

Stradivari's Varnish: A Review of Scientific Findings—Part II

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Abstract

The first part of this article discussed the scientific analysis of the inorganic composition and the structure of Stradivari's violin finish. The second part focuses on the organic composition and the principles of coloring. The basic medium of Stradivari's finish is resinous drying oil, as revealed by modern chemical analysis, possibly also containing some proteins or carbohydrates. A summary table of 24 identified substances in Cremonese finishes is given, including oils, resins, minerals, and pigments. What scientific analysis has taught us about Cremonese finishes differs significantly from the traditional views held from the early 1800s to about 1970. The scientific information also provides insights into the birth and the disappearance of classic finishes. In the second half of the 17th century, resinous drying oil became obsolete in most arts and crafts, as it was replaced by spirit varnishes and essential oil varnishes. Violin making was not spared from this trend. Given the complexity of the Cremonese finishing system so far uncovered, it seems to be easily forgotten but difficult to recreate—even with the help of modern science.

In Part I of this review [1], I discussed why many are interested in the wood finish composition of Antonio Stradivari and other Cremonese masters, as well as some of the traditional views on the subject. I also discussed the scientific findings with regard to wood finish stratigraphy and inorganic constituents. To remind the reader of the basic features of Cremonese finishes, the results of a few significant studies (not included in Part I) will be described.

An instrument made by Andrea Guarneri in 1689 was included in Geary Baese's [2] studies of Cremonese finishes. He used a microtome to cut out a cross section for examination. Under light microscopy, the wood finish appeared to have two principal layers: the ground coat and the color varnish. The ground coat over the wood was transparent and lightly colored, containing mineral particulates. The color varnish contained several pigmented layers. Baese also found the finish on an instrument made almost 70 years later (in 1758) by Giovanni Battista Guadagnini (1711–1786, Italy) to be similar to the Guarneri specimen. The ground on the Guadagnini instru-

ment was analyzed by energy-dispersive X-ray fluorescence (EDXRF) under a scanning electron microscope (SEM). The major elements found were silicon, aluminum, calcium, and potassium, comparable to inorganic particles (calcium carbonate, silicon oxide, and aluminum potassium silicate) found in the finish on a cello by Andrea Guarneri, as reported by Nagyvary and Ehrman [3], also using SEM/EDXRF. A micrograph of Guarneri's particulate ground coat is shown in Fig. 1 [4].

As more analytical evidence is accumulated, it is becoming clear that many similarities exist between the finishes of Cremonese and non-Cremonese violins, and between violins and plucked string instruments made in Italy. The similarities are found in both inorganic components (see Part 1 [1]) and organic components (the key study is Ref. [5], discussed in the next section). Nearly 80 years ago, the Hill brothers [6] mentioned such similarities, and the similarity between the Guarneri and the Guadagnini finishes discussed here is consistent with their observations. They considered Guadagnini, who worked briefly in Cremona around 1758, to have been one of the

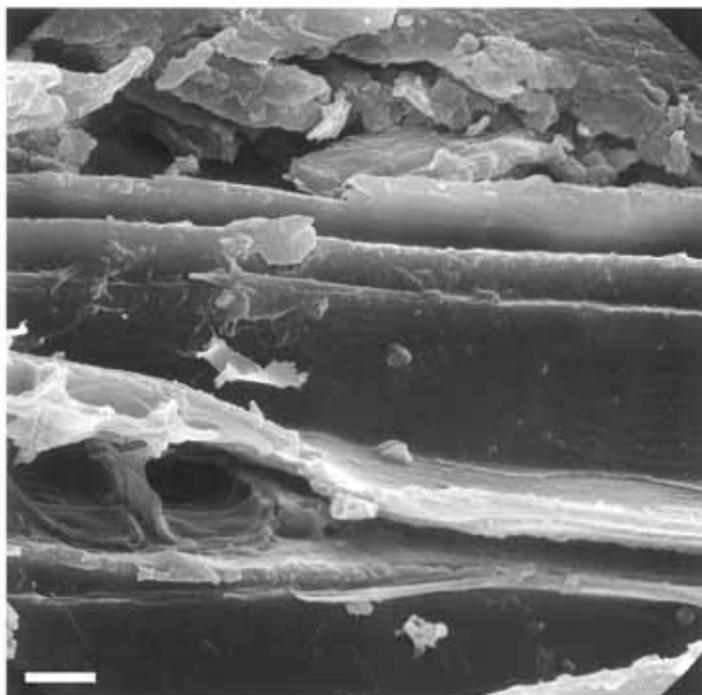


Figure 1. A particulate ground coat over the spruce top of an Andrea Guarneri cello. This image was originally published over 30 years ago in this journal (Ref. [4]), representing the first scanning electron micrograph of a Cremonese wood finish. At the time, it was mislabeled as having been made by Giuseppe Guarneri filius Andrea, ca. 1690. Reproduced with permission of Joseph Nagyvary, with an added scale bar representing 5 μm .

last practitioners of the Cremonese finish [7]. (They were, however, quite puzzled by why Guadagnini only occasionally used Cremonese-style oil varnish.)

Using SEM/EDXRF to examine wood finishes, Meyer [8] identified calcium-containing minerals on a cello by Domenico Montagnana and silicon-containing minerals on a double bass by Francesco Goffriller. It remains possible that those mineral particles in the ground were residues of chalk or pumice stone used for wood polishing. However, in electron micrographs of Stradivari's ground ([1], Figs. 1 and 3), the particle size (below 2 μm) and amount are more consistent with a deliberate application of particulate composite coatings.

On a Stradivari rib fragment, Meyer [8] observed a very chippy wood finish consisting of a red-brown color varnish over a ground. The color partially originated from iron-containing red particles (probably Venetian red) and charcoal. He also noticed that the ground coat of Cremonese instruments did not penetrate or fill wood pores, while the Venetian ground (also

colorless but with unknown mineral content) sank further into the pores. In the next section, attention is given to the organic components in the color varnish and the ground layers.

WOOD FINISH COMPOSITION: ORGANIC MATERIALS

Modern chemical analysis is just now beginning to be used to unravel the organic constituents of the Cremonese wood finish. The most important question is whether or not Cremonese masters applied oil varnishes, as suggested by many experts on the subject [6, 7, 9, 10]. As discussed in Part I [1], Stradivari's own letter, in which he apologized for the delay due to the need to put varnished instruments under the sun, strongly implicated the use of oil varnish.

In this article, oil varnish will denote fixed (meaning non-volatile) oil varnish, made of resins dissolved in drying oil (resinous drying oil). Unless otherwise specified, oil will refer to drying (or siccative) oil (like linseed oil), instead of non-drying oil (like olive oil) or essential (mean-

ing volatile) oil (like oil of turpentine). Essential oil can also dissolve resins to make essential oil varnishes. Spirit varnishes are resins dissolved in alcohol or, in some cases, in volatile solvents of mineral origin like naphtha. To be even more clear, alcohol obtained by fermentation and distillation, called spirits of wine in older times, is a mixture of ethanol with some water (4% or more depending on distillation conditions). Resin is a rather broad and vague term, but in this article it refers to viscous, hydrophobic substances exuded by trees, which are capable of hardening, as well as their hardened products. On the other hand, viscous, water-soluble substances exuded by trees (mainly carbohydrates) are called gums, and we need not consider a third class of exudate which is rubbery [11]. Spirit and essential oil varnishes will dry very quickly upon the evaporation of volatile solvents. When essential oil or alcohol is mixed with drying oil in the varnish medium, we still consider it a fixed oil varnish because its drying still requires the slow polymerization process of unsaturated fatty acids.

Despite countless attempts to ascertain the organic composition of Cremonese finishes through historical and empirical approaches (see reviews by Joseph Michelman [12] and Martin Zemitis [10]), the issue remains heatedly debated. Numerous claims of the rediscovery of the Cremonese recipe have been made. However, actual scientific progress is rather limited in this field and often underappreciated. In the following I will summarize what modern science has taught us about the organic materials that went into Cremonese finishes.

The chemical structures of organic compounds are much more complex than inorganic compounds and therefore harder to identify. Complex mixtures of organic molecules from natural products can be combined and processed into even more complex materials. To identify organic molecules in a complex mixture, the general strategy is to separate the components so they can be individually characterized. The most useful separation technique in modern chemical analysis is called chromatography. In chromatography, analytes are carried by a gas or a liquid to flow through a solid support. As analytes interact with the solid support, the flow speed depends on the strength of the interaction. For instance, when a strip of filter paper has one end

dipped into a mixture of soluble dyes, the pigments travel up the paper by capillary action and separate into bands of different colors, and hence the technique was termed chromatography [13]. Today, gas-phase chromatography (GC) has been successfully applied to identify the oil and resin used on old violins.

Oil and resin identified

A recent study by Échard and coworkers [5] has convincingly identified some of the organic molecules contained in classic instrument finishes using GC coupled to mass spectrometry (MS). The samples included the 1724 *Sarasate* violin by Antonio Stradivari ([1], Fig. 4), the early-16th-century Laux Maler lute mentioned in Part I, and a 1606 theorboe (a lute family instrument) by Wendelio Venere of Padua. Each wood finish sample was dissolved in organic solvents, with all of its sublayers analyzed as a whole. Necessary chemical modifications were applied to make certain molecules suitable for GC separation. As different substances sequentially eluted off the GC column, they were analyzed by the mass spectrometer. In the mass spectrometer, molecules are turned into ions whose flight patterns in an electric field are measured to determine their masses.

Figure 2 shows the profile of various compounds from the Stradivari sample eluting off the GC column. The area under each peak is roughly proportional to the abundance of the compound(s) coming off the column at that time. The masses of different molecular ions and their fragments can be used as molecular fingerprints for chemical identification. The first compounds to elute off the column are the fatty acids from the oil. The significant presence of azelaic acid [13, 14] suggests the use of drying oil (Fig. 2). The common drying oils in Europe at the time were linseed oil (from seeds of flax, *Linum usitatissimum*) and walnut oil (from kernels of *Juglans regia*), which can be distinguished from the ratio between palmitic and stearic acid. As seen in Fig. 2, the palmitic/stearic ratio of 1.57 in Stradivari's wood finish suggests linseed oil (typically 2.6 for walnut oil [13]).

To identify the resins, Échard and coworkers analyzed a selection of candidate substances: turpentine oil, lavender oil, benzoin, Venetian turpentine, colophony, Manila copal, sandarac,

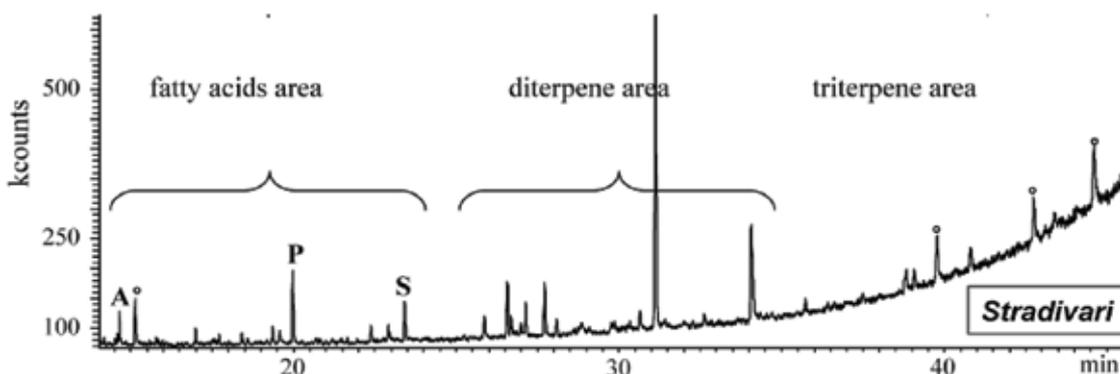


Figure 2. Gas-phase chromatography elution profile of Stradivari's wood finish. Fatty acids from oils travel faster in the column and come off at earlier times. Letters A, P, and S designate azelaic (C_9), palmitic (C_{16}) and stearic (C_{18}) acids. Diterpene and triterpene compounds are indicative of tree resin components. Circles over peaks denote extraneous substances introduced during sample preparation. Reproduced from Ref. [5] with permission of Elsevier, Inc.

dammar, and mastic. They found that compounds from the Stradivari sample matched the molecules from Venetian turpentine and colophony. For example, at 25'52" a compound came off the GC column and yielded ions with mass/charge ratios of 301, 288, 275, 273, 121, 105, 91, and 79. This profile matched with a compound called larixol, which is specific to the larch tree [13]. This indicates the use of Venetian turpentine by Stradivari, which is the exudate of the European larch tree (*Larix decidua*). On the other hand, the source of the colophony (rosin) can be traced with no more specificity than to the *Pinaceae* family. The main component of tree resins is a class of complex but related molecules called terpenoids. Terpenoids are synthesized by plants using a common building block called isoprene, but combined and modified in thousands of ways [15]. Hence, there usually exists some ambiguity in tracing the terpenoids in a sample back to its botanic origin, unless a very specific marker like larixol is available.

