TALK FOR BVMA CONFERENCE 10.10.15
FROM THE STABLE TO THE WORKSHOP – INVESTIGATING THE USE OF SALTPETRE IN VIOLIN PRIMERS

INTRODUCTION

Most of you will know about Koen Padding, who died three years ago. He was one of my contemporaries at Newark in the 1970s and went on to do an enormous amount of research into violin varnishes, selling the results of his labours through his Magister company. When he died he left no record of how he formulated his products.

Over the last two and a half years I put together all the information I could find about his work; articles he wrote, notes that accompanied his products and information that others passed on to me. I also had analysis done of the products. All this information is in my recently published book: 'Violin Varnish: notes and articles from the workshop of Koen Padding'.

The subject of my talk today is a discussion of some ideas resulting from this work. I would emphasise that this is highly speculative, and I am at the beginning of the research and experimentation. It seemed however worth sharing this today in the hope that others will have ideas to contribute and that a number of you will take the bit between your teeth and try experiments of your own.

I have prepared a written version of this talk which I am happy to email to anyone who wants - the info will come at the end.

MAGISTER PRIMERS

Probably the most-used of the Magister products was the range of primers. There were several different types but they all had in common that they were thin, watery liquids, golden in colour, which were brushed or sponged onto the white wood of the violin. After a day or two in the UV or sunshine the colour deepened to a warm golden-brown which developed further over time and provided some sort of protection to the bare wood. It's important to emphasise that this was not a simple dye – although there was some colour in the liquid, most of the colouring it gave the wood was due to an oxidisation reaction, enhanced by exposure to UV, which enhanced the grain and figure of the wood and deepened the colour, rather than staining the wood as would happen with a dye.

Over the years I heard a number of ideas about what might have been the components of the primers, and rumours that people had had them analysed. On closer questioning the analysis seemed like a contemporary urban myth – you could never find anyone who had actually seen it! I was also told that the primers were simply potassium nitrite or nitrate and you could save yourself a lot of money by using that instead. Having tested industrial nitrates and nitrites thoroughly, I can confirm that whilst they give an oxidising result on the wood, the effect is by no means the same, and neither is the colour.

I was fortunate that Peter Greiner put me in touch with the lab in Germany run by Drs Elisabeth and Erhard Jägers, who specialise in scientific analysis of cultural artefacts. They kindly ran tests on a number of Magister products, and their report is included in my book. The tests they ran, using infrared spectroscopy, identified the inorganic, not the organic, components of the primers.

The elements they found in the different primers were as follows. Not every primer contained every element or compound.

Ammonium nitrate
Calcium
Calcium nitrate
Chlorine
Nitrites
Potassium nitrate
Potassium
Potassium hydrogen carbonate (potassium bicarbonate)
Silicon

The principal ingredients were paired; in some primers ammonium nitrate with potassium hydrogen carbonate, in others potassium nitrate with calcium nitrate.

The potassium nitrate is indeed there, but part of a richer spectrum of elements. Immediately you can see that some of these other elements could have a role in protecting and strengthening the wood, notably calcium and silicon. You might also surmise that even if the colour produced by the oxidising properties of potassium nitrate is your goal, this richer cocktail of elements might be more akin to getting your vitamin C from an orange rather than a pill – a lot of other things that are good for you are included.

The Jägers evaporated the solvent of the primers for analysis. Their description of the residue shows that each primer had a different form – some were roughly cubic crystals, some needle-like, some a mixture of crystals and amorphous material and one so hygroscopic that the solvent couldn't be evaporated totally.

Primers 1 and 2: partly crystalline, partly amorphous
Cremonese wood preparation Primo: large cubic crystals
Cremonese wood preparation Secundo: needle-shaped crystals
Linea Cremonese M1 light: fine crystalline
Linea Cremonese M1 dark: too hygroscopic to evaporate
Linea Cremonese M2: semi solid, partly crystalline

IF NOT INDUSTRIAL NITRATES, THEN WHAT?

So, if not industrially produced nitrates, how were the primers made? There were a few clues. I was able to acquire Koen's varnish-related books, and one that caught my eye was about the historical production of gunpowder.

