

OF OLD WOOD AND VARNISH: PEERING INTO THE CAN OF WORMS

by

C Y Barlow and J Woodhouse
University of Cambridge

Introduction

Violin varnish, for the moment using the word loosely to signify all substances applied to the wood of a finished instrument, exerts a widespread fascination. Makers aspire to find ways of giving new instruments something of the appearance of the classic Italians, and the general public has somehow got the odd notion that varnish in itself accounts for the unique esteem in which the instruments of Stradivarius and a select few other Italian makers are held. Over the years investigations have been made with a wide range of depth and scientific credibility, from the eminently respectable all the way to the decidedly crackpot. In the hope of avoiding the latter label, we preface this contribution to the subject with an attempt to set our work in the wider context of what has been done and what could be done in the way of scientific study of the whole problem. One consequence will be a level of scientific caution which is proper but perhaps rather dull — when we come to discuss our recent results we will give pointers and indications, and plenty of fodder for further work of many kinds, but no definite pronouncements, recipes or “secrets of Stradivari”.

Studies of varnish (still in the broadest sense) can be grouped into three categories, although naturally there is some overlap. First comes the historical/archaeological group: what can be deduced from surviving instruments or fragments of them, or from contemporary literature, about what the great makers did? Second, there is the “recipes” group: definite suggestions to modern makers about how they might treat their wood. Such suggestions might or might not grow out of investigations in the first category, but they are surely to be judged primarily by results and not by historical authenticity. Finally, there are studies of the effect of wood treatment on vibrational behaviour and thus on the sound of the instrument. The priorities of a maker are presumably to find a method of finishing an instrument which makes it look good and continue to look good, which protects the instrument from the rigours of active life, and then which combines with all the other aspects of construction and setting-up to give satisfactory sound and playing characteristics. Only when a method satisfies the first requirements is it of interest to enquire about the effect on vibration, since no-one will buy the instrument unless its appearance is acceptable.

The present study falls in the first group. We will show pictures and analyses of several samples from authenticated old instruments, and will discuss what can be deduced about the materials and methods of the makers in question. Considerable diversity will be revealed, and the dangers of basing any sweeping conclusions on only a few samples (as has sometimes been done in the past) will be highlighted. At least in this preliminary stage of the investigation, nothing sufficiently definite to constitute a “recipe” will emerge, although we will be able to rule out (for these particular samples) a few of the possibilities which have been canvassed. The only things we shall have to say about possible acoustical consequences of any wood-treatment processes will be in the form of some general remarks about the sort of effects to be expected, and some indications of the type of scientific investigation which would be necessary to investigate such issues further.

Before going any further, it is important to address some questions of terminology. So far we have used the term “varnish” very loosely, but it is in fact central to this investigation to distinguish between at least two components of the treatment applied to the surface of the

wood. We shall show shortly that to a greater or lesser extent, at least half of the fragments of old instruments studied here have an under-layer containing particulate matter, and a layer of varnish proper on top of this, largely devoid of particles. This underlayer usually corresponds to the layer which remains stuck firmly to the wood when the varnish chips or wears off. What to call it proves to be an issue capable of arousing deep feelings — restorers, when pointing to the layer in question, will call it the ground layer, but an instrument maker may think of “ground layer” specifically in connection with the varnishing process, and that might be quite misleading. Since we are discussing pieces of old instruments obtained through the generosity of various restorers we shall use their description here, but it should be understood that we are not thereby making any statement about what the makers had in mind when applying this layer to the wood. It might have been thought of as an underlayer or filler as part of the varnishing process, or as a wood strengthening process of some kind carried out earlier in the constructional process. Alternatively, it could have been an incidental effect of some other operation, such as using an abrasive substance in the finishing process. We will return to a discussion of some of these possibilities later.

Another terminological issue concerns such words as “hardness”, “toughness”, “stiffness” and “strength”. When describing the effects of the ground layer on the properties of the wood, such words are often used somewhat indiscriminately. In scientific usage, these words all have specific and quite distinct meanings, and different measurement techniques are used to determine the values of the quantities signified. We can illustrate the scientific usage of some of these terms by analysing what we mean by describing varnish as “chippy”. The fact that the varnish breaks up into small pieces is a result of its being brittle rather than tough. If one were to pick up a fragment of the varnish which had flaked off, one would have no hesitation in describing it as hard, a term which may for a particular material be defined quite properly by reference to how difficult it is to scratch. If the fragment were large enough, one could bend it in one’s fingers and estimate its stiffness from the force one had to apply.

That the varnish was damaged at all by treatment which we did not regard as excessively rough was a consequence of its strength being rather low. While we shall try to stick to scientific usage, it is a little unfortunate that all the good colloquial words for the qualitative concepts of “hardness” etc. have been scientifically hijacked. A good ground layer obviously imparts something with this general quality to the underlying wood, especially when applied to spruce, but whether that quality should be described primarily as “strength”, “hardness” etc. requires a range of measurements to be made, some of which seem hardly possible with the very small samples with which we shall be dealing here. We simply do not yet know which of these words is the most appropriate, in the technical sense.

Experimental techniques used here

This study has used a Scanning Electron Microscope (SEM) as its the principal tool. We use this in two distinct ways. First, we obtain pictures of the topography of the sample, and we shall see when we come to discuss examples in detail that quite a lot can be learnt from studying these. Second, we can use X-ray analysis to discover which chemical elements are present in the part of the sample which is being examined, subject to some limitations which we discuss shortly.

