to us suggests that the Cremonese ground erred on the side of a slightly higher particulate content than this.

Working with emulsions can be a time-consuming and messy business. Each ingredient has an effect on the balance of the other ingredients. If one makes a mistake or overshoots, it is very difficult to "recover" the emulsion. It is better to clean up and start again. As the emulsion is an oil-in-water type, the glassware can be cleaned with water. We make the emulsion using a glass pestle and mortar. The resulting consistency is like thick mayonnaise, best applied with the hand or thumb. It is easy to apply an even first coat over the surface of the wood. Happily, this seems to deposit a thickness of approximately $35 \ \mu m$, which is quite close to the thickness of the samples shown by Barlow et al. [5].

As a guide to formulating an emulsion with the lowest penetration, we give the controlling criteria and suggest a recipe that will optimize the performance of our emulsion ground varnish.

The oil-resin mix. Historic examples probably varied widely in the choice of oil and resin and their relative proportions. We cook 40 g of lin-

seed oil and 30 g of rosin until the "firm pill" stage is reached. After preparation the mix may need to be diluted with turpentine to be workable at room temperature, but no more than necessary. Increasing the dilution increases the penetration of the emulsion. We add 15 ml of turpentine while cooling, but not before the oil/rosin temperature has dropped well below the boiling point of the turpentine.

The clay. Kaolin, aka China clay, has a refractive index that is close to that of the dried oilresin film and will therefore minimize any loss of transparency. The optimum amount of clay can best be determined by testing the holdout of the emulsion on paper and thin spruce shavings. We have found that approximately 25% kaolin was sufficient to maximize the holdout. If the clay content is increased beyond this, the emulsified film is more likely to leave a crater around an open pore. So, for 5 ml of the above varnish we thoroughly grind in 1.7 g of kaolin.

The glue. We use 6 g of dry rabbit skin glue soaked in 30 ml of water heated in a water bath. Just enough glue is added to form an oil-in-water emulsion. For 5 ml of varnish, we mix in 30 drops of the glue mix.

The water. After making the emulsion, water can be added to lower its viscosity to a workable consistency. The water may be added, a couple of drops at a time, until the emulsion can be applied by the thumb. We found that about 10 drops was sufficient for the above quantities.

This recipe gives the following approximate proportions: 24.7% of China clay and 2.6% of glue by weight in the dried varnish film. These are the minimum percentages required to perform their function. The varnish has poor selfleveling, but it is not difficult to apply an even coating with the thumb. When dry, the applied film has a matte surface, or possibly a very low sheen, not unlike a meringue, and a slightly chalky appearance.² If the cooking is done at low temperature, the color of the dried film will be a pale yellow. The ground takes over-coating very well and is transparent.

CONCLUSIONS

Emulsions of the pre-polymerized oil-resin varnish can be made using violinmakers' glue as an emulsifying agent and clay-sized mineral material as a stabilizer. These varnishes greatly reduce penetration into the wood and thereby increase the frequency range of the radiated sound, as well as its projection. They function as both a sealer and ground layer. Of the emulsions we formulated, we found that the oil-in-water type was the easiest to manufacture and it exhibited better holdout and stability. Because of its reliance on particulate material, we think that it could be the most authentic. We call this formulation the "Harris & Sheldon ground varnish," and we believe that it is a recreation of the family of ground varnishes used by many of the classical violinmakers. Their varnishes varied, but the Harris & Sheldon ground varnish can be adjusted in oil and resin type and in the nature and quantity of the mineral content to replicate most classical ground varnishes. A specific formulation is given that has been designed to optimize the acoustic and visual properties.

The addition of clay-sized mineral material has an essential part to play in the construction of this oil-in-water emulsion. Not only does it reduce the amount of water-borne emulsifying agent (glue) required, but it also stabilizes the resulting emulsion. Similar ground varnish layers may have been widely used before 1750, and because of the low penetration of emulsions into wood, they would have bestowed certain tonal benefits. However, it may have been only in Cremona that the emulsion was specifically formulated to minimize penetration into the wood, perhaps explaining the superiority of many Cremonese violins.

FURTHER RESEARCH

Recent advances in analytical methods used in materials science offer the possibility of furthering our research. What we need are small samples of varnish of unquestioned authenticity from instruments made by distinguished Cremonese makers. Please contact us if you can offer such samples.

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NOTES

1. The various substances applied to violins have been varyingly referred to as fillers, sealers, grounds, and varnishes. Terminology can raise strong feelings, so we have given careful consideration to the wording of the title "particulate ground varnish layer." The coating material discussed in this paper was very carefully formulated to not penetrate the wood. To call it a "filler" would be very misleading. It certainly seals the wood against penetration by subsequent coats and in that sense it is a "sealer," but it is much thicker than merely a sealer and forms a ground. A ground is the stuff one sees when the top varnish layer wears off of an instrument made in the classical era. Writers have traditionally referred to this layer as a "ground," and we adopt this term. To distinguish it from alternative types of ground layers, we add the word "particulate" in recognition of the fact that it contains particulate material. It is made essentially as an oil varnish. Hence, we describe it as a "particulate ground varnish," but it does act also as a sealer.

2. We have seen the back from a violin made by Andrea Amati (in the collection of Charles Beare) that has had the top varnish removed with solvents to expose the unworn virginal ground varnish. The surface of this ground has very low sheen and a slightly chalky appearance. The appearance of our Harris & Sheldon ground varnish is similar in this regard.

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