The oxidising agent of gunpowder is saltpetre, which is one of those confusing, imprecise terms that covers a number of compounds of greater or lesser purity – in this case, mainly either calcium nitrate or potassium nitrate. Historically, it was produced from a mixture of manure, urine and wood ashes. Interestingly, when I contacted the editor of the book to ask if she knew of anyone involved in trying to recreate these early techniques, she said that the last person to ask this question was one Koen Padding.

Another clue came from Roger Hargrave, who says that he and Koen had started work together on this idea years ago, but that Koen had developed it further. And I was forwarded a copy of an email from Koen where he states categorically that industrial nitrates are not the same as his primers.

A recurrent theme in the Jägers' analysis is the presence of an unidentified brown substance presumed to be a largely decomposed organic component. The colour and smell suggested that it had been subjected to strong heat. This also corresponds with the historical method of saltpetre production.

Lastly, we know that Koen kept horses, and therefore would have had the ingredients for the production of saltpetre readily to hand.

THE THEORY OF SALTPETRE PRODUCTION

The materials needed to produce saltpetre are urine, soil, manure and wood ash. The manure and urine often come from horses but a wide range of sources were used historically.

The chemistry of saltpetre production is still not perfectly understood, but the basic process is this.

During digestion, the bodies of humans and other animals produce compounds of nitrogen and hydrogen as waste matter. This is present as ammonia, which is toxic, so the liver converts the ammonia to urea which is then expelled in urine.

The first stage of the saltpetre process is to turn the urea back to ammonia, which done by an enzyme present in soil, urease. Then the nitrosomona bacteria also present in soil convert the ammonia to nitrite. Finally the nitrobacter bacteria present in soil and in manure convert the nitrates to nitrites. The nitrates produced in this manner are mainly calcium nitrate. To produce potassium nitrate, wood ash is introduced. This is rich in potash (potassium carbonate) which reacts with the calcium nitrate to produce calcium carbonate and potassium nitrate. The wood ashes are either introduced as part of the decomposition process just described, or later as part of the refining process.

SALTPETRE PRODUCTION AS DESCRIBED IN HISTORICAL DOCUMENTS

The earliest sources of saltpetre were caves, cellars etc, where a white deposit had grown. The necessary condition was that there had been some form of manure deposited nearby over a long period – for example the cellar of a house where horse manure had been piled up outside, and the nitrates had leached through the walls. This would be usable with little additional treatment, but availability was limited.

As demand grew, techniques were developed to manufacture saltpetre. This was a was a considerable industry from the middle ages up until at least the time of the American Civil War. Only with the invention of gun cotton did production cease to be a major industry. Demand for nitre-rich soil, for example from stables or dove-houses, was considerable. The test for the presence of nitrates and other salts was taste – on the tongue it should be 'biting' as the 16th century writer Biringuccio says; strong and salty.

SALTPETRE BEDS

Techniques for manufacturing saltpetre were first documented by the end of the 14th century. Nitre-rich soil was mixed with manure,straw and often wood ashes, and made into big piles. Lime was added to the mix to reduce the acidity. These piles were irrigated with urine, and the liquid that ran off the piles was collected and reused. After several months, the surface of the piles developed a white deposit. This was the nitrates that had been produced in the pile.

The three prints reproduced from *Treatise on Ores and Assaying*
by Lazarus Erker, 1580

LEACHING SALTPETRE FROM SOIL

To extract the nitrates from the white-encrusted soil scraped from the surface of the piles, barrels were prepared which had a tap near the bottom and some form of filtration, usually sticks and straw. These barrels were then filled about three quarters with the nitrate-rich earth and topped up with water. The liquid was stirred and then left to settle. The water washed the nitrates out of the soil. The resulting nitrate-rich water could then be carefully poured off via the tap, the filtration ensuring that minimal sediment was included.

BOILING DOWN SALTPETRE

This liquid was then boiled down. Impurities were skimmed off as it boiled, and sometimes alum or glue added which helped the scum to form into clumps that were easier to skim.

The resulting liquid was ladled off, poured into trays and left to cool slowly, when crystals of saltpetre would precipitate out.

This mixture would still be quite impure, but further processes could be undertaken to refine this product.

Much early saltpetre was calcium nitrate rather than potassium nitrate. This was problematical for the production of gunpowder as calcium nitrate is much more hygroscopic - and damp gunpowder doesn't burn. For our purposes, whilst a proportion of calcium nitrate might be useful for strengthening the wood, it doesn't have the colouring effect of potassium nitrate. So the inclusion of potash is a vital step. Some recipes suggest straining the hot liquid through ashes.

