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Conserving Tangible and Intangible Cultural Heritage: Cleaning Degraded East Asian Lacquer

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Abstract

East Asian lacquer (*urushi*) is a natural, thermosetting polymer, characterised by its durability and gloss. Prolonged exposure to light, however, causes photodegradation, which initiates microcracking in the surface layers. Accumulation of dirt, grease, or non-original materials, such as varnishes applied during attempted restoration, contributes to deterioration of the lacquer's appearance through discolouration. This build up must be removed in order to conserve affected pieces, and the potential use of solvents to achieve this aim is investigated here.

This work presents a review of the chemistry of this unique material, and the distinction between different East Asian lacquers is investigated. Valuable, rare lacquer samples could not be taken from naturally aged museum pieces in order to investigate the applicability of solvents in cleaning conservation processes, and so the damage featured on the models used was recreated artificially. The advantages and limitations of such an approach are assessed in terms of the practical value of the resulting samples as credible models compared to the naturally aged material.

In free film studies, solubility parameters were determined for a range of lacquers, and the morphological changes that result from solvent exposure are also investigated to determine potential 'safe' solvents for conservation cleaning. These studies show that most solvents are damaging to photodegraded lacquers to some extent, and the possible risks must be assessed against the need for removal of a damaging layer. The findings reported here have implications for the choice of solvents used in conservation cleaning, but other solvent properties and behaviours must be considered along with these data when identifying the least damaging, yet effective solvents.

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Introduction

The aim of this research was to investigate the use of solvents in the conservation cleaning of photodegraded, original Japanese (*urushi*) lacquer artefacts, and the focus of this work, therefore, is the interaction of solvents with these natural, polymeric materials. This research project was based on the Mazarin Chest conservation project,[1] a major collaborative venture which involved conservators and scientists from around the globe.

Japanese, Chinese and Korean lacquer is obtained as sap from the *Rhus vernicifera* tree, and in its refined form it cures under high humidity to a glossy and durable finish that resists water, heat, acids and alkalis.[2] Over time, the lacquer ages due to photodegradation and its structure becomes increasingly crosslinked and damaged. The thermosetting material remains insoluble, although it becomes increasingly sensitive to some solvents, including water and cleaning agents. Aged *urushi* models are used in this work to determine whether any solvent system can be considered ‘safe’ to use on such a vulnerable material, whilst also being an effective cleaning agent of photodegraded resin varnishes and dirt and accretions built up over the years.

The popularity of lacquered furniture of East Asian origin is examined from a historical perspective in the first chapter. The valued lacquered-surface aesthetic is a result of skilled application by experienced artists, and also its inability to be successfully reproduced in Europe. These pieces were scarce and expensive,[3] and demand outweighed supply in Europe during the 17th-18th centuries, and, as a consequence, imitation materials were keenly sought. The technique for producing imitation surfaces of *urushi* lacquer is termed ‘japanning’ and it became widely used in Europe to produce furniture and decorative pieces displaying a ‘lacquered’ effect.

Japanning materials were based on spirit or oil-based varnishes, which were widely available in Europe from the 17th century. The most common varnish materials and published recipes for japanning, and other high-gloss surfaces, are discussed in Chapter 2. These recipes illustrate the types of materials that were available and popular during this time that may have been used in the restoration of glossy surfaces.

Numerous studies on the chemistry of *urushi* have been carried out since the 1950s, and Chapter 3 reviews the literature from those studies available in the English language to highlight the unique nature of this natural polymer. Specific modes of curing and deterioration, and the implications of the latter on conservation, including the damaging effects of high levels of light exposure towards lacquer are discussed.[4] The photodegraded material loses the characteristic gloss and surface integrity associated with East Asian lacquer due to the formation of microcracks on its surface.[5] Other problems experienced by these lacquers, such as abrasion, environmental damages and even restoration attempts that have involved the addition of non-original materials such as waxes, oils or resin-based varnishes contribute to an overall deterioration of the lacquer in terms of quality and aesthetic.

A range of lacquers are produced in East Asia, the properties of which vary according to the geographical region of collection, and the type of sumac tree from which the sap is obtained. Differences in colour are also observed in cured lacquers harvested at different times, those which have been exposed to refining processes, and those which have had additives introduced.[6] Chapter 4 discusses these different types, and determines whether the cured, aged lacquers can be distinguished by solid-state analysis, and more importantly, whether the origin of lacquer present on an artefact can be identified using such methods.

The use of naturally aged lacquers for chemical analysis and solubility testing is severely restricted in this research due to the fragile and valuable nature of the materials. Consequently, a range of artificial ageing and damaging processes have been carried out in order to produce a sufficient sample size. Fresh lacquer samples were exposed to harsh conditions, and their effects monitored in terms of chemical and optical changes, and these changes are discussed in Chapter 5. This conservation chemistry approach examined the changes in *urushi* over time by means of accelerating the breakdown of the polymer structure, morphology and surface appearance, comparing them, where possible, to naturally aged standards. In the case of the insoluble, crosslinked *urushi*, only solid-state analysis is useful in monitoring the changes that occur. The artificially deteriorated film models were used to determine how increasingly aged lacquers respond to a range of solvents. This work aims to quantify this response in terms of calculated solubility parameters, values that can then be applied to other models such as the *Teas fractional solubility parameter system*, which is a predictive model of solvent-artefact surface interaction that is familiar to many conservators.[7]

In addressing the behaviours of natural, ancient materials for conservation practises, no two pieces will display the same features in terms of original materials, techniques used and extent of damage. The best means of approaching treatment, therefore, is to be familiar with the behavioural *trends* of a range of solvents towards the materials.

The assessment of damaged surfaces with regards to its stability is often carried out visually by experienced conservators. Trial and error investigations, however, using small areas to test the responses to solvents can cause irreversible damage such as blanching due to leached components, swelling and movement of the surface, delamination, and pooling of solvents in lower layers. Conservators need to know which, if any, solvents can be safely used to remove contaminants such as dirt and dust trapped in fine cracks, grease from fingerprints, or non-original materials such as waxes, oils or resin-based varnishes, and this will be the focus of this work.

To restore an object's aesthetic quality, whilst conserving the piece as a whole, there is a need to reduce the discoloration of the original surface due to gloss reduction or from the presence of aged, yellowed varnish, or an accumulation of dirt or oils. Since solvents have been successfully used in the cleaning of oil paintings,[8-10] it is reasonable to speculate that they have potential benefit as cleaning agents for damaged lacquers too; the use of solvents as cleaning agents is discussed in Chapter 6.

The main objective of this research is to determine the effects of solvents on vulnerable lacquer surfaces, particularly in terms of swelling and leaching effects. Solubility tests, including immersion and vapour sorption tests, are carried out to determine the relative uptakes of different solvent types on aged lacquer films. The solubility parameters of lacquer in degraded states are determined in Chapter 7, and the effects of solvents on the morphology of lacquer surfaces are investigated using scanning electron microscopy. Taken together, these data imply general trends in the responses of damaged lacquer models to different solvent classes, indicating which are the most, and least, damaging.

The risks associated with applying organic solvents and water to the surfaces of photodegraded lacquers are discussed in Chapter 8, in relation to the potential benefits that may be gained in terms of cleaning unwanted layers from the original surface. Solvent characteristics other than their swelling properties, including diffusion and evaporation rates, have a significant influence on their potential use in conservation cleaning, and these are also discussed in reference to the materials under investigation.

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Chapter 1

Exported lacquered furniture and the Mazarin Chest

For centuries East Asian lacquer has been used to decorate and protect the surfaces of furniture, ornaments and functional items. This unique, thermosetting polymeric material, *urushi*, is obtained as tree sap and cures to a glossy, stable and mirror-like surface. Pieces displaying *urushi* were highly collectable,[1] and interest in obtaining such items was at its height in Europe during the 17th century. The condition of the pieces remaining from this period depends on the way they have been treated, the surroundings in which they were stored, and also the quality of the original workmanship. Since exposure to light causes the dulling of the surface,[2-5] as will be discussed later in this work, many pieces are found in a dull and matt state, and feature evidence of restoration attempts.

The historical use of *urushi* in the creation of remarkably intricate decorative features will be discussed in this chapter; of particular interest are the pieces from the 'Fine Period'[1] (1630-1640s), during which time particularly high quality pieces were created in an identifiable style. The collectability of such pieces meant that there was more demand than could be met, and so artists and furniture-makers began to look in earnest for a means of producing similar finishes without using *urushi*. Decades of investigation yielded several varnish compositions and application techniques which attempted to produce the lustre of *urushi*; this technique was termed 'japanning'.

1.1 A history of lacquering and decorative style

The traditional Japanese art of lacquering has always been handed down through generations; this highly skilled technique takes a lifetime of work to acquire. The intricate planning, painstaking effort, and superlative artistry required to create these elaborately decorated items is developed over many years. Skills such as these, and the intangible cultural properties that they contribute to Japan, are so valued that the Japanese government have adopted the term ‘Living National Treasure’ to be used for a specific few uniquely skilled and experienced masters of crafts such as pottery, paper-making and lacquer art.[6] Lacquer artists developed a variety of innovative techniques which expanded the different decorative styles. Techniques and designs were altered over time, and specific periods in Japanese history can be associated with identifiable features. For example, many important lacquer artists worked in the Momoyama period (1568-1600); one of their most favoured techniques was to create a smooth black background and to painstakingly add detailed relief decoration in silver, gold, and mother-of-pearl, featuring flower or animal decoration.[7]

The beginning of the Edo period (1603-1867) saw the production of extremely high quality lacquer pieces. Using black or gold backgrounds, artists were able to create elegant styles, and the competitive nature of the profession promoted the creation of increasingly impressive pieces, leading to abandonment of the traditional bare style. The second half of the Edo period was a prosperous time in Japan, and many lacquered furniture and inro (small receptacles for items such as medicines, which were attached to the belt by a cord) pieces were made for merchants who provided their wealthy clients with these fashionable items. A pioneering technique of this era was the creation of a different style using *maki-e* (a decorative Japanese gold or silver lacquer created by the sprinkling of metal powder) decoration with less definition than previous styles. Depth and perspective obtained through experimentation with different materials were extremely popular.

Foreign influence on decorative style

Following the arrival of Portuguese merchants in 1543 on the island of Tanegashima, near Nagasaki, a mutually-beneficial and exclusive trading relationship was established between Portugal and Japan. During the time that the Portuguese held their position as exclusive traders, they moved large amounts of Chinese textiles to Japan, as well as a variety of products from the West, including wine, food products, clothes, hour-glasses, optical lenses and carpets.[8] These novel items proved popular with the Japanese.

In turn, the Portuguese developed an interest in exotic lacquer ware, particularly that involving *hiramaki-e*, a technique producing a low-relief effect where a single layer of lacquer is applied to the ground, sprinkled with gold, dried, consolidated and polished. The Portuguese began to order lacquer wares made in Western-style shapes and depicting non-traditional symbols, the so-called Namban or Southern Barbarian[9] style, characterised by densely crowded decoration such as that illustrated in Figure 1.1.

Namban lacquer was characterised by thick applications of lacquer layers, rather crudely spread upon the wooden carcass without the usual foundation and fabric layers. This type contrasted with the traditional lacquer ware style and did not use elegant decorative techniques such as *maki-e*, although it was based on the traditional *urushi* material, unlike the imitation technique of japanning, which used very different materials, as discussed later.

Figure 1.1: A wooden tankard coated with black and gold lacquer inlaid with mother-of -pearl in Namban style, from early 17th century (Museum number FE.23-1982). Photograph courtesy of the Victoria and Albert Museum.

Domestic furniture was ordered in large quantities from Kyoto workshops with a specific aesthetic style in mind. The Portuguese preferred mother-of-pearl inlay decoration and designs typically included images of animal and plants. Frameworks and geometric patterned borders seen on some pieces show the great influence of traditional Chinese styles. The vast blank spaces seen and valued in traditional Japanese design were densely filled with foliage or other detailed patterns, a very un-Japanese style.

This exclusive trade continued until the arrival of the Spanish half a century later, followed by the Dutch and the English, ending the Portuguese's authority and prominence. The Spanish and Portuguese were forced out of Japan following the first Shogun of the Edo period's anti-Christian ruling. Following this political change, Japan isolated itself from the Western world for nearly 200 years, retaining contracts only with the VOC (Vereenigde Oostindische Compagnie) for trading purposes. The Dutch were permitted to trade with the Japanese as the Dutch East India Company (VOC), established in 1602, because as Calvinists they were not viewed as Catholics by the Japanese.[10] The Edo period lasted from 1603 until 1867, beginning when Tokugawa Ieyasu took military control of Japan.

The Dutch mostly purchased copper, silver and gold, and some lacquer and porcelain from the Japanese, for distribution throughout Europe. Dutch VOC records show that nine lacquered chests arrived in Holland in a Japanese cargo in 1610.[9] The first English voyage to Japan was in the Clove ship, belonging to the East India Company. According to its records, in September 1614, it arrived at a London port bringing several items of furniture and items of kitchen equipment which were coated in "a most excellent varnish", according to the company's chief agent.[11] Around this time, newly discovered items such as these pieces were generally kept as gifts for nobility, although some were auctioned. Impey and Jorg have catalogued documentation relating to the trade in Japanese lacquers with the English during the period of their residence in Japan. An extract from this record reads as follows: "1618, 1 January. Richard Cocks' diary: I gave these new years giftes following, *viz*: To Capt. Adames a nest of 5 maky beakers, To Mr Wedmore 2 maky beakers". The 'maky' refers to the traditional Japanese *maki-e* technique.[1]

There was a decline in the production of larger pieces of export lacquer furniture in the latter part of the 17th century. English japanners had petitioned to reduce the amount of imported lacquer that hindered their trade, and also the cost of these pieces had become too high. Japanese lacquer was regarded as being superior in quality to Chinese lacquer. According to Rein, “none have so quickly disengaged themselves from their Chinese masters and patterns … and won eminence among all civilised people”.[12] Such pieces consequently became very expensive, more than the VOC could afford.[9] Private Dutch merchants continued to import lacquered items, but the VOC ceased dealing in these items.

Following the expulsion of the Portuguese and English, and up until the late 18th century, there were notable changes in the designs on lacquered pieces. The Portuguese-influenced crowded style of the 17th century was replaced by ‘a more restrained and pictorial decoration with a plain black lacquer background’.[9] The Namban style of decoration, incorporating foliage masses and geometrical designs, did not appeal to the Dutch and consequently there were changes in style by the end of the 1640s. Mother-of-pearl was used to a lesser degree, and larger plain areas of black lacquer or gold *maki-e* (Figure 1.2) were included; this style was most apparent during the 1630-1640s, during these decades fine Japanese pieces were produced. Expensive lacquer pieces of this style were regarded as status symbols in the West.

The Tokugawa government would not allow export lacquers to include pictures of Japanese towns, weapons, or castles, as of August 1641,[13] and the ‘pictorial style’ which was less crowded, usually depicting landscapes and mountains, plants, water birdlife and classic tales and legends, became very popular.

Figure 1.2: Japanese Inro displaying gold and silver *maki-e* techniques: *hiramaki-e* (low sprinkled picture) and *takamaki-e* (high sprinkled picture (1775-1850) (Museum number W.477-1910). Photograph courtesy of the Victoria and Albert Museum.

The mountain, water, and plant life scenery was presented on a large, black background using *maki-e* techniques. The lacquer was of a finer quality[14] and the use of borders was rapidly disappearing. This lacquer was more typical of the traditional Japanese style, which increased the popularity and commercial value of the export lacquer ware. Some 'foreign' symbols continued to be found however, such as Indian, Chinese and Japanese characters. Figure 1.3 shows a cabinet and stand from the 17th century, the cabinet is a piece of export lacquer made in Japan to Western style. The stand was added later on in Europe to add practicality to the piece.

Figure 1.3: Cabinet on stand (cabinet made in 1630 in Japan, and stand made between 1680-1700 in Europe) decorated with lacquer (Museum number FE.38:1 to 13-1978) Photograph courtesy of the Victoria and Albert Museum.

In addition to reverting to the more traditional Japanese style, other East Asian elements were in demand, including Chinese and Korean figures. Changes in style were accompanied by changes in furniture shape according to European demand. Furniture from the 1630s typically had two doors and two side-opening panels – a style which remained popular well into the 18th century.[14] Smaller items were also in demand; particularly chests, small boxes and nests of boxes. Pieces of exceptional quality were produced in the 1630-1640s.

1.2 The surviving pieces of the Fine Period

Examples of very fine quality Japanese lacquer exist today outside of Japan. Lacquer pieces surviving from the 'Fine Period' (1630-1640s), the time following the exclusion of the Portuguese, are scarce. Impey and Whitehead identify a few surviving pieces: the Mazarin Chest and Lawrence chest (currently lost); the Chiddington Casket, which was a

European style chest; and the smaller van Diemen and Buys box. The Victoria and Albert Jewel box and Western box were both jewellery boxes supposedly owned by English collector William Beckford at some point.[15]

The Mazarin Chest, held in the Victoria and Albert Museum, London, is currently undergoing conservation. Although little is known of its early years, it is estimated that the export piece was brought over to Europe more than 350 years ago. The chest is thought to have been produced in Kyoto workshops during the 1630s and is likely to have been shipped directly to Europe or to a Dutch East India Company official. The chest was almost certainly produced, to order, for nobility in the Parisian courts where there was a large demand for such luxury goods. Over the next 160 years it was in the possession of the Mazarin-La Meilleraye family, the evidence for this assumption being that the steel key belonging to the chest bears the coat-of-arms of the family. By the end of the 18th century, the chest was passed to the Duc de Bouillon who held a large collection in Paris.

The Mazarin Chest (Figure 1.4) is adorned in traditional Japanese decoration on a piece of European-style furniture. This European-Japanese hybrid is very rare, with the quality of both the surface decoration and foundations being exceptional for a piece not intended for domestic use within Japan.

Figure 1.4: A side-view of the Mazarin Chest. Image courtesy of the Victoria and Albert Museum.

1.3 Decoration on the Mazarin Chest

Remarkably fine details are present on the chest which required intricate techniques to effect. Figure 1.5 shows a small section of a building which has raised decoration depicting its construction. The roof ridge has been constructed from metal sheet, whereas gold and silver twisted wire (*marusen*) has been used to represent railings. Drops of dew on the tree branches are represented by silver studs (*ginbyo*). A *maki-e* technique, whereby a sharpened piece of bamboo is used to scratch away part of a sprinkled picture design prior to hardening, has been used for the windows.

Figure 1.5: A building depicted on the chest, illustrating a range of fine techniques used. Image courtesy of the Victoria and Albert Museum.

The attention to fine detail on the chest is notable by the efforts made to add facial features and textile clothing patterns on to the smallest of figures. The boat in Figure 1.6 is 7 cm long, and the inset picture shows the extensive detail of the man’s face, despite it being only 3 mm high.

Another example of the minute details presented can be observed in Figure 1.7, where part of a dragons face can be seen. This is a very small part of a scroll design around the edge of the chest lid. The eyes of the dragon have been designed so that the pupil of the eye has been set into the surface of the lid, and a glass eye inset into the raised lacquer with which the dragon has been constructed; this indicates extensive forward planning in the design of the chest.

Figure 1.6: A small area of decoration on the Mazarin Chest: two figures in a boat, and, inset, the delicate features added to the man's face. Image courtesy of the Victoria and Albert Museum.

Figure 1.7: A dragon's face as part of the edging of the lid. Image courtesy of the Victoria and Albert Museum.

In 1800 the Mazarin Chest was acquired by English eccentric William Beckford, who was a collector of lacquer and other art pieces, particularly "small-scale, exquisitely crafted works of art".[16] The Victoria and Albert Museum archives[17] show evidence of Beckford's acquisition in 1797, when he instructed his agent to begin the purchase process. It was sold in 1800, and the three years difference indicates some degree of preparation was required for its sale. There are anecdotal suggestions that the Mazarin Chest was, at some point, treated to restore the gloss. If this did indeed occur, there is no documented evidence to confirm it, although there are areas on the chest which seem to have been japanned, and possibly varnished. Shiny surfaces were fashionable in France at this time, and Beckford himself was well known for his Francophilic tastes.[16] By this time England also had a taste for bright and shiny furniture;[18] dimly lit rooms required bright pieces of furniture. The French nobility and upper-classes were keen collectors of fine Japanese lacquers.

1.4 Treatment of the Mazarin Chest

As previously mentioned, there is speculation that some treatment has been carried out on the surface of the chest. If restorative treatment was in fact carried out on the Mazarin Chest, it is unlikely to have required this prior to 1688, as East Asian lacquer can retain its lustre for 75-100 years under reasonable conditions. Assuming that great care was taken with this piece, and that environmental impacts were restricted, then its gloss would have been retained well. Additionally, the Mazarin Chest was acquired by the Victoria and Albert museum during the 1880s, and whilst it is not documented to the contrary, any restoration is unlikely to have been carried out whilst in the Museum's possession without having been recorded. The latter can be reasonably assumed since the Museum register from 1882 gives details of the chest and its acquisition, which does not list any accidents, repairs or restorations, but does describe its condition on acquisition as being ‘rubbed, and small portions missing’. This implies that a degree of damage was visible on the chest when it was acquired. The ‘rubbed’ condition may refer to a scratched or dulled surface, with detriment to its gloss. Victoria and Albert museum records state that, prior to the Museum’s acquisition of the chest, it was passed to Beckford’s daughter, the Duchess of Hamilton, and remained at Hamilton Palace in Scotland. In 1882 the Mazarin Chest appeared in the catalogue of the Hamilton Palace sale, from where it was purchased by the Victoria and Albert Museum.

Over time revisions are added to these records. For example, it was originally stated in the archived documentation that the chest belonged to Napoleon I, however later revisions state that this is inaccurate. Records found, for the same year, for oil on canvas paintings in the Victoria and Albert Museum detail all of the cleaning and re-varnishing processes that the objects underwent. It is unlikely, therefore, that the addition of varnish to parts of the chest would not be recorded.

In a letter from Beckford in 1797 to his agent, to whom he insists that he acquire the Mazarin Chest, he speaks of his being “affected with the Japan-mania in a violent, incurable degree”.[17] He was eager to acquire a large lacquer collection of the finest quality, and he had a particular partiality to purchasing pieces from the collections of people such as Madame de Pompadour, the Duc de Bouillon, and Cardinal Mazarin. He is thought to have kept the chest alongside the van Diemen Box and the Buys box in Fonthill Abbey. Interestingly, Beckford was known for having pieces of lacquer ware taken apart and used as components on other pieces, a typically French practice. Whilst it is not known for whom the Mazarin Chest was originally created, it has been traced to the Mazarin-La Meilleraye and the Duc de Bouillon (a Parisian Collector). During the later part of the 17th century, and throughout the 18th century, the chest is thought to have resided in aristocratic homes in Paris, and so it is interesting to briefly look at the way in which East Asian lacquers influenced French furniture of this time.

1.5 Influences of East Asian styles on French furniture c. 1650-1800

The Mazarin Chest resided in France during an age where there were many influences over furniture style. Louis XIV the ‘Sun King’ (reigned 1643-1715), for example, was the ruler most associated with the 17th century period of extravagance for the French Monarchy.[19] With his court based at Versailles, the King enhanced his elaborate lifestyle by surrounding himself with musicians, writers, architects, artists and furniture makers. His furniture preference was for large, ‘masculine’, square, bold forms; this furniture is referred to as ‘Baroque’, with surfaces rich in colour and high gloss.

During the reign of Louis XV (reigned 1715-1774) the majority of the population were poverty stricken peasants who were bitter towards the elaborate lifestyles of the nobles. The elaborate Louis XV furniture style is often referred to as the ‘Rococo’ style which thrived during the greater part of the 18th century (1730-1775). This style contrasts greatly with the style of the previous ruler, being designed for comfort and beauty, with a ‘feminine’ and ‘romantic’ imagery. Flowing curves feature on legs, seats and backs of chairs and tables, whereas straight lines were seldom found on any furniture or architecture of this period. The decorative style was elaborate and exquisitely detailed, increasingly featuring *Chinoiserie* as French furniture became more and more influenced by Asian design. East Asian lacquer began to emerge on wood furniture.

Production of 18th century furniture, Paris

18th century French furniture, made mostly in Paris, was beautiful and refined, displaying supreme artistry and technical skill. These pieces were sought after by the wealthy to furnish residences all over Europe; the style had a considerable impact on the fashions of cabinet-making outside France.[20] Craftsmen such as Jean-Henri Riesener (1734-1806) created items in Paris, for Marie Antoinette, including opulent furniture pieces displaying Japanese lacquer panels, surrounded by gilt-bronze flowers, fruit and wheat symbols.

There were strict regulations governing the way in which craftsmen constructed this furniture, enforced by the Furniture-Making Guild (Corporation des Menuisiers), which was finally dissolved in the French Revolution in 1791. The menuisiers were responsible mainly for the carpentry work, whereas the ébénistes applied the veneered finish. Louis XIV's finance minister, Jean-Baptiste Colbert, structured the guild into an effective professional organization for its specialized members and craftsmen of French furniture. As the ébénistes' art of veneering continued to develop, the guild was renamed the 'Corporation des Menuisiers-Ébénistes' in 1743.

The traditional black and gold aesthetic was well received and highly valued in French society where such opulent and complexly decorated pieces were in fashion, and the collectors took pains to maintain the effect. Evidence of this is indicated on the damaged *urushi* panel shown in Figure 1.8. Brown patches show areas of photodegraded *urushi*, and on close inspection of the areas surrounding the gold branches there is evidence of re-varnishing with a black varnish in an attempt to restore the original effect.[21]

Figure 1.8: Damaged *urushi* panel. Image courtesy of the Victoria and Albert Museum.

1.6 The demand for lacquer

Europeans greeted lacquered furniture from Asia with great admiration, and they rapidly became status symbols amongst the very wealthy and nobility. From the end of the 17th century, the vogue for Japanese lacquered furniture had spread throughout Europe, but Japanese production could not satisfy demand. Also, *urushi* in its liquid form could not be transported from Asia over long distances since it was too reactive with the air and would have cured in its containers by the time it had reached its European destination.

One solution to this was to cannibalize the lacquered screens and boxes imported from Japan to create new furniture in the Western style. This was a practise that went on in France and England in particular, and an example of a commode made in Paris displaying Japanese lacquer panels and japanned borders is presented in Figure 1.9.

Figure 1.9: Commode made in Paris (1750-1760), veneered with Japanese lacquer panels and japanned borders (Museum number 1094-1882). Photograph courtesy of the Victoria and Albert Museum.

Many lacquered panels were ordered with the intention to be used to adapt Western style furniture.[22] Screens were also acquired for their ability to be divided and added to enhance and adapt other furniture pieces. Pairs of furniture pieces such as chests or cabinets were often decorated in mirror images, although the individual pieces were generally lacquered with asymmetric design and large areas of blank spaces for aesthetic reasons, as discussed above, also allowing the addition of extra features such as lock plates.[1] It is for this reason that genuine lacquered pieces from Japan are not often found as complete, undamaged pieces.

When adding panels of *urushi* lacquer to Western pieces it was necessary to fill in the gaps between the panels, legs, stands, and so forth, and to decorate these joining parts to blend with the lacquered panels. The technique known as japanning, was used for this purpose. Japanning was developed back in the 17th century as European artists and furniture makers had strived for decades to produce a substitute for East Asian lacquer, and this is discussed further in the following section.

1.7 Japanning

Japanning is a European technique which is used on furniture and other objects as a decorative and protective coating. The process uses varnishes that have a resin base, and it involves the application of several coats of varnish, which are each heat-dried and polished. The method was popularised amongst skilled artists and amateurs by ‘A Treatise of Japanning and Varnishing’ published by John Stalker and George Parker in 1688,[23] a manual which gave detailed instructions as well as stencilled ‘Oriental’ designs to copy. This fashion continued through to the 19th century, particularly as better varnish formulations were increasingly being produced to create the required effect.

In France, japanning and *urushi* were frequently seen in combination. The example shown in Figure 1.10 is a French commode from the mid-18th century showing original *urushi* panels surrounded by japanned legs, and a polished marble top.

On the corner of a commode from the mid-18th century (Figure 1.11), the juxtaposition of the *urushi* and Western material can be seen, and their differences are apparent. The *urushi* panel has been over-varnished, and over time has become dull and matt, whereas the japanned panel is crackled on the surface. The two finishing effects are obtained using very different materials, and therefore deteriorate at different rates.

Figure 1.10: Mid-18th century French lacquered commode. Image courtesy of the Victoria and Albert Museum.

Figure 1.11: A closer look at the surfaces of the commode shown in Figure 1.10. Image courtesy of the Victoria and Albert Museum.

Examination of French pieces of this time illustrates the preference for a highly glossy finish on their furniture surfaces; lacquer pieces were often re-varnished in order to maintain the gloss. Attempting to revive the dull *urushi* with Western oils or varnishes may give an immediate effect by seeming to improve the gloss of the surface; however it will in no way replicate the original appearance or subtlety of the surface, and could potentially cause damage in the long term.

Owing to the close links that Portugal held with Asian societies during the 17th century, the imitation methods were more reluctantly accepted by the Portuguese, although fashionable trends slowly encouraged acceptance of japanning techniques.[24] For example

Portuguese cathedral choir-stalls dating from 1731 have been found to feature japanned panels.

The desire to imitate Japanese lacquer

The desire to produce pieces which displayed the Japanese style of glossy black areas with extensive amounts of gold decoration increased, since there was simply not enough *urushi* lacquer ware on the market.

The attempt to recreate the *urushi* lacquer effect was pursued for a long time. In Amsterdam, a successful varnish was patented by William Kick in 1609, and patented again several years later as an improved recipe.[1] It was during the 1730s that the French Martin brothers developed and patented a varnish, the Vernis Martin, which was intended to imitate East Asian lacquers to such an extent that it could compete with the original material. Heating oil with copal and adding Venetian turpentine, and then painting thin layers on top of wood or paper surfaces, which were hardened in a furnace, was the general procedure for producing the effect.

This formulation was very successful: in 1740 the Martin brothers secured a Royal patent on their recipe. The varnish became popular and fashionable on the continent, and also at Court, where it was used for many of the Versailles Palace rooms. To meet popular demand for their japanned ware, they opened three factories in France (1730-1785) to produce replicated lacquer wares, using their 'perfected' varnish.[25] The 'Vernis Martin' was frequently used to restore damaged lacquer or to blend japanned panels with *urushi* panels.[26] The publication of "A genuine receipt for making the famous Vernis Martin"[25] in 1776 meant that good imitation East Asian lacquer pieces could be prepared. After the initial enthusiasm over Japanning in England during the 17th century, the reduced volume of literature indicates that there was a lull until the mid-18th century.

Western designs saw the increased experimentation with coloured japanning produced by the addition of pigments. Although the gloss effect was still the key aim, the unsubtle, bright colours were uncharacteristic of the traditional Japanese aesthetic. These pieces were very much influenced instead by Chinese red lacquer pieces, and were characterised by a monochrome background (red, black, blue and green) with gold decoration.

Coloured japanning – how the colours were achieved

Japanned items are characteristically strikingly colourful, with pigmentation being used to create rich colours - very different from the traditional black and gold effect. Impey and Jorg highlight the lack of paintings that depict lacquer wares, and they hypothesized that the black objects did not act as very good background imagery.[1] It is also possible that artists found these complexly decorated items time-costly to reproduce when painting portraits, preferring simple background objects.

Figure 1.12: Black japanned cabinet, mid-18th century. Image courtesy of the Victoria and Albert Museum (Museum number W.61:1 to 8-1931).

The literature of the time has very specific directions on the production of the coloured japanning formulations, and it is interesting to briefly look at the literature for the best means of obtaining these colours. William Salmon's extensive work on a range of subjects, Polygraphice,[27] published in 1675, directs that the production of black japanning requires that three layers of seedlac coloured with lampblack is applied, followed by six layers of seedlac and Venice turpentine, and then another 12 layers of lampblack-coloured seedlac, allowed long periods of drying time inbetween layers. After drying for 6-7 days, and polishing with Tripoli until smooth, the surface is finished with oil and lampblack. Evelyn also presents a recipe for 'Japan of China varnish' which contains spirit of wine, gum lac, a small amount of sandarac (alternatively mastic and white amber), with extensive preparation procedure and details of its application.[28] According to Stalker and Parker[23] the basic recipe for black Japan (such as that shown in Figure 1.12) involved the addition of lampblack, a black pigment, to shellac. Lampblack is a sooty, greasy substance produced during the production of dry turpentine resin.

The production of Red Japan required not only vermillion pigment, but also the build up of subsequent layers of tinted transparent varnishes. "Dragon's blood" mixed in to the varnish is recommended by Stalker and Parker.[23] Dragon's blood is a bright red resin and is collected from dried fruit of the genus *Daemonorops*, and after grinding can be dissolved into spirit varnishes.

In the preparation of common, red Japan, Salmon[27] recommends the use of isinglass size, or preferably seedlac only, since this withstands polishing, a statement which conflicts with Boyle's opinion of its inability to do so.[29] The seedlac is coloured with vermillion, applied in four layers, washed over with eight layers of ordinary shellac, and then ten layers of best seedlac varnish, followed by thorough drying and polishing with Tripoli. A deeper red can be produced by adding Dragon's blood to the final seedlac varnish to heighten the colour. For a paler red, vermillion is mixed with white lead, until a slightly paler colour is obtained than ultimately required, since it will be heightened by subsequent varnish layers. These pigments are again added to a seedlac varnish.

White Japan was generally used to imitate the effect of ivory, which is naturally an off-white colour. The tendency for varnishes to yellow meant that it was difficult to achieve a pure white colour, although some formulations were more successful than others. Stalker and Parker's complex formulation consists of eight resins.[23] To achieve the whitest colour possible, a white ground layer is also required.

Salmon[27] does not recommend the use of off-white resins in the preparation of White Japanning materials, preferring instead the use of isinglass which is a fish glue extracted from parts of fish bladder in boiling water, yielding an insoluble gelatine component. Isinglass size was frequently used as a varnish in a similar way to gum Arabic or egg constituents[30] - if sugar is added it has fewer tendencies to crack. This coating is susceptible to damp conditions however, and also tends to yellow over time. One of the main advantages of such a material is that it can be sponged off the surface it has been applied to using hot water. In Salmon's recipe he states that three isinglass size layers are polished with Dutch rushes, followed by two layers of boiled and thickened starch solution.