Although GC/MS is a powerful analytical tool, it still has numerous technical limitations when applied to the violin finish. One obvious problem is that some compounds will not dissolve or vaporize, such as salts and organic polymers. The solidification of drying oil is a polymerization process between polyunsaturated fatty acids. Unsaturated compounds from tree resins can copolymerize with the oil and become insoluble. Other compounds may be unstable during the analysis and breakdown. Moreover, experimenters need to make certain assumptions

about what types of molecules may be present to choose the appropriate experimental condition. MS analysis also has many limitations. For example, not all molecules will ionize efficiently and some compounds may therefore go undetected. Abundant ionic species will also suppress the signal of low-abundance species. Therefore, the failure to detect a substance by GC/MS analysis is not necessarily a proof of absence, nor does it provide quantitative information.

The word "turpentine" can be confusing at times and warrants some additional discussion. Generally speaking, the resinous sap exuded from conifers is classified as oleoresin because it contains both oils and resins. When distilled, the volatile fraction is considered as an essential oil or ethereal oil, while the residue forms a solid material. The term "resin" can denote both the viscous exudate and the solid left behind. Oleoresins from trees in the *Pinaceae* family are historically called turpentines, but turpentine can also denote both liquid and solid components derived from oleoresins. The volatile fraction obtained by distillation is called oil of turpentine, turpentine oil, or (gum) spirit of turpentine. The solid that remains is called rosin or colophony, or, in older times, pitch or Greek pitch [16, 17]. What is commonly called rosin today may be from pine or fir trees [18] (both in the *Pinaceae* family). In modern times, turpentine usually denotes oil of turpentine rather than the undistilled exudates. However, the undistilled oleoresinous exudates of silver fir (*Abies alba*) and larch (both in the *Pinaceae* family) trees are still called

Strasbourg turpentine and Venetian turpentine, respectively [19]. Venetian turpentine hardened by exposure to air is often sold as a semi-solid. How it was collected and processed 400 years ago is difficult to determine. It is thought that the distillation of the raw larch oleoresin to obtain an oil of turpentine was rarely performed, though the 17th-century de Mayerne manuscript had described such practices [13].

Resins from non-coniferous trees can also be useful for varnishing. In fact, the word “turpentine” evolved from *trementina* or *terebithina* [20], which historically denoted the “Chian turpentine” produced by *Pistacia atlantica* (formerly *P. terebinthus* [13]) on the Greek island of Chios. Over time the demand for turpentine far exceeded the Chian production and various coniferous oleoresins took its place. The island of Chios is also the historical origin of mastic resin, produced by *Pistacia lentiscus* [13]. The nomenclature of resinous materials has always been confusing, especially before the 19th century, due to their chemical complexity and the lack of systematic botanic classification.

Some molecules from the Stradivari sample matched those from modern French colophony, but not turpentine oil [5]. This may be interpreted as the use of some type of rosin from the *Pinaceae* family. GC/MS demonstrated that pine rosin and Venetian turpentine contain many of the same molecules, and we cannot determine which resin was more abundant. It should be noted that the volatile components of historical wood finishes will not appear in modern analysis because they evaporated long ago. The use of alcohol and oil of turpentine for quick-drying varnishes appeared in Europe in the 16th century [21], which means that their use in Cremonese finishes cannot be ruled out based on historical reasons. Furthermore, compounds in historical samples may have undergone chemical changes over time, which further confounds our chemical analysis.

The Venere theorboe had a GC profile similar to the Strad violin, showing linseed oil, Venetian turpentine, and rosin [5]. In the Laux Maler lute, linseed oil and *Pinaceae* resin were found, with additional triterpene compounds that seemed to indicate frankincense from some *Boswellia* species. Compounds specific to Venetian turpentine were not detected, but it remained possible that

the negative result was caused by four centuries of aging.

More oils and resins

The results of Échard et al.'s GC/MS analysis [5] are in general agreement with an earlier study by Raymond White, who used only GC [22, 23]. In White's experiments, the GC instrument was fitted with a nonspecific detector that determined how much organic compound was exiting the column. In this setup, the identity of a compound could only be inferred from its retention time compared to known standards. One of the samples White analyzed was a Santo Serafin (1699–ca. 1758, Venice) violin finish. Microscopic examination revealed a hydrophilic (with an affinity for water) ground layer and a hydrophobic (with an affinity for oil) top varnish, with little interaction between the two. In an earlier study, Louis Condax [24] also noted the hydrophilic property of the ground coating on a Strad cello.

Ideally, the ground and the color varnish from a wood finish should be analyzed separately using GC, but this has not yet been achieved. The Serafin finish as a whole was first extracted with methanol and ethanol. A fraction of the extract was methylated to render it suitable for GC analysis. The main ingredient identified by GC was a conifer oleoresin from some *Pinus* species (pine resin). Minor components probably originated from sandarac (resin of the African conifer *Tetraclinis articulata* [13, 25]) and some type of copal (resin of the *Leguminosae* family [11, 13]). In a second experiment, benzene was used for extraction but no wax was detected. The insoluble part was saponified (hydrolysis of fat by base) and methylated to facilitate fatty acid detection. The palmitic/stearic ratio of 3.35 suggested walnut oil [13]. Generally speaking, linseed oil dries faster than walnut oil due to the higher degree of unsaturation (more double bonds in its lipids) [13], but the actual drying rate is highly dependent on how the oil was prepared and the addition of chemical driers [26].

White's analyses of a cello by Giuseppe Guarneri *filius* Andrea indicated linseed oil, pine oleoresin, and a small amount of mastic. David Tecchler (ca. 1668–ca. 1747, Venice) and Francesco Goffriller (1691–ca. 1750, Udine) samples both contained pine oleoresin and drying oil

(linseed and walnut, respectively) [22]. The Zanetto viola from Brescia in the early 18th century showed walnut oil and pine oleoresin. A Tononi cello made in Bologna around the same period contained walnut oil and pine oleoresin, as well as some triterpene molecules indicative of mastic. The ether extraction of the Tononi sample showed a variety of long-chain hydrocarbons that pointed to beeswax. Beeswax was long known to be an artists' material [27, 28] and it was sometimes said that a wax-resin mixture can be as protective as an oil-resin varnish [21]. The presence of beeswax may also indicate the use of propolis (bee glue), as proposed by Sacconi [9] and Fulton [16]. Propolis is secreted by bees as a hive-sealing material [29] that contains beeswax, resins, and volatiles (the latter two are collected from plants).

In addition, GC studies by Baese [2] found walnut oil and substances resembling oxidized pine resin in a Rogeri sample, and Caruso et al. [30] identified by GC/MS walnut oil on a Vincenzo Trusiano Panormo (1734–1813) bass labeled 1752 (possibly made in Palermo). Meyer identified drying oil, pine resin, and mastic in two D. Montagnana cello finishes, presumably using GC but details were unclear [8]. Using GC/MS, Chiavari, Montalbani, and Otero [31] found drying oil and rosin in the finish of a violin by Giovanni Marchi (1727–1807, Bologna). Pollens [32] also identified drying oil (probably linseed) and conifer resin (probably oxidized pine colophony) from a Stradivari violin. Taken together, it is quite obvious that classic Italian violin finishes were primarily based on drying oil (linseed or walnut) and *Pinacea* oleoresin.

Infrared (IR) absorption spectroscopy has also been applied to resin analysis. Infrared light can be absorbed by vibrating chemical bonds at certain frequencies. However, the number of vibrating chemical bonds in a mixture of oil and resins is very large, resulting in complex spectra that are hard to assign to specific substances. Using IR spectroscopy, Condax observed in an A. Guarneri sample absorption peaks that seemed to correspond to aliphatic hydrocarbons (alkanes and olefins), stearic and palmitic acids, and high molecular weight materials [33]. These tentative chemical assignments are consistent with resins dissolved in drying oils. In other samples, Condax observed substances that may

represent rosin. In other studies, IR spectroscopy has successfully identified adulterants such as alkyd resin (applied as a modern overcoat) [34] and silicone rubber (used for modern casting) [35]. Korte and Staat [36] applied a more sophisticated form of infrared spectroscopy for *in situ* examination and observed spectra resembling aged mastic in two Venetian instruments from the 16th and 17th centuries.

Oils and resins demystified?

Based on current data, it appears that, during the Golden Age of Italian violins, master makers predominantly used fixed oil varnishes. The drying oil was either linseed or walnut oil, and the major resins were from the trees of the *Pinacea* family, such as pine rosin or Venetian turpentine. This basic formulation appeared to be conserved between major makers in Cremona and other parts of Italy. Occasionally, modern analyses detected additional resins: mastic, copal, and sandarac. It should be emphasized that current analytical methods probably only detect the more abundant or more soluble organic components. Detailed characterization of natural products in a historical sample remains very challenging. Even for something as abundant and commercially important as Coca-Cola, it is not yet possible to reconstruct its recipe of natural flavors by chemical analysis.

We cannot formally rule out that some resins may have been dissolved in spirits or essential oils, and may have been mixed with drying oils when they were applied. Therefore we should consider if the resins identified are directly soluble in drying oils. Judging from both modern reports [10, 25, 26, 37, 38] and old manuscripts [20, 21, 27, 28, 39], we know that resins found in classic Italian violins (rosin, Venetian turpentine, mastic, sandarac, copal, and frankincense) are all soluble in drying oils, and so are resins like amber and dammar. For some resins, dissolving into drying oil requires considerable heating and expertise in handling, and may be potentially hazardous, but it is difficult to determine how ancients performed this task.

Linseed oil itself is also a natural product of considerable complexity. Important factors in linseed oil processing include the extraction method, pre-polymerization by heating or ultraviolet (UV) radiation, pH adjustment, and

the addition of metal driers (commonly lead, cobalt, or manganese) [14, 26]. Historic studies indicate that old master painters were very picky about the oils they used, and a good discussion of artists' oil had been given by Eastlake; even Leonardo da Vinci wrote down some tips on preparing walnut oil [28]. The choice of the chemical drier can affect the speed of drying and other properties [26]. For example, it is said that red lead (Pb_3O_4) makes the dried film hard and brittle, while litharge (PbO , yellow) makes it elastic [40]. Lead was the traditional drier known to Italians [20] and has been detected in many Cremonese finishes [1], but it remains unclear in what form it was incorporated [3, 33, 56]. According to Laurie [21], the preparation of drying oils for artists has evolved little since the Renaissance. Hence, the oil used in Cremona was probably prepared according to one of the procedures described in old texts, but we cannot ascertain which one.

A Cremonese finish often has two or more sublayers, but we do not understand the layer distribution of identified resins. We must admit that, despite the progress in analytical chemistry, our understanding of the Cremonese oil-resin medium is obviously incomplete. At best, modern science can teach us how *not* to make a Cremonese finish, not how to make it. For instance, White [22, 23] appeared to have ruled out the use of metal rosins proposed by Michelman [12] or polymerized turpentine proposed by Fulton [16], but admitted that a small amount of amber could have gone undetected in his study. The varnishing method proposed by Fry [41], which includes nitric acid as an oxidizing agent, also appears unsatisfactory according to some modern luthiers and varnish researchers [22], and others are concerned about the injurious effect of nitric acid on the wood [42].

