The Chemistry of a Stradivarius

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By the sheer beauty of its vibrant sound, the voice of the violin can be intimate and enchanting like no other musical instrument. The enormous complexity of this odd resonator box has long attracted some of the best minds in science to play on it and think about how it functions. The letters of Galileo, for example, show how impatiently he awaited the completion of a violin from Cremona while he was under house arrest in 1635. Einstein was an aficionado of the violin, and a fair player throughout his life. The German chemist Richard Kuhn, winner of the Nobel Prize in 1938 for his work on carotenoids and vitamins, was an accomplished violinist.

The violin also is a great cultural and scientific puzzle. It evolved from simpler, more ancient stringed instruments during the middle of the 18th century through the innovations of Italian instrument makers, such as Andrea Amati. And it was brought to a peak by two other Italian artisans, Antonio Stradivari and Giuseppe Guarneri, in the early 18th century.

Violins, music critics, and music lovers have long marveled at the rich sound produced by string instruments skillfully crafted in Cremona more than 200 years ago—and have theorized about what set these instruments apart from any made before or since. Despite increasing research into the materials and character of these classic Italian instruments, however, controversy continues unabated over their secret. This special report, which is a considerably departure from the typical special reports CAEN has published previously, presents one chemist's contribution to unraveling the secret of the classic violin, a mystery that may never be resolved to everyone's satisfaction. Many present violin makers and researchers disagree sharply with Joseph Nagyvary's approach and conclusions, centered as they are on materials. Certainly, structural issues are also important and a fine instrument's acoustical properties are dependent on its shape. And as one well-known violin maker pointed out, the secret of Stradivari may not be one thing but rather many, all combined in the correct proportion as in a properly designed culinary recipe or a well-engineered automobile engine. Nevertheless, we think CAEN's readers will find Nagyvary's chemical focus on the mysteries of fine violins both interesting and provocative.

The Messiah violin, made in 1716, is in mint condition—one of the few instruments produced by Stradivari that has escaped the vagaries and ravages of time. It has stayed with the Stradivari family and in other loving hands for many years until it was deposited at the Ashmolean Museum of Oxford University, where it is now on display. Its varnish is highly colored and far from transparent, although it is not so opaque as that on some other Stradivari instruments still in mint condition. The varnishes on these instruments have a raw-Orange peel-like texture. Such an uneven surface, with a silky or pearly gloss, is typical of unpolished composite resins. For understandable reasons, no chip of varnish is available from the undamaged Messiah for chemical analysis.

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In contrast, the typical concert Stradivarius has a battered appearance, with much of the color varnish missing and often replaced with a glossy layer of shellac. The layer of original varnish is difficult to blame on normal wear and tear, although the carelessness of players should not be underestimated. Perhaps some of the original varnish has been deliberately rubbed away by compulsive owners or restorers to improve the shine of the instrument. Some experts believe, however, that the partial loss of the outer varnish layer is beneficial to the sound, as it helps unmask the woody brilliance that makes the music produced by the greatest Strads so attractive.

Wood treatment

Although wood quality has a decisive role in acoustical performance, just what makes a particular piece of wood an ideal "tone wood" (that is, wood with the acoustical properties suitable for a musical instrument) remains ill defined. Not just any piece of spruce or maple will do. Many modern violin makers believe that unadulterated wood will become good tone wood if it is merely aged for a long period, perhaps 10 to 30 years. They contend that any use of chemicals to artificially mature the wood is a condemnable shortcut to natural aging: one that will cause the instrument to deteriorate in time.

Others, however, admit to using artificial seasoning, a practice deeply rooted in the craft of wood carving because some treatment often is required to avoid the cracking or rotting of wood. Chemicals such as potassium hydroxide, potassium permanganate, and various chromates, which have been used in the past to stain wood, or potassium silicate solution, which has been used as a wood filler, may weaken lignin-cellulose bonds, however; thereby damaging the matrix of the wood and decreasing its structural stability.