Boyle and Stalker and Parker do use resins in their recipes for white japan, although they instruct the use of the whitest and clearest materials. According to Boyle[29] white varnish is prepared by using two drachms of white resin, melted, 1 oz of white amber added (finely powdered) heated gently until the mixture dissolves. Small amounts of oil of turpentine are added as required.
The white resin component is not specified here, but Stalker and Parker give the following recipe for 'the best white varnish':

1 lb whitest gum sandarac
1 oz whitest gum mastic
3 oz clearest Venice turpentine
1 ½ oz gum copal
½ oz gum elemi
½ oz gum benzoin/Benjamin
1 ½ oz clearest gum animae
½ oz white rosin

Only the white component of Benjamin was used - a clear colourless varnish which was soluble in alcohol.[31] Gum anima is generally marbled with white, opaque and yellow transparent veins, the white will have been used here, and appears the same as copal but is more brittle and softer, melts easily. By itself it has limited use in varnishes but is sometime added to other resins.

For Blue Japan, Stalker and Parker detail the use of a white lead and smalt mixture, the latter component being obtained by finely grinding up blue cobalt glass, the quantity added affecting the intensity of the colour. The use of Prussian blue in Japanning was first documented in 1771 according to Brunskog,[32] although it could well have been used earlier on in the century when it was first invented. Repeated over-varnishing on a blue Japanned background with varnish that has a tendency to yellow, means that japanning that was originally intended to be blue may develop a green tone to it over time.
According to Polygraphice,[27] Lapis Lazuli for blue japan uses several layers of isinglass size or thick seedlac mixed with white lead, and after drying and smoothing, five or six layers of seedlac mixed with smalt are applied. A layer of best white varnish is added, followed by a final layer of smalt, a cobalt-derived pigment, mixed with white varnish (or pure ultramarine). Green Japan was generally produced by a mixture of blue and yellow pigments, such as Prussian blue and King’s yellow.[30]

A good example of a piece of japanned *chinoiserie* furniture is The Badminton Bed (Figure 1.13; V&A Museum reference number W.143:1 to 26-1921), which was constructed in 1754 from beech wood and was japanned in red, yellow and blue, with gilding, displaying carved wood dragons and open lattice work.

Figure 1.13: The Badminton Bed. Image courtesy of the Victoria and Albert Museum.

Japanware: A thriving industry

Japanning was not confined to the coating of wooden furniture; metal, papier-mache, leather and tortoiseshell were also common substrates. According to van der Reyden and Williams[33] a thriving industry in japanned papier-mache existed in England from the mid-18th to mid-19th centuries. From the 17th century Pontypool in South Wales was home to tinplate and iron works, and it was here that Japanning techniques were used in order to finish these metals. The production of thin iron sheets had been problematic before the end of the 17th century; however a method for producing thin and even sheets was developed by John Hanbury in Pontypool, who used a heavy rolling mill to produce these sheets. The product was used in the manufacture of kitchenware, to which a protective coating of japanning was added.

In his publication on Pontypool Japan, John[34] gave details on a long-standing recipe for black japanning, suitable for use on metals and papier mache, which required:

448 pounds of raw linseed oil
22 pounds of lump umber
20 pounds of flake litharge
100 pounds of asphaltum
5 pounds of cobalt resinate
406 pounds of white spirit or turpentine

The oil is heated with the umber and the bituminous substance asphaltum, followed by the gradual addition of the cobalt resinate and flake litharge. This is diluted with turpentine when the mixture is cooled. A black glossy effect is obtained after the addition of three coatings. By this time the preference for shellac-based formulations seems to have been abandoned, although this could be due to industrial costs.

This trade began to go into decline from around the middle of the 19th century, the development of new materials possibly contributing to this. However, since the 'Oriental' style glossy objects were no longer rare, and no longer found in wealthy homes only, a result of the availability of imitation pieces, and the sight of such items was becoming common. Their value and desirability began to change. Some japanning did continue in the Midlands well into the 20th century, but for functional products; a thin layer of japanning served as a protection layer rather than a decorative one.

More muted, subtle surfaces were increasingly required on furniture surfaces as the industry moved towards the contemporary furniture that has more emphasis on the functional rather than surface effects and ornamentation, with aesthetic being provided by materials and structure. The full gloss look remained in vogue in France however, for much longer.

1.8 Summary

The scarcity of East Asian lacquers in the West resulted from high costs, difficulties involved in acquiring such pieces from abroad so that only the very wealthy were able to obtain them, and the inability to create these objects using *urushi* in the West. This led to the destruction of many genuine lacquered pieces, being dismantled so that partial panels could be incorporated into new furniture. Over time, lacquer dulls as it is exposed to light, and attempts to restore the original effect were sometimes carried out in Western collections using inappropriate materials. Varnishes designed to give an immediate gloss effect added to the surface of the damaged pieces are potentially damaging to lacquer surfaces as they age and deteriorate.

The introduction of japanning meant that the original segments could, to a certain extent, be blended onto new pieces, although coloured japanning pieces were conspicuously different to the traditional Japanese lacquered aesthetic, and resembled the Chinese lacquer to a greater extent. Finding a varnish formulation which could match the effect of the *urushi* lacquer was a challenge to artists during the late 17th and the early 18th centuries. Some of the many recipes formulated to achieve the effect, including the famous Vernis Martin, are discussed in the next chapter. Reviewing these recipes from key literature provides us with some insight into the types of varnish materials that were used with a high gloss as the objective, and therefore may have been used during restoration attempts on lacquer pieces in Europe.

In conserving these collectable items, it is necessary to understand the materials present on their surfaces. Fresh, natural resin varnishes have very different properties to East Asian lacquers. Resins are soluble in a particular range of solvents; however as they age and oxidize more-polar solvents are required to remove them from surfaces. Oil-based varnishes such as copal, and also long-chain polymeric synthetic coatings, crosslink over time and become very insoluble, and can only be removed if they can be swelled significantly. Increasingly insoluble materials are difficult and unsafe to remove.

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Chapter 2

A history of material selection in achieving imitation East Asian lacquer finishes

A common problem encountered in Western lacquer collections is that attempted restoration results in valuable pieces displaying a coating, or partial coating, of non-lacquer material used in the absence of original *urushi*. Materials that were in common use amongst artists and craftsmen, to create glossy coatings on furniture and decorative items, are considered in this section, with particular focus on the time around which the Mazarin Chest was produced, up until its acquisition by the Victoria and Albert Museum in 1882. Notable texts of the time are consulted; the authors being key figures in science or the arts during the 17th-late 19th century.

Traditional methods and materials for protecting and decorating furniture have been appreciated for a long time and remain in use today. Over time, new materials have emerged and their optimum use developed by experiment and observation. The advancement of scientific discoveries in the area of finishing materials features in technical artistry literature from the beginning of the 19th century. The advancement of knowledge regarding such materials and their manipulation is illustrated by the huge amount of associated literature, such as treatises and artist's manuals, popular literature and dictionaries offering practical guidance on their use. Formulations presented by artists and varnish-makers were developed by observation and repeated use; these personal recipes were increasingly cited and shared by the inventor by the 19th century.

2.1 Protection and decoration of furniture

The purposes of adding a finish to furniture were to enhance the aesthetic of the piece, to protect against environmental or everyday use, to disguise the original wood or base material, or to achieve a particular optical effect. 'Oriental' lacquer from East Asia, as discussed in the previous chapter, was very much in fashion during the 17-18th century, but limited in its availability. These luxury goods were valued for their exquisitely ornamented and glossy decoration, which relied on the skilful preparation of the surface, not just the form of the piece. The limited supply of these goods led skilled craftsmen to create their own imitations, a process which became popularly known as 'japanning' in which spirit varnishes were built up in many thin layers to produce a gloss intended to resemble that seen on *urushi* lacquered pieces.

As discussed in the previous chapter, japanning briefly thrived in industry during the 19th century; skilled, experienced practitioners of the craft wrote numerous texts describing the processes involved, in treatises and reference guides. Such writings were a popular venture with experts of various professions, such as sculptors and architects;[1] with printing press availability, literature on such interests could be produced widely. A particularly popular area of technical literature throughout the 18th century was for painters' coating and protecting materials[i-iii] and methods of adding protective coatings. With the expertise and extensive work done by skilled artists and scientists alike, knowledge regarding the best ways of treating and combining raw materials was advancing; specific details of varnish preparation were publicly shared.

This study will draw upon several key authority texts from the 17th to 19th centuries which detail the materials, preparation and application methods used during furniture finishing, both in a decorative and protective role, particularly those materials or techniques used to imitate East Asian lacquer's gloss. The texts are representative of the type of literature made available at the time by authors who wished to share their expertise in the advancement of such arts amongst professionals and amateurs alike.

i) Bardwell, T., 'The Practice of Painting and Perspective Made Easy' (1756), ii) The anonymously published 'The Artist's Assistant Or School of Science' (1801), iii) Enfield, W., 'Young Artist's Assistant', (1822) Recipes are taken from highly respected professionals who kept detailed accounts of their work, thoughts and theories, such as the ‘Great Mr Boyle’s’ collection of his previously unpublished manuscripts, written for the use of gentlemen and ladies’ hobbies including drawing, japanning, varnishing and painting on glass. The organisation of the literature was novel. The purpose of “*The method of learning to draw in perspective made easy and fully explained*”, is, according to the foreword to Boyle’s manuscript, to present information in such a way that enables the student to avoid having to search through large volumes of literature, thereby taking the form of a reference manual.[2] The purpose of Dossie’s “Handmaid to the Arts”, 1758, is, according to the author, to convey extensive information to artists with accuracy, and is aimed at those persons who desire to imitate arts with complete instructions regarding the use of the various materials.[3] These instructive publications were largely based on the authors’ extensive experience, which was highly valued. Watin states that the details he presents in ‘L’art du peintre, doreur, vernissuer’ convey his opinion only, however, being acquired from thirty years of experience, a great deal of useful information is to be acquired from his records.[4]

Varnish recipes from English and French manuscripts, treatises, art manuals, trade records, sales journals, and workshop records, illustrate the common resins and solvents used over time. Application and drying procedures and manipulation of varnish formulations were as important as the materials used in achieving optimum properties. Such literature successfully communicated production methods for the much sought after East Asian aesthetic. All the literature includes extensive detail regarding the execution of this craft, although the format of the literature varies, some being set out in diaries or collections of papers and not as an organised reference manual.

The disclosure of techniques and recipes for achieving specific effects was not general practise amongst artists; trade secrets, such as the Italian Cremona varnish used for musical instruments, from 1550-1750, as ‘nature’s own varnish for the violin’,[5] were not documented and, therefore, could only be poorly imitated. This varnish ceased being used after the mid-18th century, and its method of production and application is now unknown.

Despite rumoured possibilities of the recipe having been handed down to descendents, such a document has never come to light and is considered a lost secret.

2.2 Surface coating formulations: a need for secrecy?

Centuries before the implementation of protections such as copyright, patents and peer-reviewed journals, the potential wealth and merit to be had from new findings were closely guarded; from artists closely shielding their methods of emulating the notoriously difficult flesh shade in watercolours, to alchemists who carefully safeguarded their work on the transmutation of metals. There were a growing number of individuals, however, who regarded this secrecy as a hindrance to progress. Practical instruction manuals and 'how-to' books by artisans were fundamental in the promotion of modern science according to William Eamon's "Science and the secrets of nature".[6] He states that during the 17th century, opinion amongst the natural philosophers changed from secrecy to open disclosure; keeping scientific knowledge from the public was no longer desirable, commenting that "esotericism in alchemy and the crafts as [are] obstacles to the growth of knowledge".

The debate over whether the public should share 'scientific' knowledge continued over time; in 1659 John Evelyn proposed an exclusive and secretive society for discussion and practical work, keeping strict control on when and where the public may be admitted. Other scientists such as Robert Boyle believed that the sharing of knowledge was in the public's best interest, and this view was shared with many scientists and natural philosophers, who founded the Royal Society in London, or 'invisible college of natural philosophers' in 1660.[7] One of the first books the society produced was John Evelyn's *Sylva*, cataloguing many varnish recipes.

The abundance of literature available from the late 17th century on the subject of coating and decorative finishes, such as varnishing and japanning of furniture pieces, is, therefore, fortunate.

Protection of intellectual property

In the prefaces and introductions to some of the literature discussed here, the authors state their intentions to accurately communicate the instructions for reproducing certain finishes by sharing their own recipes or those which they have tried out and deemed suitable and effective for a particular use. This sharing of knowledge indicates that there was no general concern over any loss in business involved with such recipes (contrasting with Cremona varnish). This particular era coincided with the introduction of copyright and patent laws in the UK, which possibly had some effect. According to the UK Intellectual Property Office[8] the Statute of Anne was passed in 1709, and passed into law the following year, and stated that copyright in publications was protected by Parliament. Patents were not so straightforward although they are thought to have originated from the 15th century when specific grants of privilege were assigned to the makers of stained glass windows.

The Martin Brothers, in France, obtained a Royal patent for their secret Vernis Martin recipe, which they were widely using in their factories throughout France, as they required protection for their business. There are no such UK records (at least none yet found in this study) for protection of japanning recipes, and the first US patent registered relating to japanning is not for its recipe but for the use of japanning in coating springs for the improvement of their mechanical properties, registered in 1884.[9]

Artists, or those authors who considered themselves chemists, were less concerned with protecting business interests, and by this time their publications were also protected, meaning that such authors were pleased to impart their detailed knowledge. Another reason for the production of such literature is that it was thought to protect the good name of the profession. By the mid-19th century, varnish recipes and their optimum production methods were widely publicised, however, in industry the published details were still limited. The Sales journals of Holland and Sons cabinet makers[10] (1850-1851) itemise orders made to the company ranging from creation of large and elaborate pieces of furniture to minor repairs, and make frequent mention to the supply of French polish, mahogany polish and reviver polish. Of course it is unlikely that the composition of their special varnishes would be disclosed to those buying it, even the sales journals (which meticulously list every tack, nail or hook required for the manufacture or repair of each sale) do not actually list of ingredients required for polishing and re-finishing solutions. A typical entry for a refinish is as follows:

3 pints polish, 2 gills spirits, 2 gill varnish, 1 gill oil, glass paper

There is no record of the exact material used; presumably it would be to the detriment of the company to reveal too many secrets regarding the materials present in their polish products, as their records indicate that a significant amount of business was made in supplying varnishes for particular uses. This type of document has therefore not been able to yield any useful information regarding the resins or oils used.

2.3 Japanning: secrets revealed

The historical use of natural materials in decorative roles can be dated back to prehistoric times, and are even seen on stone-age art.[11] Naturally occurring polymers have long been employed in surface coatings, including conifer (pine) resins, vegetable oils, waxes, gums, alcohol-soluble resins, such as shellac, which consists of a complex mixture of crosslinked polyesters, and ambers and copals, which consist of terpenoids that have undergone extensive polymerization and structural rearrangement during fossilization.[12] Japanning relied upon the use of such materials to produce glossy, durable coatings. Pigmented resin varnishes were applied in many thin layers, with heat-drying and polishing carried out carefully at each stage, to produce a hard surface with full gloss.

Diarist John Evelyn revealed the ‘rare’ secrets of Japanning, he claims, for the first time in his 1670 Sylva Royal Society publication.[13] In it he gives the following recipe for japanning varnish using the spirit-soluble resins gum-lacq and sandarac:

“Take a pint of spirit wine exquisitely dephlegmed, four ounces of gum-lacq, which thus cleanse: break it first from the sticks and rubbish, and roughly contusing it in a mortar, put it to steep in Fountain-water, tied up in a bag of coarse linen, together with a very small morsel of the best of the castile-soap, for twelve hours; then rub out all the tincture from it, to which add a little alum, and reserve it apart: the gum-lacq remaining in the bag, with one ounce of sandarac (some add as much mastic and white-amber) dissolve in

a large matras (well stopped) with the spirit of wine, by a two days digestion, frequently agitating it, that it adhere not to the glass: then strain and press it forth into a lesser vessel: some after the first infusion upon the ashes, after twenty four hours, augment the heat, and transfer the matras to the sandbath, till the liquor begins to simper: and when the upper part of the matras grows a little hot, and that the gum-lacq is melted … strain it through a linen-cloth, and press it betwixt two sticks into the glass, to be kept for use, which it will eternally be, if well stopped".

Several layers of the pigmented varnishes are applied to the substrate, followed by several layers of clear varnish to give a glassy finish. Materials used in achieving the 'oriental' lacquer effect were abundant, and interest in how they could be used for this purpose was growing.

2.4 An influential Treatise

In 1688, Stalker and Parkers' hugely influential *A treatise on japanning and varnishing* was published; it focused on the materials and well-developed techniques required in achieving the so-called oriental style of lacquer finish. Stalker and Parker addressed the great demand for the East Asian style by offering individuals the means to reproduce, in stages, the desired effect using spirit-based varnish rather than the *urushi* lacquer, the latter being difficult to obtain and handle.

The publication was an important technical manual giving comprehensive instructions on the production of imitation 'oriental' lacquer. Not only did the publication present detailed recipes, it also included pattern illustrations, which were believed to be of 'oriental design' as illustrated in Figure 2.1, enabling English, French and other Europeans to apply a lacquer-type finish to their pieces whilst copying specific designs that are suggested in the text. This Treatise was one of the earliest pieces of English literature covering the subject in such detail.[14]

Figure 2.1: Design idea for decorating a powder box in ‘oriental’ motif presented in Stalker and Parker’s *A Treatise of Japaning and Varnishing* (1688).[14]

Landscapes, such as that illustrated in Figure 2.1, were popular choices for adorning the surface decoration, but figures and scenes from tales and legends also featured. The inclusion of these designs by Stalker and Parker enhanced the usability of their book to the ultimate achievements of the user: to imitate East Asian style finishes. Similar designs can still be observed on surviving pieces, for example, a clock case held at the Royal Ontario Museum has been reported by Webb[15] as having chinoiserie decoration on the surface similar to that shown by Stalker and Parkers’ published patterns. Intended recipients of the information contained in the Treatise were both amateurs and professionals. The Treatise was influential at a time when several ‘ladies’ pursuits’ were coming into fashion; over the next century such pursuits as drawing and painting were deemed reasonable for well-bred women. Evidence of this trend can be found in the literature, for instance, Bickham’s ‘The Economy of Arts’ from 1747 is also entitled ‘A companion for the ingenious of either sex’.[16]

Stalker and Parker claim to have written the treatise based on their own experience and knowledge, having either developed or experimented with the recipes repeatedly to be ensured of their success. Their preface highlights the durability of japanning as a coating material, the inalterability of ‘Japan’ and its contribution to furniture’s ‘splendor and preservation’ being of key importance. Its properties include impregnability against ‘time and weather’, and it resists fire, mould, damp, woodworm, and corrosion. Clearly such a formulation offered craftsmen a beneficial means of protecting their products. The authors discuss the superiority of Japan as a country which has products which ‘exceed in beauty and magnificence all the pride of the Vatican at this time’.

In their ‘epistle to the reader and practitioners’ the authors explain their intention to produce Japan which is so close to the original lacquer that ‘no one but an Artist should be able to distinguish ‘em’, assuming, of course, that it is carried out by a competent person. They warn consumers about the influence of different levels of skill on probable outcomes: there are those who have ‘more confidence than skill and ingenuity’ who impose ‘trash’ on their consumers. The authors evidently have a low opinion of unqualified and unskilled individuals who promote themselves as other than amateur, and who, amongst their offences, claim to be able to tutor ladies in the art, and claim to be Japanners and painters - much to the detriment of the good name of these professions.

The status and fashion of pieces made in the ‘oriental’ design is also apparent from their observations: their recipes enable homes to be furnished with entire sets of Japan rather than the occasional piece. The reliability of Stalker and Parker’s knowledge regarding use of materials appear to be in agreement with other authors of the time, however, writing in The Burlington Magazine for Connoisseurs in 1911, British author Herbert Cercinsky, who was considered to be a specialist in Sheraton and Georgian furniture, voiced his conflicting opinion regarding the validity of Stalker and Parker’s work.[17] Cercinsky claimed that their work was ‘absolutely worthless’, written by individuals who had ‘not even a prentice knowledge of the art they professed to teach’. It was for this reason, that is their lack of knowledge regarding individual components, that the authors recommended the use of mixtures including a solution in spirit of wine ‘of practically every kind of resin and gum known to commerce'; rather than discussing limited, preferred materials as seen in other texts. He is also disparaging of other texts of the time, concluding that 'lackering' (japanning) was mainly a subject to be taught in young ladies schools rather than being used at a serious technical level. Those likely to be skilled and knowledgeable on the subject, he claims, were unlikely to want treatises such as that which Stalker and Parker published. However, the treatise's recipes generally correspond with other recipes of the time, which endorse the methods and materials chosen: details of the main resins and gums are discussed here.

The natural resin varnish materials are of interest in this work, since the focus is to determine the suitability of using solvents to remove aged, degraded resin-based materials from degraded lacquer surfaces, and it is, therefore, useful to review the resins that may be used in adding gloss to furniture surfaces.

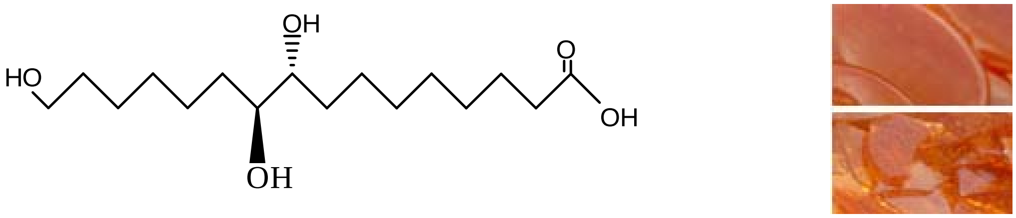
2.5 Resin varnishes for japanning

Shellac

Seedlac and shellac resin is of notable importance in the early japanning recipes. Lac is the only known commercial resin of animal origin, and has been used for centuries as a protective and decorative surface coating for wood or metals. Secreted from the *Laccifer lacca* insect, the stick-lac is collected on twigs, scraped off and then repeatedly cleaned, crushed and filtered. After drying it is winnowed and sieved to produce the commercial seedlac which contains 3-5% impurity.

Seedlac can be treated to produce bleached lac, and other lighter shades, either by traditional hand methods or modern machine processes, and gives a very strong varnish. Shellac is melted and formed into laminae – a principal component of sealing wax, coloured with vermillion to form red wax, or with lamp black for black wax.

Shellac is composed of 30-40% aleuritic acid (9,10,16-trihydroxyhexadecanoic acid), see Figure 2.2a, which forms a complex polyester on esterification,[18] containing alcohol and aldehyde groups, therefore, it is soluble in solvents which are hydrogen-bond donating.



a) b)

Figure 2.2: a) Aleuritic acid (9,10,16-trihydroxyhexadecanoic acid) and b) amber-toned shellac pieces (buttons and flakes).

Seedlac has a warm, neutral brown colour, and buttonlac has a golden, light brownish amber tone (Figure 2.2b). Lemon and orange lacs have a pale yellow-orange colour, whereas garnet lac has a deep rich brown colour. Blonde and super blonde lacs are very pale and clear and require chemical bleaching.

As one of the most commonly used 18th century spirit varnishes, it requires ethanol ("spirits of wine") as a solvent, which was obtained from impure wine or brandy of up to 50% water, which required repeated distillation.

In agreement with Evelyn's best japanning recipe shown above, Stalker and Parker present a spirit-soluble, shellac-based recipe for varnishing black japan:
"pour fome of the thickeft seed-lac-varnifh into a Gallipot, adding to it as much lampblack as will at the firfh wafh blacken and difcolour the work…with this varnish and black mixt together varnish over your thing three times, permitting it to dry thoroughly between every turn. After this take more of the lac-varnish, and mix it with lampblack to the same degree of thickness with the former". The coloured seed-lac is applied in several layers.

Seedlac also makes an appearance in William Salmon's 'seed-lake' and 'shell-lake' published recipes for Indian varnishes in Polygraphice (1672), although he does not specify these for use in Japanning, subsequent literature has cited his recipes as being appropriate for this use.[19]

Robert Boyle also experimented with making seed-lac based varnish, as featured in his recipe:[20]
A quart of strong spirit into a glass vessel and add 6 lbs seed lac. Let this stand for 2 days, with frequent shaking. Take a flannel bag with a 'Hippocrate's sleeve' (the bag is a square piece of flannel, having the opposite corners joined, so as to make it triangular) and let it pass through, allowing the liquor to drop through into a receiver, until all the liquor has been strained and all the dregs are dry. Allow the remainder to stand in glass bottles for a few days, after which time the thicker parts will settle at the bottom – pour off the clear varnish into a separate container ready for use.

Although Boyle appreciated the frequent recommendation of seedlac, he was of a different opinion regarding its usefulness, stating that it is 'not of any great service' owing to its inability to withstand vigorous polishing. Shellac remained a very important varnish up until the introduction of nitrocellulose materials which largely replaced it in around 1925. It was used frequently on furniture rather than paintings, due to its tendency to darken with age.[21] The main drawback in using this material is that due to its dark colour it is difficult to obtain white and blue japanning varnishes. The latter require another resin type, as discussed in the previous chapter.

So far this discussion has focused on the use of varnishes to create an *urushi* lacquer type finish, however there were other popular and fashionable optical effects desired on furniture pieces during the 18th century. The application of a highly glossy yet transparent varnish, which highlighted the texture and natural pattern of the wood used to create the furniture, known as French Polishing, was also very popular.

French polishing is a technique that uses liquefied shellac (and sometimes small amounts of sandarac), originated in France in the 17th-18th centuries, and has been used internationally since the early 1800s for fine furniture. The most popular varnish used to achieve the high gloss on furniture of the Baroque and Rococo periods was shellac.[22] Using a polishing pad instead of a brush, many layer applications and polishing could produce a mirror-like shine. Shellac has rich red or yellow tones; however by exposing thin layers of shellac to the sun, lighter colours could be obtained, and it was these shades that were used for the French polishing technique.

Non-shellac resins

During the 18th century, prominent japanning experts published recipes for closely reproducing the glossy *urushi* lacquer effect which did not feature shellac resin. The famous Vernis Martin uses amber as a main resin with turpentine solvent. Pontypool japan recipes make use of linseed drying oils and turpentine. As a substitute for oil, which requires lengthy drying times, turpentine is recommended as a suitable solvent when preparing mastic or sandarac-based varnishes, also offering advantages over the use of spirits. In turpentine, the varnish is much easier to handle, spreading more evenly and drying at a rate which prevents blooming or ‘chilling’ sometimes caused by rapidly evaporating spirits. Turpentines and rosin are known to degrade fairly rapidly however.

Resins such as mastic, sandarac, and copal were used to enhance the durability of other varnishes. Dominance of a particular resin and the measures of each constituent alter the properties of the resulting varnish, and furniture makers and conservators must find the best techniques and formulations to produce a suitable effect. In “L’art du menuisier” (The art of the woodworker), Andre Jacob Roubo presented a recipe[23] for clear varnish based on sandarac which had little effect on the colour of the piece:-

A pint or 2 pounds of spirit of wine, 5 ounces of the palest sandarac, 2 ounces mastic tears, 1 ounce gum elemi, 1 oz aspic (oil of lavender)

He instructed that the ingredients should be dissolved in a ‘bain-marie’, which allowed a controlled heating of the varnish, ensuring it did not boil. Once the varnish has cooled and been filtered, it can be used for the required eight coats. In Mauclerc's treatise on varnish making, "Traite de couleurs et vernis" he advocates the use of direct heat in ensuring a complete combination of the varnish components during their preparation,[24] opposing the idea of using a bain-marie as a means of producing high quality varnish. This is disputed not only by Roubo's use of the bain-marie but also by Watin[25] who disagrees with this from a safety point of view: the flammable nature of the varnish materials means that the use of direct heat is not a wise idea.

Where colourless and transparent varnishes were required, the most useful varnish resins were the sandarac, mastic and dammar resins. Sandarac (sometimes called gum juniper) is a colourless and transparent material, which was used in the 18th century for producing transparent glossy finishes. On its own it can become brittle and required the addition of other softer resins, such as mastic or gum elemi, to improve its strength. Camphor, which was added to varnishes as a softening additive, is a vegetable substance that dissolves in alcohol and mixes well with oils. Its volatility and aromatic properties led chemists to class it as an essential oil as opposed to a resin.[26] Sandarac crystallises and re-crystallizing depending on the humidity and temperature of the atmosphere, limiting its use as a varnish on its own. The addition of copal improved the stability of this, and other, varnishes. Less expensive copal fragments were sometimes passed off as good quality sandarac by unscrupulous suppliers.[26]

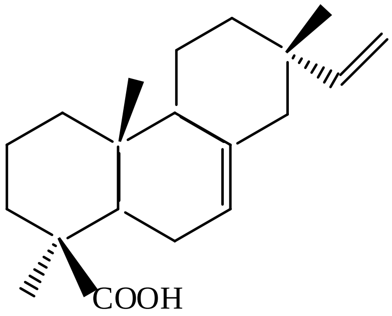


Figure 2.3: Sandaracopimaric acid.

Sandarac resin is made up largely of sandaracopimaric acid (Figure 2.3), and was used less frequently where clear and colourless coatings were not required. Its brittleness means it has a tendency to crack with age. In the 18th century, sandarac was in high demand, as it was widely used for light-coloured finishes, despite needing the addition of plasticizing materials for it to be of use for any length of time. Sandarac forms the bulk material in Watin's recipe for a clear varnish which also contains smaller proportions of mastic, gum lac, Venice turpentine, elemi and spirit of wine.[25]

Mastic is a resin soluble in alcohol but not in water. Formed as transparent tears with a lemon colour and sweet aromatic smell, it is used to make a very tough varnish. Mastic (Figure 2.4) is a soft triterpenoid resin, obtained from the bark of the *Pistacia lentiscus* tree. It is a perfectly clear varnish and is soluble in polar solvents including alcohol and turpentine, and is oxidized upon ageing.

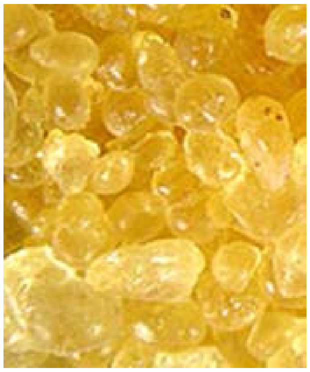


Figure 2.4: Mastic 'tears'.

Mastic is generally used as an additive in varnishes rather than as the main resin. It has a yellow tint which deepens on ageing. It is generally used as a paintings varnish, and is easily brushed to a smooth and even film.

Another triterpenoid resin, dammar, is exuded from the *Diptocarpaceae* tree. It consists of dipterocarpol which, on ageing, forms dammarenolic acid (Figure 2.5). It forms a hard and colourless varnish film, although it is a brittle substance and the film is easily scratched, and yellows by thermal oxidation over time. The most appropriate solvent for dammar is turpentine.[21] At high humidity this coating is susceptible to blooming (the clouded appearance on a varnished surface), the extent of which is dependent on how it was applied. A persistent bloom will be observed where condensation has been present on the surface when it is drying.

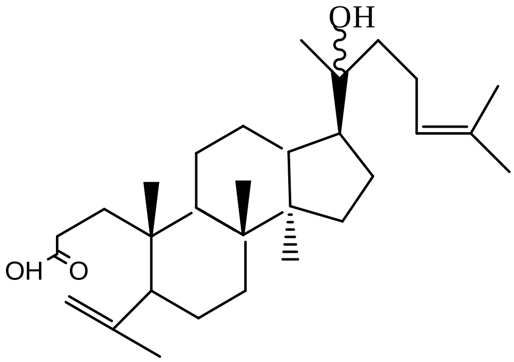


Figure 2.5: Dammarenolic acid.

Dammar was not widely known in England during the mid 19th century, with only a couple of artists experimenting with it. Mastic was much easier to work with, and to remove, although it had a tendency to darken with age and crack considerably. The latter part of the 19th century saw a general preference for the use of mastic-based varnishes, and this trend continued early into the 20th century, despite its deficiencies. The mastic varnish had generally been modified with drying oils, other resins and balsamic additives to improve their properties. Whilst the use of cheaper dammar in turpentine was becoming widespread in the rest of Europe, its use in England was rare, despite its superior qualities in terms of retention of its original colour, lack of blooming and a high refractive index. It is known to have been available from 1859, combined with poppy oil, but not widely used.

2.6 Oil varnishes for japanning

Hard fossil resins, such as amber, copal and colophony, are relatively stable polymeric materials that have lost volatile components following a prolonged period of burial under pressure. These resins require some degree of heating in order for them to dissolve into oil. These varnishes typically took a long time to dry but added durability to the finish. Fossil resins appear in recipes for japanning finishes, for example, a ‘receipt’ for a Strong Japan by Boyle[20] (p44) is summarised here:

½ oz colophony is melted, and 1 ½ oz amber is sprinkled in. It is then stirred and spirit of turpentine added. When melted, 1 ½ oz fine sarcacole is introduced, the mixture is stirred and more spirit of turpentine is added. Then this is passed through a coarse hair-bag, *placed between two hot boards, and pressed gently. The product is put into a glazed, warm vessel, where ivory black is added.*

This recipe is for the final layers of a japanned papier-mache, or similar, item. Heat is required to set this varnish, resulting in a highly stable coating.

The colophony material used by Boyle is from the distillation of turpentine with water, which leaves a solid, non-volatile residue, which when removed and melted forms colophonium. Amber is the hardest natural fossil resin available; it is very insoluble, however, and can be difficult to work with. It exhibits different properties: white and opaque, sometimes yellow and transparent, sometimes dark gold. For this reason amber is the basis of a recipe Boyle presents for the preparation of a varnish to imitate the gold effect seen against the monochrome background in japanning, to produce the 'oriental' effect:

Colophony, melted, add 2 oz amber and some spirit of turpentine as the mixture thickens. Continue stirring and then add 1 oz powdered gum elemi and more spirit of turpentine. Care should be taken to keep the volume of spirit of turpentine used to a minimum since a thicker varnish will make a harder coating. This varnish is applied to gently warmed pieces, in front of a fire, and hardened 'by degrees'.

After the drying process is complete, the vessel will look like polished gold, according to Boyle (p46), who had a great interest in japanning recipes and had accurately predicted in his writings from the 1660s that the art and trade of lacquer imitation using varnish would appear very soon in London as he had witnessed it already in Paris.

By itself, amber produces a dry, brittle, and inflammable film although it yields a hard, fine polish, often combined with colophony as illustrated by another of Boyle's recipes. An example of a hard varnish containing amber is documented by Boyle,[20] and is used over metals to prevent tarnishing. Amber is particularly good as a vehicle for pigments, and consequently was popular with artists who frequently combined it with linseed oil, since the amber increased the oil's drying rate.