The SEM works by hurling a fine beam of electrons at the sample under examination. Some electrons rebound from or are re-emitted by the surface layers of the specimen, and these are picked up by a detector. An image is formed by sending this signal to a television screen, and by scanning the beam across the specimen in synchronisation with the raster on the screen. The resulting pictures have a remarkable three-dimensional quality, with an enormous depth of field, and high magnifications can readily be obtained. If one examined specimens suitable for SEM imaging in an ordinary light microscope, then high magnifications and depth of field

would prove mutually incompatible. Another contrast with light microscopy is that wood is quite transparent to light, whereas electrons cannot penetrate far and so only show the topography of the surface. Some immediately relevant examples of SEM pictures may be seen in reference [1], where a range of wood surface finishes (scraped, sanded etc) is shown.

In fact, electrons are very easily distracted from their intended job, and this leads to one of the more tiresome aspects of working with SEMs: everything must be done under a high vacuum (10⁻⁴ torr). Fortunately, most things are remarkably little affected by being put under vacuum, and in any case it is usually possible to tell whether they have been disturbed in any way. The other indignity inflicted on the sample follows from the fact that not all the electrons fired at the specimen escape from it to aid imaging: many of them remain there, and unless there is an electrically conducting path by which they can escape, they will cause the specimen to charge up, which will in turn cause distortion in the image. To prevent this, specimens are given a very thin and even coating of an electrically conductive substance (usually gold or carbon). Except when something goes wrong with this coating process, one cannot tell from the SEM pictures that the coating is there. To complete the electrical circuit, the specimen must be earthed to the microscope. This involves sticking it to a mounting "stub" with conducting glue of some kind. More details of just how our specimens were prepared for the microscope will be given when we discuss results later on.

The electrons fired at the sample excite the atoms in such a way that they emit radiation which is characteristic of their chemical species. This radiation is in the form of X-rays, and a suitable detector can pick them up and allow a distribution of number of counts against energy to be obtained, giving what is called an EDAX spectrum (Energy Dispersive Analysis by X-rays). This distribution will have peaks in it corresponding to the characteristic energies of the various elements present, and the relative sizes of these peaks can be used to deduce something about the relative abundances of the various elements in the sample. A simple plot of this spectrum can, however, be misleading. If we want quantitative estimates of the relative amounts of different elements, we must take into account the fact that the method has different sensitivities to different elements. It cannot detect elements of lower atomic number than sodium (i.e. hydrogen, helium, lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine or neon), nor elements of very high atomic number, of which the only relevant one here is perhaps lead. For the range of elements which are detected, a computer program can be used to process the raw EDAX spectrum to compensate for the variations in sensitivity and give relative abundances of elements in the sample.

When interpreting the details of such EDAX spectra, a further cautionary note is necessary. The numbers obtained are influenced to an extent by the topography of the surface under study. Accurately reproducible results may be obtained from smooth metal specimens, for example, but from the kind of rough and irregular surfaces studied here a degree of variability is inevitable. However, the range of behaviour to be revealed here is far greater than these experimental uncertainties, so that the main conclusions are not jeopardised.

Most organic material consists largely of carbon, oxygen, hydrogen and nitrogen, so that it is a great pity that EDAX is unable to detect these light elements. However, this is not the loss that it might at first sight appear. The different properties of the enormous range of organic materials are governed by the way in which these elements are combined, not merely by their relative abundances. Thus we would in any case be able to deduce little from such measurements even if they could be made. Highly-developed techniques of organic analysis are of course available, but lie outside the scope of the present investigation. Applications of such analysis to the organic constituents of varnish have been described at the first of these meetings two years ago, by Raymond White of the National Gallery [2]. We would of course obtain the most thorough results by combining the analysis used here for inorganic constituents

with that kind of organic analysis on the same range of samples, and it is hoped to carry out such collaborative studies in the future.

Some possible materials and methods

It should be clear from the above description of the experimental methods used here that we are only able to deduce a limited range of things about any given sample. Our analysis alone cannot give definitive pronouncements about what was applied or how. The best use of our results is to combine them with other things which are known about the processes of wood finishing. We have knowledge from various quarters — on historical practices we can look to documentary evidence on instrument making, as well as the associated areas of furniture making and painting, and we can add to that the experiences of modern-day makers in trying out ideas. Of course this latter area is something of a minefield, since every maker seems to have a pet theory about some aspect of varnishing, so that their evidence on the effectiveness of any particular approach may be not entirely unbiassed.

An incidental reflection arising from this last observation is to ask whether instrument makers are likely to have been very different in days gone by. Is it really credible that there can have been any “secret” which was both agreed by a wide range of makers in different regions of Italy for a long span of time, and also kept from outsiders? Neither half of that proposal seems on the face of it very convincing. We are thus led, tentatively at least, to the other school of thought on such matters, that instruments were finished using the usual methods of the day, which did not strike anyone at the time as worthy of comment. We are, perhaps, looking for the Polyfilla and Ronseal of the seventeenth and eighteenth centuries.

Our main concern here is with the ground layer. Our pictures reveal very clearly the presence of a substantial fraction of solid, particulate matter in this layer, and the EDAX analysis method is quite suitable for finding out something at least about what those particles might be. We first review what kind of substances might be expected, which elements they contain, and thus what we might look for in an EDAX spectrum to discriminate between the many possibilities. We should make it clear in advance that this line of argument is primarily useful in providing negative evidence. If a key element in some particular substance is definitely not found, then that substance can be ruled out. However, if the right elements for a particular substance are found, that only shows that the substance is possibly present — many minerals share the same elements, and there are likely to be other possibilities which match the data equally well. Thus we may be able to disprove a few pet theories (at least for the particular samples examined), but we shall not be able to prove any.