By comparing the refractive indices (RI) of identified minerals and the wood, it has been proposed that the RI of the Cremonese ground medium should be ~ 1.55 [3, 43]. While linseed oil as a liquid has an RI around 1.48, dried linseed oil films on old paintings increased in RI from ~ 1.52 to 1.57 after 100 to 400 years of aging; walnut oil shows similar trends [44]. All common varnish resins have similar RI ~ 1.53 – 1.54 [44], including rosin, copal, dammar, sandarac, and dried Venetian turpentine. Thus, the

oils and resins identified so far all satisfy the RI criterion for making a transparent coating over the wood.

In a nutshell, it can be said that oils and resins identified in classic Italian wood finishes contain no surprises, although we cannot formally rule out the presence of more exotic substances. The presence of drying oil (walnut and linseed) was easily predicted from both historical and empirical perspectives. Experiments with non-drying oils such as olive oil produced expectedly messy coatings [16]. The resins identified to date are already familiar to most violinmakers. They all appeared in Heron-Allen's violin-making treatise published in 1885 [37] and numerous other violin-making manuals. We have come a long way from two centuries of confusion and debate to the scientific characterization of the oil-resin medium, but for luthiers looking for exact recipes and protocols, a satisfactory answer cannot yet be formulated on a scientific basis.

Proteins and carbohydrates

When White [22, 23] applied ninhydrin to stain for proteins in Old Italian violin finishes, the results were in most cases weakly positive. This seems to indicate a small amount of protein, although the possibility of wood contamination could not be completely ruled out. Condax [33, 45] reported that the alcohol-insoluble fraction of an Amati cello finish sample (color varnish and ground analyzed together) contained 7% nitrogen, indicating the presence of proteins (oils, gums, and resins contain little nitrogen). He also found proteins on a 1669 Guarneri, an 18th-century Tecchler, and a 1707 Venetian instrument, by two different staining methods [33]. Without noting which instrument was analyzed, wood finish scrapings were dissolved in hot hydrochloric acid, and amino acid analysis implicated the presence of gelatin (partially hydrolyzed collagen, from animal or fish glue) and an unidentified protein. Amino acid analysis of the ground layer by paper chromatography implicated egg white. From this, Condax proposed that a proteinaceous coating was applied over the ground, or perhaps the protein was a part of an emulsion medium.

Sacconi [9] proposed that a colorless isolation layer separates the mineral ground from the color varnish. He thought the isolating com-

pound might be *vernice bianca* (egg white, gum arabic or cherry gum, candied sugar, and honey), based on chemical tests that detected albumen and sugar, but no analytical details were given. Judging from the fluorescence color table given in the book, some of his chemical claims may have been based on UV fluorescence. UV light is invisible to the eye, but after molecules or crystals absorb it, the emitted light may be in the visible range (perceived as colors). Overall, UV fluorescence is a convenient but rather unreliable way of identifying materials [46]. Baese [47] reported the use of an unspecified protein stain to reveal a protein layer between the ground and the color varnish in an A. Guarneri sample.

Evidence of proteins in Old Italian lute finishes has also been reported by Échard et al. [49]. A Magno Dieffopruchar lute from late-16th-century Venice was examined with IR beams from a synchrotron source (a type of particle accelerator). The bright and focused beam provided spectroscopic measurements with the spatial resolution of 5–10 μm [50]. The IR spectra revealed organic and inorganic substances from individual coating layers and individual particles. Échard also used the synchrotron X-ray beam to measure the diffraction pattern of embedded crystals. In the ground layer (~40 μm thick) he found calcium carbonate, calcium sulfate hemihydrate, and quartz [49], similar to what have been found in Cremonese finishes [3]. Surprisingly, the major organic binder in the ground is not oil and resin, but proteins (identified by the vibration of peptide bonds). Above the ground, there is a second particulate layer of red-brown hue. It contains calcium carbonate, calcium sulfate, kaolinite, and iron earth particles, and the binder is also proteinaceous. In the third topmost layer, no minerals or proteins were detected [49]. Whole-finish sample from this instrument has been previously analyzed by GC/MS—walnut oil, diterpenoid resin of the *Pinacea* family, and unassigned sesquiterpenoid compounds were found, but the experimental protocol was not designed for protein detection [5]. Therefore, the particle-free top varnish appeared to be an oil-resin mixture.

From these results, we are tempted to speculate about the “two kinds of varnishes” mentioned by master lute maker Sigismond Mahler in 1526 (Ref. [7], p. 73): one is an oil-resin var-

nish and the other is a proteinaceous varnish. An unpublished study by Meyer also reported protein detection by an unspecified microchemical test on a cross section of an archlute finish (cited in Ref. [49]). We do not yet know what proteins were applied in lute finishes. A Stradivari viola d’amore sample examined by Échard [48] by pyrolysis (heat-induced decomposition) and GC/MS showed biomarkers that may implicate egg yolk. IR analysis of the *Davidoff* Stradivari violin from the same study also found putative signs of proteins [49]. In an earlier study, White [22] analyzed the amino acids from a D. Montagnana cello ground coat and putatively identified collagen.

Pollens [32] reported a study of the chloroform-insoluble fraction of Stradivari’s wood finish that showed proteins and cellulosic materials, but the analytical method he used was not described. Cellulose-like compounds may have come from the wood fiber or carbohydrates in the finish. Using the furfural test, which detects pentose sugars [13], White [22] found some carbohydrates in a D. Montagnana cello finish. We cannot yet ascertain if the presence of proteins and carbohydrates is related to the use of *vernice bianca* proposed by Sacconi [9], which is a protein-carbohydrate mixture.

In summary, there is fairly convincing evidence that at least a small amount of protein was incorporated into some classic Italian violin finishes. Judging from historical practices, proteins on old violins had four potential sources: animal (or fish) glue (also called gelatin or collagen glue), egg white, egg yolk, and casein glue (from milk or cheese) [13, 27]. Plant gums also contain glycosylated proteins but the protein content is generally quite low. At this point, there is some tentative evidence for the presence of glue and egg proteins, but further verification is required. Possible sources of carbohydrates include plant gums (like gum arabic), colored gum-resins (like aloe or gamboge), or oleo-gum-resins (like myrrh gum) [11]. The majority of proteins in higher organisms are glycosylated, some of which have very small sugar moieties, while some are mostly made up of sugars. Without further details about the source and layer profile of proteins and carbohydrates, it is difficult to understand their potential purpose in a wood finish.

How about the unvarnished inside of violin

plates, did it receive some transparent coating? Condax [45] thought it was a general practice to apply some surface treatment to the interior of plates in Old Italian violins, while Sacconi [9] thought Stradivari used *vernice bianca* for this purpose. We are not informed on how they came to such conclusions. It is known that the back of old wooden panel paintings sometimes had proteinaceous protective coatings [28]. While using proteins to seal wood pores is a common practice in many crafts, including violin making [17], I do not know if plant gums have been used for this purpose. Tove and coworkers [51, 52] have used Rutherford backscattering and EDXRF to examine the unvarnished plate surface of antique Italian violins, but these elemental analysis methods were unsuitable for detecting organic coatings such as *vernice bianca*. The comparison between the unvarnished portion of a violin back and a cello belly both made by Stradivari found higher iron and tin levels in the latter. It is unclear if this reflects the inherent difference in the types of wood involved (maple vs. spruce), or some kind of superficial or penetrating wood treatment.

A COLORFUL ISSUE

No authority has claimed that the color of Cremonese violins correlates to their tone. Nevertheless, how to color the wood finish has attracted the attention of many violinmakers and scholars. The Hills' opinion on coloring is rather pessimistic, calling it "the stumbling block in the way of so many makers" [7]. For them, the key to coloring is to avoid its negative impact on the acoustics. Others are fascinated about coloring because they wish to replicate the unequalled beauty of Stradivari's finish [9, 12, 53]. It is no secret that the appearance of a violin has a great impact on its market value.

Cremonese instruments came in a variety of colors [10, 12]. For instance, Stradivari started with a yellow color long used by the Amatis and later experimented with many variations [7]. The basic Cremonese colors were yellow, red, and brown. Generally speaking, varnishes can be colored in four ways. The first is to add organic or inorganic pigments, which are insoluble in the medium, such as colored particles of vermilion shown in Part I, Fig. 4 [1]. Secondly, organic dyes can be fixed onto transparent inorganic par-

ticles. The generic name for this type of pigment is lake, such as madder lake. A third possibility is to dissolve organic dyes or colored resins, such as dragon's blood, in the oil-resin medium, with or without the help of volatile solvents. Lastly, drying oils and resinous constituents themselves may be colored.

Inorganic pigments identified in Cremonese finishes to date include, as discussed in Part I [1], vermilion/cinnabar (mercury sulfide), orpiment (arsenic sulfide), and iron-earth (iron oxides). The excessive use of these pigments, having RI around 2.5–3, would lead to opacity because the RI of oil-resin medium is ~1.54 [46]. Count Cozio di Salabue [54] mentioned arsenic being added to 18th-century Italian varnishes, which has been detected in the instruments of Stradivari [35, 56] and a 1740 violin of Genoese master Bernardo Calcagni [56]. Sacconi believed that Stradivari sometimes used cinnabar while Guarneri *del Gesù* sometimes used Venetian red (Fe_2O_3) [9]. Interestingly, when Échard [56] examined 15 Old Italian instruments from 1550–1750, the only three that contained mercury all belonged to Stradivari. Iron oxides appeared to be a common pigment in Old Italian violins, including Cremonese instruments by Ruggieri [57], Stradivari [8, 32, 57, 65], and A. Guarneri [3]. On one of the Stradivari violins, iron oxide was found alongside manganese oxide, indicating the use of umber earth [48]. It is also known that iron and manganese are effective driers in fixed oil varnishes [26], and therefore the distinction between a drier and a pigment is not clear-cut. Also, iron could be an adulterant from tools or other minerals.

Interestingly, blue pigment particles had been observed by light microscopy on a Stradivari sample dated 1690 [57, 58]. This could potentially explain the purple tint of Cremonese finishes observed by some authors [2, 59]. The reported identity of the pigment was either indigo or Prussian blue. These two pigments often appear similar under light microscopy [60]. It is well established that Prussian blue (ferric ferrocyanide) was first synthesized in Germany in 1704 and introduced as an artists' pigment around 1720 [19, 61]. It can therefore be assumed that Stradivari's blue pigment was indigo (from the leaves of *Indigofera tinctoria* or *Isatis tinctoria* [13]), which was known to ancient Rome [61].

Moreover, three independent studies reported carbon black (charcoal) particles in Stradivari's color varnish [8, 32, 57].

Under light microscopy, several researchers had observed particles that resembled lake pigments [2, 3, 23, 33, 34, 57]. However, the organic dye in lake pigments is generally difficult to ascertain [13]. Since the first synthetic organic dye did not appear until the 1850s [13], Cremonese masters must have used natural ones. Based on light microscopy studies, Schmidt [34] and Nagyvary [57, 58] reported madder lake in Stradivari varnishes. Madder is a red dye extracted from the root of the madder plant (*Rubia tinctorum*), known in Italy since antiquity [13, 62]. Madder is the most important red natural dye of vegetable origin [13], and its lake can be permanent [18, 19, 21, 63]. The identification of madder lake is further supported by two microchemical studies. Michelman [64] reported madder lake in a Ruggieri cello using an unspecified microchemical test, and Condax [33] observed lake pigments in Old Italian varnishes showing orange in acetic acid and purple in potassium hydroxide, and concluded the presence of madder lake. Although such pH testing suggests the presence of some organic dye, it is not an unequivocal demonstration of madder. First, there may be other organic dyes showing similar color changes. Moreover, the extract of madder contains several different dyes, most notably alizarin and pupurin [13], and their colors strongly depend on metal ions present [62]. As such, it is difficult to predict the color of madder lake under different pH values.