Amber forms the base of some European varnishes, most notably the Vernis Martin, publicised in 1776 in Paris and Dublin.[27] The four Martin brothers perfected a varnish to imitate East Asian lacquers in around 1730. Fired and hardened sheets of paper stuck to furniture surfaces were painted and varnished before being glazed with gum Arabic. Dossie[3] identifies the advantages of using water-soluble gum Arabic as a protective coating on paintings as being its ease in application and of removal, when compared to those prepared in turpentine oil or alcohol. However its tendency to crack makes it unusable unless it is modified with, as Dossie suggests, sugar which prevents cracking, although problems associated with this include the increases stickiness of the material which sullies the surface. He suggests that the use of egg white spread thinly can be used as a suitable substitute for gum Arabic, which cracks to a lesser degree, although it is not long lasting, being affected by moisture and a dry atmosphere. The addition of alcohol and sugar make the material easier to apply.

The Vernis Martin (vernis parisien or vernis de Paris) varnish recipe was published as a substitute for *urushi* lacquer sheen.[27] The recipe stated that the following materials were used:-

1 pound gamboge
4 ounces ornotto (annatto – from achiote treem red pigment)
4 ounces Venice turpentine
1 pint turpentine
Add some amber varnish (sometimes an ounce of seedlac is also added)

Gamboge, referred to in this recipe is a partly water-soluble and partly alcohol-soluble resin, used as a golden-yellow colouring agent, obtained from trees of the genus *Garcinia* of south-central Asia. Generally used in water colours, it is an irritant, especially to painters who clean brushes with their mouths.[26] The Vernis Martin was so successful in reproducing the lacquer effect that the French process became imitated itself. In *Veneers of Authority*[28] it is stated that Maria Theresa wrote of her delight in a ‘lacquered’ box from Vienna which “could fool anyone into believing it had been made in France”.

The use of oil varnishes has already been mentioned with amber resin; however it is important to mention another important fossil resin, copal, whose use is favoured particularly by Watin.[25] Hard fossilized resins such as copal (Figure 2.6) requires some heating before they can be dissolved. The term copal covers a wide range of resins, which melt at high temperatures, and linseed oil is added along with driers. Over time these materials darken and suffer cracking.


Figure 2.6: Copal resin.

A survey of varnish types found on paintings in the National Gallery during the 19th-20th centuries, by White and Kirby,[29] gives useful information regarding the general attitudes towards the use of some of the varnishes mentioned in this section. Although the information is based on oil paintings, not furniture, the survey still enables the availability of some materials at this time to be understood further. For example, copal-oil varnish was unfavourable with some artists during the 19th century – there were difficulties associated with removal and a tendency to discolour quickly: to yellow and then to brown. It was difficult to apply, and alkali substances were needed to remove it. However there were some who found its persistence an advantage in its role as a protective layer. In Carlyle's study of resins and gums in oil paint medium she observes the lack of recipes which include the fossil resins used as stand-alone varnishes, citing only three, although they are popular as components in 19th century painting materials.[30]

2.7 Material awareness

Advancements in and awareness of materials used by artists and furniture makers of the late 18th-19th century arguably affected the approach to decorative finishes; increased knowledge of the chemistry of the materials meant that they could be used to optimum effect. Tingry, a professor of applied chemistry, in his 1804 edition of 'The Painter and

Varnisher's Guide',[26] makes frequent reference to the chemists of the time, while his writing takes a more scientific approach when considering the materials used. For example, his advice includes the addition of pounded glass to the varnish during its preparation to improve the finished product, having noticed that the glass specks acted as a nucleus or reaction base. The scientific manner of his guide is evidently another turning point in the development of varnish formulations, and coincides with another significant time – that of the industrial revolution when technological innovations saw the replacement of manual labour with machinery.

According to Tingry (chapter II), modern chemistry was at that time considered an exact science, particularly involving those materials and substances used in painting. Knowledge of this science is, according to Tingry, necessary for a painter to become skilled in such an art.[26] Significantly, he presents his information with reference to chemical states rather than their more traditional names (for example, he uses 'red oxide of lead' instead of 'red lead', 'carbonate of lead' instead of 'white lead'). By the end of the 19th century, literature explaining the preparation of artists and craftmen's material was being presented in a highly scientific context.

The impact of an enhanced understanding of materials on furniture-makers, artists and craftsmen is the production of higher quality substances, more efficient use of raw materials, and a better understanding of the quality of resins and gums being supplied. A good knowledge of the chemical behaviour of materials meant that they could be enhanced, and natural materials could be cleaned and purified to a greater extent using chemicals such as treatment acids. The use of sulphuric acid in the treatment of drying oils is such an example, although it is one which causes some disagreement between artists. The acid was once used to remove mucilage from linseed oil, and the remaining acid removed using steam.[31] However, sulphuric acid has a destructive effect on pigments and other components, and this raises doubts about the quality of the resulting oil exposed to such a treatment.

Enhanced understanding and manipulation of materials could also be used more deceitfully; Carlyle[32] highlights the widespread adulteration of ingredients including resins and oils used in varnish preparation during the 18th/19th century, for example she discusses how rosin was frequently added to varnishes and linseed oil. Williams, in 1787, also warned of this practice producing manipulated materials as being inferior and ‘not fit for use in painters’ medium’.[33] Sometimes cheaper resins were substituted, so unless the artists prepared their own materials and obtained them from a reliable source, they could not know exactly what varnish components they were using. Chemist Frederick Accum (1820) studied adulteration of food products with chemicals (sometime with toxic substances such as lead), Indian ink and pigments, and he concluded that “the increased division of labour” rather than deliberate substitution of cheaper, less effective materials were responsible for these adulterations.[32] This meant that individuals were unaware of the intended use of the tarnished products further up the process. Whether deliberate or just a result of too many layers of involvement, not having a good understanding of the materials being used was disadvantageous to craftsmen.

Traditional coating materials offer a good level of protection to furniture pieces, whilst enhancing beauty and ornamental value. These natural materials age over time, their components oxidise and chemical stability decreases as the surface becomes more polar. The durability of the coating is considerably dependant on the preparation of the varnish; carefully developed recipes have featured the inclusion of preservative materials which impede its degradation, tendency to crack, yellow or cloud. However, it is inevitable that furniture coatings will degrade, and so, towards the mid-19th century chemists began to seek new materials for a variety of purposes including coating materials which possessed enhanced durability and optical properties.

2.8 *Urushi* – an unknown material

Although European artists were familiar with resin and oil-based varnishes, they knew little about the East Asian *urushi* lacquer that they were imitating. Genuine *urushi* was difficult to obtain and handle. In the next chapter the chemistry of *urushi* lacquer is discussed in detail; clearly it is a very different material to those found in spirit or oil-based varnishes. The popularity of the decorative effect of *urushi* was accompanied by a rather closely guarded knowledge of its handling and application.

Some attempt is made to understand the unknown material in the literature. Dossie included an explanation of the difference between Japanning materials and *urushi* lacquer in his instructions on the preparation of grounding layers for Japanning in his 1758 ‘Handmaid to the Arts’,[3] which, according to Webb[34] was the first publication in which the difference had been explained. In his 1670 edition of Sylva, Evelyn refers to a Chinese tree lacquer, described in the publication *China Illustrata* which disclosed details of a tree-exuded gum called Cie, a material known in China for its ability to beautify wood, but kept secret from Europe, until a monk named Imart was able to obtain it.

In later editions of Sylva, Evelyn updates his varnish recipes to include the natural lacquers, such as those cited in the Philosophical Transactions journal. This particular journal gave details on oriental lacquer sent by the China Missionaries to the Great Duke of Tuscany and communicated by Dr Sherards.[35] The Grand Duke of Tuscany acquired a sample of lacquer sap, and its properties were described to the Royal Society under the name ‘Indian varnish’. This vague term was used in the 18th century for all East or South Asian pieces, including Japan.[28] Knowledge of these such far-off locations were improved to some extent as contact through trading increased. Europeans became more knowledgeable about East Asia, began to distinguish between the different countries, although according to Yonan[28] “old myths about a fantastic China ... persisted”.

In his communication, Dr Sherards noted the allergen effects and uniqueness of the oriental ‘Indian’ lacquer, including the temporary itching and swelling caused by direct contact with the substance.[35] As regards its physical properties, the author determined that the so-called ‘Indian varnish’ is in great part a gummy substance, light, does not dissolve in water or spirits, but is taken up in oil, has some resistance to fire but does burn completely. He concludes that there is no mercury present in the lacquer, since it is light and floats on spirits. Only the outer part exposed to air becomes hard and black, whilst the underneath lacquer remains ‘of the colour and consistence of honey’. These are the first attempts to understand a novel and unknown material in the West.

Over the last few decades, much has been written on the chemistry of *urushi* lacquer, and this literature is reviewed in the next chapter. The resin or oil-based materials discussed here are very different to the unique East Asian lacquer-based coatings, in terms of their physical and chemical properties. The chemistry of *urushi* helps to explain its durability and gloss, and the reasons that these surfaces become damaged in unsuitable conditions. The implications of its properties and behaviour, in terms of its conservation, will also be discussed.

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Chapter 3

The chemistry of East Asian lacquer: A review of the scientific literature and implications for conservation

Urushi has been used by skilled lacquer artists for thousands of years, predominantly in the East Asian countries of Japan, Korea and China, where there is an abundance of *urushi*-producing trees. Spectacular lacquered artefacts still exist due to the stability of the material, as already discussed in Chapter 1, and numerous conservation efforts endeavour to preserve these pieces. The following chapter will discuss the chemical properties of this complex material, with particular reference to its stability and durability, and the conditions that contribute to its deterioration. The importance of understanding these properties is discussed with regards to the conservation of *urushi*-based objects.

3.1 *Urushi* lacquer

Urushi lacquer is a complex natural material obtained from the *Rhus vernicifera* Stokes or *Rhus vernicifera* D.C. tree, of the sumac family and a relative of the poison ivy tree. There are several different types of *urushi*, the terminology for which varies depending on the region of its origin. For example, the transparent non-glossy *urushi kijiro* as it is known in Tokyo would be termed *akaro* in many other parts of Japan. Transparent black *urushi* is termed *roiro* in Tokyo, but *hon roiro, kuro roiro* or *kuro-ro* in other parts of Japan. This work will make frequent reference to *ki-urushi* (the raw matured form), *kijiro* (*urushi* refined by removal of water) and *roiro* (refined *urushi* reacted with iron (II) hydroxide or iron acetate to chemically alter the colour to black) *urushi* in particular.

The uses of urushi

East Asian lacquer of wide ranging origin, and therefore quality, has been used for centuries for its decorative and protective properties. Following the collection of the slightly acidic raw sap, it is matured and refined to produce a material which, when applied in several thin coatings, cures to give a hard, durable coating of great aesthetic beauty and gloss.

Urushi has been applied to wood, ceramics, metal, leather and tortoiseshell. It is also used in the preparation of priming layers, and subsequent foundation layers which are constructed using *urushi* mixed with clay and other materials, starting with coarse material and then using gradually finer grains with careful polishing and curing between each application. It is also an excellent adhesive. In its uncured state the material is an irritant, producing moderate to severe allergic reactions in a large proportion of individuals during filtration (Figure 3.1) and application processes.[1]

Figure 3.1: Filtration of *urushi* lacquer to remove dust particles.

Urushi has been used for centuries to decorate and protect everyday items as well as precious artefacts. Not surprisingly, a wealth of information is available on their conservation, including restoration of gloss and reattachment of flaking decorative parts.[2,3] It is also vital to understand the characteristics of this complex material when treating damaged surfaces.

Much of the literature on *urushi* focuses on its production, including traditional preparation methods, and art historical significance. In an attempt to go beyond this focus, this chapter will concentrate on journal papers produced since the 1950s by authors whose work has a primarily scientific orientation, drawing only on that available in the English language to illustrate Western understanding of this complex material. These papers, along with an experience of traditional treatments, will inform conservators in their selection of suitable conservation materials and environmental conditions for lacquer wares.

The extensive use of lacquer imitation materials and the combination of East Asian lacquer panels with new pieces of furniture can cause difficulties in identifying the coating material. Experienced curators and conservators can sometimes distinguish these techniques by visual inspection. Solubility tests in inconspicuous areas may help in determining whether the piece is a European or East Asian lacquer, since different coatings are soluble in different types of solvent.[5] Care is required with historic objects, since the solubility properties of aged lacquer are very different to those of newly cured lacquer. For more specific information on the coating type, chemical analysis is required.

3.2 The production of *urushi*

Before looking more closely at the composition of the material, it is necessary first to consider how and where *urushi* is produced. *Urushi* is the sap from the *Rhus vernicifera* tree, valued for its ability to coat surfaces with a beautiful, luxurious and durable finish, as well as its excellent adhesive properties. Of note, at this stage the major component of lacquer is urushiol. This molecule is a phenolic material that polymerizes under the influence of an enzyme to form very strong, crosslinked, network structures.[6] *Urushi* is categorised as a thermosetting polymer due to the irreversibility of the curing reaction.

Crosslinked systems have excellent mechanical and chemical stability, and are insoluble in solvents. As the degree of crosslinking increases, the network becomes more rigid, reducing solvent swelling and increasing the glass transition temperature. Spectacular *urushi* artefacts dating from 6000–5000 BC have survived partly because of this stability.[7]

Several types of *urushi* are available, differing according to geographical source, the harvest season, and the way in which they are collected and processed. The main areas of *urushi* production are Japan, Korea and China, where *Rhus vernicifera* is abundant. Related species occur in Vietnam and Taiwan (*Rhus succedanea*, in which the phenolic lipid is laccol), and in Burma and Thailand (*Melanorrhoea usitata*, in which thitsiol is the phenolic derivative). Figure 3.2 shows the structure of the most abundant catechol isomer which has been identified in urushiol mixtures by high-performance liquid chromatography.[1] Its chemical name is 3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl) catechol, and the unsaturated aliphatic side chains play a critical part in the oxidative curing reaction, discussed later.

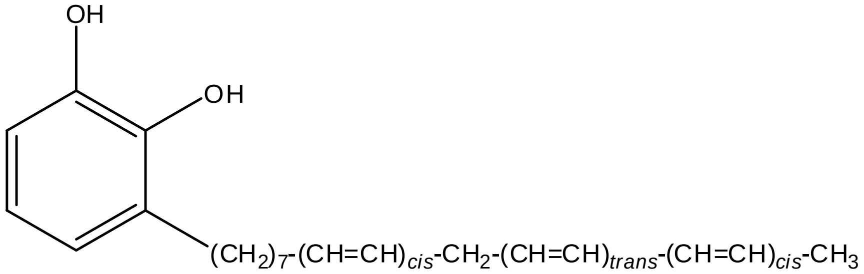

Figure 3.2: A catechol isomer found in abundance in *urushi* sap.

3.3 Chemical properties of *urushi*

Little was known about the chemical properties of this complex material until the end of the nineteenth century. The first documented separation of the sap components was reported in 1882 by Ishimatsu.[9] The composition of *urushi* has been studied since the mid-twentieth century[10] and an understanding of its structural properties has been advanced largely by Kumanotani[6] whose work is essential reading and a valuable reference tool for other researchers. Significant research was also carried out by Kenjo in the 1970s and 1980s, including studies on the production of *urushi* pieces,[11] as well as the chemical and physical properties of the lacquer, and the effect of changes in pH, humidity and other environmental factors on lacquered pieces. Her work is very useful to the study of *urushi*, however, is mostly published in Japanese, and will not be discussed further here.

Composition of sap

Freshly collected lacquer sap is an unstable water-oil emulsion. The oil phase consists of around 60% urushiol, the phenolic compound possessing unsaturated long carbon chains as shown in Figure 3.2, as well as glycoproteins (macromolecules composed of a carbohydrate bonded directly to a protein). Depending on when the sap is harvested, it can contain from 20% to 30% water – this phase contains the laccase enzyme and a small amount of densely coiled polysaccharides with branched structures, which increase the durability of the film once cured.[10] The complex branched structures of the high and low molecular weight lacquer acid-form polysaccharides present in *Rhus vernicifera* have been isolated and determined during studies involving their chemical modification.[12-16] Both the polysaccharide and glycoprotein constituents of the plant gums present in the sap are thought to play an important role in determining the structure of the lacquer matrix, particularly by controlling the specific directions in which the chemical bonds formed during the curing reaction are arranged.[6]

Collection of sap and blending processes

The sap used for lacquer is collected from trees that are around ten years old, by cutting into the phloem vessels every few days throughout the main season of June to October. Yields are low over the lifetime of the tree, thus *urushi* is a precious resource.

After collection, the sap is matured for at least 12 months, after which it is called *ki-urushi*. A degree of treatment of this matured lacquer significantly adds to the stability of the coating once it has hardened. The '*kurome*' treatment of lacquer described by Kumanotani[6] is a refining process, taking place in an open vessel at 30°C for two hours, during which time the sap composition is homogenised by the constant stirring action. The exposure to air at a precise temperature creates optimum conditions for enzyme activity. These conditions are also favourable for initiating oxidation of the urushiol component. Glycoproteins from the plant gums also begin to react with the urushiol at this stage, as indicated by Kumanotani's infrared spectroscopic analysis of the protein-bound urushiol extracted from the lacquer. At this stage of the treatment there is a reduction in the water content as some evaporates, and that remaining forms much smaller droplets within the emulsion.

As the water content drops from around 30% to 10%, the water-insoluble polysaccharides move into the oil phase to complex with the glycoproteins. A water-in-oil emulsion forms, and when the water content reaches 3% these complexes disassociate to some extent, increasing the viscosity of the lacquer.[6] If left unrefined, the matured *ki-urushi* remains high in water content, and the polysaccharide tends to form large globules within the *urushi* matrix rather than being distributed evenly around the polymerized urushiol grains that form during the *kurome* treatment. The beneficial effects of *kurome* refining of the lacquer are supported by the comparative study by Niimura and colleagues on curing rates of *kurome*-treated *urushi (kijiro)* and *ki-urushi*.[17] Through their analysis of the polymerization of alkenylcatechols they showed that crosslinking of *kurome* lacquers occurs at a faster rate than for the *ki* lacquers. The *kurome* treatment accelerates nucleus–side chain and side chain-side chain crosslinking.

Urushiols are responsible for the crosslinking that makes *urushi* so durable and strong. They couple in the presence of oxygen, to produce dimerized compounds (two similar subunits linked together) such as biphenyls and dibenzofurans (Figure 3.3) that indicate the onset of polymerization.[10]

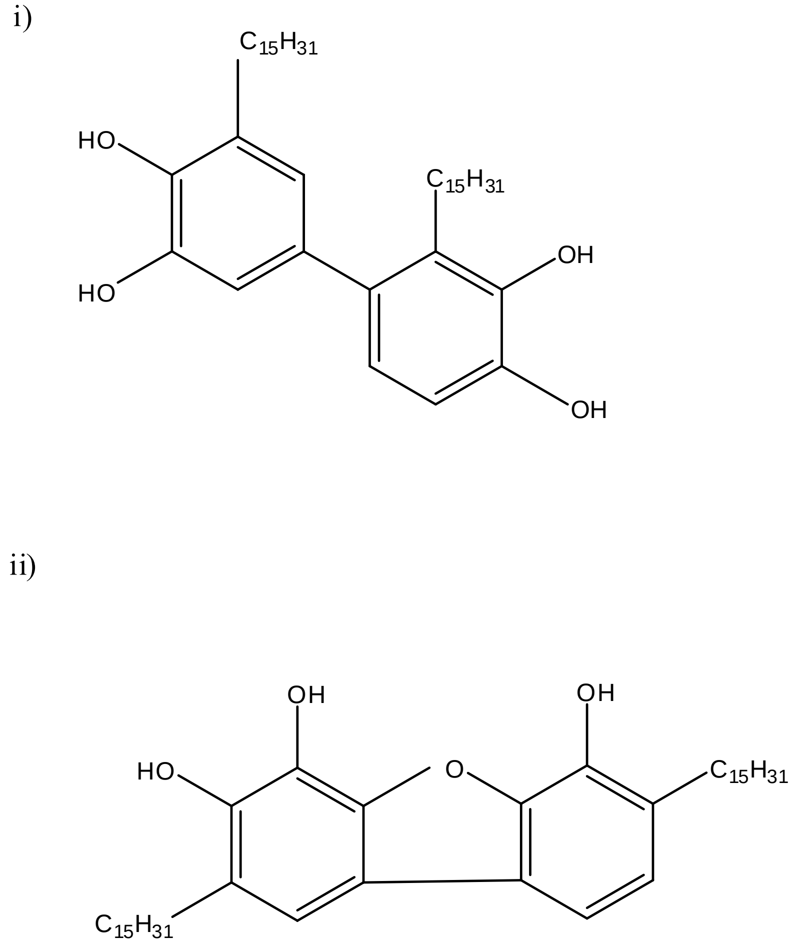

Figure 3.3: Biphenyl (i) and dibenzofuran (ii) compounds.

Polymerization generally requires an initiator and the formation of free radicals in order for the reaction to proceed. Free radicals possess unpaired electrons that make them highly reactive. *Urushi* lacquers appear to cure by a process of radical creation, formation of oxy-radicals, and the addition of polymer radicals to other reactive parts of the urushiol such as the unsaturated parts of the side-chains.[1] The crucial role played by the enzyme in the initial polymerization of urushiol is presented in a study by Kumanotani.[18] The enzyme is the copper-based laccase and is present at about 1% content. Its primary function appears to be initiating oxidation of phenolic compounds to their corresponding quinones and reducing oxygen to water. During this process the copper atoms of the enzyme are first reduced, a process in which the metal ion loses some of its positive charge, then more water is produced as the charge is restored. The water transports dissolved oxygen through the polymer film as it hardens. Dried *ki-urushi* films have been observed to gain weight over a period of 17 years due to their great susceptibility towards oxidation, whereas a smaller weight increase is seen for the *kurome*-treated (*kijiro*) lacquer film, which appears to possess some resistance to oxidation.[6]

3.4 The curing mechanism

Nearly two months is required for lacquer to reach a state that can be regarded as completely cured.[1] However, at a relative humidity of less than 50% at ambient temperature, the lacquer cannot cure to a hardened state. The effect of temperature is also significant, the increase of which has been shown to encourage the curing to occur at a faster rate.[18] Even when the lacquer is considered cured or hardened, reactions still occur in the solid film for some time, since many reactive sites still exist.

The effect of enzyme action on film formation

As noted previously, the enzyme naturally present in the sap is responsible for the initiation of the curing reactions. A study by Kumanotani in 1978 furthered understanding of the film formation reactions by monitoring molecular oxygen in lacquer films.[18] He used an oxygen electrode to measure oxygen uptake during the initiating phase of the oxidation process, concluding that the molecular oxygen is held and used by the laccase enzyme, evidently a favourable catalyst for oxidizing urushiol to its corresponding quinone.

Both the drying and degradation of the lacquer start from the outer surface.[10] Aside from the production of urushiol dimers, the hardening is also achieved by the oxidative polymerization of the unsaturated components of the urushiol side-chains. Kumanotani determined that there are four main types of urushiol dimer: carbon-carbon coupling products of urushiol, dibenzofurans, carbon-carbon and carbon-oxygen 'nucleus' side-chain-bound compounds and side-chain hydroxylated compounds.

The enzyme involved in the curing of the Taiwanese *Rhus succedanea* was isolated by Japanese researchers, and was found to be a peroxidase present in conjunction with a small amount of laccase.[19] This causes much faster oxidation of the phenols than that seen in Japanese lacquers where only laccase is present, suggesting that the enzyme type can play a key role in the rate of curing. Thus lacquers from different origins will require different curing times.

Traditional lacquer colouring pigments include haematite (iron III oxide), cinnabar (mercury sulphide) and orpiment (arsenic sulphide), giving deep red, brown-red and yellow colours, respectively. Other historic pigments such as lead white, chalk, azurite, malachite and copper chloride are not found in lacquers. These pigments decompose in the acidic *urushi*, raising the pH and resulting in enzyme deactivation, preventing the curing process from reaching completion.[20]

Initial reactions involved in the curing process – the importance of water

An ongoing reaction cycle results in oxidation of urushiol to urushiol-quinone. Semi-quinone radicals are very reactive, readily forming bonds with the urushiol. The compounds produced include diphenyl dimers, which cannot form in the absence of moisture. The relative humidity of the immediate curing environment is therefore usually kept at around 80%.

To overcome the inconvenience of requiring a high humidity during curing, fast-drying hybrid lacquers have been prepared that can cure at low humidity. Lu *et al*. combined lacquer prepared by the *kurome* method with a synthetic organic silicone, the presence of which decreases the amount of monomer present and increases the amount of polymer present, even at lower humidity.[21] Curing time is drastically shortened.

Extending the polymer

Following the initial reactions, the polymer network is further extended as bonds are formed between unsaturated side-chains and the aromatic ring part of the urushiol. Kumanotani also suggests that hydrogen is eliminated from the side-chains, a significant step since such reactions increase the unsaturation and produce more reactive sites. As the curing reactions proceed, water is expelled from the film. The water carries glycoproteins and polysaccharides as it diffuses to the surface, resulting in a segregated phase which generates the grain structure discussed later.

The oxidative polymerization reaction produces an increase in the presence of carbonyl groups in the surface of the film as it hardens.[22] An increase in the relative amount of carbonyl measured is seen due to the polymerization of urushiols to dibenzofurans, and also the concentration of glycoproteins and other plant gum materials in the surface layers. Niimura and colleagues have shed some light on the progress of polymerization through their studies on the durability of artificial films.[23] They deduced that polymerization proceeds via the enzyme-catalyzed ‘nucleus’ side-chain carbon-oxygen coupling and autoxidation of the carbon-carbon side-chain coupling, as in the natural material. Synthesized *urushi* analogues polymerized to form harder films than in the natural material due to the presence of longer side-chains containing more double bonds. The ratio of elements such as oxygen to nitrogen within the lacquer surface can be determined with spectroscopic methods, and relates to the durability of the cured polymer. The hardest of the synthetic *urushi* analogues are seen to have a higher ratio of oxygen to nitrogen, as seen in natural *urushi* films.[17]

Kurome treatment and glass transition temperature

The development of the polymer network was explored by Obataya *et al*. who studied the dynamic viscoeleastic properties of three different types of *urushi* lacquer films over a period of 1000 days.[24] The films included a clear *kurome*-treated lacquer (*kijiro urushi*), *ki-urushi*, and *roiro-urushi*. Such experiments allowed elastic modulus, viscous response and glass transition temperatures (T_g) to be determined. T_g is the temperature below which the materials are in a glassy, brittle state, and above which they are in a rubbery or liquid-like state. Both glasses and rubbers are elastic, but around the T_g viscous processes dominate which lead to significant, rate-dependent energy dissipation. The ratio of viscous to elastic response is characterised by ‘tan δ’, which peaks around T_g. It is worth noting that a number of different molecular relaxations occur at different temperatures, but it is the main chain (backbone) mobility that determines the overall glass transition.

These Dynamic Mechanical-Thermal Analysis (DMTA) experiments indicate that the glass transition of the polymerized urushiol backbone rises as the curing proceeds. The change is associated with an increase in stiffness and decrease in the magnitude of tan δ in all cases. Such effects are consistent with the development of a crosslinking network that increasingly constrains the urushiol molecular framework. The *kurome* treatment of the *kijiro-urushi* was found to have accelerated the curing reaction, but the viscoelastic behaviour of the different lacquers was similar except for the rate, and hence extent, of reaction. The incomplete curing of the *ki-urushi* samples is illustrated by the T_g data. For the *kijiro* lacquer, T_g increased from 120^oC to 170^oC over the ageing period, compared to slightly lower T_g changes of 113^oC to 158^oC and 90^oC to 133^oC for the *ki*, and *roiro* lacquers, respectively.

Kurome-treated lacquers have been reported to remain stable for many years, whereas films cast from *ki-urushi* degrade significantly within a year.[6] Thus *kurome* treatment of lacquer is crucial for durability, as indicated by the lower T_g values of the *roiro* and *ki* lacquers after the same period of ageing. A lower T_g is consistent with a lower degree of crosslinking, and a higher plasticising water content, associated with a less advanced curing reaction. Since the chemistry of the lacquers is similar, the change in curing behaviour presumably relates to the changes induced during *kurome* treatment. The overall stability of *roiro* that would be expected as a result of *kurome* treatment is reduced by the reaction with iron hydroxide. *Kijiro* (*kurome*-treated) is most stable, followed by *roiro*, which has increased stability compared to *ki-urushi*. *Ki-urushi* is the least stable as it has had no *kurome* treatment.

Synthetic lacquers

Studies of both curing and degradation processes have been advanced by the preparation of synthetic lacquers largely based on analogues such as linoleic acid and linolenic acid.[23] Other analogues have been prepared that closely copy the natural material, using for example phenol derivatives containing a primary alcohol, unsaturated fatty acids and an enzyme. Such compounds allow controlled monitoring of the crosslinking during curing, as the synthetic materials are easier to study but exhibit similar processes to those which occur in natural *urushi*.[25] Synthesized *urushi* analogues also provide reference materials for analytical methods such as chromatography, as discussed later.

3.5 Development of grain structure

The stability of *urushi* is affected by light and water, although the careful preparation of the lacquer's grounding and top layers is also crucial in establishing a durable surface. Kumanotani has suggested that films produced from *kurome*-treated lacquer owe their stability to the arrangement of a densely-packed grain structure.[10] Particles of polymerized urushiol molecules form, which are coated with a layer of polysaccharides, with the glycoproteins acting as an adhesive between the particles, and providing an oxygen barrier,[6] thereby contributing to the durable nature of the coating and protecting it from abrasion.

Under high magnification dried *kijiro* films show a closely-packed grain structure interspersed with polysaccharide grains, whereas films made from *ki-urushi* show an inhomogeneous distribution of *urushi* constituents.[10] It has been suggested that the *kurome* treatment has a strong influence on the nature of the grain structure.[24] By ensuring a uniform initiation of the polymerization process over a well-defined time, the grains develop at the same rate, producing more regular grain size, and a more even distribution of segregated polysaccharides. The occurrence of large polysaccharide agglomerates observed by microscopy increases in *ki-urushi* based films and is likely to be detrimental to its stability.

3.6 Durability: the effect of water and light

Urushi lacquer is susceptible to photodegradation if exposed to light for a prolonged period. If the binding between the grains of the upper layer of lacquer is destroyed by the effect of light exposure, these grains are lost as powder, thereby exposing a new layer of rougher grains. This leads to an overall change in the appearance of the surface, with a significant reduction in gloss. Formation of micro-cracks in the surface (Figure 3.4) is another symptom of light damage, causing serious destabilization of the lacquer structure, which can extend into the foundation layers.

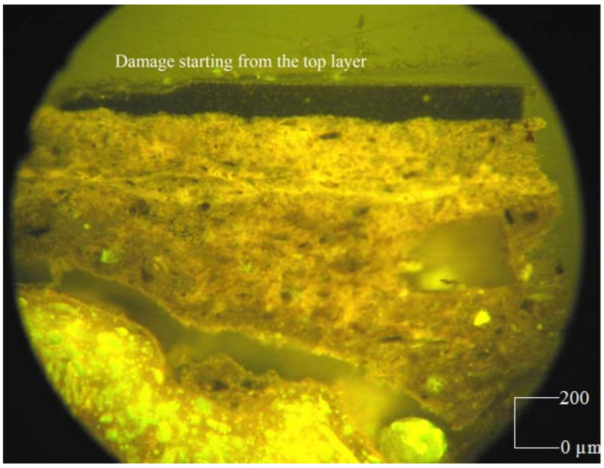

Figure 3.4: Formation of micro-cracks in the surface.

Ideally, the exposure to light of lacquered pieces displayed in museums should be controlled, as they tend to lose their colour and lustre, as illustrated in Figure 3.5 which highlights the difference between the protected interior of the bowl and the exposed exterior of the lid over many years.[26] Ultra-violet (UV) radiation can cause rapid photodegradation of the lacquer, and consequently lamps that filter out radiation below 365 nm should be used to minimise the damaging effects of light. Visible light will also damage lacquer, although at a slower rate than UV light. According to Webb, the stability of *urushi* films can be rated blue wool 4 standard.[2] Degradation may occur by fragmentation of molecules into smaller components and/or by oxidation reactions.

Figure 3.5: Japanese bowl and lid showing the difference between a light-exposed and a protected lacquered piece. Photograph courtesy of N. Schellmann.

Relative humidity levels also play a role in the degradation of lacquer. In dry conditions, the lacquer coating becomes increasingly brittle as water is lost from the polymer. The plasticizing effect of the small water molecules is well-documented.[27] Thus, the presence of absorbed water in humid atmospheres improves the toughness and flexibility of the lacquer films,[28] thereby increasing their effective strength. Evidence for this plasticizing effect is provided by DMTA measurements, which show a reduction in glass transition temperature and increase in tan δ with moisture content.[24] Such experiments have highlighted the differences between *kurome*-treated and *ki* lacquers. Cured *kurome*-treated lacquer absorbs less moisture at a given relative humidity. However, at a given moisture content, *kurome* lacquer is more effectively plasticized. This behaviour has been related to a more uniform microstructure (specifically the uniform distribution of polysaccharides), as discussed above. The rate of water absorption and desorption is dependent on the thickness of the lacquer film, and the relative humidity of the immediate environment.[29]

The moisture content of lacquer also affects the cohesion of the coating and substrate. Kitamura has observed that desorption of water from lacquer and the wooden substrate may occur at different rates, causing stress at the coating–substrate interface.[7] He has observed that in archaeological excavations lacquer-ware is frequently found in a moisture-saturated state. Uncontrolled drying of excavated lacquer can cause catastrophic shrinkage leading to delamination of the coating from the substrate. As with many waterlogged organic materials, immediate treatment is required to prevent such damage. PEG (polyethyleneglycol) impregnation or freeze-drying has been used for waterlogged archaeological lacquer.[7]

Variations in lacquer properties

Urushi lacquers harvested during different seasons or exposed to different refining procedures vary in their mode of deterioration and their stability, even when exposed to the same environmental conditions. Black lacquer (*roiro-urushi*) displays different properties to other so-called transparent *kurome*-lacquers, including the way in which it deteriorates.[30] It has been suggested that the *roiro* lacquers absorb more of the radiation to which they are exposed, thereby deteriorating more quickly. It was suggested earlier that the reaction with iron hydroxide during the colouring process may also contribute to its decreased stability. On exposure to intense UV radiation, the measurable gloss of *roiro* decreases by half within 48–96 hours of exposure, compared to 240–288 hours for *kijiro* lacquer.[30] Observing significant differences between lacquers from different sources or seasons, or that have been exposed to different treatments, is more problematic. *Ki*- and *kijiro-urushi* show no discernible differences in terms of their main functional groups (using infrared spectroscopy) or thermal stability, and therefore often require techniques such as X-ray photoelectron spectroscopy (XPS)[21] or DMTA[22] to provide useful information.