We can conveniently start a discussion of candidates for ground layers by drawing a distinction between two different ways in which particles might find themselves stuck together on the surface of a piece of wood. Essentially, they either stick themselves together, or they are stuck together with something quite different which is deliberately added for that purpose. Examples of both approaches are in common use today. French polishers often use plaster of Paris as a grain filler, a material which has a natural cementing action, hardening by chemical reaction between the solid particles as it dries. In the other category, the black mastic commonly used for decorative purposes such as setting mother-of-pearl shapes around the soundhole of a mandolin is made from ebony filings blended with glue to form a paste. The particles (of wood in this case) have no natural ability to stick together, so a separate cementing agent is added.

At least two possibilities in the first category present themselves. One is indeed plaster of Paris, or some mixture involving this as a cementing agent. Plaster of Paris is made from gypsum, and has been used since ancient times. It is a form of calcium sulphate, so we would look out for calcium and sulphur as indicating elements in an EDAX spectrum. A second possibility, suggested by Chipura [3], is pozzolana cement, or Roman cement. This is prepared from a volcanic ash ground up and heated with lime, and again has been known since ancient

times — its durability is responsible for the survival of much Roman and medieval masonry structure. The pozzolana ash itself, without the lime, also has a weak cementing action and could conceivably have been used alone. Later on we shall show an EDAX spectrum of pozzolana, as a reference against which to compare spectra of ground layers.

There are two arguments against one or both of the above substances as being the basis of the ground layer on old violins, which we should address briefly straight away. The first, which applies to both, is that Roman cement and plaster are opaque in the form in which we are most accustomed to seeing them. This contrasts strongly with the renowned clarity of the ground layer, and would seem to rule them out immediately. However, this proves not to be the problem it appears. The reason is the same as that adduced by H. G. Wells to explain the Invisible Man (although the argument applies far better to our problem than to his!). Consider, he said, ground glass. This is an opaque white powder, until it is put into water, when it becomes invisible. The reason is that the refractive index of the glass is much higher than that of air, but very similar to that of water. Thus in air, light waves are reflected and refracted from the irregular facets of the small particles, scattering the light uniformly in all directions and making the powder seem white. In water, however, the light waves are hardly aware of the existence of the particles, since the refractive index is almost identical to that of the surrounding medium. There is very little scattering of light, and the result is transparency.

A very similar effect can be produced in a thin layer of plaster or cement, or indeed many other aggregates of mineral particles, overlying wood, simply by applying rosin oil or something similar. This penetrates the spaces between the particles and fills them with something whose refractive index is similar to that of the particles themselves, making the layer transparent to light so that the structures of the underlying wood show through clearly. We should note that an explanation of this kind must be the reason for the transparency of actual old ground layers, because one definite finding of this study is that these layers certainly do contain a large amount of particulate matter of some kind, which would inevitably be opaque if the gaps between the particles were occupied by air rather than something with a suitable refractive index. As a final note on this issue, it might not be desirable to match the refractive indices too precisely: a good enough match to ensure transparency, but enough mismatch to give a little extra lustre to the mixture may well be the ideal.

The second argument which can be brought against pozzolana cement (but not in this case against plaster of Paris) has rather more force. If the cement is required as such (and the renowned durability certainly makes it an attractive idea), it should be noted that this particular variety of cement only sets if it is kept quite wet for two days or so. One might well think twice about treating a finished instrument in that way, since one would worry about glue coming undone and thin wooden plates distorting. Only experiments could reveal just how strong this objection is in practice. Perhaps one can obtain some of the benefits without such drastic treatment of the wood, or perhaps if one really wanted the full effect of the cement, one might apply it to the top and back plates, at least, when the outside surface was finished but before hollowing out, when they would be less vulnerable to long wetting. This second possibility would have the peripheral advantage that the final adjustments to the plate thicknesses would then be made with the ground layer in place, so that any influence it has on the vibrational properties could be taken into account when tuning tap tones and so on.

We now turn to our second general category of ground layer candidates, those in which the solid particles are mixed into some other medium, which serves to stick them together and to the wood. Here the range of possibilities is very wide. It can perhaps be subdivided again into two groups, those in which the solid particles were deliberately added to form the ground coat, and those in which the particles are in some sense accidental. The latter category sounds a little odd, but one suggestion which has been made is that the particles arise from the use of something like pumice as an abrasive in finishing the wood. Left-overs from this abrasive

treatment then become incorporated into whatever the first coat of the finishing process may be.

The class of possibilities in which solid particles were added deliberately to make the ground layer is the widest of all. One can imagine taking something like rosin oil and mixing virtually any finely-ground substance into it, then applying that by brush, rag or fingers, in one coat or several, to the surface of the wood. Provided a reasonable match of refractive index is achieved, as explained above, the result would be roughly the sort of thing which is observed. One would presumably want to restrict attention to additives which are reasonably inert since that is an agreed characteristic of good Italian ground layers. The choice is still wide: ground glass, just about any mineral available in finely-divided form or not too hard to grind up in a mortar and pestle (limestones, alum, clays, silt from the bed of the Po ... the range is vast), or manufactured substances known at that time, such as perhaps milk of magnesia, which when filtered yields a very fine white powder (magnesium sulphate), made by precipitation from sea water with milk of lime. (Perhaps milk of magnesia would prevent any digestive problems with varnishes of the Sacconi school, with their edible content of honey, egg white and so on!) The last two mentioned substances are perhaps not meant too seriously, but are intended to serve as illustrations of how wide the net could be cast.