The most advanced lake pigment analysis to date (reported by Échard and coworkers in 2009 [65]) was carried out using micro Raman confocal microscopy. Raman spectroscopy examines the vibration of chemical bonds in a compound, somewhat similar to IR spectroscopy. On the *Provigny* Stradivari violin (1716), the organic lake showed Raman spectra typical of an anthraquinone dye. Compared to common anthraquinone dyes found in nature (alizarin, pupurin, and carminic acid), the spectra was closest to the carminic acid, the main component of cochineal. At the time, the most popular cochineal came from the Central American insect *Dactylopius coccus*. The inorganic binder was determined by EDXRF to be aluminum hydrox-

ide (hydrated alumina), which was the standard lake binder of the time [65].

Taken together, the evidence suggests that Stradivari used red lake pigments frequently, which may partially explain the transparency of his color varnish. Madder and cochineal dyes have been identified so far, which were probably co-precipitated with aluminum hydroxide to prepare lake pigments [9, 25]. It is not yet possible to rule out the use of additional dyes and other inorganic particles for lake binders.

The appearances of classic Italian varnishes, according to White [22, 23] and Sacconi [9], do not resemble varnishes with dissolved organic dyestuffs or color resins, such as gamboge or dragon's blood. Also, such substances have not been identified by chemical analyses. However, dissolved organic colorants in small amounts may be difficult to detect. Many organic colorants are also fugitive and undergo chemical changes over time, which further complicates the issue. It has been claimed that gamboge (yellow tree gum-resin from *Garcinia hanburyi* [11, 15]) was found on a Ferdinand Gagliano (1706–1781, Naples) sample based on color changes (yellow to reddish brown) when ammonia was added (cited in Ref. [10], p. 98). However, most organic dyes show color changes when pH is adjusted, and this type of assay can hardly be considered conclusive.

One of the most useful red-color resins is shellac, also called lac, stick lac, seed lac, or gum lac. It is secreted by a scale insect (*Kerria lacca*) and contains 70–80% resin, 4–8% coloring matter, and 6–7% wax [13]. It is the most common resin in spirit varnish recipes, but the coloring matter can also be extracted by sodium carbonate solution and used as a dyestuff. If shellac (with or without some sandarac) is the main component of a finish without drying oil, it is probably a spirit varnish. Shellac spirit varnish is mainly found on Italian violins after 1750, and some German violins before that [8]. There are instances of some shellac found on Stradivari's instruments [32]. Given the many possible uses of shellac, it is difficult to interpret if it was original or due to re-varnishing by restorers. Regardless, analytical evidence clearly shows that classic (1550–1750) Italian violin finishes were primarily based on resinous drying oil, not spirit or essential oil varnishes.

Lastly, the main constituents of the medium, drying oil and *Pinaceae* oleoresins, are also colored. Linseed oil is known to yellow over time, more so than walnut oil [18, 66]. From a chemical perspective, the color of linseed oil is influenced by metals and oxidation [12, 26]. The experience of old master painters indicates that the preparation and purification of oil has strong effects on its color over time [28]. The color of rosin, depending on its source and processing, can vary from pale yellow to dark reddish brown [26], which can further change in the presence of metal ions [12]. Venetian turpentine is a viscous liquid of pale greenish-yellow [26], although impurities can make it brown [18]. Upon drying, it generally does not yellow further in the paint media, making it desirable for artistic applications [18]. Therefore, it remains possible that the oil-resin medium itself can be a main contributor to the color of Cremonese finishes.

Another question related to coloring is whether Cremonese masters tried glazing. In oil painting, glazing is the superimposition of translucent paints of different colors, which may create interesting visual effects unattainable with a single layer of paint or multiple layers of the same paint. Titian (1485–1576), the most revered of Venetian painters, was known to be obsessed with glazing [67]. Cremona in the early 1500s also had a significant presence of Venetian-school painters [6]. Bearing this in mind, we turn our attention to the two micrographs that best represent the cross section of classic Italian violin finishes. The first is for a Stradivari finish (ca. 1690), published by Nagyvary and reproduced in Part 1, Fig. 8 [1]; the second is for a Goffriller cello (1731), originally published by Condax [43] and reproduced in Ref. [50]. The Goffriller sample showed a ground coat and a five-layer varnish about 160 μm thick. Particulates are clearly visible in the second ($<10 \mu\text{m}$, fine lake pigments) and the fourth ($\sim 30 \mu\text{m}$, coarse pigment particles) layers counting from the ground. What we observe in these two specimens is compatible with a glazing technique. Both Nagyvary and Condax reported that classic Italian violin finishes were extremely brittle, making it difficult to produce an intact cross section for examination. In the Nagyvary case, the sample had a soft modern overcoat to provide some adhesion. In the Condax case, he used a heat lamp to soften

the sample before sectioning. However, there were also Stradivari samples examined by other researchers that did exhibit glazing layers [8, 48, 65]. From just a few cross sections examined to date, it is hard to draw general conclusions, but it appears that glazing could have been one of the coloring techniques of the old master luthiers.

Dichroic effects?

From the discussion above, it should be obvious that our understanding of coloring in Cremonese finishes is far from complete. Furthermore, it is often stated that Stradivari's varnish is dichroic [9, 41, 42, 53, 68–70]. Michelman [71] provided a good description for this color phenomenon:

A dichroic effect can be observed on a violin or viola or cello possessing it by viewing an area from two different directions, perpendicularly to a band of the grain on a maple back. A difference in the color of the band under observation will be seen as the direction of viewing is changed. For example, an orange colored area may change to a brown-red as the direction of viewing is shifted.

Michelman further commented that dichroic effects are often accompanied by the illusion of depth. As he correctly pointed out, this usage of dichroism is not consistent with its technical definition in physics and optics. I believe that the proper scientific term would be goniochromism, which means, literally, the change of colors resulting from different viewing/illumination angles. Goniochromism can be measured by proper optical instruments (goniophotometers) [72], but I am not aware of such measurements performed on Stradivari instruments. Goniochromism phenomena observed in natural objects can be called iridescence, pearlescence, or chatoyance, depending on the object and the underlying optical principle.

The iridescence of soap bubbles and the pearlescence of pearls are structural colors resulting from the interference of light. It is almost inconceivable that wood finishes would possess ordered structures that generate interference colors. While tiny mineral particles may show some wavelength dependence in their scattering pattern (dispersion), it is probably insufficient

to cause apparent color changes. According to Michelman's experiments [71], colored and colorless wood finishes applied on glass plates do not exhibit dichroism. He believed that dichroism is not an intrinsic property of the wood finish, but a result of its interaction with the wood. In my opinion, the dichroic effect of violin backs may resemble what woodworkers call chatoyance. Chatoyance, derived from "like cat's eye" in French, can be observed in some gemstones (cat's eye, tiger's eye, and hawk's eye), in silk cloth, and in some woods, especially the curly types. The underlying optical principle is the selective reflection of light in certain directions by a group of parallel fibers. Chatoyant gemstones show wavy bands of varying colors and luster, and these bands move as the mineral is being turned, producing the illusion of depth. The characteristic shimmer of silk garments is also the result of uneven reflection.

Woodworkers have long been familiar with many kinds of chatoyant woods, including curly maple. They have also developed various techniques to bring out the chatoyance in a piece of wood such as the smoothening of the surface and the application of transparent varnishes or wood stains [73]. How much chatoyance can be enhanced or suppressed is a part of the woodworking skill, guided by empirical experience rather than specific scientific principles. If it is true that Stradivari's maple shows unusual degrees of chatoyance, it may imply two things. First, his wood finish is particularly good for bringing out chatoyance. Alternatively, his maple may have inherently different properties from regular tonewood maple, either due to wood selection or special wood treatment.

SUMMARY OF IDENTIFIED SUBSTANCES

In Table 1 substances convincingly identified in Cremonese and other classic Italian wood finishes are compiled for quick reference. This list is by no means comprehensive or definitive, and is influenced by my interpretation of the cited studies. The chemical analysis of Cremonese finishes is a work in progress, with many obvious challenges. The small number of samples analyzed so far makes it difficult to reach a conclusion about the similarities and differences

between various makers, periods, and regional traditions. Problems such as authenticity, wear, and contamination can also undermine the validity of analytical results. Chemically similar substances may not be readily distinguishable, and details on how natural materials were collected, processed, mixed, and applied are almost always unobtainable. The spatial distribution of each material in the multi-layered wood finish is in most cases unclear. Negative results in current chemical analyses do not prove the absence of a material, especially for organic substances. Some inorganic substances already identified are not listed if the abundance is low and the function is unclear, because most inorganic materials in those times would have been impure mixtures. For example, Michelman sometimes detected boron, tin, copper, and silver in old Cremonese and non-Cremonese finishes (summarized in Ref. [10]); it is difficult to determine if they were adulterants or added intentionally. Our understanding of the Cremonese finish is bound to improve as the science advances. Therefore Table 1 should be viewed as a working draft of the "rediscovered" Cremonese ingredient shelf-list, not any sort of recipe collection.

Putting it together

While Table 1 provides what may be considered as the reclaimed, but incomplete, ingredient list of Cremonese finishes, we would like to know how these substances fit together in the actual finishing system. To achieve this, we need analytical methods that can provide both chemical identification and spatial information. While we have discussed some progress in this direction, much remains to be done. Recently, Échard and coworkers have been combining multiple analytical methods to get a head start in this direction [48]. Their analyses of seven Stradivari instruments are summarized in Table 2.

It needs to be pointed out that not all analytical methods have been applied to all seven instruments. Therefore, although no organic substance is listed under the *Longuet* Stradivari, it represents the absence of the experiment rather than the absence of organic matters. What is immediately striking about the data in Table 2 is the heterogeneity. Although researchers can generally determine the oldest wood finish on an

Table 1. Substances identified in the wood finish of classic Italian string instruments

Substance	Identification Method ^{1,2}		Refractive Index ⁵	Possible Purpose	Note
	Cremonese ³	Italian ⁴			
Linseed oil	GC ^d , GCMS ^{c,p}	GC ^{d,l} , GCMS ^c	1.53-1.57	Drying oil medium	RI of dried film
Walnut oil	GCMS ^c	GC ^{d,h} , GCMS ⁿ	1.53-1.57	Drying oil medium	RI of dried film
Venetian turpentine	GCMS ^c	GCMS ^c	~1.54	Major resin/solvent	RI of dried film
Rosin	GC ^d , GCMS ^{c,p}	GC ^{d,h} , GCMS ^{c,o}	~1.54	Major resin	Probably <i>Pinus</i> species ^d
Mastic	GC ^d	GC ^d , IR ^j	~1.54	Minor resin	
Copal		GC ^d	~1.54	Minor resin	
Sandarac		GC ^d	~1.54	Minor resin	
Protein	AAA ^e , MC ^{e,h} , IR ^c	AAA ^e , MC ^{e,h} , IR ^c	~1.54	Isolation layer ^a Binding medium ^c	Putatively identified: egg white ^e , egg yolk ^c , glued, ^e
Wax	GCMS ^c	GC ^d	~1.44	Minor medium	Found beeswax ^d
Carbohydrates	IR ^p	MC ^d	~1.53	Isolation layer ^a Wood sealer ^a	May be plant gum ^a
Calcite	PXF ^{b,g} , LM ^g	PXF ^{b,c,l} , XRD ^c , IR ^c	1.57	Inert particles	Strongly birefringent
Calcium sulfate	PXF ^b	PXF ^{b,c,l} , XRD ^c , IR ^c	~1.56	Inert particles	Found hemihydrate ^c RI for hemihydrates
Silicon oxide	PXF ^b , LM ^b	PXF ^{b,c,l} , XRD ^c	1.55	Inert particles	Found quartz ^b
Potassium feldspar	PXF ^{b,g} , LM ^g	PXF ^b	~1.52	Inert particles	Potassium aluminosilicate RI for orthoclase
Aluminum silicate	PXF ^b , LM ^b	PXF ^{b,c} , IR ^c	~1.56	Inert particles	Found kaolinite ^c RI for kaolinite
Aluminosilicates	PXF ^b	PXF ^{b,c}	Variable	Inert particles	Further identification is difficult
Barium sulfate		PXF ^b , AES ⁱ	1.64	Inert particles	
Lead	BXF ^{c,f,k,l} , AES ^{e,i}	AES ^{e,h} , RBS ^k , PXF ^b , BXF ^{c,f,k,l}	Variable	Drier/pigment	May form lead soap Found lead chloride and lead oxide/carbonate ^b
Iron oxide	PXF ^{b,c,g,l} , LM ^{b,g} RS ^{c,p}	PXF ^{b,c,l}	~2.8	Pigment/drier	RI for Venetian red
Umber earth	PXF ^c	PXF ^c	~2.4	Brown pigment	Manganese oxide and iron oxide
Vermilion/cinnabar	BXF ^c , LM ^{c,q}	BXF ^c	~3.0	Red pigment	Mercury sulfide
Orpiment	BXF ^m , PXF ^g , LM ^g	BXF ^{c,l}	~2.7	Yellow pigment	Arsenic sulfide
Carbon black	LM ^{b,l,p}		Opaque	Black pigment	
Cochineal lake	RS ^c		<1.7	Red pigment	Over aluminum hydroxide ^c
Aluminum hydroxide	PXF ^c		~1.6	Binder for lake pigment	
Madder lake	LM ^{b,g}	LM ^{d,e} , MC ^{e,i}	Variable	Red pigment	RI depends on binder
Unidentified lake	LM	LM	Variable	Pigment	Composition unclear
Indigo	LM ^b		~1.50	Blue pigment	