3.7 Deterioration and chemical modification of *urushi*

Despite the durable nature of *urushi*-coated pieces, conservation is often required for historic pieces. Studies of fresh lacquer films have shown that upon exposure to UV/visible light sources over a considerable length of time, the crosslinking density is seen to increase, causing stress on the film, and over time micro-cracking and blistering occurs.[1] The process of deterioration occurring in historic lacquer is accompanied by an overall change in the appearance, from high gloss to dull and matt.

Some experiments have taken the approach of adding stabilizing components to uncured lacquer to protect the cured films from the damaging effects of UV and visible radiation, and to indicate sites of vulnerability on a molecular level. The photo-stabilization of *urushi* lacquers using hindered amine light stabilizers (HALS) and UV absorbers has been investigated by Hong *et al.* who monitored the effect of this treatment by infrared spectroscopy. They focussed on the 1700 cm^{-1} region of the spectrum, which relates to the presence of carbonyl groups. Increasing intensity in this region can be correlated to the development of photodegradation products, such as ketone groups forming in the side-chains. The addition of 2% HALS Tinuvin 292 stabilizer into the lacquer prior to curing reduced the intensity of the carbonyl band by up to three times after ageing. Carbonyl absorbance is also seen to increase in untreated lacquer during UV exposure.[31]

Photodegradation also causes weight-loss, possibly due to evaporation of water, but more likely related to the decomposition of polymerized urushiol chains. Toyoshima suggested that some of the degradation products were volatile and that there was weight loss on degradation caused by exposure to light.[32] With the addition of HALS, the loss in mass was reduced, though the rate of curing of the lacquer was slowed. The mechanism for the photo-stabilization may involve the production of radical traps. Species such as $NO^{\cdot}$ are produced from the oxidation of $NH^{\cdot}$. These species are able to trap radicals, thereby terminating the free radical reactions, and consequently reducing oxidation. Alternatively, the acidic component of the *urushi* and these basic stabilizing compounds may form some salt products that Hong speculates might retard curing.[31] Another study that investigated the UV stabilization of lacquer involved the pre-cure addition of benzotriazole derivatives esterified (linked) with unsaturated carboxylic acids. These UV stabilizers exhibited co-polymerization of the unsaturated side-chains of the lacquer.[33]

Structural changes as a result of deterioration

The dulled appearance of a light-damaged lacquer coating is a result of structural changes which occur on the surfaces of the films, including the deterioration of the grain structure as discussed earlier. A study by Ogawa[34] that used XPS to examine the extent of oxidation of cured material found that it occurred only at the surface of the film during degradation, the extent of which increased with light exposure time. Films were exposed to a fluorescent light source, with either acrylic or glass plates covering the film, or no cover at all. Since the plates remove UV rays of wavelengths shorter than 400 nm, the films were irradiated with visible light only under these conditions. The results revealed that over a period of exposure to the unfiltered light, gloss and colour changes were seen, along with oxidation at the surface of the film. However, those samples exposed to a light source from which shorter wavelengths had been removed also exhibited such changes. XPS results indicated that increasing the time of exposure to fluorescent light led to an increase of peak intensity around the carbonyl region (a measure of degradation noted earlier), and a decrease in triene (side-chains) groups, albeit very slight. However, the lower layers were barely affected, even after 4000 hours of exposure. Ogawa demonstrated that discoloration, gloss reduction and oxidation of the film surface were caused by exposure to both fluorescent and visible light.

The accelerated photodegradation of *roiro-urushi*[30] is also associated with microstructural changes on the surface of the lacquers, including the appearance of cracks and an increase in white particulate materials after only 48 hours of UV exposure, compared to 240 hours in the case of *kijiro* lacquer. As the films deteriorated, the ratios of the carbon-hydrogen and carbon-carbon bonds seen in infrared spectra were seen to decrease as these bonds were cleaved during the oxidation process, and consequently the ratio of carbonyl bonds increased with exposure time. As with Hong's research, these chemical changes correlated with structural deterioration of the lacquer surface.

Infrared spectroscopic (IR) techniques have shown that as a lacquer surface deteriorates, the urushiol and glycoprotein fraction decrease, whilst the durable polysaccharide fraction persists.[35] At the substrate-lacquer interface, a higher concentration of polysaccharide was found, when compared to the lacquer-air interface. Fourier transform infrared spectroscopy can also be used to distinguish *urushi*-based finishes from pigmented resin-based finishes used to imitate the effect of *urushi* lacquer using microgram quantities of sample.[36]

In addition to the effects of the ambient environment, heavy pollution has been observed to affect the gloss and smoothness surface of the *urushi*. Lacquered plates were exposed to indoor air in East Asian cities over several months. Most damage to the gloss appeared during frequent fog episodes. Spots appeared on the surfaces where dense 'acidic' fog occurred: analysis showed the presence of carbonyl groups, which are a product of urushiol side-chain oxidation. The damage is likely to have been accelerated by sulfates present in the acidic fog.[37]

Once photodegradation has begun and the polymer network begins to alter, the lacquer becomes increasingly sensitive to water and organic solvents due to an increase in exposed polar components. The deterioration of the substrate due to cracking, shrinkage or expansion, may be accelerated by damage suffered by the lacquer layers. Macro and micro-cracks in the lacquer structure result in a more permeable surface, which allow greater adsorption and penetration of water into both the lacquer and the foundation layers. This may cause dimensional changes that lead to delamination and general structural deterioration.

3.8 Analytical techniques for characterization of *urushi* lacquer

The insoluble nature of cured, nondegraded lacquer films offers a good degree of protection from environmental influences, but presents a significant problem to the analytical chemist. *Urushi* is a difficult substance to study once cured, as it is resistant to acids and alkalis, and insoluble in organic solvents.[23] Since chemical analysis, such as the sensitive spectroscopic or chromatographic methods, generally requires the dissolution of the material when preparing the sample, the limitation to analysis of solid samples using solid-state methods such as Raman spectrometry, Scanning Electron Microscopy and solid-state Nuclear Magnetic Reasonance, is significant.

Much of the literature concerning the analytical study of *urushi* concentrates on methods for determining the composition of the raw or mildly oxidized sap, since at these stages it is still mainly soluble if an appropriate solvent is selected. Analysis of *urushi* sap also allows distinction between lacquers from different sources.

There are many techniques available for the analysis of the sap, particularly the *urushi* fraction, such as gas chromatography,[38] supercritical fluid chromatography, high resolution NMR spectroscopy and mass spectrometry. Liquid chromatography with a mass spectrometric detection system has allowed the study of urushiol isomers in lacquer sap,[39] providing a method that offers another means of determining *urushi* origin. Chromatographic methods, including gas-liquid chromatography,[40] liquid chromatography[41] and high-performance liquid chromatography,[42] are popular for the analysis of the urushiol components of the sap of *Rhus vernicifera*. Whilst these methods allow us to gain knowledge of the chemical composition of the *urushi*, they are limited to analysis of uncured sap.

Kumanotani separated urushiol dimers formed in mildly oxidized sap slurry by gel permeation chromatography, which enabled him to resolve at least 20 compounds and identify them by spectroscopic techniques.[6] This method allowed him to determine that the most prevalent species present in the mildly oxidized sap were the biphenyl compounds, followed by 'nucleus' side-chain bound dimers, side-chain hydroxylated compounds and dibenzofuran compounds.

Earlier in this review the different types and sources of *urushi* were discussed. Gas chromatography has been used to quantitatively analyse *Rhus vernicifera* sap, by determining the abundance of olefinic urushiols, using synthesized urushiol components for reference. This method enabled the composition of urushiols in the sap to be determined as a function of the growing conditions.[38]

Monitoring the curing progress

IR allows rapid, non-destructive monitoring of functional groups, which has facilitated the investigation of curing mechanisms, for example by showing the early oxidation of urushiol to its corresponding quinone,[43] the decrease of quinoid (carbonyl band) and olefinic bands (unsaturated part of the side chains), and a gradual increase in hydroxyl, benzene ring and conjugated triene bands.

Analysing cured lacquer

It can be helpful to know what type of *urushi* is present and to pinpoint its origin. Pyrolysis-gas chromatography with mass spectrometry (GC-MS) has been used to determine the lacquer type.[8] Gas chromatography separates molecules in a mixture, and mass spectrometry provides a means of identifying each molecule type. In pyrolysis GC–MS the organic matrix is decomposed by heat. The method is therefore destructive, although it can be carried out using very small quantities of the sample. Fragments are oxidized to different products and it is the pyrolysis products that are used to distinguish the various lacquer types.

This technique successfully detected urushiol in *Rhus vernicifera* and *Rhus succedanea* lacquer films. Laccol was only found in *Rhus succedanea*. Differentiation between species or types of treatment was achieved through identifying the specific thermally decomposed components: for example, 3-/4-heptadecadienylcatechols are the identifying species in Burmese lacquers. *Ki-urushi* and *kijiro* (*kurome)-urushi* were analysed[44] revealing that differences lay in the peak area ratios of 3-pentadecenylcatechol:3-pentadecylcatechol and 3-pentadecadienylcatechol:3-pentadecylcatechol. The method has also been used in the characterization of *Rhus vernicifera* and *Rhus succedanea* lacquer films by monitoring their pyrolysis mechanisms.[45]

Laser-desorption-mass spectrometry (LD-MS) is an alternative technique that enables urushiol and laccol-based *urushi* to be distinguished.[46] In LD-MS a laser pulse breaks the polymer into small fragments in a vacuum, so there is no oxidation of the resulting fragments. This method was shown to produce standard ‘fingerprints’ unique to each type of Chinese lacquer studied. The use of pyrolysis with chromatography will be discussed in more detail in the next chapter where the potential differentiation of various lacquers (from each other and from non-East Asian lacquer materials) will be investigated.

Uses of urushi in analytical equipment

The qualities of *urushi* have been exploited in modified analytical equipment as it makes an excellent material for ion-selective electrodes. *Urushi* matrix membranes have been applied to nitrate ion-selective electrodes in the measurement of nitrate-nitrogen in upland soils,[47] tetrafluoroborate-selective *urushi* electrodes,[48] selenocyanate-selective[49] and sodium-selective electrodes.[50] *Urushi* dip-coated electrodes are long lasting and as strong as other types of matrix, such as PVC.

3.9 Implications for conservators

The unique properties of *urushi* lacquer differ from any other decorative or coating material, and must be understood before conservation is attempted. Aged and photodegraded *urushi*-coated objects will develop a dull and matt appearance. As photodegradation advances a brown-tinged, powdery surface is produced as the surface *urushi* grains begin to separate. The cleaning treatments adopted for lacquer contrast with those adopted for materials such as oil paint. The removal of dirt or layers of aged varnishes by organic solvents from original surfaces have been studied extensively.[51, 52, 53] Consequently, the effects of solvent swabbing, penetration of solvents, and leaching and swelling behaviours are well understood in relation to such materials. However, due to the grain structure of the lacquer surface, cleaning by the mechanical action of drawing a swab over the surface to remove large, loose particles of dirt or foreign bound materials is problematic as it will also remove lacquer grains.

One of the effects of light damage is to cause cracking on the surface, which may penetrate through to the foundation layers. Micro-cracking on the surface is likely to trap dust, dirt and other materials such as moisture or oily substances, which may impair the appearance of the piece and accelerate the degradation of the surface. Before cleaning, it is important to understand the potential effects of cleaning materials or techniques on a water-, pH-, and solvent-sensitive, photodegraded lacquer surface. Cleaning is frequently required where inappropriate materials have been employed during restoration attempts. Aged varnishes become less soluble over time and may require potentially lacquer-damaging solvents to remove them. Figure 3.6 shows a lacquer piece during the removal of aged varnish.

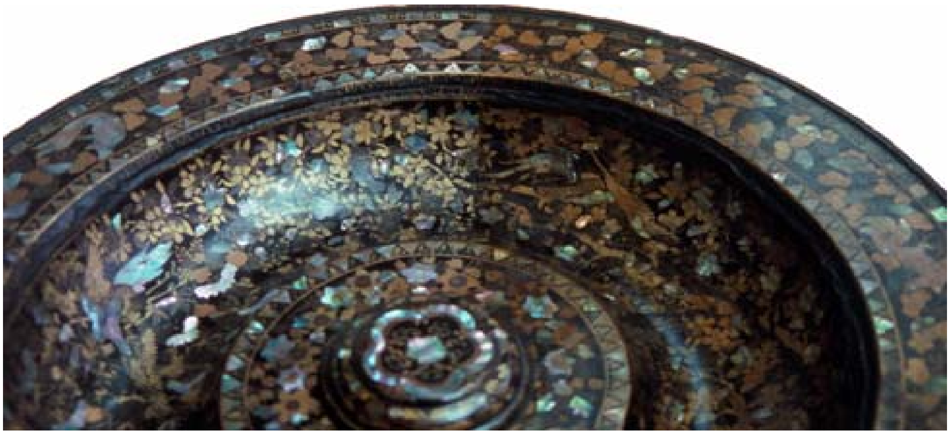

Figure 3.6: The partial removal of an aged varnish layer (left-hand side of image). Photograph courtesy of S. Rivers, V&A.

Durability has been explained in terms of the extensive crosslinking that occurs within the polymer film, particularly with *kurome*-treatment of the lacquer prior to use. It is apparent that the components of the *urushi* have crucial roles to play in the curing of lacquer to a durable film; the laccase enzyme is an initiator of polymerization, the urushiols are polymerized in the presence of oxygen and encapsulated by a layer of polysaccharide which acts as barrier adhered to the urushiol by glycoproteins. This arrangement of urushiol grains is an effective barrier that moderates the impact of fluctuations in relative humidity.

The implications of this structure are that a freshly made film is resistant to abrasion, solvents, acids and alkalis. These characteristics are beneficial when lacquer is used as a coating material, but cause difficulties in the analysis of films. One of the greatest dangers to the durability of this material is exposure to light. *Urushi* films fall into the blue wool standard 4. This rating means that if UV radiation is filtered out, a lacquer piece can be displayed for eight hours per day for 80 years at 50 lux before damage will be observed, which means that long-term exhibition of lacquered pieces is possible under strictly controlled conditions. As the effects of photodegradation advance, so the effects of fluctuations in relative humidity become more pronounced. In addition, light-damaged lacquers become very sensitive to the oils and moisture present in fingerprints as the surface becomes more hygroscopic. Therefore, the use of gloves is necessary when handling these pieces to avoid further damage.

Lacquer pieces must be kept away from direct sunlight to control the radiation that reaches the surface by the use of filters to remove wavelengths lower than approximately 400 nm. Original lacquer surfaces dating back hundreds of years often display a very high gloss if they have spent most of their life protected from light, for example enclosed in boxes or chests. Strict limitations on the periods of display are required. Display conditions must involve low lux lighting. Ideally, when in storage they should be kept in dark conditions. Colour changes may be seen on the surfaces as the surface morphology is altered, particularly in contact with solvents[54] or moisture in combination with heat. It has been observed that the combination of moisture and temperatures as low as 50°C can cause colour changes on lacquer surfaces.[2] Conservators should be aware of this thermochromatic sensitivity when using heat as part of a conservation treatment, for example when re-adhering loose flakes.

The effects of fluctuating relative humidity have been discussed earlier in this review, exemplified by the damaging effects on excavated waterlogged pieces moved into drier conditions. The effect of an extreme relative humidity decrease causes significant damage; sudden drying results in shrinkage of the substrate, causing stress to the lacquer as it becomes more brittle and cracks appear, as plasticizing molecules are removed. Relative humidity fluctuations and cycling will cause an increase in the damage on the lacquer piece, resulting in an uneven and cracked surface. The presence of water is valuable to the plasticity of the polymer. A stable relative humidity controlled at 50% to 60% is necessary for storage and display of lacquer objects.

It is worth noting that materials deposited on lacquer surfaces from the atmosphere, including settled air-borne pollutants and particulate matter,[55] may contribute to its degradation. Pollution in the atmosphere has been seen to have a detrimental effect on *urushi* surfaces; in particular, the presence of acidic fog has been seen to cause uneven deterioration of the coating, due to oxidation of patches of the surface. An atmosphere protected against such pollution is required.

3.10 Summary

This chapter has focused on the major studies of chemical information available in the English language on *urushi*, a unique coating material. In its sap form, freshly collected from a tree, it is of no particular use until it has been matured by reducing the water content, or treated using *kurome* methods to produce a more-stable, partially polymerized emulsion, which enhances the durability of the dried lacquer. A significant amount of information regarding the structure and activities of the material can be determined whilst in its sap form. However, in its cured state, its inherent durability and insoluble character poses problems for analysis. Significant contributions to the understanding of the chemistry of *urushi* have been gained from the work of Kumanotani.[6, 10, 18, 43]

One of the key considerations for conservators should be the mode of deterioration of lacquer. Central to the subject of deterioration are the damaging effects of light and fluctuations in relative humidity. Lengthy periods of exposure to light can cause significant damage to the lacquer surface, changing its sensitivity to the effects of changing moisture, pH and organic solvents. Aged lacquer is more vulnerable to the effects of fluctuating relative humidity than fresh lacquer. Suitable storage and display conditions in terms of light exposure, relative humidity and protection from polluting atmospheres are essential in conserving and maintaining lacquer artefacts.

Further research is needed to investigate the effects of solvents, including water at various pHs, on light-damaged lacquer. Solvent interactions may occur during cleaning, removal of varnish, consolidation, application of fills, retouching or if a coating is applied. Although much is understood about the process of photodegradation there is no consensus about whether such surfaces require conservation and, if so, what materials and techniques should be used? A corollary to the need for more research on potential conservation treatments for photodegraded lacquer is the need to develop reliable artificial ageing of lacquer surfaces, and this will be discussed in Chapter 5. The next chapter, however, will consider the various lacquer materials that are available for further research, the means of distinguishing the sources of different lacquers in their new or aged forms, and will identify the most suitable materials to use in preparing lacquer models for solubility analysis.

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Chapter 4

Differentiation of lacquer types

The implications of lacquer properties to conservation have been discussed briefly in the previous chapter. One of the most important objectives in conservation science is the identification of the historical materials used, prior to selecting appropriate treatments. Both sample availability and analytical techniques are limited for these aged materials; however a range of ancient lacquer samples has been obtained and analysed by pyrolysis-gas chromatography/mass spectrometry (py-GC-MS) with the expectation that their botanical source or exposure to specific treatments or conditions might be elucidated.

The range of East Asian lacquers available for decorative use is extensive, with some saps being treated with specific functions in mind. The subtle effects of mother of pearl or shell can be accentuated by a suitably clear and high quality *urushi*, whereas a yellow-based *urushi* is used to highlight gold inlay. The harvesting of sap at distinct times of the year, and the subsequent treatments and inclusion of additives, oils or pigments produce delicate to strong variations in the colour of the sap and the cured film (Figure 4.1).

Figure 4.1: A collection of brushes belonging to Japanese lacquer artist Onishi Isao, coated in protective and decorative red, pigmented lacquer.

Non-*urushi* coatings on artefacts have been shown to be distinguishable from *urushi*-based objects,[1,2] and there are reported identifications of lacquers from different botanical sources such as *Rhus vernicifera* and *Gluta usitata* by py-GC-MS.[2] There is no reported analysis that further identifies the specific *urushi* types discussed in the following chapter.

4.1 *Urushi* – a valuable commodity

In Japan, *urushi* is regarded as a valuable commodity; some sources report an '*urushi* tax'[3] introduced on this precious substance during the Edo period (1603-1867). As a result, methods have been in place for centuries to ensure its careful preparation, handling and application. *Urushi* is filtered immediately before use to remove as many dust particles as possible. In a Japanese workshop, all surfaces including tables, walls and floors would be wiped down with damp cloths to reduce the dust present. Filtration is done using fine filtration cloth or Chinese paper.

Urushi is an expensive and precious material, due partly to the limited volumes that can be collected from the lacquer tree. Traditionally, careful incisions are made on the *urushi* tree trunks over four-day cycles. Only small amounts of sap are yielded from each cut, and an entire plantation might not yield more than one pint of *urushi* per day over the most productive period.

In addition to creating a high gloss surface, *urushi* is also used as an undercoat to gilding, an adhesive, and in grounding layers. It is generally used in a rawer form in the later. Branches from depleted lacquer trees are boiled in water, and the resulting lacquer, *seshime urushi*, is used in ground layers due to its inferior quality. *Mugi urushi* acts as a very strong adhesive, and is used to attach cloth to wood or for making filler. It is a mixture of lacquer and tofu or wheat flour.[4] High quality lacquer is built up in layers, with good foundations being essential for its stability. These layers include coarse ground layers, followed by finer layers, before the smooth glossy coatings are added. Figure 4.2 shows the process of layering.

Figure 4.2: From left to right this process board shows the numerous stages involved in creating the final glossy effect upon a stable foundation, explained below.

The hinoki wood base (*Kiji*) is first consolidated (*Kiji gatame*) with raw *urushi*. A coarse layer of ground (*Ji*) is applied, and then polished after curing for three days (*Ji togi*). The ground layer is consolidated (*Ji gatame*), and a finer layer of *urushi* with *Ji* and *Sabi* powders are applied (*Kiriko*). This is again polished once dry (*Kiriko togi*), and consolidated (*Kiriko gatame*). A finer layer of *Sabi urushi* is applied, polished (*Sabi togi*) and consolidated (*Sabi gatame*). Then, the glossy coats of *urushi* are added: an under coat (*Shita nuri*), followed by polishing (*Shitanuri togi*), a second coat (*Naka nuri*) and polish (*Nakanuri togi*), and then a final coat (*Uwa nuri*). After the final layer is cured, a polishing finish process is applied (*Roiro sage*).[5]

4.2 Decorative techniques

Apart from the *urushi* lacquer there are other decorative materials present on the surface of the lacquered pieces. For example, *Raden* is the inlaying of thin pieces of mother-of-pearl which are taken from conch shells and bivalves and cut to fit the required area before being inlayed into the top layer of lacquer.

The process of *maki-e*, a sprinkled picture decoration, is a typical traditional method of decoration, and this was studied with a Japanese lacquer artist over several weeks prior to preparing samples for analysis. There are several methods each using different grades and shapes of metal powder. In the Togidashi-*maki-e* process, roughly textured gold and silver powders are sprinkled on the middle *urushi* coating which contains a design sketched out in *urushi*. Once dried, another coat of *urushi* is added to seal in the image. This area is polished with charcoal once dry so that the entire surface is even and flat, but still contains the image.

Hiramaki-e processes use fine silver or gold powders which are again sprinkled onto designs sketched out using *urushi*, this time on the final layer. A layer of *urushi* consolidates the metal, and the polishing process flattens the surface. *Takamaki-e* is the raised, sprinkled decorative method in which coarser *urushi* is used to build a raised area which is then covered with metal powder. Again, *urushi* is used for consolidation and the design is polished. The overall effect is raised away from the flat surface. Figure 4.3 shows this process being carried out during the lacquer workshop.

Figure 4.3: Charcoal polishing during the *Takamaki-e* process.

The *urushi* is applied using lacquer brushes which are made using human hair, washed in sodium hydroxide and then hardened with lacquer glue. The glue is squeezed out using fine combs, up to 100 times. Wooden plates are attached around the hair to bind the bundles. When dried, the tip of the brush is cut with a plane.

As the brush is used and worn out, the wooden part can be trimmed down (similar to sharpening a pencil) and the hair is slightly loosened from the glue using a pointed hammer (Figure 4.4). The hair used is the same length as the wooden part. *Maki-e* brushes use rabbit, rat and cats' hair, which is thin and flexible and supports the complicated movements required for this technique.

Figure 4.4: Preparation of *urushi* brushes.

Finishing urushi

The final polishing stages are essential to reveal the final glossy surface of the lacquer. There are two commonly used methods for finishing the final coat of *urushi* – it can either be left as it is after it has cured (*nuritate-shiage*), or the final layer is polished with soft charcoal, and then with powder and oil (*roiro-shiage)*. For polishing the undercoats and middle coats of *urushi*, hard charcoal (*hōzumi*) from Magnolia hypoleuca, is used. *Tsubakizumi*, a softer charcoal with dense grains, is used in its powder form for polishing *takamaki-e* and soft metal surfaces. In order to achieve high gloss, a coating of *Ki urushi* is applied and then immediately rubbed off with *washi* paper, and polished further.

4.3 Classification of *urushi*

Several types of *urushi* are available, differing according to geographical source, the harvest season, and the way in which they are collected and processed. The main areas of *urushi* production are Japan, Korea and China, where *Rhus vernicifera (verniciflua)* is abundant. Related species occur in Vietnam and Taiwan, the *Rhus succedanea*, in which the phenolic lipid is laccol, and in Burma and Thailand, the *Gluta* (*Melanorrhoea) usitata*, in which thitsiol is the phenolic derivative (Figure 4.5).

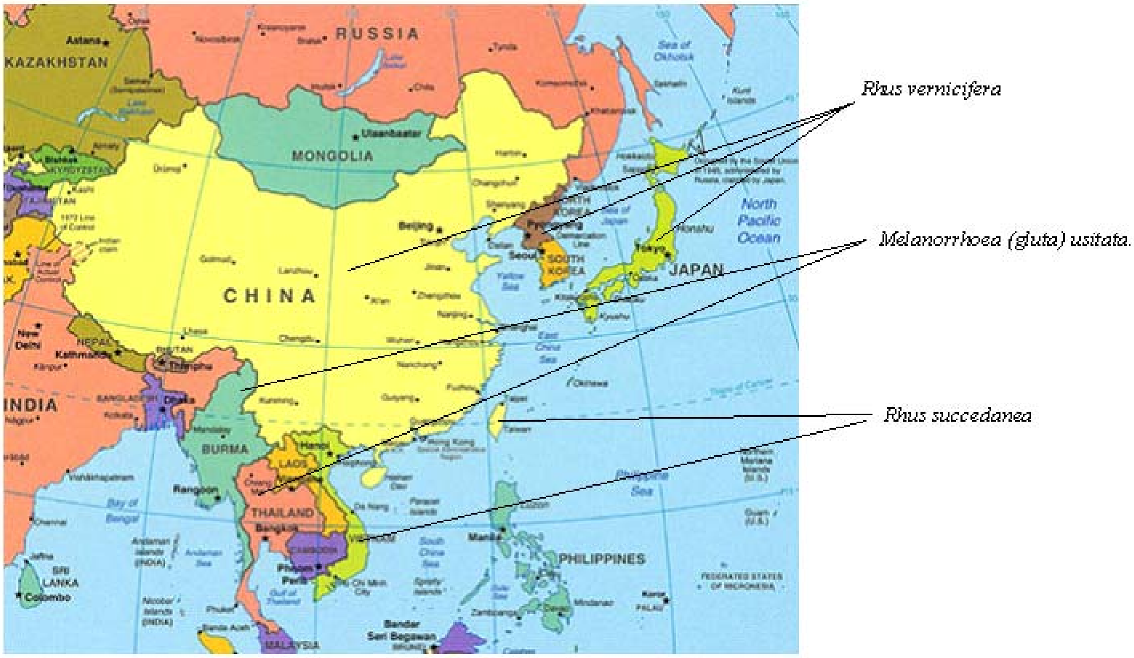


Figure 4.5: Geographical sources of lacquers from East Asia.[6]

Sap treatment

A wide range of lacquers are available depending on the time of harvesting, the refinement processes applied, or the addition of oils or pigments. The first tapping of the lacquer harvest is taken during the June-July period and is referred to as *hatsu urushi*. The second tapping is the *sakari urushi*, taken from August to October, and the third tapping is the *Oso hen* taken during November. According to '*Urushi no Waza*'[7] the *sakari hen* lacquer is regarded as the highest quality. The raw sap obtained from the tree contains a number of impurities which must be filtered off. The water content of the raw *ki urushi* is high at around 25-30%, as discussed in the previous chapter. In order to refine the lacquer, nayashi and kurome processes are applied, homogenising mixing and the removal of substantial water content, respectively.

Properties of lacquer can be altered by the addition of oils, pigments and resins. The caramel coloured lacquer which appears during the processing stage is called *seisei urushi* and in this state various materials are added to change the resulting lacquer. A much more transparent lacquer can be achieved by the addition of vegetable-based oil.[7] Rape-seed or sesame-seed oils are used depending on whether a non-drying (rape seed), or drying oil (sesame) effect is required. *Kijiro* lacquer is a transparent lacquer containing no oil, and is used in the preparation of coloured lacquers, whereas the *kijomi* is a filtered version of the raw lacquer which has received no kurome or nayashi. It is an additive-free lacquer with very high water content.

Kuro nuritate urushi is a transparent lacquer which contains up to 20% oil and has been coloured black. It forms an excellent glossy surface due to the oil content without requiring the polishing processes described later in this section. Lower grade lacquers are frequently used for coatings which are intended to be coloured – *suki nuritate urushi* is a transparent lacquer to which oil has been added will be coloured at a later stage.

Transparent black *urushi* is termed *roiro* in Tokyo, but *hon roiro, kuro roiro* or *kuro-ro* in other parts of Japan. The addition of iron filings to the raw *urushi* causes the lacquer to turn black. An alternative route to this effect is the rapid chemical reaction of iron hydroxide with the lacquer at the end of the kurome process.

Finally, *urushi* is used for attaching other materials, such as metals, to the surface. Careful consideration is required for the colour and consistency of lacquer used over such materials. *Urushi* can be adapted to contribute a variety of decorative effects. *Nashiji urushi* is a transparent *urushi* with a yellow dye or gamboge resin[7] added, and this lacquer is appropriate for the application of gold flake, adding to the brightness of the gold effect mentioned earlier. The addition of these materials adds considerably to the drying time however. In affixing lighter coloured materials to the piece, *rose urushi* is used, which is a mixture of *kuro roiro* and *kijomi* lacquer. A mixture of *kijiro* and *nashiji* (*nurikomi urushi*) is also used in the attachment of metal particles.

Clearly, there are many different types of lacquer available for different purposes, but can they be chemically distinguished in either new or aged lacquer samples?

4.4 Differentiation of seasonal lacquers: Pyrolysis-gas chromatography-mass spectrometry

The structures of various lacquers were investigated using py-GC-MS. This method is excellent for the direct analysis of a solid and insoluble sample requiring no pre-treatment, unlike other chromatographic analyses. The thermal stability of lacquers, which has already been discussed in Chapter 3, necessitates the elevated temperatures which are achieved by pyrolysis to produce volatile components suitable for GC-MS analysis. The literature suggests that the behaviour of lacquers under such conditions can be characterized by specific markers,[1,2,8,9] and the following experiment aims to firstly reproduce these markers, and then to ascertain whether they can be used to distinguish different types of Japanese lacquer.

Experimental details: Py-GC-MS analysis was carried out using an Aglient 19091S-433 gas chromatograph with mass spectrometer. The separation was carried out on a capillary column (0.25 mm i.d. x 30 m), using helium carrier gas at 130.3 ml min^{-1} splitless flow rate. The sample (minimum 0.5 mg) was suspended in the middle of a quartz tube, held in place by quartz wool, and placed into the pyrolyser holder following injection of tetramethylammonium hydroxide (TMAH). The sample was introduced into the furnace at 450^{o}C, and separated by gas chromatography. The GC was programmed to increase at 20^{o}C per minute, from an initial oven temperature of 40^{o}C to a maximum of 350^{o}C. Identification was by mass spectrometry. Trial runs determined that detection of the monomer was only possible following derivatization of the sample in the pyrolyser before analysis took place. Derivatization with TMAH renders the polar constituents more volatile and, therefore, more easily separated by the GC method. The long-chain methyl esters that appear in the results may be due to the rapidly methylated anions that are produced by the pyrolysis method, and the addition of the TMAH causes esterification of long-chain fatty acids present. A range of higher temperatures were carried out, and the 600°C program improved the detection of the monomer.

Sample details: Thin lacquer films cast from commercial *Rhus vernicifera* types, and cured in a controlled-humidity chamber (75-80% r.h.) including raw (*ki*), *roiro hen*, *sakari hen*, *oso hen* and *kijiro* (a blend of different seasons) *urushi* (properties summarised in Table 4.1), were pyrolysed at 450°C with 2 µl TMAH, and then the temperature was increased to 600°C, and the pyrolysis products were separated and detected by GC-MS with splitless injection.

Table 4.1: Properties of *Rhus vernicifera* lacquers analysed by py-GC-MS

Lacquer type	Description
Ki	Raw lacquer
Sakari hen	August-October harvest
Oso hen	November harvest
Kijiro	An oil-free blend of seasons
Roiro hen	Transparent, black lacquer, coloured by chemical reaction with iron

Studies by Kamiya *et al.*[8], who also cites previous studies by other investigators in his work, suggest that the ions at m/z 123 and 108 are specific to *urushi* pyrolysis, and represent the catechol in various states of degradation. His suggested mechanism is reproduced in Figure 4.6.

The samples were derivatized with tetramethylammonium hydroxide (TMAH) as it was determined that methylating the lacquer samples at 450°C produced more compounds for detection. The corresponding marker ions in this work were therefore m/z 151 and 136.