It is the breadth of this class of possible substances which prevents our analysis giving any positive identification — most likely combinations of elements turn out to be shared by several different minerals which could in principle have been used in this way. On the other hand, it might be argued that it doesn't matter a great deal exactly what is used in a method of this type. If self-cementing is not required, then the particles are simply embedded in whatever sticky liquid forms the medium. The qualities of adhesion to the wood which are so widely praised in the best Italian instruments would presumably stem primarily from the medium, not the particles, and that is perhaps likely to be an organic material like rosin oil, outside the scope of this investigation. If the "secret" of the Italian ground layer is just to mix large amounts of inert mineral powder with your rosin oil (or whatever is used as the first liquid coat of the finishing process), then one might expect a wide range of different minerals to perform more or less equally well, and for the actual choice to have been dictated by local availability, cost, received wisdom or personal preference.

Detailed results

We now, at last, come to some actual results. We shall show some representative SEM pictures and EDAX spectra illustrating the wide range which the samples made available to us have revealed. We have examined 15 reasonably well authenticated fragments of the varnished surfaces of instruments, mostly Italian, dating from between 1650 and 1750. The most satisfactory way of obtaining information from these is to create a fresh crack in the fragment, splitting off a still more minute sliver, the fracture surface of which is examined. These specimens are sections through the whole thickness of the original fragments, showing a slice through the varnish (where surviving), ground layer (if present) and underlying wood. It is important to emphasise that the specimens show fracture surfaces rather than cuts. Although carefully cut surfaces are ideal for investigating wood, if the varnish is cut a smooth surface is created with little topographic detail. The rough fracture surfaces on the other hand can be made to reveal considerable amounts of information about the nature of the constituents in the varnish, and also provide quite a reasonable picture of the wood.

Rombouts sample

The first example is chosen for didactic reasons only. Figure 1a shows a section as just described through the surface of a fragment of back from a cello by Pieter Rombouts, an approximate contemporary of Stradivari working in Amsterdam, which reveals the various

layers under discussion particularly clearly. The sample was made available by Gil Solomon. The picture shows an area of the specimen which is about 0.15mm in length: the magnification of the picture is indicated by a scale bar at the bottom which is measured in μm , micrometres (or microns, one micron being a thousandth of a millimetre). To help explain what is going on here, this picture is shown also in schematic form in Figure 1b. As in all of our pictures we are looking almost parallel to the varnished surface, which appears at the top, running away into the distance. Working down the picture we come to the fracture surface of the varnish and its underlayers. The varnish layer proper is quite thin, with a smooth fracture surface, and careful examination shows at least two distinct coats. Below this comes a layer some $20\mu\text{m}$ in thickness, which exhibits a rough fracture surface of a type which is characteristic of material containing discrete particles. This is the ground layer. Some individual particles can be clearly seen: they are mostly between 1 and $5\mu\text{m}$ in diameter, some being rounded and some angular. Below this layer is the wood, and there are in this case no visible cracks or fissures between the two, in accord with the observation that the layer was very firmly bonded to the wood. There is little sign of penetration of the wood by the varnish. The area labelled "oil" in the schematic is something which has been seen in a number of samples. It closely resembles the residue seen just below the surface of (newly-prepared) wood which has been treated with linseed oil. Doubtless other oils could leave a similar-looking residue.



Figure 1a. Scanning electron micrograph showing wood, ground layer and varnish on a specimen by Rombouts. The scale bar in the bottom right-hand corner gives the length scale: it corresponds to $30\mu\text{m}$, 0.03mm. The curving line at top centre is a crack in the surface of the varnish.

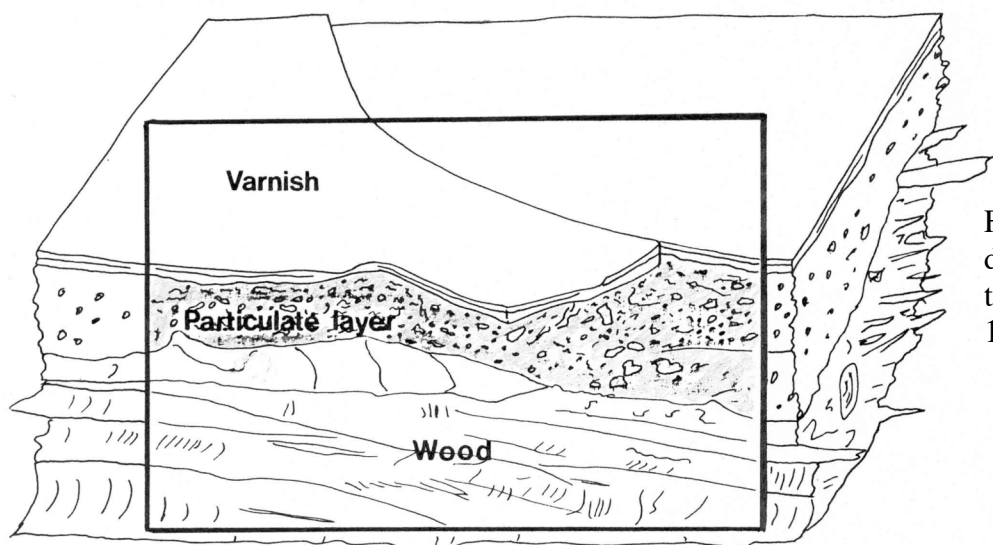


Figure 1b. Schematic diagram explaining the features from Fig. 1a, above.