1. Identification methods: AAA, amino acid analysis; AES, atomic emission spectroscopy; BXF, X-ray fluorescence of bulk samples; GC, gas chromatography; GCMS, gas chromatography coupled to mass spectrometry; IR, infrared spectroscopy; LM, light microscopy; MC, microchemical test; PXF, X-ray fluorescence of particles; RS, Raman spectroscopy; RBS, Rutherford backscattering; XRD, X-ray diffraction.
2. The superscript indicates scientific references to studies published by these investigators: a, Sacconi [9]; b, Nagyvary [3, 57–59, 74, 75]; c, Échard [5, 48–50, 56, 65, 76]; d, White [22, 23, 77]; e, Condax [24, 33, 43, 45, 68]; f, von Bohlen [35, 78–82]; g, Schmidt [34]; h, Baese [2, 25, 47, 83]; i, Michelman [64, 84–92]; j, Staat [35, 36]; k, Tove [51, 52]; l, Meyer [8, 80, 81]; m, Barlow and Woodhouse [56, 93–95]; n, Caruso [30]; o, Chiavari [31]; p, Pollens [32]; q, Greiner [96]. For details, please refer to the main text.
3. Identified in bowed instruments (1550–1760) by Cremonese master makers, including Guarneri family members who relocated elsewhere.
4. Identified in string instruments (1500–1800) by Italian makers outside Cremona.
5. For a material of variable compositions, the approximate value or a range of RI is given. For crystals with multiple RI, the average value is given. RI values are compiled from several references [38, 44, 46, 60]. The RI of wood is 1.53–1.58.

instrument using various inspection methods, it remains possible that some instruments have lost all of their original color varnish or wood finish [7, 9]. Another possibility is that Stradivari's finishing method was actually quite variable, as suggested by Sacconi [9]. Sacconi mentioned some Stradivari finishes whose thickness "is reduced even to the point of resembling a mere veil." Without further data on the stratigraphy of Stradivari finishes from unequivocal samples, a better knowledge of how the wood surface was

prepared, and the organic composition of the binding medium in the ground, it would be difficult to scientifically reconstruct the wood-finishing protocol of Stradivari from the available ingredient list or explain its physical, chemical, and acoustical properties.

Sacconi called the coating between the color varnish and the wood a "wood preparation." He noted its "strong power of penetration into the wood allowing an amalgamation and combination of the wood and the preparation," and that

Table 2. Wood finish comparison between six violins and a viola d'amore made by Antonio Stradivari.^a

Violin Name	Date	Organic Components Components	Inorganic	Structure
<i>the Longuet</i>	1692		- Pb, Fe	Upper layer 30-40 μm Underlayer
<i>the Davidoff</i>	1708	- Siccative oil (walnut?) - Diterpene resin (Pinacea)	- Al, Si, Mg, Na - Pb, Fe	Not resolved
<i>the Tua</i>	1708	- Siccative oil - Diterpene resin (Pinacea)	- Pb, Fe	
<i>the Viotti</i>	1709		- Pb, Fe - Mn (table)	
<i>the Provigny</i>	1716		- Hg (head), Pb - Fe, Mn: umber earth (table)	
<i>the Sarasate</i>	1724	- Oil (linseed) - Diterpene resin (Venetian turpentine)	- Hg (cinnabar/ vermilion)	Not resolved, sample too small
Head of a viola d'amore	Early 1700s	- Diterpene resin (Pinacea) - Siccative oil? - Egg yolk? - Sebaceous contaminants?	- Ca, S: gypsum - Al, Si, Mg, Na	Upper layer ~20 μm Underlayer Mineral particles

^a Data compiled from Table 5 of Ref. [48] and personal correspondence with J.-P. Échard. For technical details, see Ref. [48] and the references therein.

“a high superficial surface tension was needed to enable the preparation to fill and stop the pores.” As such, it seems that the wood preparation had two components. The first component was absorbed into wood fibers, and the second component formed a coating above the cells and pores. It is difficult to interpret his comments about the properties of the “wood preparation” without knowing the relationship between these two components. The second component appears to match the mineral ground observed by electron microscopy. We do not know whether the first component, if it ever existed, resulted from the ground medium seeping into wood fibers during the drying process. Others propose that a separate transparent coating could have been applied before the particulate ground, in which case it may be called a sealer [17, 97].

A comprehensive study comparing five different Stradivari instruments was recently conducted by Échard and coworkers [65]. These included four violins (a long pattern from ca. 1692, the *Davidoff* of 1708, the *Provigny* of 1716, the *Sarasate* of 1724) and one head of a viola d’amore (ca. 1720). The techniques used to investigate their wood finishes included Fourier transform IR spectroscopy using a synchrotron

beam line, Raman confocal spectroscopy, SEM/EDXRF, UV/visible microscopy, and pyrolysis-GC/MS. They examined varnish/wood cross sections using UV/visible microscopy and found two main layers. The lower layer penetrated ~10-30 μm into the spruce and 30-100 μm into the maple, and barely rose above the wood. The upper layer was tinted and some red pigments were identified (iron oxide and cochineal lake). Both layers are predominantly organic (not filled with mineral particles), containing mostly drying oil as revealed by IR spectroscopy. Protein, waxes, and carbohydrates were not detectable, but their presence in small amounts could not be ruled out. The resinous component was detectable in the upper layer, and by GC/MS appeared to be diterpene resins of the *Pinacea* family.

The biggest surprise in the latest study by Échard et al. [65] is the absence of the mineral ground. Based on this study alone, it seems that Stradivari simply applied a layer of drying oil as the ground. But this may be an oversimplified interpretation. First of all, the analysis did not rule out that small amounts of proteins, carbohydrates, or amber could have been added. Secondly, I would like to point to another electron micrograph recently published by Barlow [95]

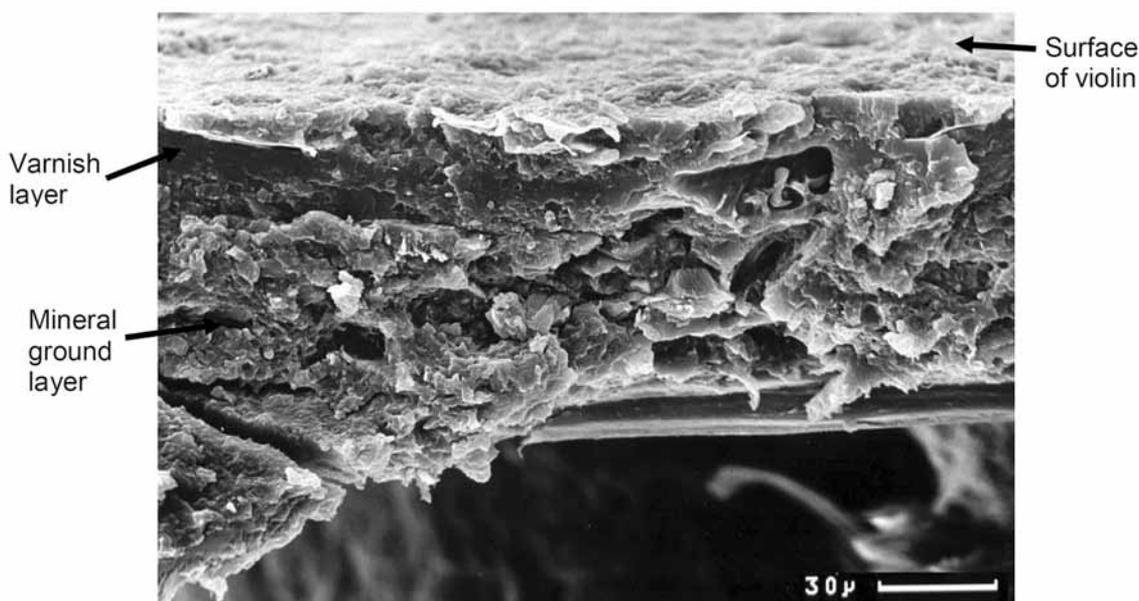


Figure 3. Scanning electron micrograph showing the cross section through a mineral ground layer on a 1728 Stradivari violin. The wood below appears to be maple. Reproduced from Ref. [95] with permission of the author C. Barlow.

in 2008 (Fig. 3). It clearly shows Stradivari's application of mineral ground over the wood (maple). This is very similar to what is shown in Fig. 1, *viz.*, that Andrea Guarneri applied a mineral ground over the spruce. Additional evidence that Cremonese makers adopted mineral grounds was discussed in Part I of this article [1]. The discrepancy with regard to the mineral ground cannot be easily explained at this moment. Perhaps different instruments simply received different wood finishes. Since all five of the Stradivari instruments analyzed by Échard et al. [65] have belonged to Cité de la musique for over a century, and thus share a common history, it is not inconceivable that they had been similarly re-varnished in the past, although there is no indication that they were. Can the lower coating penetrating into the wood be the original sealer, while the mineral ground is already lost? Clearly, additional studies are required to clarify the many questions that still surround the ground and the potential sealer coatings used by Cremonese makers.

TIME FOR A PARADIGM SHIFT?

In Part I of this review [1], I mentioned what can be considered the “traditional material paradigms” with regard to Stradivari's wood finish. With the emergence of recent chemical analysis data, it appears that these century-old ideas often miss the mark.

The traditional belief was that the Cremonese color varnish was based on oil-resin media. There have also been many who disagreed, insisting that the media was alcohol- or essential oil-based [37, 98]. They observed that oil varnishes do not dissolve in alcohol but Cremonese varnishes do. I think this apparent paradox can be resolved when we realize that chemical changes (mainly oxidation) can continue to take place in a varnish film for hundreds of years. Merrifield [20] mentioned a 19th-century Italian painter, who restored old oil paintings, saying that alcohol dissolves old oil paintings but not new ones, because of chemical transformations brought by aging. From the positive identification of drying oil and resin in almost every classic Italian finish analyzed to date, we may conclude that fixed oil varnish was the standard practice.

To account for the extraordinary properties

of Stradivari's finish, many old (and modern) theories suggest the use of exotic substances as binders or colorants. Modern chemical analyses did not identify any exotic ingredient, just standard materials used by craftsmen and artists from those times (Table 1). In fact, the resins identified so far in Cremonese finishes—mastic, rosin, and Venetian turpentine—could not have been more traditional. They all appeared in the oldest recipe of oil-resin varnish found in Europe, recorded in the 8th-century Lucca manuscript [28]:

. . . mixtures of transparent substances, forming a varnish to be applied to colored surfaces: linseed oil 4 parts, turpentine resin 2, galbanum 2, larch resin 3, frankincense 3, myrrh 3, mastic 3, veronice [could mean amber, copal, or sandarac] 1, cherry-tree gum 2, flore puppli [unknown substance] 1, almond-tree gum 2, fir resin 2.