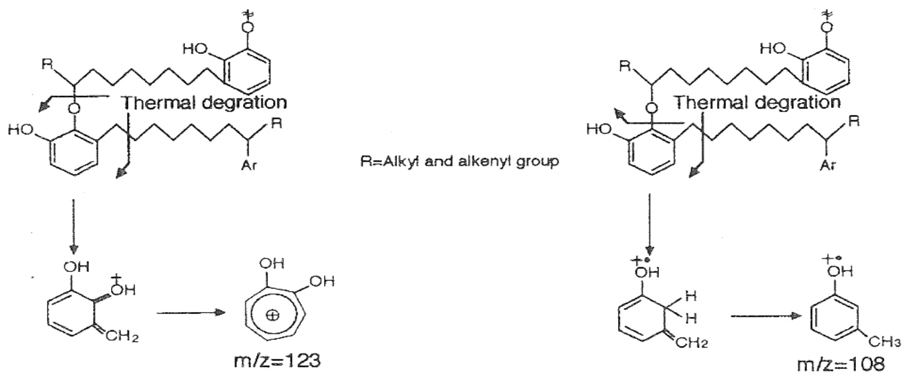
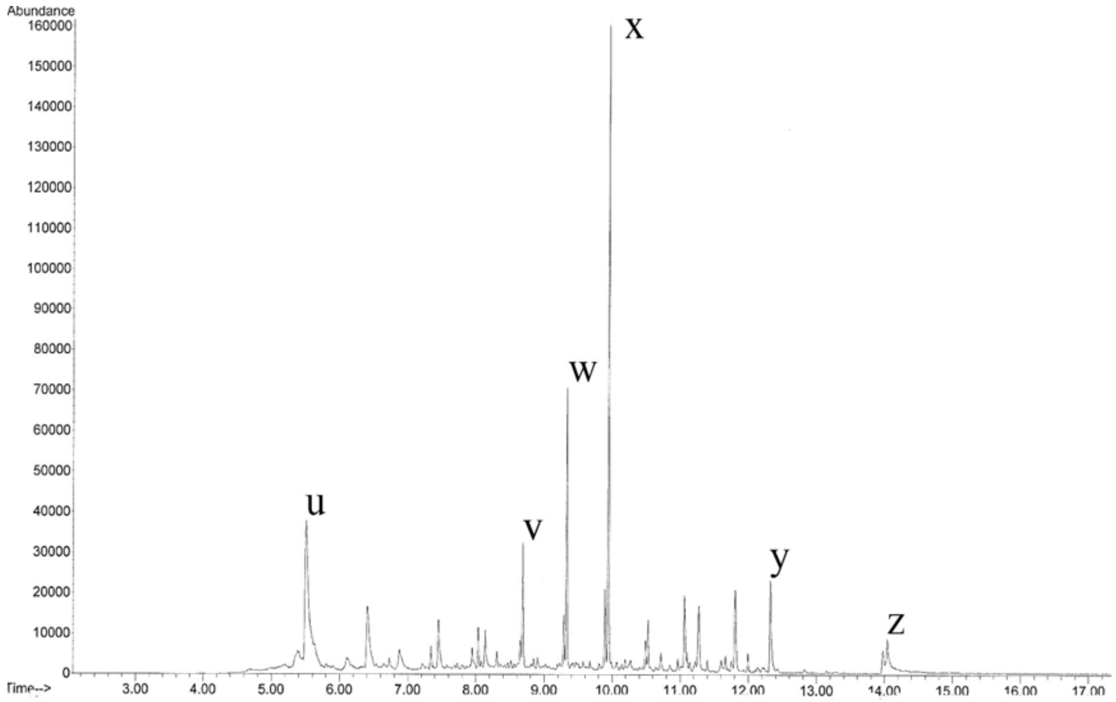
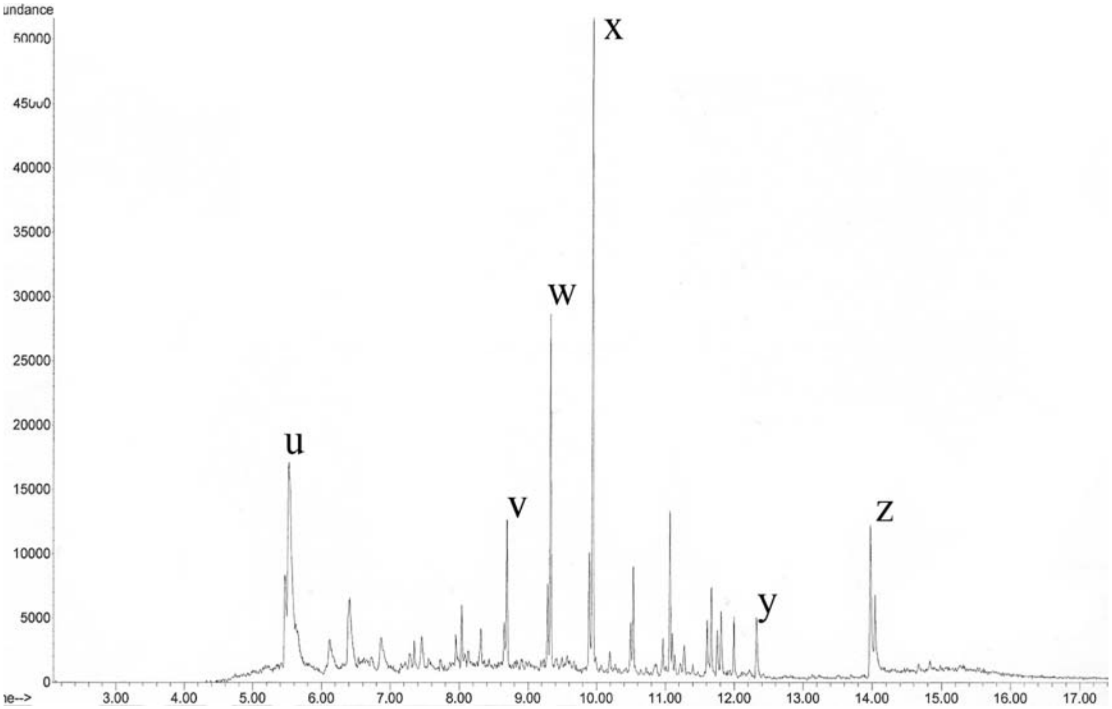


Figure 4.6: Degradation of *urushi* lacquer, generating m/z 123 (151 after derivatization) and m/z108 (136 after derivatization) from Kamiya *et al.*[8]

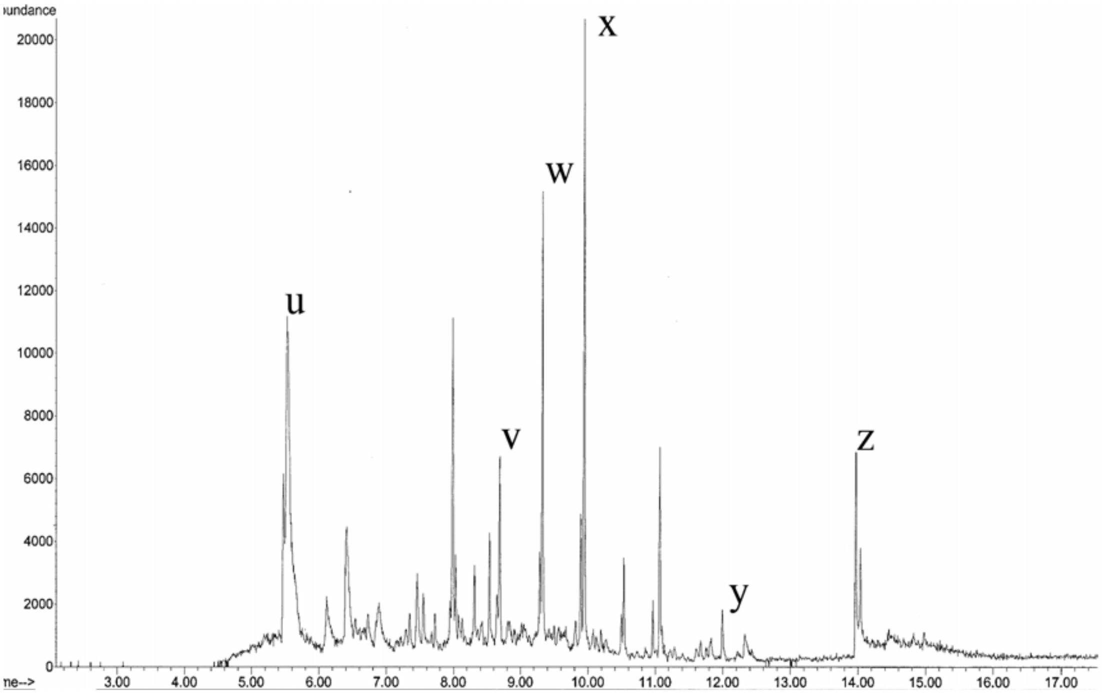
Figure 4.7 shows the selective scanning for m/z 136 of a *kijiro* sample, and the main peaks at u-z have been identified in the literature as 2-methylphenol (u), 2-pentenylphenol/2-pentylphenol (v), 2-hexenylphenol and 2-hexylphenol (w), 2-heptenylphenol and 2-heptylphenol (x), 2-dodecenylphenol/2-dodecylphenol (y), and 3-pentadecenylphenol and 3-pentadecylphenol (z).[8]



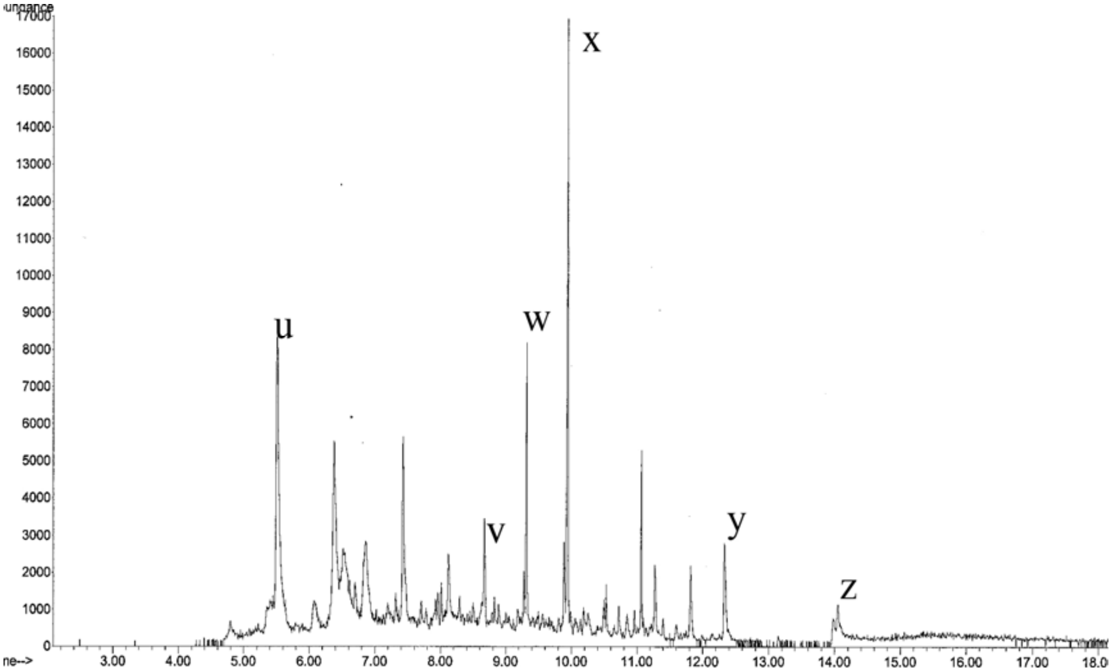
a) *oso hen*



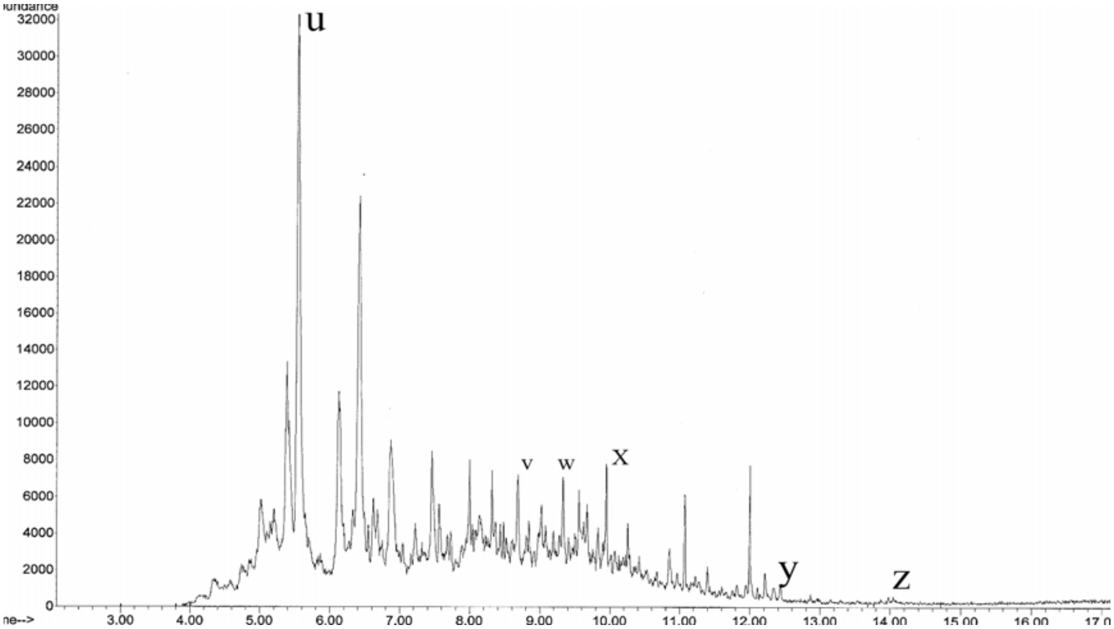
b) *roiro hen*



c) *kijiro*



d) *sakari hen*



e) raw - *ki*

Figure 4.7: Abundance of components of m/z 136 ion species for a) *oso hen*, b) *roiro hen*, c) *kijiro*, d) *sakari hen* and e) raw (*ki*) *urushi* films, showing areas of interest u-z.

The y-axis scales illustrating component abundances in Figure 4.7 are significantly different from each other, making comparisons difficult. However, it is notable that the

C7 (peak X) components are in highest abundance in all the different seasonal lacquers, with the exception of raw *ki* lacquer, and therefore this peak can be used to compare the relative abundances of the other components. The different lacquer types exhibited a similar abundance of C7 (X) and C6 (W) chain length products in this analysis, with the exception of raw (*ki*) lacquer which has a low abundance. The ethyl (C2) phenol products, however, were in high proportion in the raw *urushi* compared with the other types, but had a negligible abundance of the longest (C15 chain), as did the lacquers obtained late in the year. The treated and blended lacquers, the *kijiro* and *roiro hen*, however, had a relatively high abundance of the very long chain urushiols. The high yields of the heptyl/heptenylphenols have been explained by Lu *et al*. as being a result of preferential cleavage of the chain at the unsaturated alpha-position, where the chains are coupled through C-O.[1] The high abundance of the long chain is only seen in the refined lacquers, where water volume has been reduced. This observation may be a result of the pre-treatment of these lacquers prior to curing, which means that the crosslinking has already been initiated. In the case of the untreated saps or those obtained later in the year containing more water, less crosslinking occurs, therefore there are more ‘free’ urushiol molecules present, and consequently the thermal breakdown to heptyl-, and hexyl- chains dominates.

The *roiro* and *kijiro*, being refined lacquers, have a higher density of crosslinking when cured, and so the polymer is formed from longer monomers, which gives a more stable network, and in these cases the breakdown of the structures will produce larger components such as the C15 phenols. A higher abundance of the longer-chain urushiols might indicate a higher quality lacquer, but does not give any indication from which season it may have been produced. These experiments have only taken into account the behaviour of newly cured films as opposed to aged and heavily degraded films.

Derivatized marker ions typical of *urushi* degradation products have also been identified in the literature as m/z 222, 346 and 348. Figure 4.8 shows the typical fragmentation pattern associated with the m/z 346 marker ion, and the relative abundances of this marker can be compared for all the lacquer types.

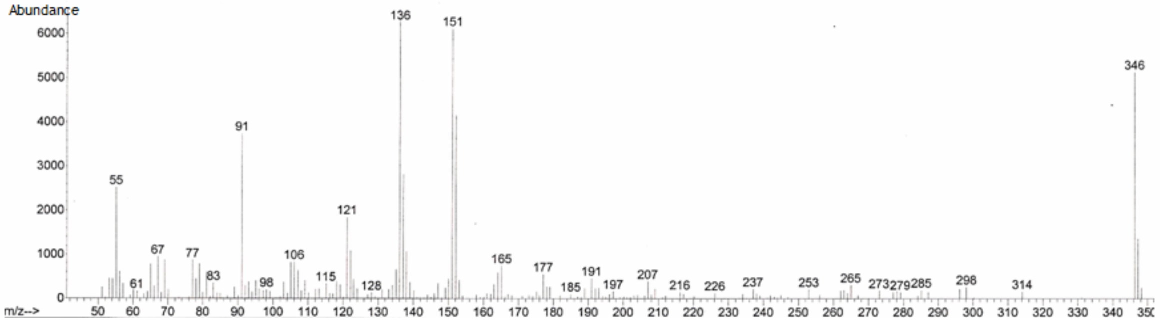


Figure 4.8: Fragmentation pattern for the m/z 346 ion of a new *Oso hen urushi* sample.

The marker ion m/z 346 was searched for with screening software, and the relative abundances of this ion within each of the lacquer types were compared for all derivatized lacquers at 450^{o}C. The fragmentation patterns were determined for the components with retention times occurring at ~14 minutes, and the results are listed in Table 4.2. The fragmentation patterns show similarities in that all the refined lacquers show the same marker ions with only the raw, unrefined sap lacking the same ions. The relative abundances of the m/z 346 marker ion are lower for the lacquers obtained at the end of the year compared with those which are blended or subject to additional processing stages, such as the *kijiro*. This may imply that the lacquers harvested in the later part of the year have a higher content of water (they are observed to have a frothy consistency when used) and, therefore, a lower urushiol concentration.

Table 4.2: Relative abundance of m/z 346 marker ion in various lacquer types

Lacquer description	Retention time (min)	Fragmentation pattern	Abundance of m/z 346 marker
Ki (raw)	13.870	346, 320	185
Sakari hen (late year harvest)	13.984	346, 151, 136, 91	580
Oso hen (late year harvest)	13.979	346, 151, 136, 91	5000
Kijiro (a blend of seasons)	13.961	346, 151, 136, 91	154,000
Roiro hen (treated with iron)	13.973	346, 151, 136, 91	210,000

There has been no reported analysis in the literature to show the difference between pyrolytic products of *urushi* obtained from different times of the year, although Wan *et* *al*. have cited previous research by Du *et al*. which reports changes in concentrations of monoene, diene and triene components in the uncured sap harvested during the summer and winter months, due to wide ranging urushiol concentrations depending on the time of year.[9] The *sakari hen* and *oso hen*, collected in the late summer/autumn months and the winter, respectively, both show an equally low abundance of pentadecenyl/decylphenol components relative to the other components, therefore a low yield of the long chain (C15) cannot be used as a means of differentiating between these seasons. Clearly there is a significantly different result for the raw lacquer than for the rest of the *Rhus vernicifera* types; the raw (*ki*) *urushi* displays a very low composition of the chains longer than C4. These observations, therefore, indicate that, whilst raw lacquer may be differentiated from the refined and seasonal *urushi* types, it is difficult, however, to distinguish those harvested at different times of the year. The patterns observed in the spectra for *oso hen*, *roiro hen* and *sakari hen* are all very similar, while the *kijiro* (blend) spectra exhibits some significant differences, most prominently at ~7.9 minutes which indicates the higher abundance of propenylphenol or propylphenol in this material. The similarities between these lacquers in terms of functional groups have been confirmed by infrared analysis of these films.

4.5 Differentiation of seasonal lacquers: Infrared spectroscopy

Functional groups have well-defined vibration frequencies; therefore IR is a reliable and straightforward means of determining changes in functional groups of *urushi* during curing and ageing.

Sample preparation details: Lacquer films from different harvests were cast out in thin films (7 microns thickness) on glass slides and allowed to cure for three days under high humidity (80%) and ambient temperature. After curing they were stored away from light at ambient temperature and relative humidity for two months, and then removed from the glass slides.

Fourier transform infrared (FTIR) spectra were taken weekly for thin films for 3 months on a Mattson Instruments model Satellite FTIR in transmission mode, and then once monthly for 15 subsequent months, to monitor changes taking place in the *urushi* films immediately after drying, to determine any functional group changes during the curing process, and finally to determine whether FTIR is a suitable method for distinguishing the lacquer types from each other (Table 4.3). The FTIR spectrum for freshly cured *kijiro* is shown in Figure 4.9.

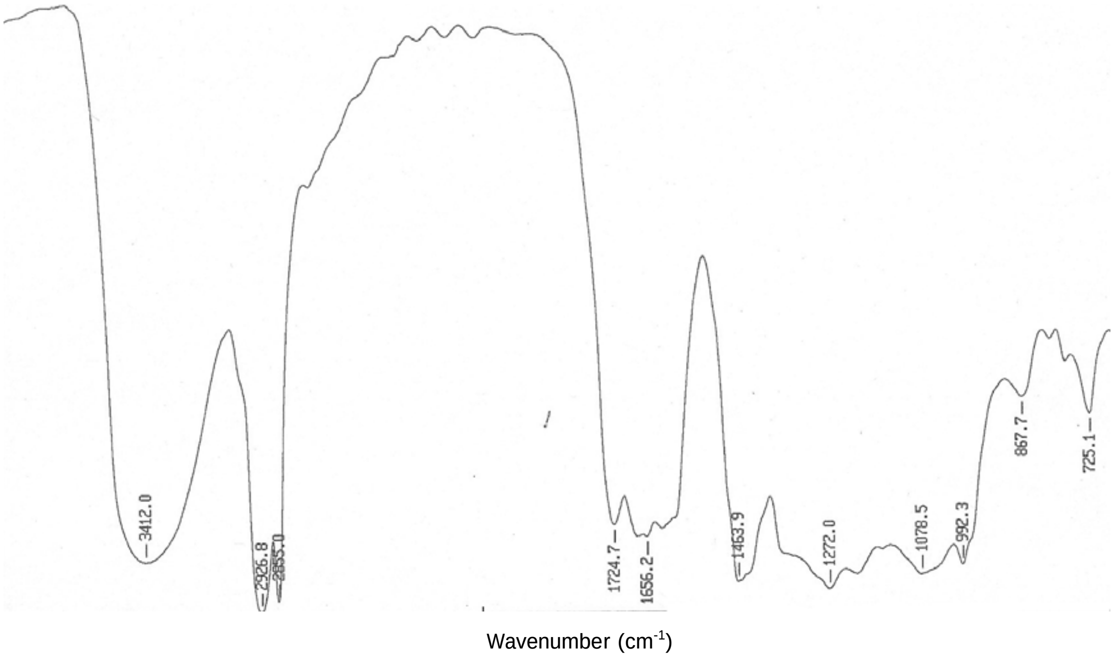


Figure 4.9 FTIR spectra for freshly cured *kijiro* lacquer.

Table 4.3: A comparison of the main functional groups present in freshly cured *Rhus vernicifera* (stored in darkness for 2 months following curing)

Main groups	*Oso hen*	*Roiro hen*	*Kijiro*	*Sakari hen*	Raw (*ki*)
Freshly cured lacquer					
Hydroxyl	3410 cm^{-1}	3400 cm^{-1}	3407 cm^{-1}	3419 cm^{-1}	3403 cm^{-1}
C-H stretches	2852 cm^{-1}	2903 cm^{-1}	2850 cm^{-1}	2850-3010 cm^{-1}	2845-3011 cm^{-1}
C=O, C-O groups	1612 cm^{-1} (shoulder at 1648 cm^{-1})	1598 cm^{-1}	1618 cm^{-1} (shoulder at 1648 cm^{-1})	1612 cm^{-1} (shoulder at 1650 cm^{-1})	1608 cm^{-1}
Carbonyl groups	1722 cm^{-1}	1722 cm^{-1}	1721 cm^{-1}	1723 cm^{-1}	1722 cm^{-1}
Polysaccharide (glycosidic bond)	1077 cm^{-1}	1078 cm^{-1}	1077 cm^{-1}	1077 cm^{-1}	1077 cm^{-1}
Triene (conjugated)	993 cm^{-1}	993 cm^{-1}	993 cm^{-1}	993 cm^{-1}	993 cm^{-1}

After 12 months, with the films being stored in ambient laboratory conditions, in terms of light and humidity, hydroxyl peaks (~3400 cm^{-1}) remain strong and broad. The carbon-hydrogen stretches and carbonyl peaks also remain strong and improve in resolution, the latter due to increased quinoid bands over time as a result of oxidative polymerization. Peaks are still seen at 1077cm^{-1} for the glycosidic bonds of the polysaccharides however they have become weaker, whilst the out-of-plane bending of the hydrogens on the double bonds of the conjugated triene stretch is at 993 cm^{-1} and the peak intensity decreases considerably as oxidative polymerization continues to occur in these active sites, that is, the side-chains where the *urushi* is known to start degrading. Some degree of error is introduced in determining the peak positions of specific carbonyl bonds due to a large range of carbonyl stretches in each sample. On ageing, the carbonyl stretch becomes sharper and more resolved.

Urushi lacquer is highly durable, and so over a period of 12 months no change would be expected. This was confirmed by FTIR analysis; the *roiro* lacquer would be the only type that could potentially demonstrate some change after a period of 12 months in terms of functional groups, since it is destabilised by the addition of iron hydroxide during kurome treatment; however no changes were detected by this method. The spectrum for this lacquer has the least resolved carbonyl peak region, possibly due to the darker colour of this 'transparent' film. The IR spectra display similar functional groups possibly because the sap used in these experiments has been obtained from commercial sources, having been exposed to the *kurome* (oxidative polymerization) processing in Japan, which will have continued during storage handling time in the laboratory. The small changes occurring on the molecular level, measured by functional groups changes, are too similar and too slight for the different seasonal lacquers, therefore this method cannot be used to distinguish lacquers from different seasonal sources.

In summary, the freshly cured *urushi* films of different *Rhus vernicifera* materials exhibited a similar pattern of functional groups, that is, hydroxyl peaks at ~3400 cm^{-1}, particularly broad for raw (*ki*) *urushi*, CH stretches at ~2850 cm^{-1}; carbonyl peaks which improve in resolution over time due to a marked increase in the abundance of carbonyl groups due to oxidation of the side-chain, polysaccharide peaks of decreasing intensity as the films age, at 1077 cm^{-1}, and a sharp triene peak at 993 cm^{-1} which also decreases sharply over time owing to the side-chain degradation. These patterns are consistent between all the films studied here, and confirm the results of the pyrolysis that determine that the *Rhus vernicifera* lacquers collected at various times of the year could not be differentiated by these methods. The functional groups present are the same for all the samples, and these groups change in their abundances only slightly; no distinguishing features are available from the spectra to differentiate the lacquer types from each other.

Wan *et al*.[9] studied the spectra for the uncured lacquer saps obtained from various countries, and these too displayed very similar spectra by IR spectroscopy. A study of cured lacquers has not been reported before in the literature, however, and the results indicate that the solid-state samples cannot be differentiated using this method.

4.6 Analysis of lacquers from different botanical sources

In the characterization of lacquer relics from different parts of East Asia, py-GC-MS is an effective method. Along with the identification of organic components, the method can be applied to the identification of inorganic materials that are present, such as pigments including cinnabar (mercury sulphide) found on Chinese lacquered objects.[10] The differentiation of lacquers from different origins has been achieved by the identification of marker components formed by thermal degradation of the distinct monomers, and measurement of side-chain lengths.

Analysis of lacquer from different botanical origins

As already discussed in Chapter 3, the most commonly available East Asian lacquers are obtained from the *Rhus vernicifera* (Japan and China), *Rhus succedanea* (Vietnam and Taiwan) and *Gluta usitata* (Burma and Thailand) species. Japanese lacquers are, therefore, assumed to consist of the *urushi*-based materials. However, some studies[11] indicate that a shortage of *urushi* occurred during the late 16th century, preceding the Edo period during which time the ‘fine period’ pieces such as the Mazarin Chest were produced, which necessitated the import of lacquers from other parts of Asia to supplement the lacquers available in Kyoto. The origin of lacquer cannot, therefore, be assumed based on the location of manufacture of the piece.

In the following experiments, the differentiation of East Asian lacquers on specific objects is investigated by py-GC-MS. *Rhus vernicifera* has been differentiated from the *Rhus succedanea* and *Gluta usitata* in previous work,[1,2,8-13] and the same procedure has been applied to freshly cured and lacquered museum pieces to confirm their origin.

As previously discussed, the East Asian lacquers differ in their basic structures: those from Japan and China possess an urushiol component, from Taiwan and Vietnam a laccol component, and the lacquer from Burma and Thailand has a thitsiol component. The literature shows that when pyrolysed, these three types yield different products which enable the lacquer's botanical origin to be determined.

Lu *et al.*[1] concluded that the main pyrolytic products of the *urushi*-, laccol- and thitsiol-based lacquers were 3-pentadecylcatechol, 3-heptadecylcatechol, and 4-heptadecylcatechol, respectively. According to their research, differentiation could be achieved by identifying the monomers in the pyrolysis products (Table 4.4). Pentadecyl catechols are the longest side-chain pyrolysis products in *Rhus vernicifera*, whereas hepatadecyl catechols are seen in *Rhus succedanea*. 3-heptylcatechol and pentadecylphenol is more abundant in *Rhus vernicifera*, and 3-nonylcatechol and heptadecylphenol most abundant in *Rhus succedanea*. The cleavage of double bonds in the side chain is most likely to occur at the alpha and beta positions, therefore yielding the heptyl- (Figure 4.10) or nonyl- components (Figure 4.11).

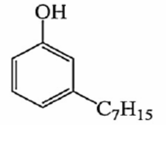


Figure 4.10: 3-heptylphenol

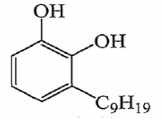


Figure 4.11: 3-nonylcatechol

Table 4.4: Summary of monomers in pyrolysis products of different lacquer types

Lacquer type	Monomer MW
Rhus vernicifera, urushiol	320
Rhus succedanea, laccol	320, 348
Gluta usitata, thitsiol	346, 348, 310, 326, 338, 354

3- and 4-heptadecadienylcatechols are the main components of thitsiol.[1] Upon pyrolysis the main products are: 4-hepatadecenylcatechol (molecular weight 346); 4-hepatadecenylcatechol (molecular weight 348); 3-(10-phenyldecyl)phenol (molecular weight 310); 3-(10-phenyldecyl)catechol (molecular weight 326); 4-(10-phenyldodecyl)phenol (molecular weight 338); 4-(12-phenyldodecyl)catechol (molecular weight 354).

The larger monomer molecular weights are not observed for the *urushi* lacquer; an example of the fragmentation pattern obtained for the 3-(10-phenyldecyl)catechol m/z 326 (354 with derivatization) ion is shown in Figure 4.12, while Figure 4.13 shows the fragmentation pattern of the m/z 318 urushiol (346 with derivatization) marker ion for *urushi* lacquer.

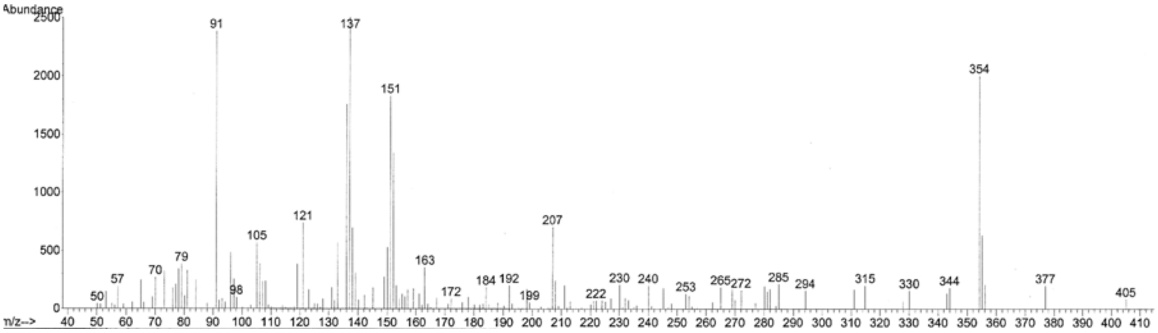


Figure 4.12: Freshly cured Burmese lacquer pyrolysed at 600°C; scanned at 15.007 min.

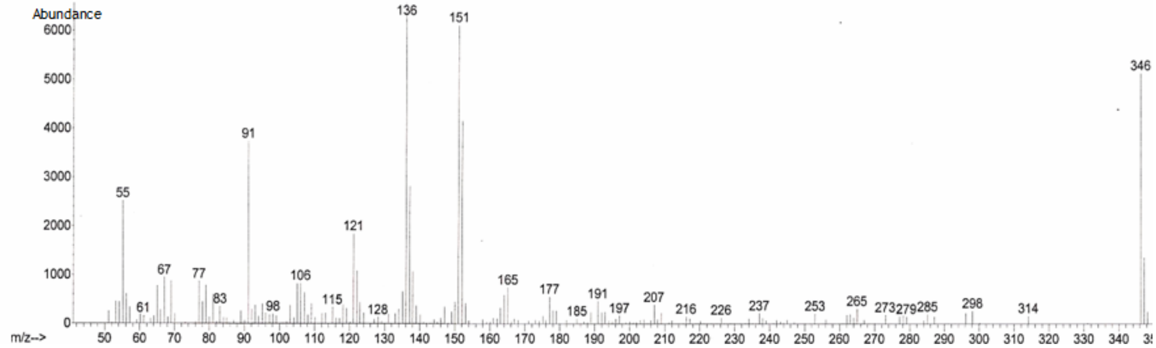


Figure 4.13: Freshly cured Japanese lacquer, pyrolysed at 450°C; scanned at 13.961 min.

Having a method by which the botanical origin of lacquer-coated objects (both new and aged), including the Mazarin Chest, is of great interest in this work since the sample materials for further investigation need to be prepared to represent the original as closely as possible, and so the correct lacquer type needs to be selected. Some literature has suggested the possibility of non-Japanese lacquer being used on Japanese pieces in Kyoto workshops at the same time that the Mazarin chest was produced, and so it is necessary to check the origin before attempting to reproduce the degraded version of the material.

Confirming the origin of museum pieces

Assumed origin: Thailand

A newly lacquered candlestick holder (Figure 4.14) obtained from Thailand in 2007, and therefore assumed to be coated in *Gluta usitata* lacquer, was sampled (0.3 mg from the base of the object) and analysed by py-GC-MS. A total ion chromatogram obtained for this sample contained specific marker ions, as suggested in the literature, indicative of thitsiol, including m/z 346, 348 and 382 (derivatized). At 600°C, strong peaks are seen at the site of these ions; Figure 4.15 shows the fragmentation of the m/z 354 (382) ion. Thus, the pyrolysis method confirms the presence of thitsiol in the finishing surface.

Figure 4.14: Thai candlestick holder.

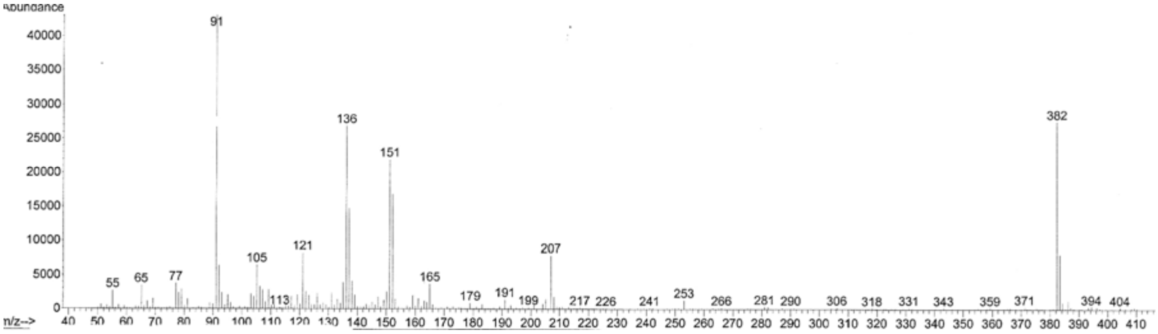


Figure 4.15: m/z 382 thitsiol marker components analysed at 600°C for Thai candlestick; scanned at 15.819 min.