Stradivari samples

The Rombouts sample, not being Italian, does not make an especially interesting example for analysis. We thus turn to two samples from the most famous maker of all, kindly made available by W. E. Hill and Sons. One is definitely attributable to Stradivari, the other probably so. Seen in SEM pictures both show a similar structure to that in Fig. 1a, with a particulate ground layer, only in both cases here the varnish proper has largely gone, leaving little other than ground on top of the wood (although both samples have some colour, chestnut-brown). Figure 2 shows an area of the first, definitely attributed, sample. The other has a ground layer which is extremely similar to look at.

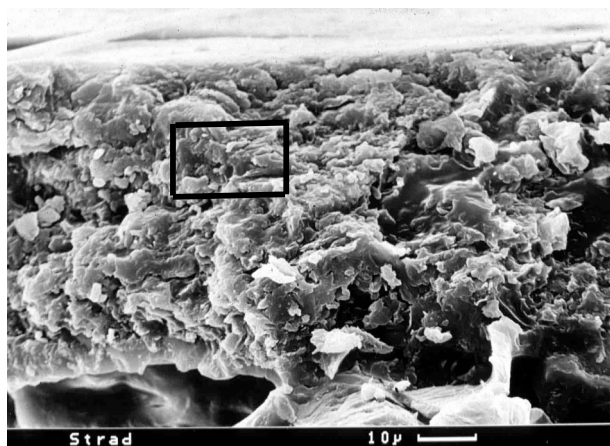


Figure 2. SEM picture of wood, ground and (not very much) varnish on a sample by Stradivari. Orientation is as for Figs. 1. The rectangular box shows the area used for EDAX analysis.

As a first example of EDAX results, Figure 3 [*not included in this version*] shows the spectrum derived from analysing the rectangular area marked on Fig. 2. The curve shows the X-ray intensity as a function of energy, as described earlier. The various peaks correspond to specific elements in the area of the sample analysed, and the main ones are marked with the appropriate chemical symbols. The relative abundances of these elements, deduced from the spectrum after processing to allow for variations in sensitivity, appear in the first row of Table 1. What is revealed is a lot of silicon, followed by, in decreasing order, iron, aluminium, calcium, sulphur, potassium, sodium and chlorine, with small amounts of other elements. (Note that some copper and zinc can arise from interactions of the electron beam with other things inside the microscope, so these elements are best ignored.)

We can begin to draw some conclusions from these figures. The analysed area consists mainly of the ground layer, and we can rule out some of the substances discussed in the previous section as possible candidates for this layer. We see no magnesium, for example, which rules out milk of magnesia and Dolomitic limestones. Before going into more detail, though, we look at some analyses of neighbouring areas of the same sample. These appear in the next three rows of Table 1, and they reveal extraordinary variations in the relative abundance of elements: calcium, for example, ranges from 6% to 24%, and iron from 6% to 36%! All have moderate to high levels of silicon, suggesting that silicates are present but not exclusively so. This ground layer certainly does not consist purely of water glass (sodium silicate or potassium silicate) or ground glass (silica, silicon dioxide), although neither substance can be ruled out as an ingredient in a mixture.

The diversity and the rich mixture of elements give some clues as to the origin of this layer. The variations between different areas of the sample are significantly greater than any experimental uncertainties, so the particulate matter is either made from a mixture of several different things or from grinding up something with significant variations from point to point, and in either case the powder is not sufficiently thoroughly stirred to produce a completely uniform composition. This suggests either a cocktail of some kind, which could also account for the wide range of elements present, or something like volcanic ash, which is very

Table 1. Relative abundances of elements deduced from the various EDAX spectra discussed in the text. For each case, the numbers indicate the percentage of atoms of each particular species among the list of elements included in the analysis. No account is taken of elements not included, and it must be remembered that the most abundant elements in organic material are not seen here. The rows of the table are as follows: (1)–(4) four different areas from the ground layer of the Stradivari sample shown in Fig. 2; (5) ground layer of the other (probable) Stradivari sample; (6) typical spectrum of finely-ground red pozzolana ash from Valentana; and (7) ground layer of the Gofriller sample shown in Fig. 4.

Sample	Na sodium	Mg magnesium	Al aluminium	Si silicon	P phosphorus	S sulphur	Cl chlorine	K potassium	Ca calcium	Ti titanium	Fe iron	Cu copper	Zn zinc	As arsenic	Ba barium
1	4	0	10	39	1	6	5	6	8	0	17	2	1	1	0
2	3	1	8	21	1	8	11	2	6	0	35	2	1	1	0
3	4	0	8	11	0	13	12	3	12	0	17	6	3	5	0
4	0	2	3	12	2	17	12	6	21	0	5	9	2	0	1
5	2	0	39	14	0	23	6	2	5	0	4	2	1	0	1
6	1	1	24	56	1	2	1	4	2	1	7	0	0	0	0
7	2	4	10	20	3	11	11	4	29	1	4	1	0	1	0