Nevertheless, some sort of chemical manipulation seems to be indispensable to achieving a beautiful sound. Violins made from untreated wood are characterized by a degree of harshness, which results from tension in the stiff wood. This leads to the dominance of a few sharp resonance peaks in the "musical" frequency region of sound (2 to 6 kHz), which can be a noticeable contribution of sound in the "noise" frequency range (6 to 12 kHz), causing shrill, high-pitched notes.
Scanning electron micrographs of wood samples taken during repair work on three old violins show remnants of microorganisms. Well-exposed hyphae of fungi are visible (below) at a magnification of 1000x on a sample taken from a Stradivarius, the Berti, of 1724, as a channel-etched fungal growth in a wood cell wall. The photomicrograph, at 2000x, of a sample from a Guarneri violin of 1735 shows several hyphae, one of them growing from an intercellular opening, and numerous round particles. A sample from a viola made by Guarneri in 1750 (opposite page, bottom), at 7000x, shows the area of an intercellular opening, a favorite target of bacteria, the remnants of which are present in large numbers in this specimen. In this example, Count Carlo di Salabue, the patron of Guarneri, warmed future violin makers against using wood from the shipyard of Venice. The high salt and microbial content of this sample suggest, however, past exposure to salt water. Delicate misinformation could have been a device for guarding craftsmen's secrets.

A milder and more easily controllable treatment—microbial modification of green wood in water—can achieve desirable effects without causing the deleterious results of high temperature. In the 17th and 18th centuries, such treatment may have been the spontaneous result of the delivery of wood by floating or barging it down rivers.

The great violin makers of northern Italy benefited from such treatment. Their choice wood was cut in northern forests and might have been carried down river to Venice; there to remain floating in the lagoon until needed. Such wood would become extensively colonized by bacteria and fungi, but its degradation was minor and selective. Mainly, it is the system of cellular valves or openings in the walls of the long tubular cells of the wood—openings that permit the flow of liquids between two cells—that are degraded by microbial enzymes, along with the cell membranes and other-exposed surfaces. However, extraction of some hemicellulose also is likely. This results in a 50-fold increase in the permeability of the wood over that of wood that has been dried susceptibly, although the mechanical strength of the wood remains practically unchanged. When wood is simply dried, the cell wall holes close. In the more permeable wood that has soaked in seawater, air moves freely through open holes from cell to cell, thereby removing additional pressure. In addition, the overall stiffness and damping characteristics of the wood can be affected because the open holes allow deep penetration of varnish or filler materials.

What does this have to do with the violins made by the Italian master craftsmen of the 18th century? An analysis of old Italian instruments might add credence to the notion that microbes had a role in making great violins. Unfortunately, authentic wood samples from such instruments are not readily available for testing. However, I have acquired six spruce specimens from instruments made by Stradivari, Guarneri, Jeannes Baptista Guarneri, and Francesco Ruggeri and examined them by scanning electron microscopy. Filaments of fungi are clearly preserved in all of these samples, while remnants of bacteria are present in some of them. More open or damaged holes are present in the cell walls of the wood in the six samples than in modern commercial wood used for violins. Also present are many mineral deposits, including clay and calcium carbonate. Concentration of salt in the six samples also is high, ranging from 10 to 50 times that found in wood that has not been immersed in seawater.

These observations are compatible with other imaginable treatments; for example, a few coatings of Mrs. Stradivari's saffron chicken soup would have done the trick. But the scenario described above appears more plausible. And if it is correct, then the wood in other Italian instruments from 18th century Cremona, Brescia, and Venice also should reveal evidence of microorganisms, open or damaged holes in the cell walls, and increased mineral content. Not enough samples have been examined yet, however, to demonstrate that this is indeed the case.

In the past 10 years, I have completed, in collaboration with professional violin makers, 30 violins using boiled or fermented wood, and their sound supports my hypothesis that the way the Italians seasoned wood in water results in better acoustical performance than do current methods of seasoning it in the atmosphere. With current methods, the sap drains in the wood cells, closing their pores and making them impervious to solutes. Permeability is the key consequence of aqueous treatment and enhances the penetration of varnish into the wood. And it is the combined performance of wood and varnish that I believe is critical to violin quality.

Violin varnish

Varnish is one of the most glorious aspects of a violin, and may have more to do with the price of the instrument than its tonal beauty. Originally, the purpose of varnish was to improve tone, or to achieve the same as that for used on furniture: protection of the wood against dirt and deterioration. Mechanical properties of the varnish—film, such as its durability and

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impact resistance, were important considerations. So were pleasing visual effects, such as attractive color, transparency, and glossiness. Ease of application and drying also were desirable factors.