Two samples were taken from naturally aged Thai lacquer pieces (19^{th} c.). The first was a black lacquer (0.4 mg) scraped from the surface of a piece of mother-of-pearl shell, and was possibly a foundation layer, and when analysed by the pyrolysis method, the higher temperature of 600°C was required in order to obtain the marker compounds to confirm its thitsiol content: m/z 382 (Figure 4.16), 354, 348 and 346, although the lower-weight markers m/z 136 and 151 were observed during the run at 450°C. The second sample was a red Thai sample (0.3 mg) of lacquer that also yielded 382 ions at 15.7-16.3 min, again confirming the presence of thitsiol (Figure 4.17).

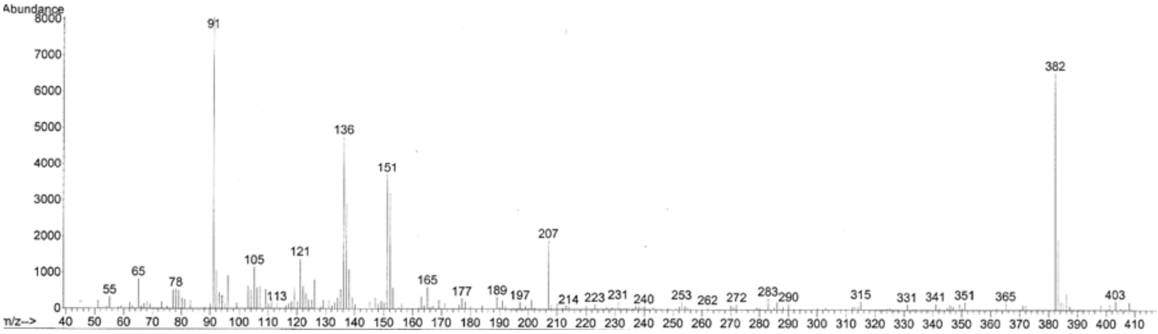


Figure 4.16: Aged, black Thai lacquer taken from back of shell, 600°C; scanned at 15.819 min.

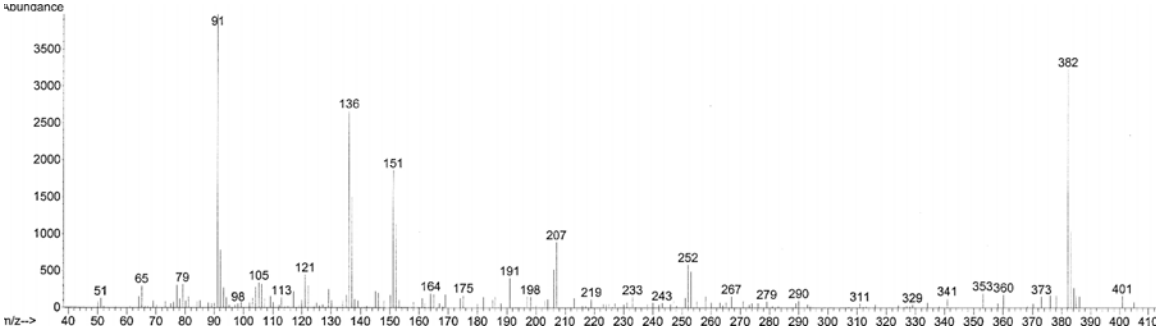


Figure 4.17: Aged, red Thai lacquer, 450°C, 15.819 min.

Assumed origin: Burma

Fresh Burmese lacquer obtained from artists in Burma during the summer of 2008 was cured and analysed by the method described earlier. Some *urushi* markers are seen at 450°C (m/z 136, 151), and at 600°C thitsiol marker components are seen but in very low abundance (Figure 4.10).

A newly prepared soup bowl obtained from Burma in 2007 (Figure 4.18) was sampled (0.2mg) from the base and subjected to the pyrolysis method. Lacquer markers were observed at m/z 136 and 151, but no further sign of the higher molecular weight lacquer markers were observed for this piece (Figure 4.19). The pyrolysis spectra library indicated that the other main peaks observed correspond to levopimaric acid methyl esters (a compound that could be found in pine gums or rosin) and hexadecanoic acid methyl esters. Fatty acid methyl esters are found in natural materials such as wax, resins and gums; however, the available sample was too small yield further information. When the oven temperature was raised to 600^{o}C (Figure 4.20), some thitsiol markers become apparent (m/z 382, with fragmentation at 151, 136), however the spectrum does also indicate the presence of a non-lacquer material.

Figure 4.18: Burmese soup bowl.

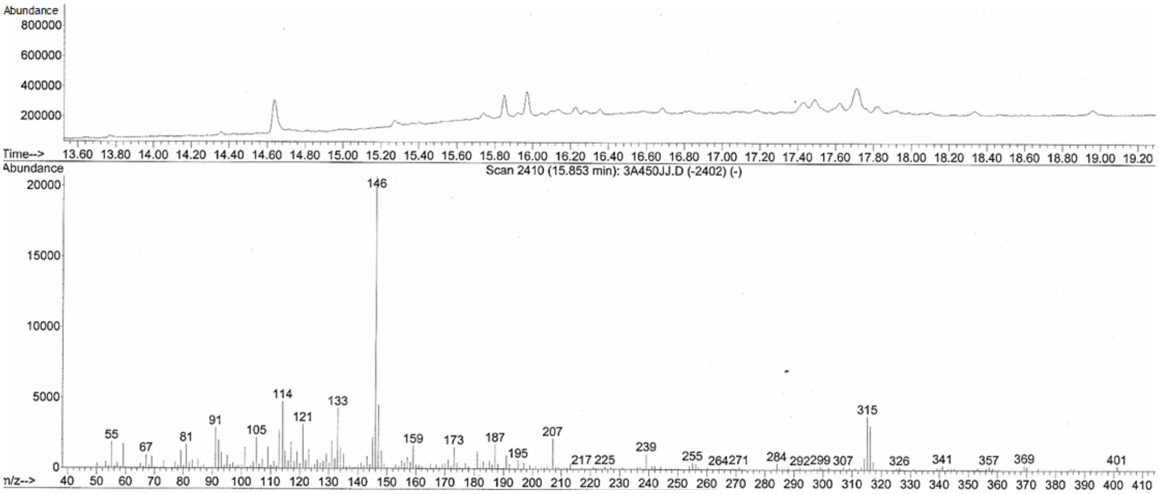


Figure 4.19: Black lacquer taken from base of orange bowl, 450^{o}C.

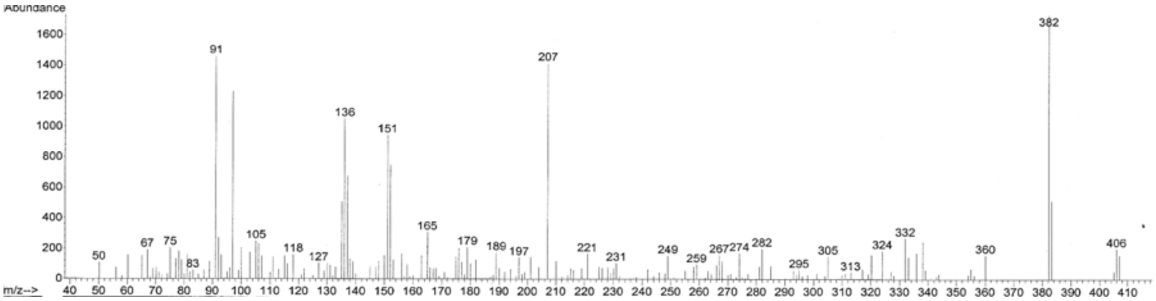


Figure 4.20: Black lacquer taken from base of orange bowl, 600°C, thitsiol markers.

A very small sample (0.1 mg) was taken from the black area of an orange and black 18th c. Burmese bowl which was being kept in storage at the Victoria and Albert Museum (ref: I.M. 202-1927). Analysis shows no marker compounds for lacquer-based material at 450°C, although the spectra library suggests the presence of benzoic acid methyl esters, which is found in some essential oils and varnish resins. When the temperature was increased to 600°C, the mass spectra still failed to show any marker components of thitsiol or urushiol (Figure 4.21); although an ion is observed at m/z 348, its fragmentation pattern does not indicate lacquer either. The spectra library indicates octacosanoic acid methyl esters (16.28 min) and undecylbenzene (10.29 min) (m/z 348), which again indicate the presence of another natural material. The sample was possibly too small to yield the lacquer markers – as discussed earlier the method determined for this requires a minimum of 0.5 mg sample, alternatively the piece may have undergone restorative treatment using non-lacquer based materials.

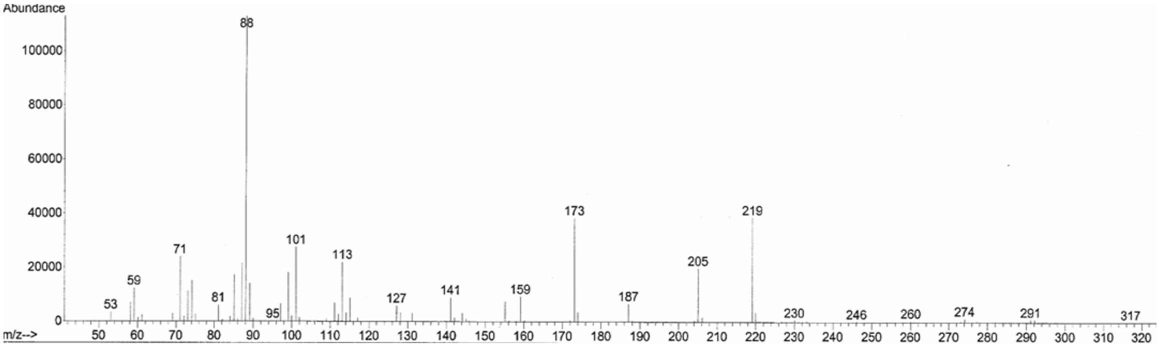


Figure 4.21: Orange Burmese sample, from pyrolysis at 600°C.

Assumed origin: China

Raw *ki urushi* was obtained from the same commercial source as the *kijiro* standards, cast out in thin films (10 µm), allowed to cure for three days under high humidity and stored in the dark for a period of 8 weeks. A sample (0.5 mg) of the cured lacquer was analysed using the pyrolysis method described above, and the resulting spectra indicated that there was a low abundance of the m/z 346 marker ion for *urushi*, but no other monomers were found.

A 15th century Chinese object (FE7-1973) was sampled (<0.2 mg), derivatized and pyrolysed using the method above. Unfortunately the sample was too small to get any useful data.

Assumed origin: Japan

A 19th century Japanese screen frame was sampled and analysed using the method described above. Swabs were taken from the sample initially, but the results were not useful since the swab was pyrolysed along with the coating, because attempts at extraction had been unsuccessful. The blank taken for the swab, when subtracted from the resulting spectra showed that there was nothing detected for these samples. A 0.4 mg sample was scraped from the surface of the matt, damaged part of the screen and analysed by py-GC-MS.

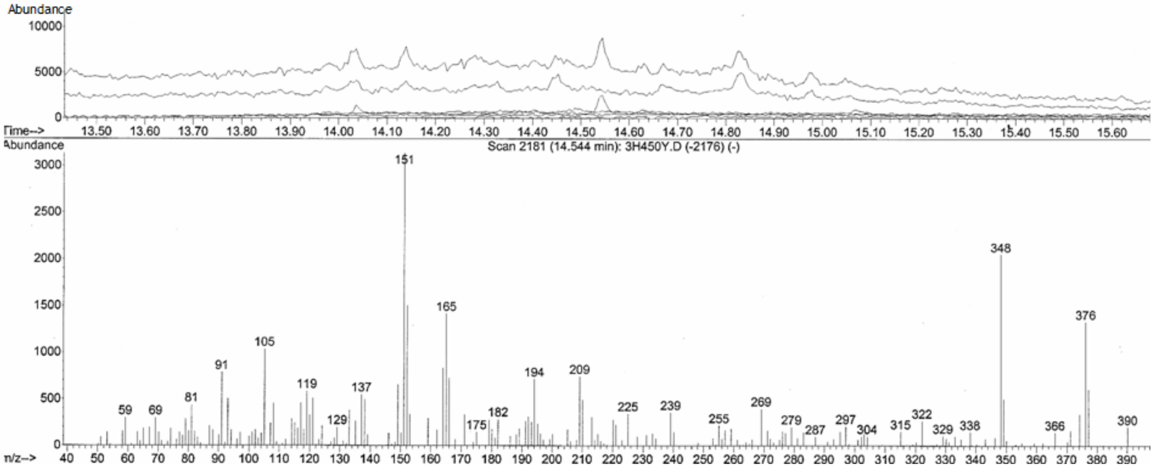


Figure 4.22: Total ion chromatogram for 19th century Japanese screen frame, 450°C, and fragmentation pattern for peak at 14.544 minutes.

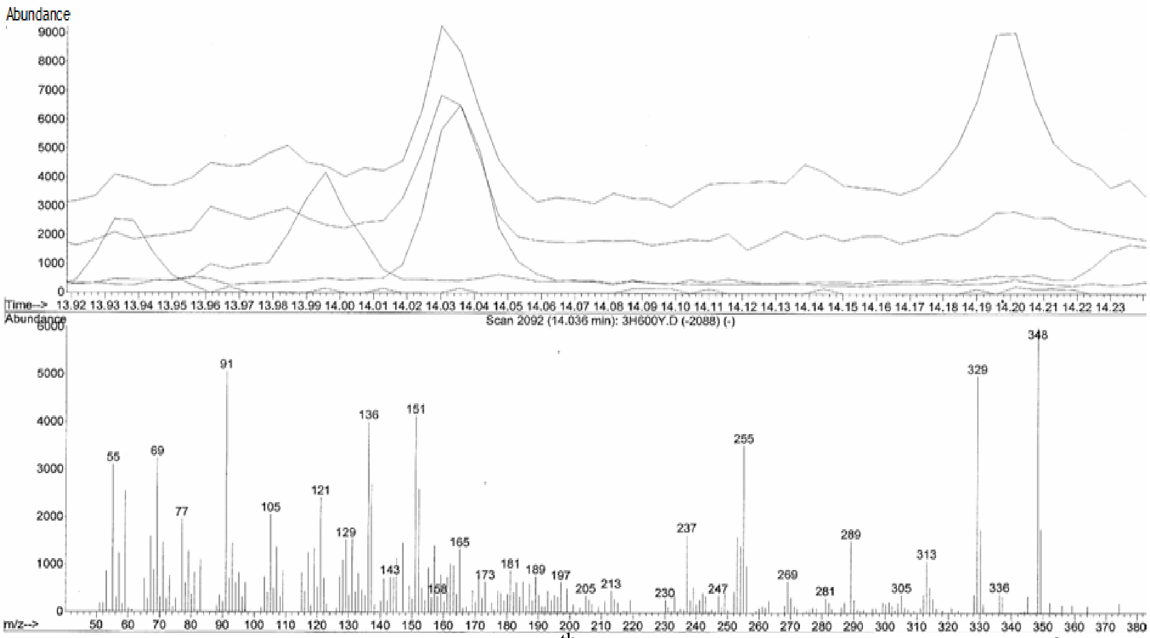


Figure 4.23: Total ion chromatogram of 19th century Japanese screen frame, 600°C, and fragmentation pattern for peak at 14.036 minutes.

The spectra obtained (Figures 4.22 and 4.23) by scanning for multiple ions simultaneously (m/z 136, 151, 346, 348 354, and 382) do show some lacquer markers (m/z 136, 151, 348), such as those shown at 14.036 minutes in Figure 4.23, which confirm that the sample taken was from a lacquer-based material, although they are found in low abundance, even at the higher temperature cycle. The m/z 136 (108) species was selectively plotted, and the total ion chromatography scan (Figure 4.24) shows a high abundance of peaks at ~9 mins relative to those seen at ~10.8 mins, which could indicate a high amount of heptenylphenols and heptylphenols in comparison to the nonylphenols, the former being indicative of *urushi* based lacquer.

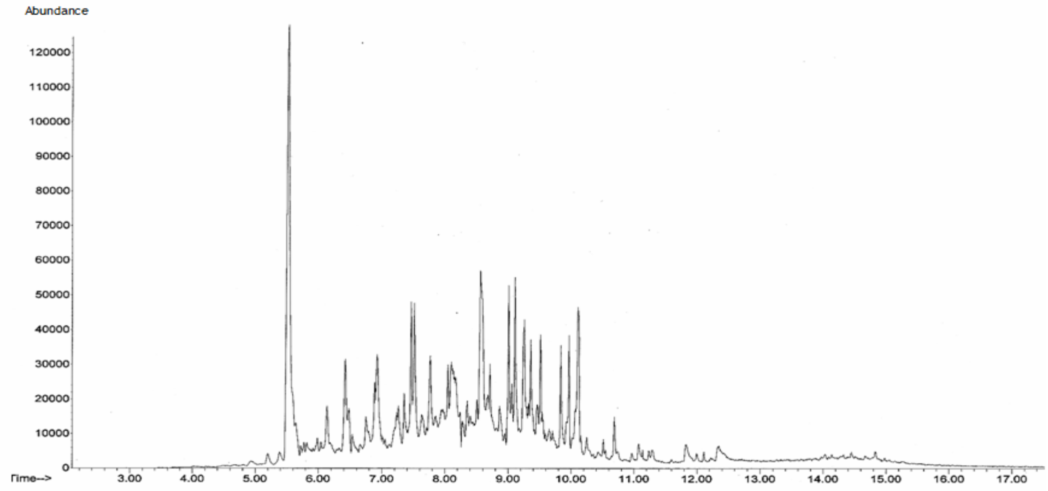


Figure 4.24: Total ion chromatogram from 19th century Japanese screen frame.

A separate part of the screen, which was glossier in appearance, despite the damage which was evident in terms of patchy regions of gloss/matt and scratches, was also analysed – however no markers could be discovered to identify this material as lacquer based. Although m/z 382 does occur (354 ion) in low abundance, the fragmentation pattern was not of *urushi* or thitsiol, and MS library searches suggested that tetracosanoic acid methyl esters/lignoceric acid methyl esters were present, again an indicator of fatty acid methyl ester components of natural resins having been added to the surface at some point (Appendix A).

The Mazarin Chest, produced in Kyoto, Japan, could not be sampled from directly, and so this investigation made use of cleaning procedures that had been previously carried out on the chest. Solvent cleaning, where industrial methylated spirit and water had been applied with cleaning wands, had removed some of the debris including the material presumed to be degraded lacquer, from the surface of the chest, and the residue was collected together on a piece of cotton cloth (Figure 4.25).

Figure 4.25: Residue from solvent cleaning collected on cotton cloth.

The cleaning was carried out in at the Victoria and Albert Museum in September 2007 at two locations on the piece: the back of the chest (Figure 4.26), and the black, matt surface of the chest lid (Figure 4.27). Since extraction of the nonsoluble surface material from the cloth was not possible, the samples were analysed by pyrolysing a portion of the cloth piece (taking a blank reference spectra as well).

Figure 4.26: Back of Mazarin Chest.

A problematic aspect of using this system is that a very small (but immeasurable in mass) sample of the actual coating is analysed, as seen with the screen sample, and so this investigation primarily sought to determine whether the residual material could be identified as lacquer based, and to then confirm that the degraded lacquer was *urushi*.

Figure 4.27: Surface of the Mazarin Chest showing cleaned area of the black surface.

First, the samples obtained from the back of the chest were pyrolysed, and the TIC obtained for the selectively scanned m/z 136 (108) species is shown in Figure 4.28. Owing to the small sample relative to the cloth, the resolution of the peaks <14 mins are not very good, although some useful information can be obtained from the clear peaks seen at 14.8 mins.

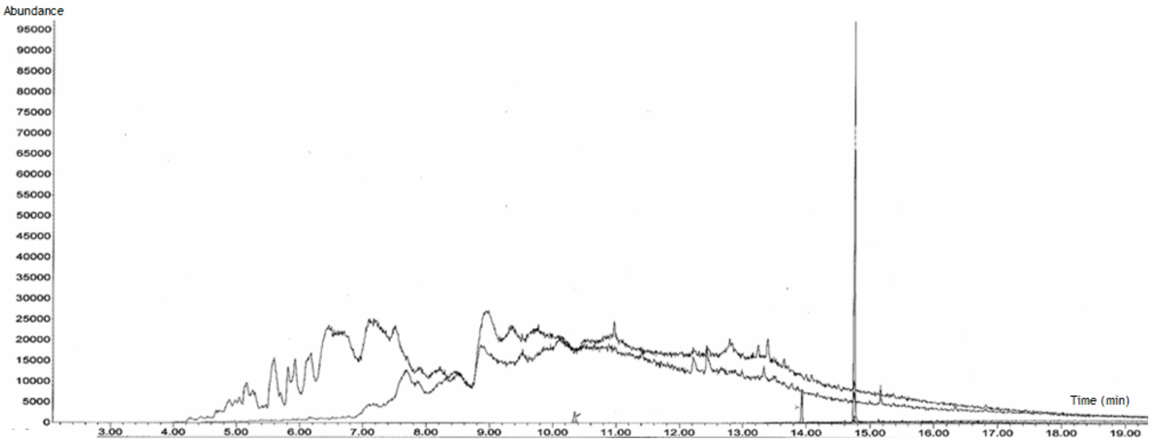


Figure 4.28: Total ion chromatogram with selective scanning for m/z 136 (108) species for cleaning sample taken from the back of the Mazarin Chest.

Residue from the back of the chest could not be confirmed as lacquer based, although markers for lacquer were seen at m/z 382, the fragmentation pattern did not represent one of lacquer, but was suggested to be tetracosanoic acid methyl esters. This could be attributed to aside product of the TMAH derivatization or to the presence of a long-chain fatty acid methyl ester-varnish constituent. However, the residue taken from the cleaning of the surface of the chest, when analysed in the same way, showed definite lacquer markers (m/z 136, 151) and the m/z 382 species may be representative of an oxidized component, but could not be definitively identified as *urushi*.

The TIC (Figure 4.29) shows that there is not a clear resolution for the individual phenolic components, when scanned selectively for the m/z 136 (108) ion species, however, the complete absence of peaks at around 11 mins and some fairly strong peaks at 9.5 min is indicative of heptylphenol components and an absence of nonylphenol components, which therefore implies the presence of an *urushi* based coating, as expected on a high quality piece of Japanese origin.

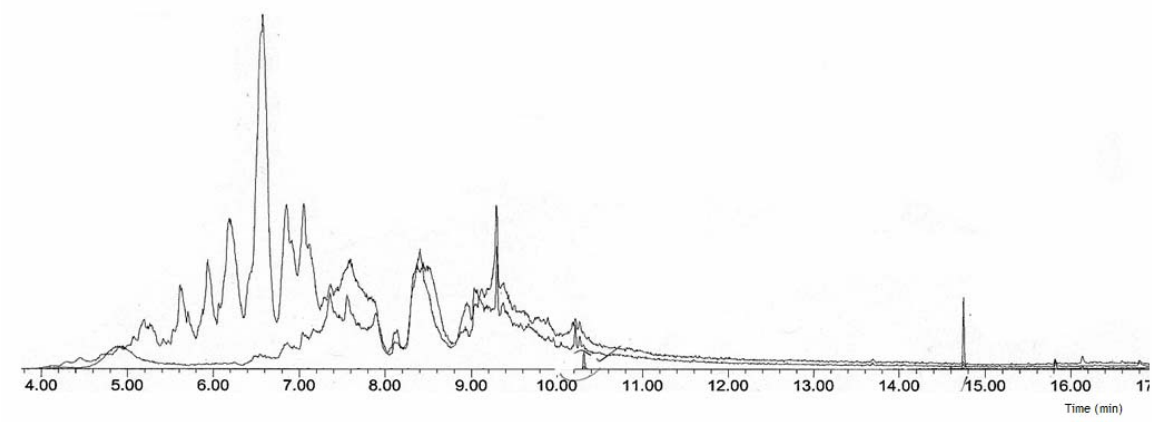


Figure 4.29: Total ion chromatogram of the sample swabbed from the black surface of the Mazarin Chest.

4.7 Conclusion

A wide range of lacquers are available for decorative purposes, varying in terms of their colour, chemical stability and drying time; these properties alter depending on their season or region of harvest, and the subsequent treatments to which they are exposed. Pyrolysis is a good method for determining a lacquer's botanical origin from very small sample sizes, and determining the presence of non-lacquer based materials on a decorative piece. However, this is always a destructive, non-reversible method of analysis – the sample taken from the surface is completely pyrolysed and cannot be returned to the piece afterwards, and the successful analysis requires at least 0.5 mg of sample. Lacquers obtained at various times of the year show distinct changes in their properties in terms of colour, however, in terms of functional groups they cannot be distinguished from each other using infrared spectroscopy, and the degradation products on pyrolysis are also too similar to yield any means of differentiating the lacquers obtained at different times for the same species.

As a result of lacquer shortages in some regions towards the end of the 16th century, there is suggestion that lacquer saps were imported from other parts of Asia to supplement these deficiencies. Therefore while the pyrolysis method described here can be used to confirm the botanical origin of the material present on unknown artefacts, this identification does not necessarily confirm the location of its manufacture.

The stability of lacquer is dependent on the quality of materials used, in addition to the workmanship that has gone into the production. The latter is very important because the build up of lacquer layers using appropriate foundation layers is necessary to prepare a stable structure for the top lacquer layers to rest upon. A high quality lacquer applied in many thin layers with polishing yields the best surface aesthetic. Japanese lacquer is believed to be one of the highest quality lacquers available, however, the fine pieces produced in Kyoto, Japan, might not necessarily display only the Japanese *urushi* (of *Rhus vernicifera* origin), although the two Japanese aged pieces studied here do seem to be *urushi*-based.

The py-GC-MS method described here can be used to accurately determine whether the coating material was lacquer based or non-lacquer based, however it cannot always conclusively prove the specific species from which the lacquer was obtained. In the aged samples, the monomer specific to each species might not be detected due to the oxidative ageing and subsequent breakdown of the polymer network, although the smaller marker compounds which are specific to lacquer based materials are generally present in the spectra. Analysis of the back of the Mazarin Chest was inconclusive since direct sampling from the piece was not possible. Instead, the materials removed from the chest on swabs used in cleaning were analysed, and the traces of lacquer degradation products were analysed by py-GC-MS. The results obtained from this investigation indicated the presence of a non-lacquer based material, which may be attributed to the presence of a varnish resin, although the swab cloth material may hinder the definitive identification of these organic materials. Swabbing with solvents in this way is also potentially destructive on an unidentified or unstable surface.

In the following experimental work, the effect of solvents on a delicate and aged surface containing lacquer degradation products will be investigated to determine just how harmful this treatment can be. In order to do this, various means of causing artificial damage will be applied to lacquer samples so that degraded models are available for solvent testing. The suitability of these accelerated damage methods is discussed in detail in the following chapter. In future experiments, the high quality Japanese *Kijiro urushi* will be used in the preparation of all standards and samples, being a blend of the year's harvested sap, thereby providing a good representative material for experiments on its ageing characteristics. The accessibility of this lacquer type, which is transparent in colour, changing to brown once cured, and is mostly used as a protective top later over decorative areas of lacquered items, also directs its choice as a standard material.

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Chapter 5

Accelerated ageing of *urushi* lacquer

Accelerated ageing processes are applied to conservation science investigations where aged sample material models are required to predict how an important artefact might be affected by a particular course of treatment. Such processes can be employed to drastically reduce the time required to obtain information on the durability and stability of materials; in addition, artificial conditions can be closely controlled in the laboratory. Reproducible methods are not readily accessible in the literature, although there are some reports of studies on coating materials and varnishes. The general consensus seems to follow Saunders and Kirkby's survey conclusions, that 'no common procedure' exists for light ageing in the conservation environment.[1] The rates at which degradation processes occur are increased by exposing the material to extreme conditions − light, humidity, thermal shock − in a short space of time in a climate or light chamber. When employing ageing regimes for this purpose, certain assumptions must be made – specifically, that changes occurring at a molecular level are the same as those that occur under natural, long-term ageing conditions, and that the irreversible changes to surface morphology are consistent in all samples exposed to the uniform conditions. Accelerated ageing might be able to recreate the physical changes of a material, yielding a surface which appears to be aged in the same way as it would be naturally, as regards dullness, matt texture or cracks and blistering of a surface. However, upon analysis of the chemical changes, cracking patterns and other measurable parameters, significant disparity is shown in this work between artificial and natural ageing of conservation materials. In his extensive work, *Accelerated Ageing,* Feller[2] cites Kockolt (1989) who recommends that an acceleration factor should not exceed 5-10, and Minsker (1982) who advises that UV irradiance must not exceed three times the solar intensity; Feller's own recommendation is that the near UV should not constitute more than a maximum of 20% of the total radiant power of the artificial light source. The limitations of rapidly increasing damage by artificial processes will be discussed here.

5.1 Accelerated ageing of *urushi* lacquer

Aged lacquer can be characterized visually by the observed change from high gloss to dull matt; a rough and uneven, powdered or cracked topography is observed under microscopy. Prolonged ageing causes *urushi* films to become difficult to handle owing to their delicate and brittle state. When studying *urushi* lacquer, the insolubility of the material limits the analysis to solid-state only. In this work, therefore, the progress of the accelerated ageing and response of lacquer were characterized by changes observed by pyrolysis-gas chromatography-mass spectrometry (py-GC-MS), changes in the functional groups of the films monitored by Fourier transform-infrared spectroscopy (FTIR), and a range of optical analyses showing surface changes in terms of gloss, colour and morphological changes (cracking and powdering) observed by scanning electron microscopy. Water-soluble fragments of the degraded surfaces were analysed by liquid chromatography-mass spectrometry (LC-MS), and cross-sections of damaged layers examined under fluorescence microscopy show how far the damage extends following short-term, accelerated ageing.

An overall increase in film damage was evident as the ageing processes were applied; these changes were observed as an increased brittleness and associated handling difficulties, gloss and colour fading, and changes in functional groups. The rapid changes monitored here show that the limited ageing instruments available show great promise in the production of damaged lacquer models for solvent-lacquer interaction analysis. However, the data that emerge from closer study of these films will provide greater insight into the validity and usefulness of such regimes.

In this chapter, a range of ageing processes were investigated to potentially determine the most reproducible lacquer ageing method for producing test material for solvent-lacquer analysis. The accelerated ageing of *kijiro* lacquer was carried out in order to attempt the simulation of long-term changes in thin films or boards, such as response to solvent interaction, water resistance, light stability and changes on a molecular level. Accelerated ageing processes were applied to speed up the damage and destabilisation of this material's initially durable characteristics. This chapter will also discuss the degree of degradation required to produce a useful sample for further investigation of proposed treatments.

As discussed in Chapter 3, the exposure of freshly cured (1 month old) *urushi* lacquer films and boards to harsh lighting conditions is expected to alter the structure of the polymer's crosslinked system and change its optical properties. The damage does not necessarily take place via the same mechanism as a naturally aged process that would occur over a prolonged period. Accelerated ageing is based on the assumption that exposing a material to a high intensity dose of UV radiation for a short time produces the same effect as a low intensity dose for a prolonged period of time. This approach neither takes into account the behaviour of sensitive materials, which may experience dehydration or bleaching, nor how the heat generated from an intense light source will also affect the behaviour of polymeric materials where the glass transition temperature is exceeded.

5.2 The predictive value and limitations of accelerated ageing

Three main purposes exist for attempting to accelerate the ageing of materials in a conservation setting.[1] The first is to study the degree to which a material is sensitive to light, giving curators a useful indication of the appropriate display conditions for artefacts in museums; the second, to provide understanding that the appearance of a particular object is a direct result of the light on the materials that were originally used; and third, to obtain a usable model for study of the behaviour of a substance, and to study its deterioration path. The most commonly used accelerated ageing regimes include light and thermal ageing, in which materials are subjected to either high temperatures, or UV light sources, or both. An accelerated ageing regime may also involve cyclic loading (stress-strain), changes in humidity and freeze-thaw cycles to simulate natural long-term ageing processes.

There are two main methods for attempting accelerating ageing: concentrating the impact of a particular environmental condition such as light, or by subjecting the materials to extreme conditions involving all of the environmental factors that it is likely to experience in its real surroundings, specifically, cycles of light, heat, and moisture. The extreme conditions should include those that would be experienced in normal conditions, but magnified considerably.[3]

When using sources of light to simulate natural daylight, the range and distribution of wavelengths present in the light source must be considered. For example, radiation reaching the earth, and subsequently the objects or surfaces that are being studied, contains wavelengths around 290 nm. Whilst shorter wavelengths would result in the speeding up of the processes of degradation, these will not occur via the same chemical paths as in natural aged conditions. Window glass will generally filter out wavelengths of less than 315 nm, preventing shorter radiation reaching the object beneath it.[2] In the study of museum object surfaces, which can generally be assumed to have been stored with care, a strong, unfiltered UV source would be unsuitable in recreating ‘real’ conditions.

5.3 Artificial versus natural changes

Research carried out since the 1980s highlights the discrepancies between the outcome of artificially-induced and naturally-induced changes in coating materials. Ageing a varnish resin will result in oxidation, crosslinking and polymerisation, and consequently decomposition of the original films compounds. Although oxidation of resins will still take place under dark conditions, it occurs at a much higher rate under light conditions. Auto-oxidation, which involves the consumption of molecular oxygen, gives rise to the presence of polar compounds.

In Van der Doelen’s[4] varnish-ageing research, changes at the molecular level that occur naturally were not faithfully reproduced by artificial means. Yellowing is one of the most significant outcomes of naturally ageing varnish resin. During accelerated ageing, damage is evident from changes in solubility and cracking of the surface; yellowing, however, does not occur. Thermal ageing can be seen to cause yellowing to some extent, although no significant change in the solubility of the varnish is observed when applying these conditions. In a study by De la Rie,[5] films of dammar and mastic were aged by heat and light, and changes were monitored. Only in the presence of light did autoxidation occur – the samples formed polar groups and thereby altered their solubility, but there was limited yellowing. Heat application that followed caused secondary, non-oxidative thermal processes, which caused yellowing. De la Rie proposed that aldol condensation and dehydration reactions in the film are the likely cause of the colour change and fluorescence under UV, and a combination of light and thermal ageing is therefore required to reproduce this effect.