inhomogeneous. Row 5 of the table shows a typical EDAX spectrum of a specimen of pozzolana ash, this particular example being of the red variety (hence the high iron content) from Valentana. The range of elements seen here is broadly similar to that in the Stradivari spectra, enough to keep pozzolana in the running as a possible ingredient. There does not seem to be enough calcium in the ground layer spectra to support Chipura's original suggestion of pozzolana cement, in which significant amounts of lime are added to the pozzolana ash, but pozzolana was also used commonly as a red pigment, and that might be a reason to include it in a mixture. If we are looking at a mineral cocktail, then a great many possibilities remain open. Most siliceous minerals, in moderation, would not be inconsistent with the spectra. Alum (potassium aluminium sulphate) could perhaps account for some of the high levels of sulphur. The second, more tentative, Stradivari sample shows significantly different results. Aluminium is here the most abundant element. Sulphur is present in large quantity, silicon in moderation, calcium is quite scarce. It seems unlikely that all this aluminium is in the form of silicate minerals, and neither can it arise predominantly from alum since there is insufficient potassium here. It could be in some form of aluminium sulphate, or perhaps as alumina (aluminium oxide), which occurs naturally as the mineral bauxite. Pozzolana is made fairly implausible by the low silicon levels. On the other hand, the physical appearance and thickness of the ground layer here is remarkably similar to that of the previous sample. The simplest explanation which this suggests is that of a ground-up mineral mixture put on with some kind of organic binder like rosin oil, where the method of application was similar in both cases so that a similar appearance was produced, but the precise mixture had changed, perhaps because the local Cremona hardware store had something different in stock on the two occasions. Obviously, though, studies of a wider range of samples are needed to see if these very tenuous deductions have any substance.

Gofriller sample

Our next sample for discussion comes from a section of rib from a bass by F. Gofriller (Venice, ca 1720), supplied by John Dilworth of J and A Beare. This is selected on the strength of certain curious features, rather than for the fame of the maker or the excellence of the varnish. Figure 4 shows an SEM picture of a chip of varnish barely managing to cling on to the wood surface. It reveals more clearly than any other sample we have examined the distinction between ground layer and varnish layer. The fracture surface of the chip is clearly divided into a smooth region (varnish) and an underlying region showing particulate matter, in this case clearly occurring in layers. Gofriller seems not to have mastered the art of anchoring his ground layer to the wood in the much-praised manner of the Cremonese, since the chip is quite obviously cracking away from the wood, leaving only a little of the ground behind and taking most of it away. The cylindrical object sticking out from beneath the chip appears to be a brush hair.

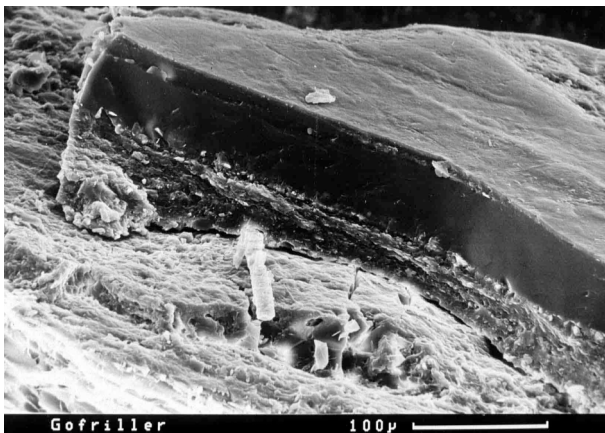


Figure 4. SEM picture of a sample by Gofriller, showing a chip of varnish and ground on the verge of parting company with the surface of the wood.

Row 7 of Table 1 shows EDAX results for the varnish/ground fracture surface of this sample. It reveals a lot of calcium, sulphur and aluminium, and a fair amount of other things, including some manganese. This last finding is in some doubt, since it seems that there might have been some manganese contamination of this particular specimen during the process of applying the electrically-conducting coating. However, manganese is sometimes found. It can be absorbed from the soil by the growing tree, and it might also have been added to the varnish or ground, since manganese is used in modern paints as a drier.

What can we deduce from the other elements which are present here? The low level of silicon means that the calcium and aluminium cannot be present primarily as silicates. This rules out, for example, clays, Roman cement, water glass and ground glass. Calcium sulphate is a possible compound, which might suggest plaster of Paris. Alum might also be present, accounting for the potassium and some of the aluminium and sulphur.

Amati sample

Our final sample for discussion is from a rib of a violin by Nicolaus Amati (ca 1660), provided by Gil Solomon. The SEM picture of this, Fig. 5, shows only a very thin layer on top of the wood. It shows no obvious sign of particulate matter. It has, however, bridged across the open end of a vessel (at the top left-hand side of the picture) very efficiently, so that something seems to have sealed the wood surface against penetration. Perhaps what we see here is just the last vestige of a layer which was originally much thicker — we cannot tell. With so little substance to work on, EDAX analysis seemed to have little useful to offer here. Incidentally, the small globular objects visible in the large vessel are fungal spores. They appeared to be alive, and thus of no great antiquity.

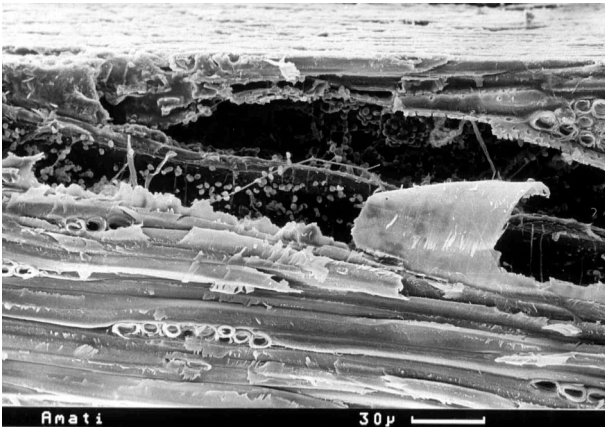


Figure 5. SEM picture of a sample by Nicolaus Amati, showing a very thin layer of varnish or ground.