In addition, however, violin varnish should have suitable vibrational properties, which are dictated by the stiffness of the wood. For example, with spruce that is used as a violin top plate, Young's modulus should be about 12 GPa longitudinally and 1.2 GPa across the grain. If the Young's modulus of the varnish is below 1 GPa, the film may be too plastic, which degrades the sound, or too elastic, which may cause selective damping and the enhancement of low frequencies. If the varnish film is too stiff (has a

amber, is an insoluble resin that can only be used after destructive melting. In addition, various colored resins, such as dragon's blood (red), aloes (brown), and gamboge (yellow), were used.

Varnish makers classify their varnishes as either alcohol varnish or oil varnish, depending on the solvent used. Alcohol varnishes dry fast because they contain no drying oil. They also form films that are more transparent and brilliant. The initial coats of such varnishes also act as fillers, entering and interacting with the wood cells. Oil varnishes usually contain a nonpolar solvent, such as turpentine or petroleum, in addition to a drying oil, such as linseed or walnut oil. Because of the extensive crosslinking that occurs in the drying oil as the varnish dries, oil varnishes are tougher and more durable than alcohol varnishes.

Modern violin makers are about evenly divided in their preference for alcohol or oil varnish. The ease of application and greater brilliance of the former often win out over the greater durability of the latter. Acoustical measurements were made by J. S. Schellenberg of various varnishes on glass led him to conclude that the influence of the varnish on the sound of a violin is minor and, if anything, in fact, is negative.

This echoes the old adage that "the varnish is a necessary evil" in violin making. Carleen Malley Hutchins, an American violin maker who explored the acoustics of many instruments with Harvard physicist Frederick Saunders, for example, thinks that a varnish and varnish "can be detrimental to an instrument." If nothing else, she notes, adjustments must be made in tuning the top and back plates of a violin while it is being built to compensate for the effects of varnish on its sound. And because varnish coatings continue to change for more than two years after they are applied, she adds, it may be several years before a newly varnished instrument shows its true musical qualities. Indeed, most violin makers continue to insist that the key to violin quality is the acoustical characteristics of the violin plates and of the entire finished instrument, rather than the chemical characteristics of the instrument's wood and coating.

On the other hand, the Hill brothers, in their 1902 biography of Stradivari, declare that the varnish was the major determinant of the tonal distinction of Stradivari's instruments. And it seems to me that it is no more possible to separate the chemistry of the materials from the acoustics of the plates or of the whole violin than it is to reproduce the sound of a silver bell in a bell made of aluminum.

The varnish used by Stradivari probably was the same as used on other fine wooden objects, such as furniture, of his period in northern Italy. According to Charles Reade, a mid-19th-century English writer, it was highly colored and often opaque in its original form. Reade concluded that Stradivari used a few coats of oil varnish followed by an alcohol solution of "divine" dragon's blood.

On the other hand, the Larivian violin maker M. R. Zemits, in his 1977 book "Violin Varnish and Coloration," suggests that an ancient varnish of amber in oil might have been used by the classic Italian luthiers. Geary Base and Joseph Curtin, two contemporary American violin makers, think they have duplicated 17th-century Cremonese violin varnish by dissolving one part of a fused amber resin in three parts of linseed oil. They use this varnish as a ground, over which they spread a colored coating consisting of one part mastic in three parts linseed oil and containing lake pigments.

Zemits points out, however, in describing Stradivari's varnishes, that "in respect to refraction and reflection of light, these varnishes appear to be similar to pre-
varnishes actually were two-phase heterogeneous systems.

Some long-ignored varnish recipes from the 18th and early 19th centuries, in fact, include significant amounts of such ingredients as glass powder (soda, con,
dioxide), white vitrific (calk sulfate), crab eyes and egg shells (calcium carbonate), and porcelain and amber powders. If these mineral components were of very fine size—down to that of the wavelength of light—their optical properties might indeed impact some of the gemlike effects described by Zemits.