Ageing methods and results of polymer durability tests were surveyed by Brown;[6] users of these methods generally regarded the accelerated ageing process as being unable to simulate the natural processes with accuracy on a molecular scale. He concludes in his research that the correlation between natural and accelerated processes is inversely related to the degree of ageing.[6] For example, van der Doelen[4] worked on triterpenoid varnishes where the use of a xenon-arc source with fluorescent tubes devices were shown to produce molecular species which differed from real samples. The production of these species, detected by mass spectrometry, affected the solubility of the varnish because additional acidic groups were generated during the accelerated conditions. However, on filtering out the UV component, a more realistic molecular surface was observed.

Comparison of the chemical processes occurring under natural and accelerated conditions indicate that artificial UV light increased the oxidation reactions that occur naturally to a very limited extent, generating other compounds not found in the naturally aged samples.[4] However, in conditions where the UV exposure is limited, natural processes are simulated more effectively. In agreement with the positive influence of an effective UV filter, Feller states in his work[2] that a xenon-arc light source with suitable filtration to represent daylight through glass has become one of the most useful and accepted sources in studies of photochemical stability of materials.

The results achieved by different ageing methods were also discussed by van der Doelen,[4] who studied the chemical changes in dammar varnishes using GC-MS. In his research, dammar film is exposed to 370 hours (~2.2 weeks) of xenon-arc light source, either with or without an extra UV filter based on plexiglass, in addition to the borosilicate and soda-lime filter already present. Comparisons are also made with a naturally aged piece of dammar and a fresh sample of dammar. Once again, a UV filter is required to approximate natural ageing. Significant differences were observed in the characteristic indicators in the dammar structures of the natural and artificial aged samples. An abundance of functional groups were also found to exist in the accelerated aged material which are not present in the natural samples. The type of oxidation which does not occur in natural ageing is caused by the UV component, and has an influence on the degree of solubility of the varnish. In the experimental section, the effect of applying UV filters during the ageing process is investigated using pyrolysis-mass spectrometry, to determine whether indicators might be observed for varying degrees of degradation of *urushi* lacquer.

The action of UV light is significant in the photodegradation of both varnish and lacquer films, and evidence for this is suggested by De la Rie and McGlinchey[7] who proposed a method for stabilizing dammar resins against UV-photodegradation using a hindered amine light stabilizer (HALS), with the addition of a UV absorber. HALS acts as a radical scavenger and enables the films to remain intact after 3700 hours (22 weeks) of accelerated ageing, with the original components of the varnish remaining (degradation normally would occur after a much shorter period of time). The films are removable by the same solvent that was used prior to ageing as UV radiation is absorbed by the additive before it can affect the material. Hong *et al.*'s study on the photo-stability of *urushi* lacquer, with and without accelerated ageing taking place,[8] showed that the addition of 2% HALS into the lacquer improved the photo-stabilisation by a factor of three. HALS is also thought to retard the curing reaction of the lacquer.

Ageing in solution

Other kinetic limitations on material ageing include a low diffusion rate of oxygen into films. Whilst such limitations are clearly beneficial in terms of materials conservation, these rates are a hindrance for ageing studies. The rates of degradation have, however, been accelerated by ageing terpenoid varnishes in solution.[9] Using mastic and dammar, the varnishes were dissolved in dichloromethane and acetone (with photosensitisers used to simulate oxidation processes) and were then exposed to fluorescent light. According to the authors this method provides a means of preparing crosslinked aged varnishes which reproduce the oxidation processes that occur in naturally aged samples, and overcome the kinetic limitations of diffusion rates into films. The ageing of *urushi* in solution, however, is not a viable means of increasing the ageing process rate, since the successful curing of *urushi* liquid sap requires very specific conditions in terms of temperature and relative humidity, and, as discussed in Chapter 3, the quality and durability of cured *urushi* can become impaired by too little or too much water content. Furthermore, this liquid-phase accelerated approach is suitable only for coatings that form films physically, that is, by solvent evaporation, rather than chemical reaction, as in *urushi*.

5.4 Ageing equipment used in conservation environments

When assessing the effectiveness of accelerated ageing, it is necessary to consider the variations in results obtained using different instrument types. Ageing equipment varies from laboratory to laboratory because apparatus is uniquely set up to meet the requirements of different experiments being carried out. The 'home-made' nature of these instruments means that consistency in conditions between institutions is improbable. A study of light-accelerated methods performed in six different institutions in the UK and the Netherlands by Saunders and Kirby[1] highlights the range of bespoke light boxes and chambers used. The conditions within the light-boxes surveyed by the authors are summarised in Table 5.1.

The study shows that the most common light sources include the use of fluorescent lamps over a range of 10,000-40,000 lux, the equivalent irradiance seen during a very clear, bright sky at midday. An overcast day may be measured at around 5,000 lux – the Commission Internationale de l'Eclairage (CIE) standard for an overcast sky, defined as the *total unobstructed illumination of an overcast sky measured at the horizontal plane* is assigned this value.[10]

Table 5.1: Summary of ageing equipment across UK/Netherlands institutions surveyed by Saunders and Kirby[1]

Institute	**Light source**	**Relative humidity/ temperature**	**Comments**
National Gallery	12 65W General Electric artificial daylight lamps, 22000 lux	36±4%, 25.5±1°C	
National Gallery	4 Philips Colour 84 fluorescent lamps = 14000 lux	Wide range available	Controllable climatic conditions
British Museum	500W Philips ML (mercury-tungsten discharge fluorescent lamp) (av.28000 lux)	51°C generated by lamps	Light fastness tester
British Museum	9 35W Philips Colour 84 fluorescent lamps = 40000 lux	37°C, achieved by two fans dissipating heat generated by lamps	No base
Tate Gallery	6 58W Philips Colour 94 fluorescent lamps = 20000 lux (in 1990), 13000 lux in recent apparatus	28-30°C, and 27-30% r.h., respectively	Permanent Perspex VE filter (eliminating <400nm)
Victoria and Albert Museum	150W tungsten lamp, fibre optic cable used to project 12mm diam. beam onto surface	21-26°C, and 32-49% r.h. ambient	Optivex UV filter used, exposed sample temp. raised approx 2°C above ambient
Courtauld Institute of Art	6 58W Philips Colour 95 fluorescent lamps = 20000 lux	Fan-cooled cabinet, av. temp. 32°C, r.h. 21%	
Stichting Restauratie Atelier Limburg	36W Philips Colour 96 fluorescent lamps = 10000 lux	20-24°C, 40-44%	

Saunders and Kirby[1] studied a range of colour changes in paper and textiles in order to compare these regimes, and, overall, some definite trends could be observed, noticeably that the filtering-out of the UV component reduced the extent of the colour change of the material. Also, the trends in the greatest and least amount of colour change were the same for each specified method. However, the results, whilst being useful for comparative purposes, are not conclusive owing to the differences in the ways in which the equipment is assembled, temperature fluctuations due to heat generated by light sources, and humidity conditions. The use of weatherometers, as used in the automotive industry, enables more control over these conditions. Outdoor accelerated weathering uses xenon-arc based sources, which are thought to most closely simulate UV-visible solar radiation compared to other artificial light sources.[11]

Light-ageing, as reported in conservation science work,[12] generally aims to create the same effect as if long-term exposure to daylight had occurred. In this work, fluorescent-bulb, mercury tungsten (HgW), and xenon-arc lamps were available (to variable extents), and lacquers were exposed to these sources to determine the method most suitable for preparing damaged *urushi* models for further analysis. Lacquer samples were compared in terms of appearance, morphology and chemistry.

Spectral characteristics

The various light sources used (summarised in Table 5.2) display different spectral characteristics. Fluorescent lamps exhibit diffuse illumination, since the inner surface of the fluorescent lamp is coated with a phosphor which also acts as a filter or diffuser. Consequently, the diffuse nature of this radiation means it is potentially less effective at causing damage to high gloss systems.[13] In xenon-arc lamps, the output is continuous from the visible part of the spectrum to far into the UV. Strong emissions are seen in the 800-1000 nm (IR) region. The chamber's temperature is 35°C, and the UV irradiance programmed to 0.5 W/m^2 at 340 nm. Some research indicates that tungsten lamps show the closest similarity to daylight.[13] The HgW lamp is held vertically and is contained in a protective metal casing, and light measurements taken in different areas of the container reveal a non-uniform light emission from different parts of the bulb. This system produces a high thermal load and a water-cooling system is required. Half of the output of such a light source is in the UV part of the spectrum, with a prominent emission at 366nm. 20% of the source output is measured as a continuous spectrum from 400-750 nm.[14]

Owing to the inconsistencies in light exposure, environmental conditions, and sample preparation, it is not possible to have a defined quantity of light exposure over a specified period of time to indicate the degree of ageing, however, clear overall trends of stabilities can become apparent from such experiments. According to Saunders and Kirby, the heat generated by lamps used in these accelerated ageing processes leads to an over-estimation of the effect of a particular quantity of light. Readings taken inside the Victoria and Albert Museum's HgW-lamp encasing, for example, show fluctuations in the temperature and relative humidity depending on the season, or even the time of day (absolute temperature range 35-50^{o}C; RH range 8-13% (RH data courtesy of J. Thei), since this equipment is not entirely encased and is subject to environmental effects. Clearly, there are limitations and inaccuracies associated with these ageing regimes.

5.5 Monitoring the accelerated ageing process

The outcomes of short-term and long-term ageing, and the use of different ageing sources, are compared here. In determining what actually constitutes damage to the surface, two end points were chosen. The first end point was determined by the surface changes measured by SEM and colour change, which was the period of time after which the surfaces were observed to have significant damage, as measured by cracking or colour change. Gloss was also measured for the samples, however, for the all methods with the exception of the HgW method, the changes were too subtle to register significant change over the initial ageing period determined. Sample numbers were restricted due to the limited availability of traditionally layered lacquer board samples. However, trends in behaviour of the lacquer exposed to each method are clearly shown and discussed here. A secondary end point was determined when the free films (8-15 micron thickness) were no longer able to be handled or cut without fragmenting; i.e. they were too brittle (Figure 5.1b). Since the samples were being prepared for solvent testing, the lacquer had to remain intact as the sorption tests required repeated removal to and from the solvent chambers. Therefore, the solubility tests were carried out using lacquers aged to the first end point.

The overall aim of this section of work was to determine whether artificial, accelerated conditions can produce a similar damaging effect to prolonged, natural ageing of *urushi* lacquer surfaces. In order to evaluate the state, quality and aesthetic of the lacquer, gloss was the first characteristic to be evaluated.

5.6 Appearance

In this work, the effects of thermal, light and natural ageing on *kijiro* lacquer films were compared. The effect of ageing on the increased fragility and curling of the lacquer that occurs as ageing progresses is demonstrated on a thin film (9 microns) in Figure 5.1. The range of ageing methods used are summarised in Table 5.2, and lacquer board samples were exposed to each method initially for a period of 0, 3, 6, 9, 12, and 20 weeks. The samples were removed and the gloss and colour changes were measured at each interval.


a) b)

Figure 5.1: A thin film of unsupported lacquer a) before ageing and b) after 36 weeks of exposure to a UV daylight simulator with polycarbonate filter.

Sample details

The board samples were prepared in 2006 on hinoki board using traditional methods, as discussed in Chapter 4, with a layer of hemp cloth, two grounding layers and three layers of lacquer. The final layer was polished with soft charcoal, and then with powder and oil (*roiro-shiage)*, in order to obtain a suitable control sample. The gloss and colour of the newly prepared surface was recorded as t = 0 weeks.

Table 5.2: Details of ageing methods used

Method	**Conditions**	**Maximum ageing time**	**Temperature (^{o}C)**	**Average Lux reading**
Natural ageing	Samples kept on a window sill, cycled light, ambient temperature, ambient humidity	12 months	Variable (range 16-21)	4,000 (over a 24 hour period)
UV daylight simulator	Polycarbonate filter/no filter	12 months	35	27,500 lux
Mercury-tungsten (HgW) source fadeometer	No filter, 366 nm (prominent wavelength), and 400-750 nm (20% of the source output)	5 months	39-44	30,000 lux
Xenon arc	340 nm; 0.5 W/m^2	4 weeks	35	341 lux
UVc source artificial ageing	No filter	20 weeks	31	n/a
Thermal ageing	Humidity kept at 60-75%	20 weeks	55-60	Nil
Aggressive atmosphere	CO2/formic acid-saturated atmosphere	20 weeks		
Naturally aged Japanese lacquer from a piece of 19th century screen has also been analysed for comparative purposes.				

5.6.1 *Urushi* lacquer gloss measurements

Gloss can be evaluated subjectively by the human eye; however the gloss meter can add quantitative values to this evaluation. Using a MICRO-TRI-Glos, multi-angle gloss meter, gloss reflection from the *urushi* surface was measured using specific illumination applied to the surface: at 20°, 60° and 85° angles to the normal, to determine the level of gloss or matt of the sample.

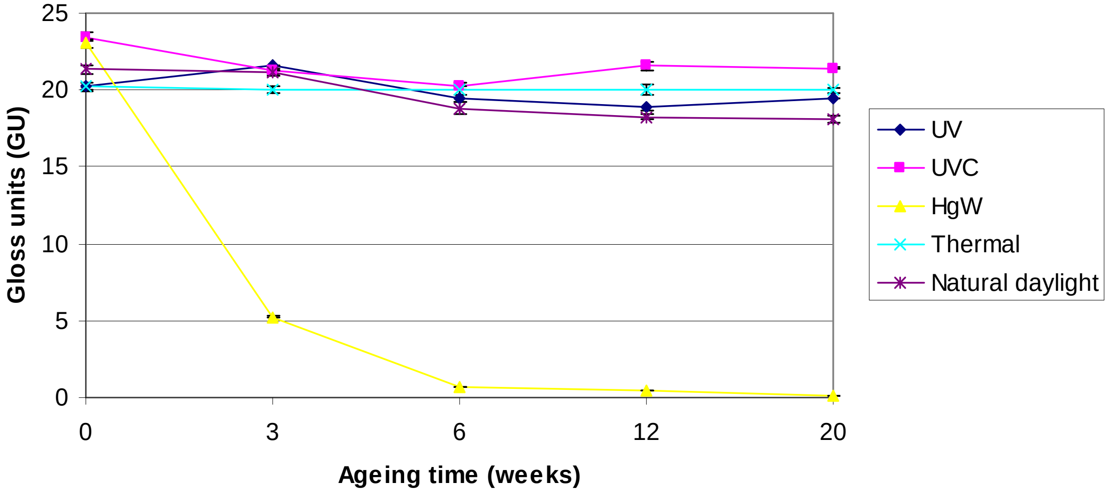
A light ray (incident ray) strikes the surface of the lacquer at an angle of incidence to the plane normal. Light rays leaving the surface of the lacquer (the reflected ray) are used to determine the angle of reflection. The reflection law states that the angle of incidence is equal to the angle of reflection. An incident ray reflects in a parallel form from a smooth, glossy surface resulting in specular (regular) reflection, therefore, for the high gloss lacquers the angle of illumination is equal to the angle of reflection. A rough surface or one composed of a semi-transparent material instead produces a diffuse (irregular) reflection. The aged lacquer sample is roughened on a microscopic level, and will therefore result in diffuse reflection of incident rays, due to multiple reflecting surfaces within the top damaged layer. As a result, a duller surface is observed compared with a new, glossy lacquer surface.

The particles within the lacquer coating may absorb some of the illumination, and pigments and impurities cause internal scatter and, therefore, diffusion, although the main (dominant) illumination is reflected in the specular direction. Some scattered light leads to a hazy yet glossy appearance. On matt surfaces, light is reflected in the specular reflection angle but also other directions. Smooth and highly polished surfaces reflect images distinctly – the incident light is directly reflected on the surface (in the main direction of reflection).

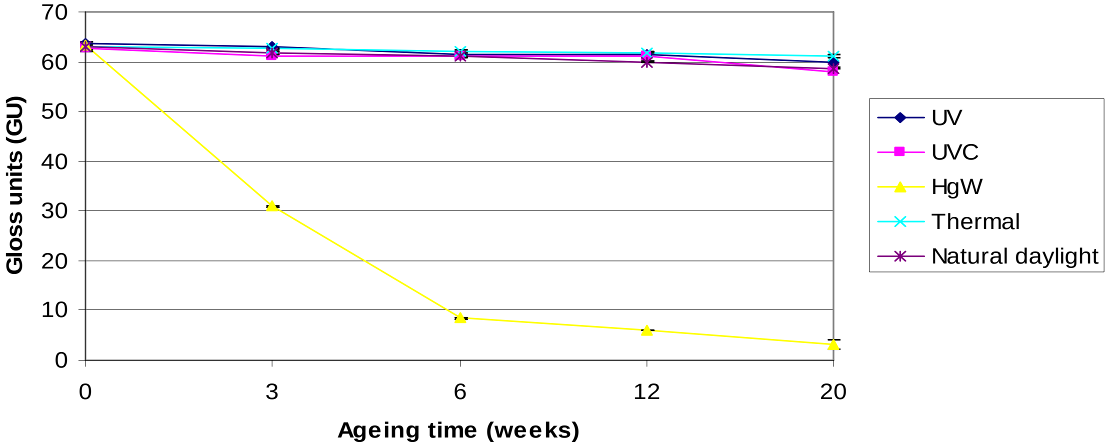
The instrumentation used is similar to that employed in industrial monitoring of paints and other coatings. The data obtained is used to assign a ‘gloss stage’ to the material according to the Trade practice in Powder Coater’s Manual VII[15], ranging from matt to eggshell, to semi-gloss and full gloss, where the latter is a smooth and mirror-like surface, and the matt surface gives readings <15 on a 85° gloss meter.

20/60/85°

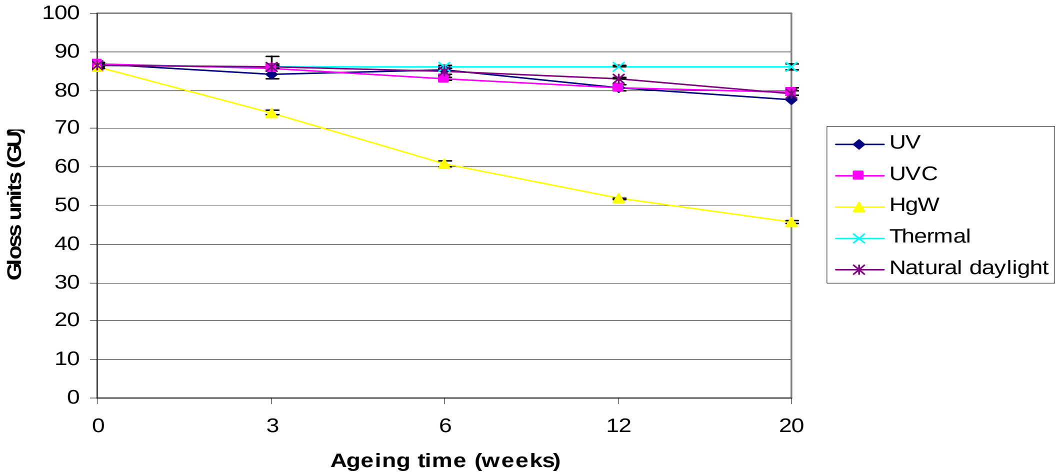
All three angles of illumination are required for this experiment since the lacquers ranged from glossy black to matt and brown, thereby showing a range of geometries. Calibration was carried out using highly polished black glass and a ceramic white tile. The expected outcome of this experiment is that as the lacquer becomes more damaged, the surface will become rougher, cracked or powdery and will increasingly scatter the radiation. All of the samples were initially measured using the 60° angle of illuminance, which is generally suitable if the outcome reading is 10-70°; however above this range the 20° was used, and below this range the 85° was used. Since the matt surfaces will scatter the reflected light, only some will be detected by the reflectometer sensor, and so different angles are used to determine the reflected light more accurately. Seven readings were taken on each specimen, and the effect of ageing on the lacquer's gloss is illustrated in Figure 5.2a-c.



a) Change in gloss units of aged lacquer measured at 20°



b) Change in gloss units of aged lacquer measured at 60°



c) Change in gloss units of aged lacquer measured at 85°

Figure 5.2: Change in measured gloss on lacquer surface (gloss units) over a total period of 20 weeks of ageing observed at a) 20°, b) 60° and c) 85°.

Observations

HgW has the most negative impact on gloss. The slight damage caused by the UV daylight simulator/UVc is evident from visual inspection. The smooth surface seems intact and has a slight noticeable dulling of the gloss for the UV daylight simulator/UVc, natural ageing or thermal ageing; however, some of their results fluctuate slightly over time. The errors are relatively small, as indicated by the error bars, and are tabulated in Appendix B. The sample area for gloss measurement is relatively large in comparison to other techniques used in this work (area, 16 mm x 4 mm). Unevenness on the surface caused by lower layers showing through (hemp cloth) may cause the fluctuations in the results over time. A cross-section taken by fluorescence microscopy of a section of the board aged by HgW for 15 weeks is shown in Figure 5.3, where the lower layers are still intact; only the very top layer (12 µm) displays damage. The reduction in gloss is rapid for the HgW but slow for both UV methods, since, as mentioned earlier, the diffuse UV radiation has a less damaging effect. As expected, control samples kept in dark conditions exhibit no change. There are limitations to this method, despite clear trends being observed. The monitoring of the lacquer colour change, with specular component excluded and included, requires a smaller measurement area, and may give clearer results.

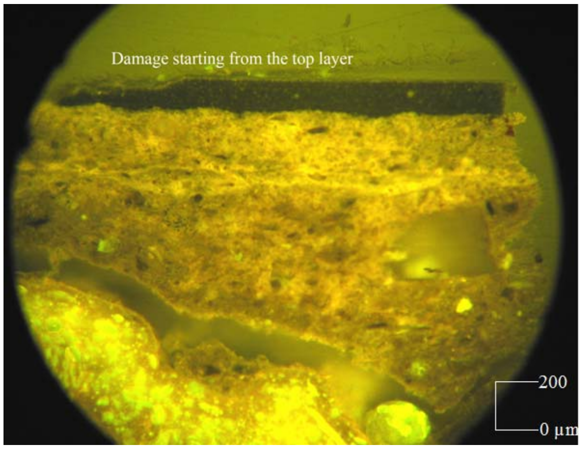


Figure 5.3: Cross-section of a lacquer board exposed to HgW for 15 weeks.

5.6.2 *Urushi* lacquer colour measurements

When inspected visually, there are clear changes to the surface of the aged lacquers: dulling and a colour change have taken place (the colour change is more obvious for the transparent films than for the boards). Colour was monitored as it changed over the period of ageing, with lightness (L*) used as the changing parameter; L* = 0, black; L* = 100, white. A positive L* refers to the brightness of the sample, whilst a negative one refers to the darkness of the sample. Hue value (h) defines the colour in terms of its red, blue, yellow and green contribution, and is calculated from a* and b* values. Positive values of a* refer to red hue, negative values are green, positive b* values are yellow, negative are blue. Overall colour change can be calculated by:

$$\Delta E^* = [(\Delta L^*) + (\Delta a^*) + (\Delta b^*)^2]^{1/2}$$

The colour measurements taken with exclusion of the specular component eliminates the light contribution due to gloss, therefore the colour values obtained here are independent of the glossiness of the new lacquer surface.

The first set of measurements was taken on an unaged piece of board which had been protected from light exposure. Ten 8mm diameter colour readings were taken using a Minolta Chroma Meter CR-2600 tristimulus colorimeter that uses the Commission Internationale d'Eclairage (CIE) colour parameters. The readings included those taken by SCI (specular component included) and SCE (specular component excluded).

Two naturally aged lacquer samples were also measured: Specimen A was taken from the back of a Japanese screen frame (19th c.) which had been protected to a certain extent from light; Specimen B was from the front of the same screen which exhibited a dulled and abraded surface (Figure 5.4). The results for effects of ageing on the measured lightness of the lacquer for SCI are shown in Figure 5.5.

Figure 5.4: Dulled and abraded naturally aged lacquer from front of 19th c. Japanese screen.

The average lightness (L*) SCI reading for A was 25.2 and for B was 26.7 and the SCE reading for A was 19.5, and B was 28.9. Comparing the SCI readings for naturally aged and artificially aged lacquers, the samples would reach the equivalent level of discoloration as an exposed lacquer (B) after 12 weeks of HgW exposure (according to the SCI data). This level of discoloration was not reached by the UV daylight simulator/UVc methods until around 20 weeks of exposure. The glossy deterioration, however, never reaches the same level for the UV daylight simulator-damaged samples, and there appears to be less surface disruption by this method of ageing compared to the harsher HgW source.

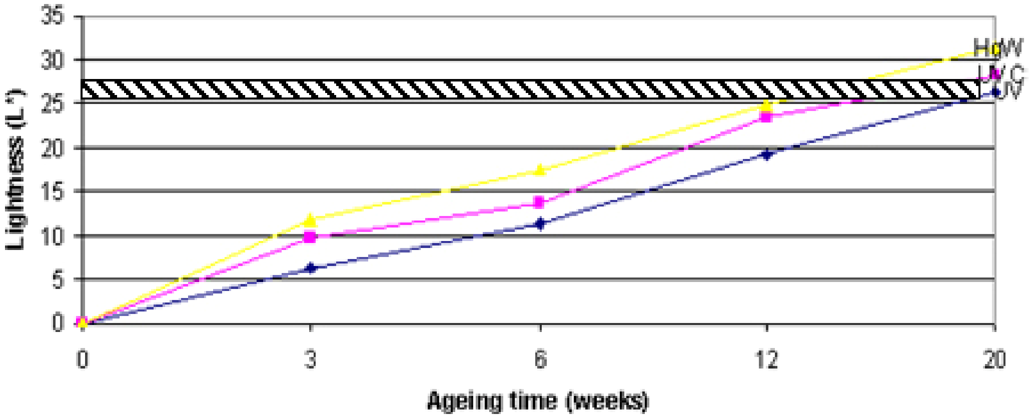


Figure 5.5: Mean lightness (L*) measure of aged *urushi* lacquer boards with specular component included; shaded band indicates L* for naturally aged lacquer.

5.6.3 Morphology

At each of these stages (i.e. 12 weeks and 20 weeks, for HgW and UV daylight simulator-damaged lacquers, respectively) the surfaces were carefully examined, along with the control (unaged) sample (Figure 5.6), using Scanning Electron Microscopy (SEM; Hitachi S3400-N variable pressure, acceleration voltage 15.0 kV). The UVc ageing method was not applied here since the chamber lamp was found to be uneven in its power output, and the samples in the chamber were observed to be receiving different amounts of radiation. Figures 5.7 and 5.8 compare the cracking in the 200-year-old naturally aged screen and the 12-week HgW aged sample, respectively. The cracking patterns are surprisingly similar, for example, the average spacing of a sample of 4 of the larger cracks measured 39.0 and 41.0 μm, respectively. The cracks are more sharply defined and have more uniform width in the HgW-exposed samples.

As discussed, the natural colour change measured by the lightness parameter, L*, correlated with approximately 20 weeks of filtered UV daylight simulator ageing, however, no significant morphological changes were observed by SEM, except for scratches probably caused during the polishing process (Figure 5.9). In fact, these are the only features on which to focus during the SEM experiment.

Although *urushi* lacquer aged under the xenon arc lamp for several weeks was not available for either colour or gloss measurements, it is still interesting to compare xenon arc-aged boards with the UV daylight simulation ageing over the same period by SEM. Xenon arc produces noticeable damage, shown in Figure 5.10, although no cracks can be seen – the surface appears instead to be of a powder-grain consistency, due to initiation of the breakdown of the grain structure, which was discussed in Chapter 3, illustrating the different responses of the lacquer surfaces to different ageing mechanisms.

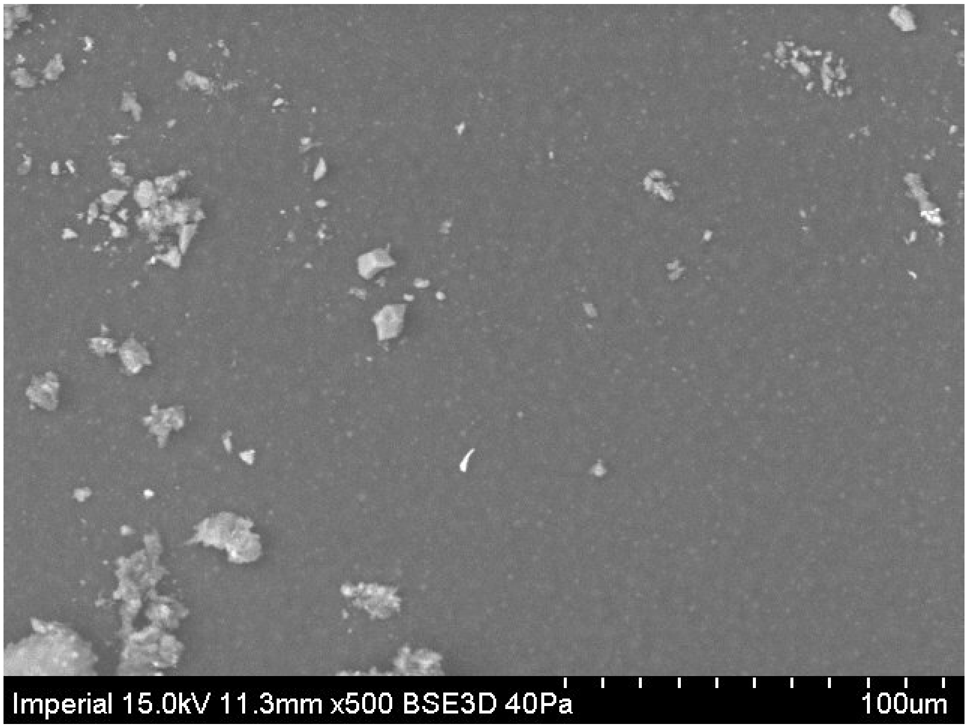


Figure 5.6: Scanning electron microscopy image of unaged lacquer (control sample) showing no cracks, the dust on the surface is the only means of focus.

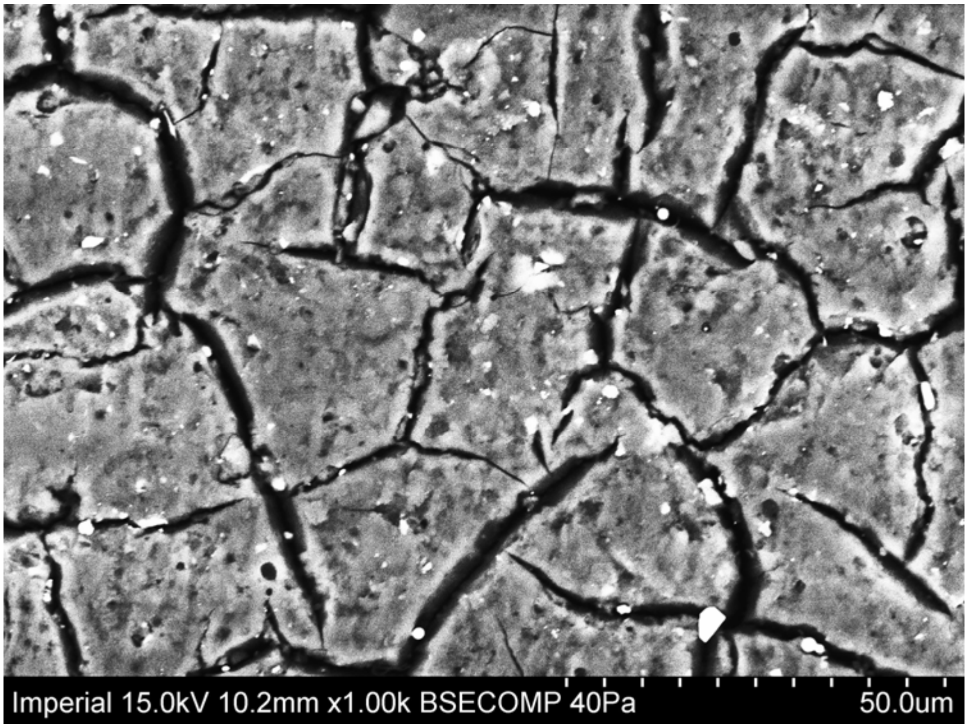


Figure 5.7: Scanning electron microscopy image taken of the surface of a naturally aged Japanese screen (approximately 200 years old).

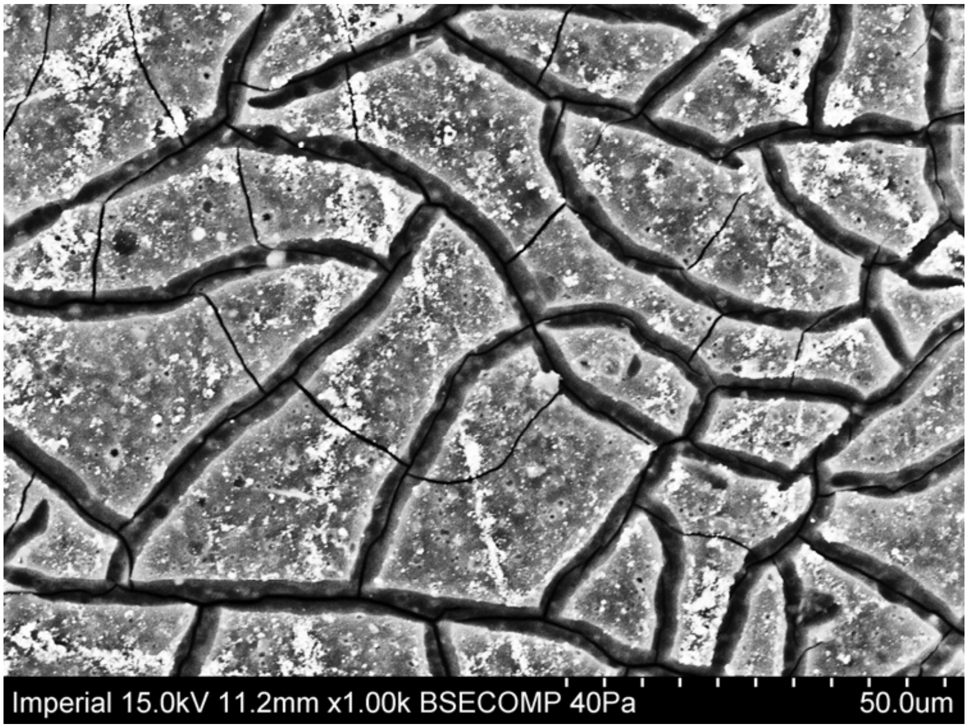


Figure 5.8: Scanning electron microscopy image taken of the surface of a lacquer sample aged for 12 weeks under an HgW lamp.