Remarks on other old samples

In addition to the samples discussed above, we have looked at another ten or so. These reveal characteristics within the wide range already revealed. For what it is worth, from the fifteen or so samples which we have studied, about half have clear particulate ground layers of the kind seen in the Rombouts, Stradivari and Gofriller samples. Of the rest, some are like the Amati sample here, where it is not easy to say just what does remain on the wood, varnish or the residuum of a worn-down ground layer. Finally there are a few which seem definitely to lack such a layer. A smooth, varnish-like fracture surface extends through a layer of reasonable thickness, all the way to the surface of the wood. Little can be deduced from the statistics of such a small number of specimens, though. Perhaps as more samples are made available for study, some kind of coherent picture will emerge of where, when and by whom such particulate ground layers were used.

Modern samples

Finally, we can draw a few interesting conclusions from SEM pictures of modern samples, prepared in known ways. It is obviously of direct interest to take various present-day concoctions, and treat them in the same way as the old samples to see whether any resemblances can be discerned. Anyone who, in George Stoppani's splendid phrase [4], has "seen some old violins, read some old recipes and been suddenly struck by the truth" is cordially invited to lay themselves on the line by sending us a small specimen of what they produce.

For the purposes of this short account, we show two examples of newly-prepared samples, to test explicitly two of the possibilities aired earlier. In both cases, we are thinking about possible methods rather than specific materials. First, it has been suggested that the particulate matter which we observe arises more or less accidentally from the use of pumice or some similar powder as an abrasive. Some was perhaps left behind, and became incorporated in the first layers of the varnishing process. To try this out, various powders were rubbed over a fine-scraped spruce surface, with and without liquid added. All results were somewhat similar, and we show one example here. Figure 6 shows the effect of using ground pozzolana with turpentine. The powder-laden surface appears at the top of the picture, while the lower half shows a section through wood and surface layer. In this case the section is made with a scalpel, across the end grain of the spruce: it is not a split surface as in the previous pictures. The thin layer of particles on the surface is clearly seen. It has not penetrated beyond the first layer of cell walls, nor has it built up in anything like the thickness observed in the Rombouts, Stradivari or Gofriller ground layers. This possibility for the origin of the particles looks decidedly implausible.

A second possibility which is easily investigated is that the particles were put on as part of a grain-filling process. To test this, we show in Figure 7 the effect of using a thoroughly modern

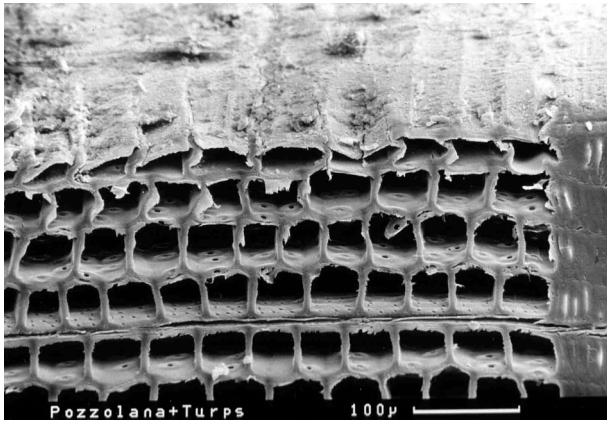


Figure 6. Sample of spruce on which ground pozzolana ash has been used as an abrasive, lubricated with turpentine. The resulting thin layer of particulate matter is clearly visible on the surface. The end-grain of the spruce has been sectioned with a sharp knife, showing (i) that the powder/turpentine combination has not penetrated the first layer of cell walls, and (ii) the slight squashing of the cells as a result of surface preparation with a fine and sharp scraper.

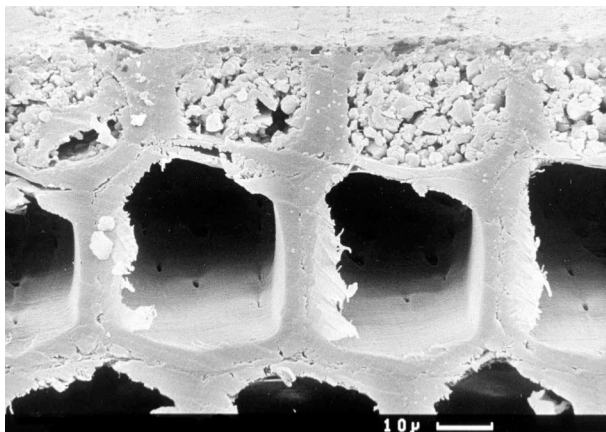


Figure 7. A surface of spruce on which Fine Surface Polyfilla has been used to fill the grain. The surface was originally sanded in this case, and the filler was burnished in after setting. The magnification is higher than in the case of Fig. 6. Again, there has been no penetration of the cell walls and the layer of particles thus created is very thin.

grain filler (fine surface Polyfilla) on spruce. The specimen was then prepared in the same way as for Fig. 6, with a scalpel-cut across the end grain. Again, we see that there is no penetration of particles beyond the first layer of cell walls, and the resulting layer is far thinner than is observed in the old ground layers. If all one was trying to do was fill grain to give a smooth finish, one would not apply the quantity of particulate matter which is in fact found.