These old varnish recipes are also intriguing for reasons unrelated to their attractive optical properties. The mineral components can aggregate within the varnish and the resulting hard layer would then make a significant contribution to the violin's overall stiffness. The bell-like crisp response of the great old violins, one of their most remarkable characteristics, thus might be explained as the result of a sedimented composite varnish.

Samples of 18th-century Italian violin varnish are difficult to obtain. Little or nothing now remains of the original varnish on most violins dating from then, most of which have been restored at sometime in the past. And what does remain usually is diluted by copious amounts of shellac, or other recent adulterants. The owners of the few instruments still in mint condition are unwilling, moreover, to sacrifice even a milligram from their precious Cremonese varnish for study. However, under the microscope, the extremely brittle Venetian varnish reveals a large concentration of both crystalline and amorphous materials. About 18% of the varnish is insoluble in methanol, acetone, or toluene, with the residue consisting of compact particles large in the 1- to 2-μm size range. The study of examined by energy dispersive x-ray spectroscopy contains 22 different minerals, the major ones being calcium, quartz, and feldspar. The absence of a few present are particles of some gemstones as garnet, rutile, and argentine.

Two of these Cremonese varnishes contain particles that are much finer in size, with a substantial number of them being smaller 1 μm, and were often amorphous. Scanning electron microscopy of their fracture images suggests that between 50 and 70% of the space is filled with particles. Not more than 30% of these varnishes could be dissolved with solvents. The particles in two Cremonese varnishes similar but contain a smaller concentration of particles, perhaps because they are from instruments that have been restored.

The appearance of these varnishes is compatible with that of an oil varnish containing very finely ground minerals, together with partially melted amorphous powder. One must be impressed with the skills of the person who produced these fine powders—a difficult task—given the use of glass powder as a grinding medium.

More important, this varnish structure should impart acoustic benefits. The old varnishes resemble modern composite polymers and cements. Because of direct contact between the sedimented particles, the varnish is likely to cause a dramatic increase in the Young's modulus of the instrument's plates compared with that resulting from an organic matrix alone. Thus the varnish could be an important determinant of the acoustical behavior of the vibrating plates. It is also possible that the amount of relatively heavy crystals might absorb high-frequency vibrations, thereby reducing noise emission.

The picture now emerging of old Italian violin varnish is both interesting and poorly defined. The violin makers of Cremona may not have developed or even formulated their own varnishes. Credit for that achievement perhaps should be attributed to individuals, who most likely were local pharmacists ("chemists"). Having a knowledge of minerals, the art of levigation, and the many mysteries of alchemy—that is, people with a different education than the violin craftsmen. Stradivarius himself, may not have been responsible for two important factors—a soft, dry, permeable wood and a hard composite varnish—that set his violins so much above those of later makers. Stradivarius may not have known any more about violin making, in fact, than we do; he just was lucky enough to have the right materials.

These factors produce a system with acoustical properties that must be different from the one favored by violin makers for the past 150 years, who rely on hygroscopic wood of poor permeability combined with a rubbed varnish. The combination of soft, permeated wood and soft varnish has also been tried in recent years, but the results have been an instrument lacking in brilliance.

Of the 30 violins I have examined in the past 10 years that were made of microbially modified wood, the first few were spoiled by the use of a rubbery varnish. Use of a long-lasting liquid of chitin (from shrimp shells) dissolved in vinegar eliminated this problem. Since 1984, however, I have used eight different composite varnishes containing powdered glass to produce violins that have been quickly accepted and admired by several young concert artists. A major asset of these violins is the rapidity with which they mature, producing a low-noise sound within a few months of playing. This can lead one to believe that perhaps the violin maker is just as important, and has been at their peak at the time they were born.

The concept of violin making as a chemical as well as a technological process is now quite evident. The notion that the wood must be modified from within the cellular, or even the molecular, level, using chemicals and varnishes as tools. By this means, the relative magnitudes of the 18 or so mechanical constants on which an instrument's acoustics depend can be modulated toward an optimum. No such manipulation is possible with the traditional approach of carving, which leaves the ratios of compression and torsion modulus intact.

The combination of the optical and chemical approach will take some time, of course. But it already has created a few new string instruments that produce sound that contains low levels of noise.

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