According to traditional opinions, mineral particles were not expected to be a major component of the color varnish. Using electron microscopy, Nagyvary has shown a Stradivari varnish containing many sub-micrometer particles ([1], Fig. 6), which are basically invisible under light microscopy. How they got there is a fascinating question. Without additional high-resolution SEM studies to confirm this result, we don't know if the high particulate content is typical of Stradivari's color varnish. The presence of inert mineral particles in oil varnishes may be deliberate or coincidental. For instance, Cennini [27] recommended adding pounded bricks into liquid varnish (*vernice liquida*, an unspecified oil-resin mixture) to make waterproof coatings. It could also happen when earth pigments with high clay contents are used [40]. In Stradivari's case, the electron micrograph clearly shows mineral particles that were carefully prepared and deliberately introduced.

The traditional belief is that the ground is a film of organic materials, but modern research has sometimes found the ground to be a composite of mineral powders and organic binders, which would be much harder than simple organic coatings. Stradivari's ground was filled with micrometer-sized, colorless particles with

RI similar to the oil medium. To clearly observe such particles would require electron microscopes (Figs. 1 and 3; also Figs. 1 and 3 in Ref. [1]). Such particles probably do not scatter enough light to cause cloudiness, but are sufficient to add some brilliance [3]. It has also been proposed that having tiny particles in a chippy varnish may lead to micro-scale cracks [3]. Interestingly, a recent experiment showed that cracks in violin finishes may act as low-pass filters for noise [99].

The long-standing confusion about the organic composition of the ground remains unresolved today. The main technical challenge is the insolubility of the binder, a testament to its durability but also a stumbling block for the analytical chemist. When examined under the microscope, the insoluble ground fragments had the appearance of linoxyn particles (polymerized solids of linseed or similar oils), and their insolubility may suggest the addition of resins, perhaps amber [2, 3, 24]. Amber, a fossilized conifer resin, is supposedly the hardest and most durable of varnish resins [26]. Other ways to decrease the solubility of linoxyn may include adding proteins or carbohydrates to form emulsions. An indirect evidence of drying oil in the ground came from the elemental analysis of the color varnish and the ground coat of an A. Guarneri cello (ca. 1670) [81]. The two have comparable amounts of lead, but the color varnish has more iron. The high iron content implied the use of iron earth pigments. The lead profile implicates that a drying oil with lead drier served as the binder in both the color varnish and the ground.

As discussed earlier, recent studies also implicate the presence of proteins in the ground of Cremonese instruments. Smoothing wood surfaces with a coating of proteins and inert mineral particles is an ancient idea dating back to the Egyptians [28], and indeed Italians prepared wooden panels for painting by applying *gesso*, a mixture of collagen glue solution and calcium sulfate or calcium carbonate [27, 39]. When water evaporates from the gesso coating, it leaves tiny pockets of air (RI equal to 1) that scatter light and create a whitish look, masking the wood figure. This “whiting” effect is of course undesirable for a violin. Recent studies show that Italian lutes were gessoed before oil varnish

was applied [49]. The transparency of the gesso ground may be improved by mixing protein (egg or glue) or carbohydrates with oil to form an emulsion medium, which was probably discovered by early tempera painters [100]. Laurie [21] has observed gesso mixed with oil on some old paintings. The idea of an emulsion ground on violins was first proposed by Conday [45] when he detected proteins in an Amati sample.

While traditional views considered oil varnishes and protein (glue) coatings in separate sublayers, recent analytical evidence suggests the possibility of emulsion media. To further investigate this, we will need analytical tools that can detect protein and oil from the same sublayer. Secondly, a mixture of drying oil, resin, mineral, and protein may undergo complex chemical changes during its preparation and application, and it is difficult to predict its physical properties. Although emulsion medium is not often used in oil paintings, Laurie has found descriptions of its use in old writings [21]. In his experiments, Laurie mixed pigments with an emulsion medium of linseed oil, egg yolk, and Venetian turpentine. The initial mixture was opaque but became transparent and beautiful upon drying [21]. Some modern painters think that emulsion media have the advantage of drying evenly and quickly because the evaporation of water leaves tiny holes for the air to pass through, allowing linseed oil to polymerize throughout the film, not just starting from the surface [100]. In a recent issue of *VSA Papers*, Harris, Sheldon, and Johnston [101] studied the feasibility that emulsion grounds containing particulates were used on old violins. The authors concluded that one of the desirable properties of the emulsion-particulate ground is the lack of penetration into wood pores. Interestingly, Meyer [8] noticed that the Cremonese ground did not penetrate or fill wood pores as much as the Venetian ground.

As we can see, traditional opinions on the composition of Cremonese finishes often cannot withstand the scrutiny of modern science. Thanks to advances in chemical analysis, we have made great strides. There are still a number of critical gaps in our understanding, but we can reasonably expect more breakthroughs in the near future. After all, this is an age of rapid progress in material science. Perhaps the greatest obstacle is for researchers to find funding and

authentic samples. Since the investigation of Cremonese finishes is an archaeological endeavor, in some sense it can never be completed. What we have rediscovered so far is already useful in two respects. At the practical level, it can help modern violinmakers make informed decisions in their attempts to recreate old finishes or produce even better ones. At the curiosity level, it can provide clues to how the coating system was born and lost.

Admittedly, I am not an expert in the evolution of art materials and violin making. The following reflects what I have learned in my foray into this subject. Or, rather, they are my personal musings on the history of violin finishes, presented here for the entertainment of the reader.

THE RISE OF THE CREMONESE FINISH

Available analytical evidence has demonstrated that, between 1550 and 1750, violin finishes used in Cremona were similar to those in other parts of Italy, consistent with the opinion of the Hills [7] and Sacconi [9]. Furthermore, classic violin finishes bear a general resemblance to lute finishes used in 16th–17th-century Italy, as discussed throughout this article. In hindsight, this is not at all surprising because Stradivari also built lutes, guitars, mandolins, and harps [9]. It is reasonable to assume that the Cremonese finish evolved from the older system of lute finishes.

But how did lute finishes originate and evolve? Unfortunately, despite much research into violin finishes, lute finishes remain relatively understudied. It would be interesting to know when lutes started to receive finish coatings, what the earliest finish was, and how it evolved into an oil-resin formula. The lute predates the invention of oil painting, and its history is without doubt a fascinating subject. Of course there are many traditional views about what lute finishes were and how they evolved, but recent analytical evidence [5, 49, 50, 56, 76] is quickly challenging the validity of many hand-me-down opinions.

Looking at Table 1, there appears to be no exotic substance in the Cremonese ingredient list. There is always the caveat that some exotic materials may have eluded our investigations. However, with so many useful varnish ingredi-

ents in the list, it would be hard to imagine that Stradivari had to rely on some highly unexpected material to confer near-magical properties. He might have added a bit of amber to increase the hardness or some dragon's blood to modify the color, but these materials will not change our fundamental understanding of his finish. One of the most ingenious aspects of his wood finish is the use of tiny mineral particles, down to the sub-micrometer range. Particles of such uniform fineness probably required both milling and size-selective separation. Having a master violin shop perform sophisticated powder preparation was an unlikely scenario, but we do not know who supplied them to the violinmaker. In fact, we do not have any reliable information with regard to how Cremonese violinmakers procured their raw materials. The closest historical account was given by Victor Grivel, a 19th-century writer, who mentioned that Stradivari bought his varnish from the local druggist (translated in Ref. [83]):

The aged Boislongpré, whom I knew well in my youth, told often that a descendent of Guadagnini had affirmed that none of the Cremonese luthiers had knowledge of the recipe of the varnish they employed on their instruments; that an apothecary, from the time when Guarneri and Stradivari were still living, manufactured for the use of everyone, and which Stradivari, "*le Grand Stradivari*" as we called him, carried his bottle himself when he went to the shop, for which his friend the apothecary, never gave him the bottom of the barrel.

It is unclear how much faith one can put into Grivel's account, considering that it was something like sixth-hand information. Moreover, recent scholarship indicates that the Guadagnini family had no direct connection with the top Cremonese makers [102]. I think lute varnishes evolved out of the coatings and paints used by Medieval/Renaissance artisans. As instrument making became more specialized, instrument finishing evolved into its own system. Traditional ingredients and techniques became combined in different ways, but no radical departure appeared necessary. Current analytical evidence supports the notion that Stradivari was an inge-

nious tinkerer, rather than a guardian of secret materials and methods.

One may also reason that instrument making was too small of an industry to demand specialized raw materials. Especially if the material was a secret, the market would have been vanishingly small. Instrument makers probably shared the same material suppliers for other arts and crafts. Medieval and Renaissance artists procured raw materials from two general sources [28]. The first were cloisters that operated infirmaries or dispensaries; the second was the secular apothecary. In both cases, a druggist with medicinal and alchemical knowledge presided over the preparation or distribution of pigments, resins, oils, ointments, and herbs [20]. In large cities, the secular apothecary was probably the main source of art materials. In Florence, painters were placed under the guild of doctors and apothecaries (*Arte dei Medici e Speziali*) [103]. Titian was also said to have purchased his pigments from the apothecary at Piazza San Salvatore in Venice, and, even in the early 1800s, the Piazza still had an apothecary that claimed to sell historical pigments [20]. Moreover, great painters like da Vinci and Van Dyck befriended the great alchemists of their times [28]. Was the violinmaker more akin to the painter or the alchemist in his approach toward varnish preparation? A hint came from the writing of the Cremonese monk Arisi, a good friend of Stradivari (Ref. [10], p. 72):

In Cremona, there is also living my very close friend Antonio Stradivari, an excellent maker of all kinds of musical instruments. It will not be out of place to make special mention of his merits. His fame is unequalled as a maker of instruments of the finest qualities. He has made many of extraordinary beauty, which are richly ornamented with small figures, flowers, fruits, arabesques and graceful interlaying of fanciful ornaments. All of the ornaments are drawn perfectly. Sometimes he paints in black or inlays with ebony and ivory. They are executed with the greatest skill, and are worthy of the exalted personages to whom they are intended to be presented. So I have thought it proper, to mention

some works of this great master, in testimony of the high esteem and universal admiration he enjoys.

It is regrettable that Arisi did not make a specific reference to the violin, the wood, or the varnish. The master was noted for his skills as a draftsman-decorator, not as an alchemist-varnisher or a woodworker-acoustician. Stradivari probably could have sought some technical assistance from the druggist/alchemist for preparing varnishes, similar to what painters did in that period. We are not sure who prepared his sub-micrometer mineral particles, but it was probably sold by the apothecary, too. Recent scholarship reveals that many northern Italy painters bought pigments from color sellers (*vendecolori*) in the 16th and 17th centuries [104], whose shops specialized in artisan supplies, including oils and varnishes [105]. It seemed that *vendecolori* was an informal subdivision of apothecaries under the guild system and their business merged back into general apothecaries in the 18th century [104]. Hereafter, we will consider color sellers as apothecaries without making specific distinctions.

Over the last two centuries, an incredible amount of research has gone into old varnish recipes in hopes of magically uncovering the one adopted by Stradivari. Now that modern science can give us a much clearer picture of what went into his finish, we may revisit these old recipes to see which one fits the best. Unfortunately, none of the historical recipes that I encountered resembles the finishing system used by Stradivari. His color varnish may resemble oil painting with a resinous medium, but the ground appears to be unique. Ironically, my search for the historical origin of Cremonese recipes has taught me more about its demise than its birth, as I will explain below.

THE FALL OF THE CREMONESE FINISH

The general replacement of fixed oil varnishes by spirit varnishes in Italian violins after 1750 is a major mystery. By 1800 it appeared the transition was complete [7]. To understand why violinmakers made this switch, it is important to examine the historic context of what was happening around them. In my opinion, three

external factors must be seriously considered. First, when the last great maker of Cremona died (Carlo Bergonzi, 1682–1747), fixed oil varnishes had become obsolete in that town. Secondly, this was not an isolated incident, but throughout Europe fixed oil varnishes had been replaced by spirit and essential oil varnishes in the second half of the 18th century. Lastly, it would have made a great impact on the commercial supply of resinous drying oil and the ingredients for making it.