WHY MIGHT SALTPETRE BE USED ON VIOLINS?

Though we might speculate that Koen used saltpetre as a basis for his primers, we don't know if it was also used on classical instruments. It seems a long way from the production of one of the components of gunpowder to the coating of a violin.

Following Koen's example as is evident from his articles reproduced in my book, let's try to think ourselves into the medieval mind. Although many if not most of the people engaged in work such as saltpetre production were illiterate, there is no reason to imagine they were stupid. On the contrary, they would have had a deep understanding of the processes they were engaged in, and maybe even because they didn't have the possibility of writing things down and measuring in our 21st century sense, they had to be keen observers of the process, using all their senses - touch, smell, taste, maybe even hearing as well as sight.

They would surely notice if the barrels used to prepare and store saltpetre were resistant to woodworm attack and rot. They would certainly have noted if wooden sticks used for stirring changed colour. And we can also hypothesise that what was used on violins was used more generally; on furniture, the panels of paintings etc.
Raymond White, who in the 1980s undertook analysis of classical varnishes at the National Gallery, said that he was surprised to find what was a fairly old-fashioned medium used as varnishes on 18th century violins. So we might assume that older, well-established methods were also used for preserving and colouring the wood under the varnish.

I've been in touch with a violin maker in Brazil who tells me that even today, local farmers make a bio-fertiliser from manure, urine and wood ashes which is also used as a pesticide/fungicide and to protect against termite attack.

PRELIMINARY EXPERIMENTS

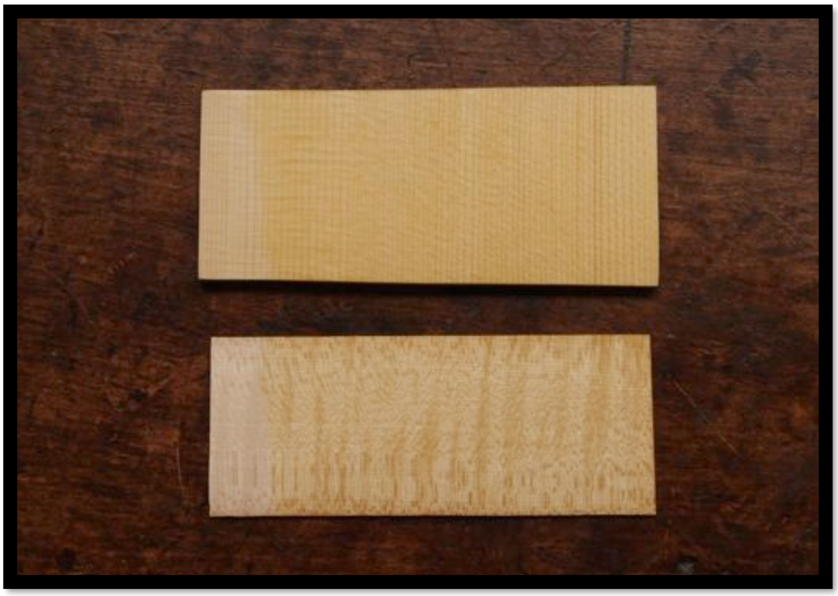
I've been working on the production of primers using horse products over the last few months, in collaboration with William Castle, who as the keeper of horses himself, has access to the raw materials.

The first ideas we came across, before I started reading in detail about saltpetre, suggested some sort of fermentation of manure, straw and urine, so William and his horses obliged. The mixture was left to stand for two or three months, and then jam jars and bottles of the resultant liquid came my way. However, when put onto wood there was no colour change.

I guessed that potash was needed to boost the potassium content, so I mixed the liquid with approximately 50% by volume of wood ashes and left it overnight. Also no effect on wood. Thinking that reactions are often better with heat, I boiled the whole mixture and cooked for about 10 minutes. This made the difference - my stirring stick was bright yellow!

I added a quantity of rainwater (to avoid the chemicals present in tap water) so that the resultant liquid would be easier to filter, and left it to stand overnight. Next day there was a thick grey sludge at the bottom and clear golden liquid at the top.

I poured off this liquid and filtered it thoroughly.