The conclusion from both of these simple tests seems to be that some at least of the old makers went out of their way to apply quite a thick layer, heavily loaded with particles. If they had merely been smoothing the surface or filling open grain, they could easily have used less. In fact, no modern sample which we have studied, prepared by any method, has produced a layer which looks very convincingly like the old ground layers shown earlier. Back to the recipe-hunters and the intrepid testers of all possibilities!

Conclusions and prospects

In summary, we have shown that particulate ground layers certainly exist on some old instruments. They are too thick to be accidental or merely grain filler. Stradivari himself seems to have used different stuff on different days, and the simplest explanation is perhaps that the apprentice on varnishing duty bought whatever hardware store had in that week, which in turn perhaps suggests mixing the particulate matter into something, not using a self-cementing mixture. Some makers didn't use it (or it has all worn off). Some quite distant makers, even in northern Europe, used something which looks very similar in the SEM. Perhaps something more like a coherent picture will emerge when we have had an opportunity to study a larger range of samples. We have yet to see a modern sample looking at all the same as the old ones, so there is still a challenge for makers with an experimental and/or historical bent, to find a combination of materials and application method which comes closer. Certain apparently possible ingredients can be ruled out for some of our samples, but different ones in

each case. There is some possibility of refining this aspect of our results by particle-by-particle analysis of ground layers, but this very laborious task is not to be entered upon lightly.

A brief note on acoustical consequences

Up to now we have studiously avoided saying anything about any possible consequences of wood treatment and varnishing for the sound of the instrument. If the subject of violin varnish as a whole is a can of worms, then this is the most seething area of it! Any treatment applied to the wood influences the vibrational properties in two ways: it can change the value of elastic constants which govern stiffness to different kinds of bending and twisting motion, and it can change the internal damping associated with these motions, which for example governs how long a tap tone rings on after striking. These quantities are well understood, and in principle can all be measured. In practice, some can be measured easily while others require considerable ingenuity [5]. The best study in the literature of the influence of varnishes on these physical constants is still that by Schelleng [6], some of the conclusions of which were summarised at this meeting two years ago by Fulton [7]. This is not the place to go into any details, but a few very simple things are worth saying in view of the amount of nonsense which is talked on this subject in the press, including the semi-scientific press which should know better.

Increasing stiffnesses raises the frequencies of tap tones, and the amount by which they are raised is a measure of the change in stiffness. Now, the plain truth here (based, admittedly, primarily on anecdotal evidence) seems to be that pretty well whatever is first put on the bare wood, once thoroughly hardened, raises tap tones by a semitone or so. Gamboge filler, rosin oil, water glass,... whatever their differences in other ways, they seem to have rather similar effects on stiffnesses. There seems to be very little scope for “secrets” and magic effects here. If anyone uses a treatment which lowers tap tones, or raises them by a fifth, the changes in stiffness will no doubt have a significant effect on the sound of the instrument, but any two things which raise tap tones one semitone will have rather similar effects on all vibration resonance frequencies. In any case, these differences can be compensated, indeed swamped, by differences in wood selection and thicknessing.

Effects on internal damping are perhaps rather more promising as a source of acoustical influences of varnish. Reliable measurements of what influence different types of finish have on damping are very few and far between, and in any case it is not easy to tell from the kind of words used to describe the “Cremona sound” whether it is felt desirable to increase or to decrease damping. Nevertheless, it does seem from those words that effects involving damping are being talked about. There is at least scope for some fruitful research in this area.

It is quite easy to describe the sort of experiment which is needed. First, one must settle on a small number of interesting candidate treatments (of all sorts — wood treatment, ground and varnish will all contribute to internal damping). Then one takes a supply of pieces of wood as similar to each other as possible: good planks of spruce as supplied for keyboard soundboards are promising here, since one can cut adjacent squares with reasonably similar botanical details. One calibrates things by measuring each piece of wood before treatment, to allow for the inevitable differences among them despite all selection efforts. One would then put each finish on one piece, keeping one untouched as a control, hang them in a suitable air-conditioned room, and measure at least the straightforward three elastic constants and corresponding damping constants perhaps once a month for a couple of years or so. That way, one would find out how the different treatments change the underlying wood, and whether they continue to change with time. The required measurements are reasonably easy [5], and we are quite keen to try just such a measurement programme when the right selection of finishes can be identified. The spruce samples are ready, and a suitable air-conditioned room has been found. Suggestions are invited for good finishes to investigate.

References

- [1] C. Y. Barlow and J. Woodhouse. Microscopy of wood finishes. J. Catgut Acoust. Soc. Series II, 1, 1, 9–15 (1988).
- [2] Raymond White. Varnishes: their chemistry and analysis. Proceedings, Tiverton conference on surface preparation and varnishing (1986).
- [3] John Chipura. Radical practices. The Strad 161-162 (1984).
- [4] George Stoppani. Proceedings, Tiverton conference on surface preparation and varnishing (1986).
- [5] M. E. McIntyre and J. Woodhouse. On measuring wood properties, Part 2. J. Catgut Acoust. Soc. 43 18–24 (1985); and Part 3, J. Catgut Acoust. Soc. 45 18–24 (1986) .
- [6] J. C. Schelleng. Acoustical effects of violin varnish. J. Acoust. Soc. America 44 1175–1183 (1968).
- [7] William Fulton. Proceedings, Tiverton conference on surface preparation and varnishing (1986).