In the Biblioteca Trivulziana in Milan, there exists a varnishing manuscript from Cremona, dated 1747 [106]. The anonymous author is assumed to be a Cremonese gentleman, an amateur enthusiast in varnish making. Judging from similar manuscripts and books from that period, varnish making was a popular hobby among many serious amateurs. Obviously, the disappearance of the Cremonese finish was not due to a lack of popular interest in varnishing. Since Cremona was a small town, it is quite possible that the author had met the Guarneris or the Stradivaris.

Surprisingly, this gentleman did not record any recipe that resembles the Cremonese finish. Instead, he was obsessed with Chinese varnishes (*verniss de la Chine*). There were 16 recipes given for Chinese varnishes, all based on resins (mainly sandarac and shellac) dissolved in alcohol. Three other recipes used oil of turpentine as the solvent. Among a total of 45 varnish recipes, only one mentioned linseed oil, as a solvent for copal, and it was called a “Turkish varnish” (*vernice turchesa*). It is ironic that an educated varnish hobbyist of Cremona would be oblivious to the fabled formulation of his own town. The fixed oil varnish was in fact the traditional varnish of Europe dating back to Medieval times [28], but to him it seemed foreign. His negligence of the Cremonese violin finish was a vivid testament to the rapid decline of this old craft and the abandonment of resinous drying oils. It can be easily understood if we examine what was happening in the varnishing industry throughout Europe at the time.

The real and the faux Chinese varnish

During the 17th century, Europe was obsessed with Chinese varnish, or Chinese lacquer in

today’s terms [107]. As a protective coating, Chinese lacquer has superior qualities: elastic, waterproof, and durable. It can form very thick coatings that will preserve wood for more than 1,000 years, as observed in ancient Chinese objects. Chinese lacquer comes from the exudate of the Chinese lacquer tree [13], *Toxicodendron vernicifluum* (formerly *Rhus verniciflua*), and its use is dated back to prehistoric times. Later, Japan imported the plant and the craft, and it also became known as Japanese lacquer.

Chinese lacquer was a fashionable and coveted material to 17th-century Europeans. Imported oriental lacquered furniture was rebuilt into European-style pieces, and European furniture was even sent to China for lacquering [107]. Given this insatiable demand, professors, alchemists, craftsmen, artists, entrepreneurs, and, of course, varnish makers throughout Europe attempted to reconstruct the Chinese lacquer. The Chinese lacquer tree only grew in East Asia, and its resinous sap, being highly toxic before it undergoes special processing, could not be transported overseas in a workable form. It was fundamentally impossible to produce the lacquer in 17th–18th-century Europe. But that did not prevent many Europeans from claiming to have recreated it in the form of hundreds of recipes. By the late 1600s, “japan” had become synonymous with durable lacquers in the English language, while Italians preferred to associate it with China.

One of the most popular varnish handbooks in Europe at the time was *A Treatise of Japaning and Varnishing*, written by John Stalker and George Parker and published in 1688 [108]. Its focus was clear: to imitate the Japanese varnish—even all the drawing patterns given were Japanese (Japanese crane, Japanese pagoda, etc.). Stalker and Parker’s closest imitation of the Japanese varnish was shellac dissolved in alcohol. The varnish hobbyist from Cremona previously mentioned, as well as countless other European artisans, basically arrived at the same conclusion, too. Resins formerly used in oil varnishes, such as mastic and sandarac, became incorporated into spirit varnishes, which were easier to prepare and apply than fixed oil varnishes and produced coatings that better resembled the Chinese lacquer. Improvements in industrial distillation also made high-purity ethanol and

essential oils cheaper and more available. With increases in the supply and demand of spirit and essential oil varnishes, fixed oil varnishes were pushed out of the market. Judging from the Cremonese manuscript of 1747, fixed oil varnish had already disappeared from everyday applications.

The fascination with Chinese varnishes had started even before Stradivari's birth. The Paduan manuscript, describing artists' methods around 1600, already offered a recipe for Chinese varnish (*vernice alla China*) based on alcohol, amber, lac resin, and sandarac [20]. The general disregard for fixed oil varnishes in 18th-century Italy also affected the fine arts. Traditionally, fixed oil varnish had been applied to Italian oil paintings as final protective coatings, and occasionally mixed into the paint medium [20, 28]. When Merrifield corresponded with eminent painting restorers of northern Italy in the early 1800s, she was surprised by their ignorance on this practice. She said, "As far as I could ascertain, oleo-resinous varnishes are not only obsolete in the north of Italy, but they appear to be almost entirely forgotten." She commented that when modern painters mentioned oil varnishes, they always meant "essential" oil varnishes. Even before the 18th century, using essential oil varnishes to protect paintings was a standard practice in England, and Stalker and Parker [108] recommended dissolving either solidified Venetian turpentine or mastic in oil of turpentine.

I also came across an extensive treatise written in English about painting and varnishing, published in 1804 in London [109]. The author, Pierre François Tingry, was a chemistry professor in Geneva. His expertise in art materials was evident in his description of the botanical origin of various turpentines and how they were processed into a dozen or more related materials like colophony, Greek pitch, Burgundy pitch, resin, naval pitch, and so on. This section of his book serves as a great information source for historical turpentine products. Tingry was sponsored by the academic society of Switzerland to author an international treatise on varnishing. He considered varnishing as a modern art and classified varnishes into two classes. The first class was from nature, using plant gums or animal gelatin, suitable for objects of natural his-

tory. The second class, divided into five genera, was for artistic applications and a true subject of marvel. The first four genres had resins dissolved in alcohol or essential oils, and the fifth was the authentic Chinese lacquer.

In Tingry's book, the word "oil" always meant essential oil, and linseed oil was called a drying oil. Pertaining to the European origin of varnishes, he said that apothecaries in the old times used to dissolve resins in "spirituous vehicles" (volatile solvents). Strangely, he did not know that European varnishes from the Middle Ages to the Renaissance were fixed oil varnishes. He thought modern varnish developments were stimulated by the import of Chinese furniture into France in the early 1700s, whose amazing varnishes were even fireproof. Tingry was aware of resins dissolved in drying oil, which he called resinous drying oil. He considered it suitable for the final coating in house painting and also for protecting masonry objects. He said resinous drying oil had qualities of a varnish and even mixed it with pigments to paint indoor objects, but he did not call it a varnish, even though aqueous solutions of animal glue and gum arabic were called varnishes. Tingry's treatise clearly portrays that, in most parts of Europe in the late 1700s, the concept of a varnish based on resinous drying oil was not only outdated, but even more alien than imported Chinese lacquer. No wonder our Cremonese gentleman [106] considered a fixed oil varnish a Turkish formulation in 1747!

While Tingry's misconception about traditional varnishes represented the viewpoint of the late 18th century, scholars in the first part of the 19th century renounced his opinion and fixed oil varnishes were reintroduced into the arts. In 1830 Jean-François-Léonor Mérimée [110] published in Paris a treatise on oil painting and advocated the use of fixed oil varnish in fine paintings, as practiced by Renaissance masters. The work was translated into English in 1839 under the recommendation of the Royal Academy. Mérimée lamented that the French school of painting reached the lowest point in its decline around the late 1700s because of the lack of material-related knowledge. A decade later, British scholars Eastlake [28] and Merrifield [20] published their treatises. The fascination of Mérimée, Eastlake, and Merrifield was not for

Chinese varnishes, but for the resinous drying oil of old master painters, their “secrets” for great colors, durability, and execution. It appeared that the general disuse of fixed oil varnishes was a temporary phenomenon in the second half of the 18th century.

Ironically, while the faux Chinese varnish may have contributed to the demise of the classic Italian violin finish, the real Chinese varnish is an excellent instrument finish in its own right. Although unsuitable for violins, Chinese lacquer is found on the most important string instrument in China, the seven-stringed wooden zither called the *qin*. Owing to the preservative power of this lacquer, there still exist dozens of top-condition zithers over 1,000 years old. There is a general preference for the sound of old zithers, and the most prized of all existing zithers, the “spring thunder” made by Wei Lei, dates back to the eighth century. More recent instruments from the Qing dynasty (1644–1912) are said to have inferior sound due to poor varnishes. Qing dynasty instruments generally had ground coats of lacquer mixed with pulverized bricks or tiles, which results in eventual cracking and flaking. Old master instruments had ground coats of lacquer mixed with powdered deer antler (containing proteins and minerals). The top varnish, made of lacquer and colorants like carbon black or vermilion, is said to have little tonal influence. The resinous sap of the Chinese lacquer tree is a natural form of water-in-oil emulsion and, when mixed with proteins and minerals from the antler, forms a durable ground coat of excellent acoustical properties. Although the analytical data are still incomplete, Cremonese ground is possibly a mineral composite with an emulsion binder (containing protein, resin, and drying oil). Maybe there is something magical after all about a ground coat composed of minerals and emulsion binders, both in the East and the West, but we need more chemical and acoustical analysis to confirm this.

Oil varnish vs. spirit varnish

As craftsmen and painters moved away from fixed oil varnishes in the late 1700s, their use by master violinmakers also decreased drastically. But why? The writings of Giovanni Antonio Marchi [111], a leading violin restorer and

maker respected by Count Cozio di Salabue, may provide a clue. His unpublished manuscript in 1786 about violin making mentioned that no one was sure of the methods of Cremonese masters. He said:

Other people believe the good quality of instruments is only to be attributed to the oil varnish used in those days—today we use spirit varnish—because it keeps the wood softer and gives the tone a human and rich character. Practice teaches us the reverse about this oil varnish: it is well known that the dryer the oily parts of the wood and more arid this wood, the better the sound.

Incidentally, GC/MS analysis of a Marchi violin found drying oil and colophony [31], the clear evidence of fixed oil varnish. I was further informed by Roberto Regazzi [112], an expert on Marchi’s life and work, that Marchi varnishes generally looked like oil varnishes. How can we reconcile Marchi’s work with his own words? One possibility is that he added alcohol to his oil varnish, but it is doubtful if it would be called a spirit varnish. Another possibility is that he was simply taking note of the popularity of spirit varnishes, but in his own efforts to mimic the old masters he used oil varnishes. In his treatise he often described his philosophies as contradictory to popular beliefs. He knew very well that old masters used oil varnishes, and his incorporation of drying oil and colophony was consistent with classic Italian violin varnishes, although other details might have differed. Marchi’s major concern was the absorption of oil by the wood, which in his experience negatively impacted the tone.

The Cremonese masters seemed to have avoided this problem by adopting what Sacconi called a “wood preparation.” Judging from modern analytical data, wood preparation may have prevented oil absorption in two ways. The first is by having a particulate ground, an impermeable coating covering the wood pores, as revealed by electron microscopes; the second possibility is by having a non-oil sealer that binds to wood fibers first. When the ground coat is a particulate composite or an emulsion, penetration of the binder into the wood appears to be limited [101]. As

mentioned earlier, it has not been possible to measure what gets absorbed into the top wood layer. Classic Italian violins outside of Cremona also had ground layers, but less is known about the ground composition and how oil absorption was addressed. Evidently, from 1550–1750, Italian master makers outside Cremona built many fine violins with fixed oil varnishes, when spirit varnishes were already available [8]. At the time, they probably thought fixed oil varnishes made violins sound better than did spirit varnishes. Most 20th-century experts also voiced similar opinions [7, 9, 10]. Why did Marchi's contemporaries prefer spirit varnishes for acoustical reasons?

One possibility was that the proper way of using resinous drying oil in violin finishing was not passed on to that generation of makers. But it is hard to understand why the apprentice system was working for two centuries and suddenly the skill became forgotten throughout Italy. A more plausible scenario, in my opinion, is that certain substances used in old violin finishes became commercially unavailable, which compromised the quality of the old finish, and many makers switched to the trendy spirit varnish. As discussed earlier, all ingredients identified thus far in classic Italian finishes (Table 1) appeared to be commonplace either before or after 1750. Hence, the key issue may have been how varnish resins were processed and sold in those days. If violinmakers used to purchase resinous drying oil prepared by the shop, would it still be available? If makers tried to dissolve solid resins by themselves, were the resins collected and processed in a way suitable for such preparation? In Stradivari's time, resinous drying oil was probably sold by the apothecary under the name of *vernice* or *vernice liquida*. To better explain the potential problem with varnish resin supply, let us first examine what “varnish” actually meant through different ages.