I wanted to see what the crystals would be like, to compare them with the Jägers' description, so I boiled down the liquid until most had evaporated, then poured the remains onto a saucer and left it to dry naturally. The crystals were roughly cubic and yellow-orange in colour, with a few white crystals dispersed amongst them.

I then dissolved some of the crystals in water with a bit of alcohol added (I understand that this increases the solubility). Interestingly a white sediment was produced, even though the original liquid was completely clear. This could possibly be calcium nitrate, which leaves a small sediment when dissolved in water. The resultant liquid was more golden and less yellow than the original, unreduced liquid.

Tested on wood, the original strong colour faded considerably when it dried. But after two coats, and a week in the UV, the colour developed and is not bad – slightly greyer than I'd like and perhaps not sufficiently intense. On the plus side, the figure and reflections of the maple are definitely enhanced.

COMPARISONS WITH GENUINE SALTPETRE

The crystals I made were of course unlikely to be anything like pure potassium nitrate saltpetre. The shape is wrong – cubic, a bit like Demerara sugar rather than the needle-shape of saltpetre. And as I didn't use soil, or refine the product as described in the saltpetre recipes, the likelihood is that it includes a whole cocktail of ingredients: traces of urea, ammonia salts and calcium nitrate.

I needed to find out more about the production of saltpetre and with luck get my hands on some of the real stuff.

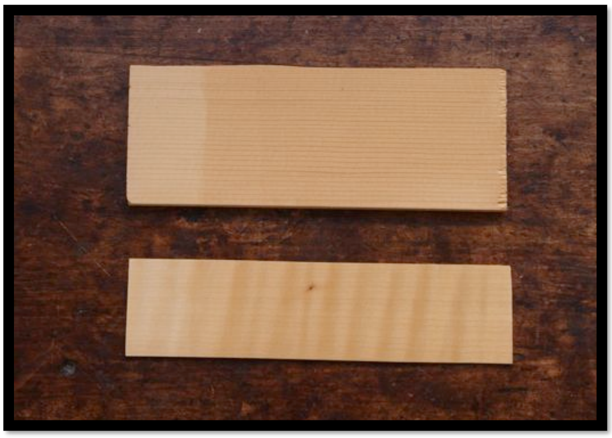
To my great good fortune, one of the world experts in historic saltpetre production, Kay Smith, lives in Leeds, a short train ride from my home in Manchester. We spent a morning together recently, and from our conversation, it became clear that practical knowledge is still scant, and particularly it's not clear how to get high yields.

UNREFINED INDIAN SALTPETRE

However, Kay was involved in an experiment undertaken in Denmark a couple of years ago by the Medieval Gunpowder Research Group (the report is available online and I will give details at the end of the talk). She generously gave me a small amount of the rather tiny amount of saltpetre they produced. As well as this, she gave me some saltpetre produced in India, where it is still manufactured, primarily as agricultural fertiliser. The first stage in the process produces something almost identical to the saltpetre they made in Denmark.

REFINED INDIAN SALTPETRE

A further stage of refinement produces these rather wonderful long crystals. They are roughly hexagonal in section, with a hole down the middle, and not at all hygroscopic.



UNREFINED INDIAN SALTPETRE ON SPRUCE AND MAPLE

I dissolved a small quantity of each and put two coats onto strips of maple and spruce. The liquids were virtually colourless. The reaction seemed slightly faster than with my homemade crystals – a reasonable colour overnight. After a few days in the UV there is not a great deal to choose between each of the samples, and the variation that is there is as likely due to my having been approximate with the concentration of the salts.

CONCLUSION

The ideas in this talk are highly speculative and there is much more work to do in order to find a manageable and consistent method for producing a usable primer for violins. Although the tests I have undertaken so far give a reasonable result, the colour is not as strong, and takes longer to develop, than Magister primers.

If Koen did use some form of saltpetre in his primers, he certainly deserves enormous credit. Making products that were consistent in quality over a long period of time from these simple raw materials is awe-inspiring. My guess is that demand for his products rose fast and unpredictably, so however he produced the primers, he was able to increase production fairly easily – I don't ever remember him being out of stock, and if he was, only for a short time. So he had surely developed a swift and efficient production process.

If Koen used some sort of saltpetre production at all, the variations between the different primers he sold must reflect different treatments of fundamentally the same raw materials. The analysis of the primers shows a narrow range of elements and compounds in different proportions and combinations. Both the way in which the main ingredients are combined and the degree of refinement of the salts produced would have an effect on the end result.

My feeling is that the relatively refined saltpetre that was made historically and that I have shown in the slides of Indian saltpetre is probably too pure. I would like to find a way of keeping a wider range of elements than just potassium nitrate in the mix. It's possible that for our purposes, a better result is gained by the combination of a spectrum of ingredients which each contribute something different to the end product.

Another question is whether the type of ashes is important. I understand the potash content can vary considerably between species of tree. The sources state a preference for hardwood ashes. Klaus Clement, in a talk he gave at one of the BVMA Dartington conferences, suggests that old household manuals counsel against using soap made from willow ash lye for washing clothes as this makes the clothes yellow - a positive advantage for us!

As violin makers, we live in an era of much greater sharing of information than the one that was around in the early days of my career. However, varnish seems to be the final outpost of secrecy. I hope that if anybody feels that there is some merit in the ideas I've outlined, that we could share our experimentation openly and learn from each other – which would also be a much faster way of reaching a result.

FURTHER READING

The Pirotechnia of Vannuccio Biringuccio translated and edited by Cyril Stanley Smith and Martha Teach Gnudi. Dover reprint, 1990.

Gunpowder, the history of an international technology edited by Brenda J. Buchanan. Bath University Press 1996

Making Saltpetre Medieval Gunpowder Research Group http://www.middelaldercentret.dk/pdf/Ho_report11.pdf

Instructions for the Manufacture of Saltpetre Joseph Leconte, 1892. http://docsouth.unc.edu/imls/lecontesalt/leconte.html

Making a double bass Roger Hargrave p.105 http://www.roger-hargrave.de/PDF/Bass/Bass_Making_Part_12_72.pdf

Ulrich Bretscher's Black Powder Page (blog) http://www.musketeer.ch/blackpowder/saltpeter.html

Varnish – from the myth to the reality Klaus Clement. Transcripts from 2001 BVMA Dartington conference

FOOTNOTE: A SUGGESTION FOR THE CONSTRUCTION OF A SMALL SALTPETRE PLANT.

With thanks to Kay Smith for her suggestions.

The heap should be a 50:50 mix of horse manure and soil. Both should be dry enough to be broken or sieved into fairly fine pieces, to enhance the reaction. Some straw should be mixed in to keep the texture open and airy. A suitable receptacle for the saltpetre plant could be a large plastic storage box. This would be prepared with a small hole at one end through which liquid runoff could be collected and reused.

The mix of soil, manure and straw would be piled loosely in the box and irrigated with urine, horse or other (apparently human urine is higher in urea after drinking wine). Some lime should be added (the bacteria work best in conditions with a pH of between 6.0 and 9.0 – 7.0 is neutral and the higher numbers are alkaline). The heap should be moist but not wet. The pile should be turned regularly to keep it well oxygenated, and the temperature at least 16-20 degrees. In time white crystals of nitrate will appear on the surface of the heap. This is likely to take several months.

When the heap is ready, it should be transferred to buckets with a hole near the bottom, plugged with a wooden plug. The bottom of the buckets should be filled with sticks and straw, which will capture the fine silt. The buckets should be about ¾ filled with the earth, and then water poured on (rainwater would be preferable). Then left overnight for the nitrates to be washed out of the soil, and for the sediment to settle. Then the plug to be removed and the nitrate-rich water collected in a fresh bucket.

This water should be boiled up and impurities and precipitated salts (which will mostly be simple sodium chloride (table salt) skimmed off.

Some time around this stage the wood ashes need to be introduced. A number of the early sources suggest ladling the hot liquid out of the pans it has been boiled in and pouring this through ashes. As we would be making less than industrial quantities, it is probably simpler just to add ashes to the liquid leached from the soil mixture and boil both together. The boiled mixture should be left overnight to settle and then the liquid poured off from the top. It should then be boiled down, skimming off impurities and salt until not much liquid is left. The residue should be transferred to some sort of clean dish or tray and left to cool as slowly as possible. As it cools, the potassium nitrate crystals will precipitate out of the solution.

It should be stressed that these crystals will not be completely pure potassium nitrate.

Note: I have read that sheep manure is high in both nitrogen and potash, though it is seldom referred to specifically in the historic texts.

Thanks to William Castle, Kay Smith and Drs Elisabeth and Erhard Jägers for their help with this project.