WHAT IS A VARNISH?

The English word “varnish” and its Italian equivalent, *vernice*, came from the Medieval Latin *vernix*, which had a number of alternative spellings. For simplicity, I will collectively refer to these related words, from Medieval Latin to modern Italian, as *vernice*. Eastlake [28] has

given a detailed account on the linguistic evolution of *vernice*, which is briefly summarized here. Initially, *vernice* referred to amber. Later, the meaning expanded to most solid resins for oil varnishes because they resemble amber. Some old varnish recipes mentioned *vernice* by weight and mixed it into drying oils measured by volume. The fixed oil varnish made in this manner was called *vernice liquida* (liquid varnish). Over time, *vernice liquida* became simply known as *vernice*; later, quick-drying varnishes based on alcohol and essential oils also became *vernice*. Pigments can be added to *vernice*, and natural solvents and resins can be substituted by synthetic ones, and the formulation is still called *vernice*. In English, the addition of pigments to a varnish creates a paint, but in Italian there is no such distinction. In his own letter, Stradivari [6] referred to his wood finish as *vernice*, which was to be expected.

In the 12th century, Theophilus [113, 114] (probably a German monk) wrote a first-rate handbook for artisans and described how to make sticky substances called *vernition* (varnish). He gave two recipes describing how to dissolve two resins in heated linseed oil. It is often difficult to ascertain the botanical origin of resins in old recipes. Scholars believe that in this case they were amber and sandarac [28, 39, 113, 114]. Around 1400 Cennini [27] wrote an influential handbook for Italian artisans, with many mentions of *vernice liquida*. Strangely enough, although the book provided many detailed recipes, it failed to mention the composition of *vernice liquida*. Around 1550 Giorgio Vasari [21, 115], a famous painter and art scholar, wrote about *vernice liquida* several times without describing its composition. In one instance he tried to mix it with egg yolk to obtain an emulsion medium, and in another he mixed it with Greek pitch (rosin), mastic, and linseed oil. From these descriptions it appeared that *vernice liquida* was a common and useful commodity, usually prepared not by artists but by professional shops. Around 1550 *vernice liquida* seemed to be some kind of thick varnish with high resin-to-drying-oil ratios, which could be further diluted with oil. Purchasing *vernice liquida* spared the artist from the toil and hazard of dissolving resins in drying oils. But what resin was used in *vernice liquida*? Was it a secret that

Table 3. Varnish recipes in the Marciana Manuscript (Italy, early 1500s, Ref. [20]).

Application	Resin	Solvent	Fire-Heated	Subsequent Diluents	Note
Protect miniatures and artworks	Benzoin	Alcohol	No		Dries in the shade
Unspecified	Amber	Linseed oil	Yes	Alcohol, naphtha, or linseed oil	
Protect everything and art works	Benzoin	Alcohol	No		Quick drying
Protect paintings, metals	Benzoin	Alcohol	No	Alcohol	Dries in the shade
For everything	Sandarac, Frankincense	Walnut oil	Yes		Thicken under the sun and take the top portion
Protect lutes, paintings, objects	Greek pitch, Mastic	Linseed oil	Yes	Linseed oil	Glass-like luster; waterproof; dries quickly
Protect lutes and various objects	Mastic	Linseed oil	Yes		
Unspecified	Mastic	Walnut oil, naphtha	Yes		
Mixed with colors in oil painting	Greek pitch, Mastic	Walnut oil	Yes		Has siccativ property
Waterproofing of pictures	Strasbourg turpentine		Yes		Melt the resin and apply directly; dries in the shade
Protect art works	Strasbourg turpentine	Linseed or walnut oil or naphtha	No		Not waterproof; dries in the shade
Protect guns, crossbows, armors	Greek pitch, sandarac	Linseed oil	Yes		Substitute Greek pitch with naval pitch for darker color
Common varnish (<i>vernice commune</i>)	Greek pitch	Linseed oil	Yes	Linseed oil	

even luminaries such as Cennini and Vasari had no knowledge of?

Cennini [27] mentioned many different uses of *vernice liquida*, such as mending broken dishes, waterproofing walls, protecting finished paintings, and so on. Could one formula satisfy so many applications, or maybe *vernice liquida* was a general term for a class of related substances? This author's opinion is that the latter was more likely, and that the apothecary probably assisted the customer in choosing one of the several formulas available. More clues can be found in the Marciana Manuscript [20], which was probably a collection of instructions used at a convent dispensary from the early 1500s.

It described multiple varnish recipes for various purposes as listed in Table 3.

From Table 3 we may infer that *vernice* sold at 16th-century pharmacies basically meant pre-dissolved resins. It could be a fixed oil varnish or a spirit varnish, or even with mixed solvents. Compared to similar recipes written for artists and craftsmen in that period [20], lead drier was missing in Marciana recipes for fixed oil varnishes. Since lead drier would reduce the shelf life of varnishes, its absence supports that these were shop recipes. Back in his house, the customer could have applied *vernice* directly, diluted it with solvents, or mixed it with other ingredients to make an adhesive, an ink, and

many other things [20]. Protective coatings containing resins were also called *vernice*. The fact that most of the fixed oil varnishes in the Marciana Manuscript required the sun to dry is consistent with Stradivari's [7] own account of putting varnished instruments under the sun. Even if Stradivari bought *vernice* (pre-dissolved resin) from the apothecary, it did not mean that the *vernice* (finish coating) on his violin had to be generic or simple.

The Marciana Manuscript sometimes used *vernice* to denote unspecified solid resins and sometimes unspecified liquid varnishes. It also mentioned *vernice liquida* and a common varnish (*vernice commune*) sold at the apothecary. According to Merrifield [20], an unspecified *vernice* resin in those days generally meant sandarac, and the *vernice commune* was Greek pitch (some kind of rosin) dissolved in linseed/walnut oil. Eastlake [28] believed that *vernice liquida* originally meant sandarac in drying oil, a reddish substance. The substitution of sandarac with some types of solid turpentine resin (pine, fir, or larch) later yielded paler varieties of *vernice liquida*. Both Merrifield and Eastlake found plenty of old recipes for *vernice liquida*, indicating that it was not a secret but a generic term for resinous drying oil.

Furthermore, we are informed by Giovanni Volpato [20] about where Italian painters obtained their varnishes around 1685. Being a painter himself, he said, "Varnishes are of different kinds: some we make ourselves, others, such as the *vernice grossa* and amber varnish, we purchase, but I make the mastic varnish myself." The homemade varnish was mastic dissolved in oil of turpentine or naphtha, with or without some Strasbourg turpentine. It appeared that, in the 16th and 17th centuries, artisans had a wide selection of *vernice* to work with, some commercially prepared and some homemade.

From the discussion above, I think two main conclusions can be drawn. First, it was not unlikely for Stradivari to have bought some sort of oil-dissolved resin at the local apothecary, as Grivel [83] had informed us. Second, it would be very difficult to know what type of pre-dissolved resin was purchased by studying old texts, because the apothecary probably sold several varieties, which could be mixed or cooked with other substances in the violin shop. We have

found rosin, mastic, and Venetian turpentine in Stradivari's finish, and we may suspect some amber as well. All of these resins were commonly found in the *vernice liquida* sold in 16th-century Italy.

The importance of resin commerce

The inventory list of a color seller in Venice in 1534 included more than a dozen solid resins, and the quantity of some resins was over 100 kg. Hence, a single shop could have stocked one to two tons of resinous materials. In a 1594 inventory list, there were fewer resins, but the liquid varnish was in stock [105]. Although these lists were probably incomplete, it was apparent that selling varnish ingredients was a thriving business. What varnish materials would the apothecary continue to carry after fixed oil varnishes fell into disfavor in the 18th century? Linseed and walnut oil were still useful for painting pictures and houses, and various solid resins could still be incorporated into essential oil or spirit varnishes. But resinous drying oil, the old *vernice liquida*, would have been discontinued if customers preferred quick-drying varnishes. According to Merrifield [20], almost no master painter in northern Italy in the early 1800s had heard of resinous drying oils, and very likely its commercial supply was scarce. Moreover, every natural resin can exhibit great quality variations due to botanical origin, collection, and processing. If resinous drying oil was no longer used, then resins would be graded and sold for their suitability for preparing spirit varnishes, not fixed oil varnishes. Both factors could have compromised the quality of resinous drying oil used in classic finishing methods, forcing violinmakers to change and adapt.

As indicated by the 1747 Cremona manuscript [106], the decline of fixed oil varnishes had already occurred in the first half of the 18th century. We can only speculate at what time the violinmakers became affected by this inevitable trend. By the second half of that century, the older violin finish was already forgotten. Even makers like Marchi and collectors like Count Cozio di Salabue could not recover the knowledge [54, 111]. The use of resinous drying oils on violins seemed to follow what happened in paintings. After fixed oil varnishes became reintroduced into French painting by the 1830s [110], French

violinmaker J. B. Vuillaume (1798–1875) started making convincing recreations of the Cremonese finish [116]. This probably reflects the dependence of violinmakers on the general availability of quality varnish ingredients, because violin making represents a very small share of the varnish commerce.

One can only speculate on how resin availability may directly contribute to the disappearance of the classic Italian violin finish. While it was easy to tell that the color varnish of classic violins was based on resinous drying oil, the presence and composition of the ground was much more difficult to ascertain by eye. It appeared that Marchi and his peers had little knowledge about the ground, arguably the most critical part of the classic finish. Even by modern analytical instruments, its composition remains somewhat uncertain. Perhaps the key to the disappearance of the classic finish lies in its ground. If the scarcity of suitable resins negatively impacted the usefulness of the old ground formulation, it might have fallen into disfavor and become forgotten.

CONCLUDING REMARKS

Over the last two centuries there have been many claims about the lost secrets of Stradivari's finish. These so-called rediscoveries were mostly misleading. Modern chemical analysis has ascertained many of the substances incorporated into Stradivari's finish, which is much more complex than traditionally assumed. Although there are still many gaps in our knowledge, we can now define some of its key features, which are shared by other Cremonese instruments.

First, we know that his color varnish is based on resinous drying oil (probably linseed oil and *Pinacea* resin) with lead drier, containing a wide array of pigments and sometimes colorless particles. The color varnish is akin to oil painting with a resinous medium over a transparent ground layer that keeps colors out of the wood. In some samples examined, the ground is highly particulate. The ground medium is yet to be determined, but drying oil, resin, and protein may be involved. How the wood was treated (including polishing, scraping, and sealer coating) is difficult to ascertain. Wood surface treatment, ground coat, and color varnish constitute the Cremonese finishing

system—the deeper it goes, the less we seem to understand, and some organic materials therein may remain to be discovered.

Has modern science found a “lost secret” or a “magic bullet”? In my opinion, the answer is still no because it is difficult to measure and define acoustic benefits associated with violin finishes. Nonetheless, modern science has suggested new directions for experimentation such as emulsion media [101] or nanocomposites [117]. There was also no secret in the sense that Stradivari's finish was similar to his neighbors'. Actually, classic violin and lute finishes used throughout Italy appeared to be closely related. We failed to detect exotic substances in Stradivari's finish, something other Italian artisans were not already using. However, the Cremonese finishing system was sufficiently complex, with many adjustable parameters (mineral particle size and amount, resin type and amount, pigment type and amount, cooking condition, layering, drying condition, etc.), so that individual practitioners could have obtained very different results. It probably needs to be understood in a systematic manner rather than as a few standardized recipes. The mysterious disappearance of the classic Italian violin finish, including the Cremonese, coincided with the general disuse of fixed oil varnishes (resinous drying oil) throughout Europe in the second half of the 18th century, replaced by spirit and essential oil varnishes, used on everything, including the violin. By the time fixed oil varnishes regained popularity in arts and crafts, the Cremonese finishing method was all but lost.

Moreover, the wood finish is only half of the Cremonese material puzzle. In fact, violin tone wood is an even more complex issue and less studied. Over the past three decades, the scientific examination of violin woods has also produced sufficient data to challenge some long-held beliefs about how they were processed and prepared. The scientific study of Cremonese materials may still hold more than a few future surprises.

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