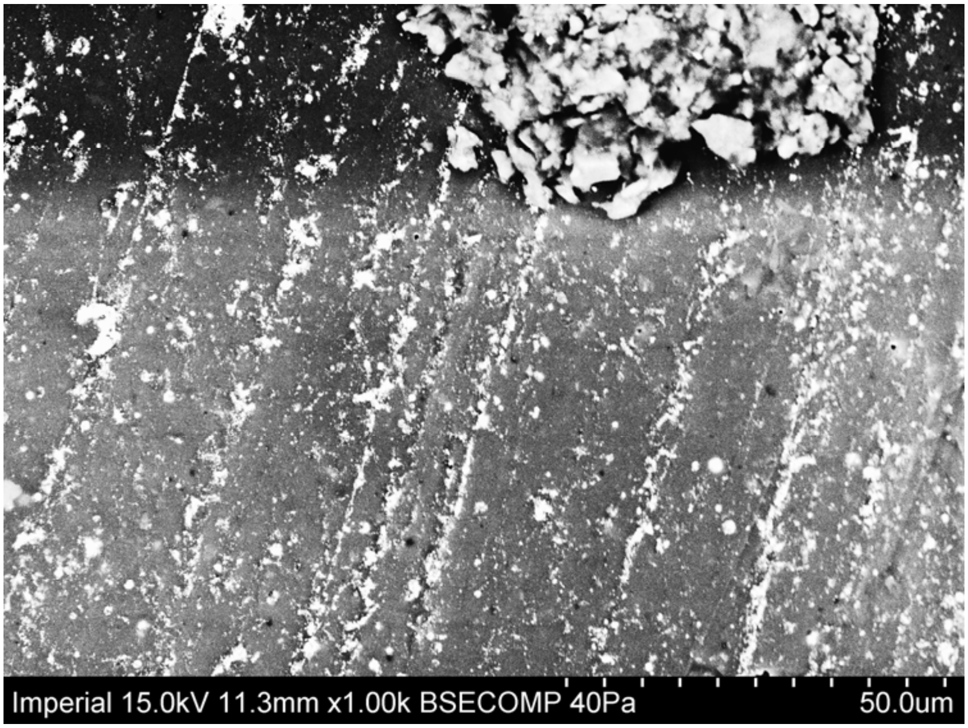


Figure 5.9: Scanning electron microscopy image taken from the surface of the UV daylight simulator-damaged *urushi* for 20 weeks.

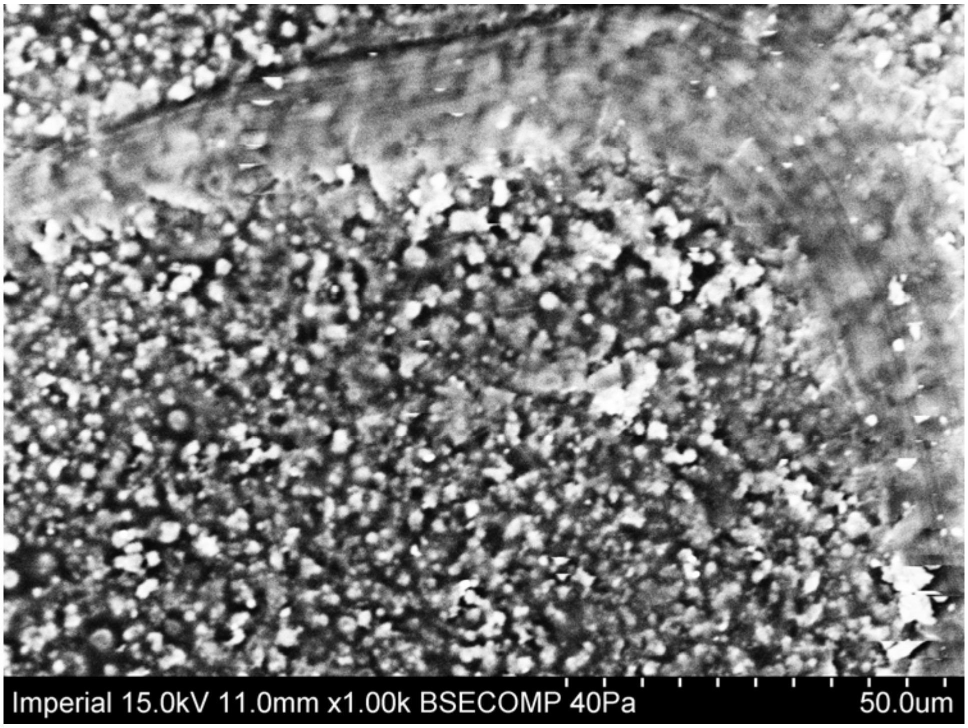


Figure 5.10: Scanning electron microscopy image taken from the surface of *urushi* aged under xenon-arc lamp for 20 weeks.

The diffuse illuminance source in the UV daylight simulator does cause a decrease in colour and a very slight decrease in gloss, although cracking is not visible after 20 weeks. At this point, only the beginnings of damage are seen, suggesting that a more prolonged exposure might produce disruption of the surface, presumably including cracking eventually, although no evidence for this speculation has yet been acquired. These samples were analysed by py-GC-MS to determine whether any chemical changes were taking place, as discussed below.

5.7 Summary of surface changes

After 13.5 weeks of HgW ageing or 31 weeks of UV daylight simulation exposure, the films fragmented upon being handled, cut, or when removal of the film from the glass was attempted. The HgW-damaged samples flaked off the slides by this stage, whereas the UV daylight simulator-damage caused the films to curl away from the surface due to the tension on the upper surface of the film. On handling, however, both types splintered. This result was taken to be the secondary end point of degradation, no further ageing of the samples would be useful for solubility tests beyond this point. The approximate exposure for both samples is calculated as a cumulative exposure of 68 x 10^6 lux hours for the HgW samples at 13.5 weeks, and 14.3 x 10^6 lux hours for the UV daylight simulator samples after 31 weeks. As discussed in Chapter 3, the maximum exposure (lux) before damage is observed in *urushi* lacquer that has been stored in museum conditions, is 40 years at 100 lux or 80 years at 50 lux, based on an exposure of 8 hours per day[16] (approximately equivalent to 11.7 x 10^6 lux hours), therefore the exposure of the artificial sources and natural ageing are in the same order of magnitude. This is the maximum cumulative exposure recommended for lacquered pieces,[16] but not necessarily the point at which degradation might commence, and the heat exposure of the artificial processes causes additional changes to the surfaces. For comparison, the HgW subjects had received 84.6% more exposure than this limit, and the UV daylight simulator samples received 18.5% more exposure than the recommended maximum at the point at which they could no longer be handled as solid films. The degree of exposure to light of lacquers not kept in museum conditions cannot be known and are likely to be very different to those kept in carefully controlled conditions.

The HgW lamp is, as discussed earlier, a harsh source with no filtration of light below 350 nm. In summary, in terms of cracking, only the HgW source generates a surface with extensive cracking that is remotely comparable with the naturally aged sample. Moreover, lacquer pieces that had been well looked after would, in general, not be exposed to harsh conditions such as these. It is, therefore, necessary to investigate not only the surface changes, but also the developments in terms of chemical changes in the lacquer layers during ageing.

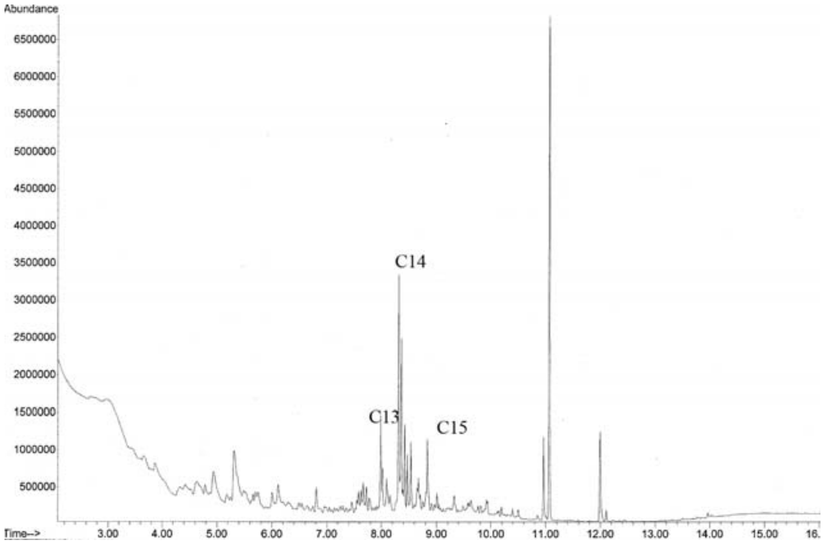
5.8 Urushiol side-chain degradation and functional group changes

5.8.1 Pyrolysis gas chromatography-mass spectrometry

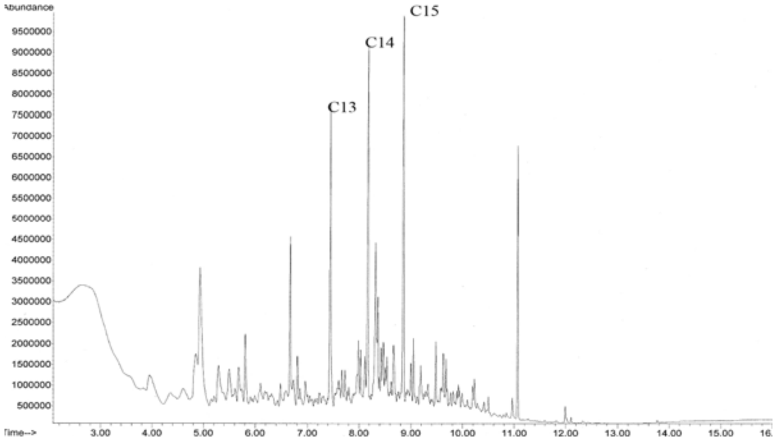
Experimental conditions: *Kijiro* films were aged in the UV daylight simulator for 23 weeks (4,000 h) under polycarbonate filter, and also for 59 weeks (10,000 h). Unaged films and films aged under natural daylight (behind glass) for 23 weeks were analysed for comparison. The decomposition of the urushiol side-chain was determined by pyrolysis

GC-MS at 450°C and 600°C following TMAH-derivatization according to the method described in section 4.3.

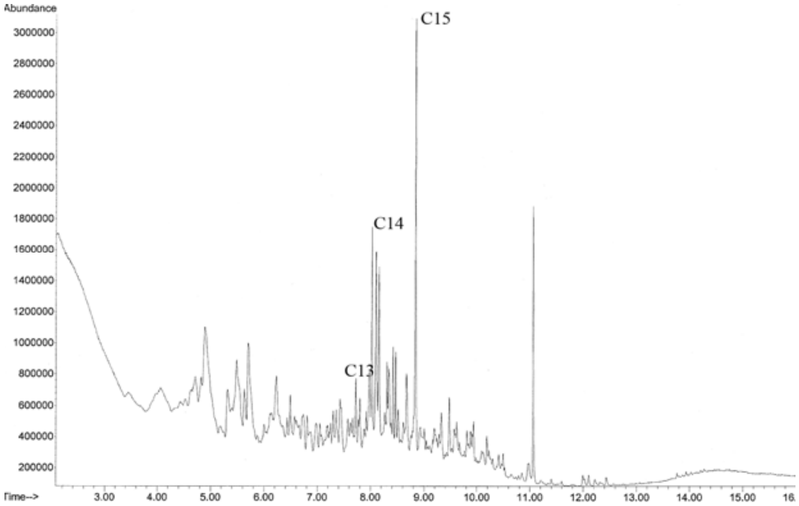
The total ion chromatograms (TIC) for each sample are shown in Figure 5.11. Due to restrictions in terms of instrument accessibility only the UV daylight simulator, unaged and naturally aged films were analysed here.



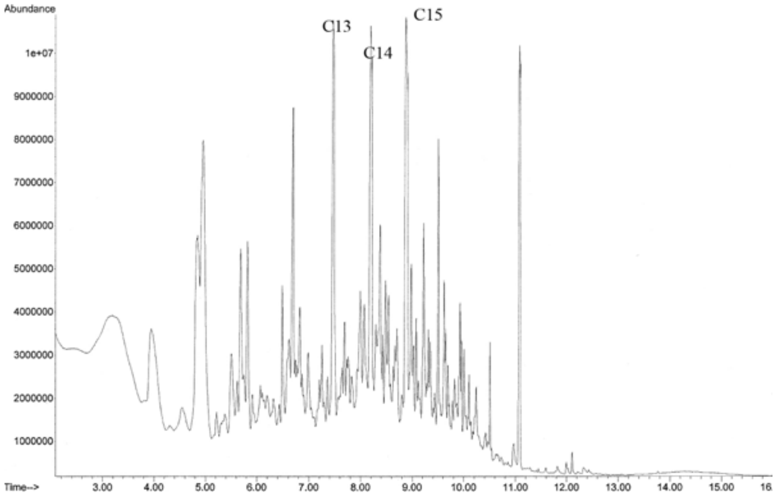
a) Unaged



b) Daylight (behind glass)



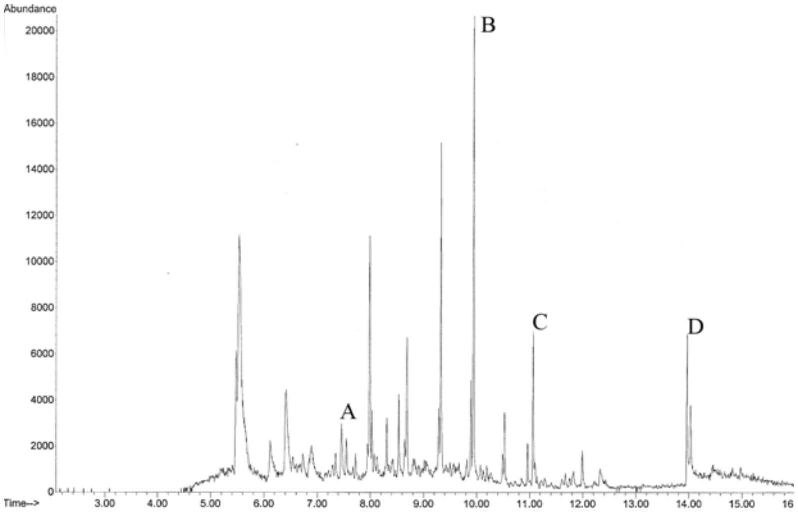
c) UV aged (23 weeks)



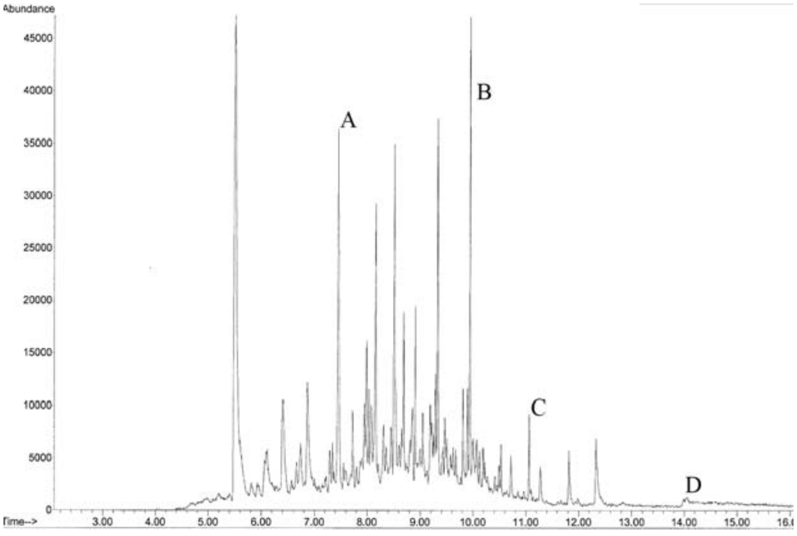
d) UV aged (59 weeks)

Figure 5.11: Total ion chromatogram of the *kijiro* films at various ageing stages: (a) unaged *kijiro*, (b) daylight ageing for 23 weeks (window as filter), (c) UV daylight simulator 23 weeks with filter, (d) UV daylight simulator 59 weeks with filter.

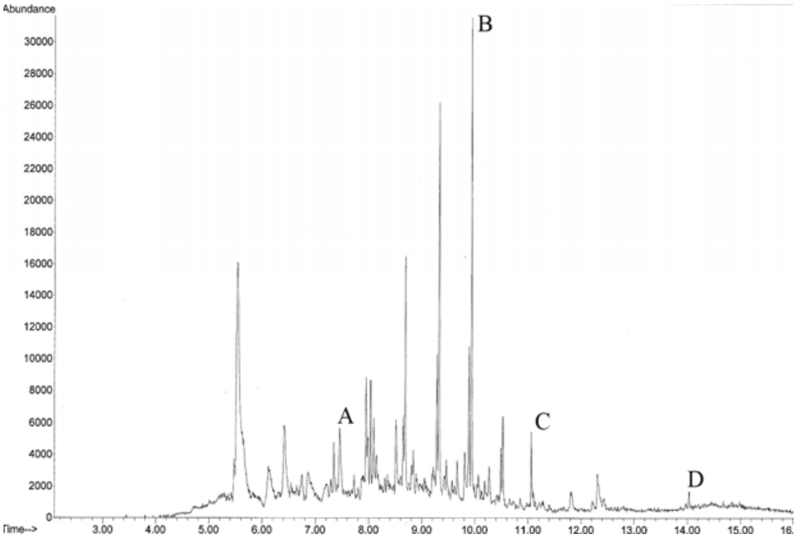
The TIC for the range of aged samples are very different. The longest carbon-chains remain in high abundance, but the shorter carbon chain pyrolysis products are seen to vary greatly. The *urushi* pyrolysis products including alkanes and alkenes were determined by the MS data; and the peaks at C13, C14 and C15 are highlighted in the spectra in Figure 5.11, and attributed to tridecane/tridecene/heptylphenol, tetradecane/tetradecene, and pentadecane/pentadecene, respectively, which are pyrolysis products described by Lu *et al.*[17] The C15 fragments were seen in higher relative abundance as the ageing progressed, as with the C14. The most harshly aged sample (Figure 5.11d) displays shorter carbon chain products as the structure is broken down, particularly at the unsaturated points of the urushiol side-chains. The high yields of C14 alkanes/alkenes are explained by Niimura as being the result of 'preferential cleavage of terminal alkyl and monoenyl side chains at the beta-position to the aromatic ring, respectively'.[18] The 136 m/z ion was isolated, and the spectrum for each ageing technique is shown in Figure 5.12.



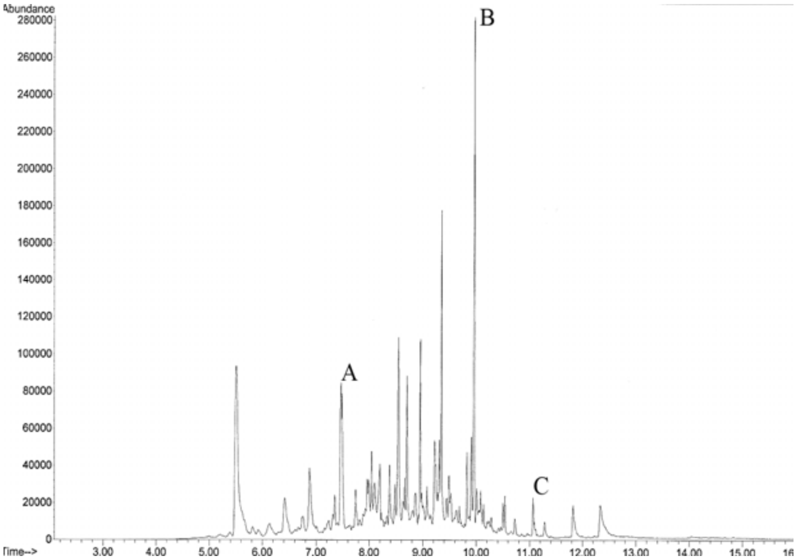
a) Unaged



b) Daylight (behind glass)



c) UV aged (23 weeks)



d) UV aged (59 weeks)

Figure 5.12: m/z 136 ion chromatograms for *kijiro* lacquer at various ageing stages: (a) unaged *kijiro*, (b) daylight ageing for 23 weeks (window as filter), (c) UV daylight simulator 23 weeks with filter, (d) UV daylight simulator 59 weeks with filter.

The main peak pairs of alkyl phenols and alkenylphenols for unaged *Rhus vernicifera* lacquer have been determined previously.[17,19,20] Aged lacquers, such as those collected from ancient pieces have been analysed using this method, however there is no mention in the literature of artificially aged lacquer. Peaks A-D (see graph) are identified as the following pyrolysis products: butylphenol and butenyl phenol (A, 7.5 min), heptylphenol and heptenylphenol (B, 10 min), decylphenol and decenylphenol (C, 11 min) and pentadecylphenol and pentadecenylphenol (D, 14 min).[20]

The structures with the longest side-chains are the pentadecyls which are abundant in the unaged lacquer, being attributed to the urushiol monomer. Figure 5.12d indicates that there is a relatively high abundance of the heptyl and butyl alkyl and alkenylphenols (B & A), however the pentadecyls (D) are completely absent from the 59-week-aged by UV daylight simulation. That said, the overall total ion chromatogram (TIC) shown in Figure 5.11d, shows long-chain alkanes and alkenes are present at abundance high enough to be detectable in the sample, including tridecane, tetradecane and pentadecane and their corresponding alkenes, even for the most prolonged ageing period, formed by the breakdown of the saturated side-chain close to the aromatic ring. The alkenes are present in less abundance but the presence of long chains result from dimerization and autoxidation. Shorter chain enyl/alkyl phenols such as butyl (7.5 mins) and heptyl (10 mins) components are relatively high abundance compared to the longer chain (pentyldecyl and decyl-) 2- and 3-alkenyl/alkyl phenols.

The effect of prolonged artificial ageing by UV daylight simulation seems to be a breakdown of the side-chain of the urushiol to shorter side chains – C4 and C7 are shown to be in high abundance. Compared to the natural ageing by daylight exposure, the butyl (C4 chains) are in lower abundance in the samples aged by 4,000 h UV daylight simulation, but after a more prolonged ageing time, 10,000 h, the abundance of these side-chains is significantly increased. Simultaneously, the long chain alkanes and alkenes (the unsaturated appear to a lesser extent as shown by the much shorter peak, as they are more prone to oxidation) are seen even in the lacquer aged for 10,000 h, because of the oxidation processes and dimerization of the urushiol formed by C-C coupling of the urushiol side-chains.

Further indications of side-chain degradation that progress with ageing were obtained by IR spectroscopy of *urushi* thin films.

5.8.2 Functional group changes determined by infrared spectrometry

FTIR analysis of unaged, naturally aged and accelerated ageing in urushi lacquers

Experimental details: Perkin-Elmer Fourier Transform Infrared Spectrometer, 16 scans. *Unaged kijiro:* The main peaks observed for the unaged *kijiro urushi*, Figure 5.13a, were hydroxyl (water) at 3412 cm^{-1}, and CH stretches at around 2926 cm^{-1}, neither of which changed significantly over the course of 52 weeks, where films were protected from light. Peaks are seen at 1620 cm^{-1} with shoulders at 1656 cm^{-1} attributed to *o*-benzoquinone, and the stretch at 1724 cm^{-1} indicates carbonyl functionalities. The polysaccharide peaks at 1078 cm^{-1}, and a sharp peak at 992 cm^{-1} indicate a conjugated triene (the olefinic bands of the dimethylurushiol)[21] which decreased in intensity over the space of a year, possibly indicating oxidation occurring in the side-chains. There was also a slight broadening of the hydroxyl peak.

Aged kijiro – natural daylight: After 52 weeks, with the films being stored in ambient laboratory conditions, in terms of light and humidity, hydroxyl peaks (3422.9 cm^{-1}) remain strong, as do the carbonyl peaks. There is a marked reduction in the intensity of the carbon-hydrogen stretch (2933.6 cm^{-1}). (Appendix C). Peaks are still seen at 1093.4 cm^{-1} for the polysaccharides, attributed to the polysaccharide groups, however they have become weaker, and the triene indicator is very weak, although still detected. These changes could be attributed to a continued oxidative polymerization reaction occurring in these active sites, or possibly due to some oxidation occurring in the side-chains where the *urushi* is known to start degrading.

Light aged kijiro: Kijiro urushi was aged up to 20 weeks using a HgW lamp source (Figure 5.13d), and UV daylight simulator (Figure 5.13i) and the IR spectra was recorded at intervals.

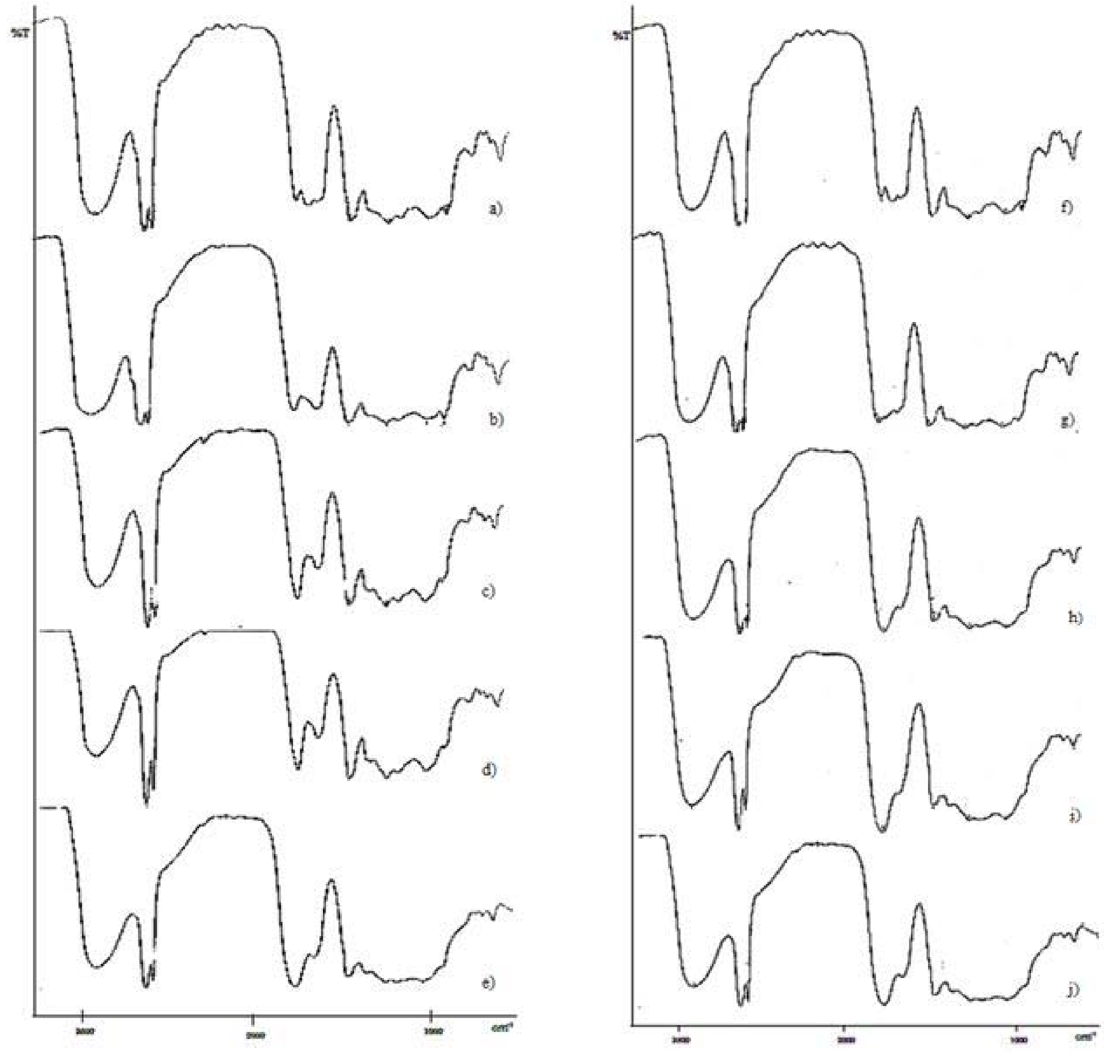


Figure 5.13: FTIR spectra of *kijiro urushi* lacquer films at (a) no ageing, (b) 4 weeks of ageing under HgW light source with no filter, (c) 10 weeks ageing, (d) 20 weeks ageing and (e) 20 weeks natural daylight ageing, (f) no ageing, (g) 4 weeks of ageing under UV daylight simulator with filter, (h) 10 weeks ageing under UV daylight simulator with filter, (i) 20 weeks ageing under UV daylight simulator with filter and (j) 20 weeks natural daylight ageing for comparison.

After 4 weeks of natural ageing, the peak at ~993 cm^{-1} is still detected; however after 10 weeks of HgW and UV daylight simulation, and 20 weeks of natural daylight ageing, this peak is no longer present, confirming that deterioration has occurred in the previously saturated urushiol side-chains. No changes in the broad OH peak around 3412 cm^{-1} were observed during UV daylight simulation ageing and, therefore, it can be assumed that the loss of free water caused by this method is negligible. There is a slight sharpening of the broad OH peak on spectra taken for 10-20 weeks of the HgW ageing that could suggest dehydration is occurring (~40^{o}C); visual inspection and handling of the lacquers aged for over 10 weeks does suggest a loss of the plasticizing water molecules (discussed in Chapter 3), as the film is brittle. When compared to the spectra for the unaged sample, there is no difference in the peaks around the 3400 cm^{-1} area, suggesting negligible water in the film. Carbonyl stretches become more defined as artificial ageing progresses for both methods.

The stretches at ~1620 cm^{-1} (1650 cm^{-1}) and ~1720 cm^{-1} are well defined after 10 weeks of HgW exposure, however, for the UV daylight simulation method, the peaks are not as clearly defined even after 20 weeks of exposure. Surface changes, including oxidation processes that generate carbonyl groups, are observed as clearly defined peaks in the shorter-term mercury tungsten experiment, and less defined peaks in the UV daylight simulation source experiment. This may correlate with the observation that the UV daylight simulation source generates less morphological surface change in terms of cracking than HgW does, even after 20 weeks of exposure.

The presence of free water was studied in films stored in a vacuum oven for 3 days at 120^{o}C (Appendix D), along with those kept in a desiccator over P_2O_5 for three days (Appendix E). The results show that the exposure to heat causes a shift in the position of the OH peak to 3062 cm^{-1}, and a much sharper, less intense peak is observed. The side-chain conjugation is still intact in this sample; however, the free water present appears to have been driven out. The P_2O_5 desiccated samples, however, show little change, indicating that heat is required to drive the water molecules out of the polymer.

A range of lacquers were also analysed by thermogravimetric analysis (TGA) on a Perkin Elmer Pyris 1 Thermogravimetric analyzer, in nitrogen. Figure 5.14 shows that there is no mass loss at 100°C, indicating a negligible volume of mobile water molecules within the film; degradation appears to begin at 190°C.

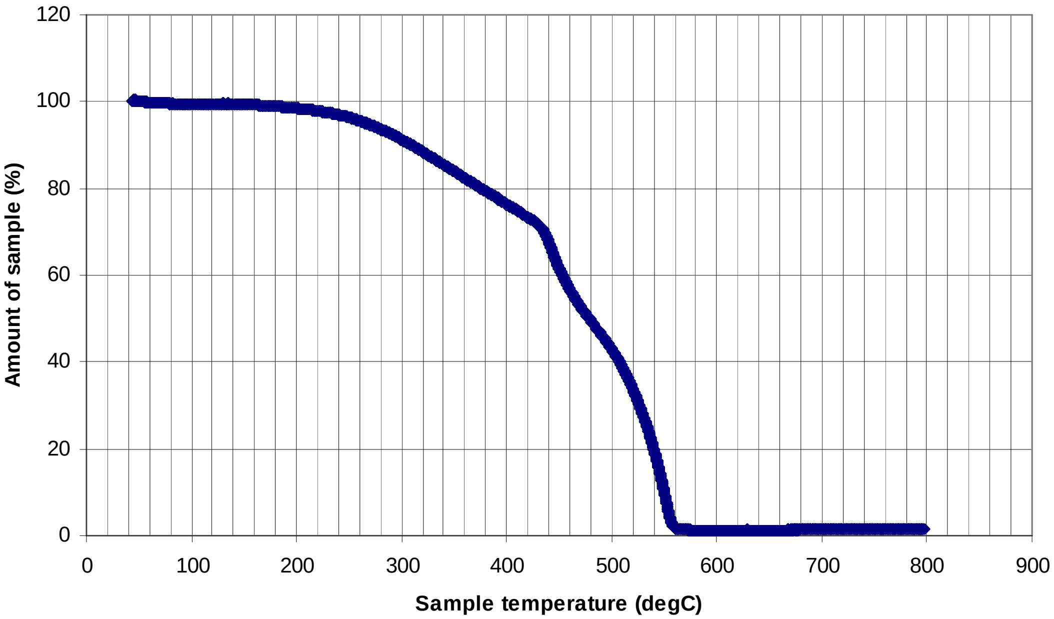


Figure 5.14: Thermogravimetric analysis of lacquer aged for 8 weeks by unfiltered HgW.

Uncured lacquer

The uncured sap was also analysed by FTIR, undiluted, between KBr discs (Table 5.3). The main differences are seen around the area of the carbonyl peaks: the carbonyl peaks at 1621 cm^{-1} with a shoulder at 1648 cm^{-1} are possibly due to an urushiol *o*-benzoquinone, whereas the 1721 cm^{-1} aldehyde groups are seen in the cured film (Table 4.3). The unhardened film displays two sharply resolved peaks at ~1621 cm^{-1} and 1596 cm^{-1}, possibly due to the C=C bending in the aromatic rings. The intensities of the peaks and their resolution, particularly around the carbonyl region, are the main differences between the cured and uncured, as expected, since oxidative polymerization increases the presence of carbonyl groups within the surface upon curing, as discussed in Chapter 3.

Table 5.3 Main functional groups observed for uncured lacquers by FTIR (KBr discs)

Main groups	*Oso hen*	*Roiro hen*	*Kijiro*	*Sakari hen*	Raw (*ki*)
Uncured lacquer					
Hydroxyl	3427.7 cm^{-1}	3408.9 cm^{-1}	3407 cm^{-1}	3390.3 cm^{-1}	3413 cm^{-1}
C-H stretches	2854.7 cm^{-1}	2854.6 cm^{-1}	2852.3 cm^{-1}	2854.0 cm^{-1}	2858.1 cm^{-1}
Phenyl ring/quinoid band	1622.6 cm^{-1} 1596.0 cm^{-1}	1621.1 cm^{-1} 1596.0 cm^{-1}	1622 cm^{-1} 1596.2 cm^{-1}	1622 cm^{-1} 1595.0 cm^{-1}	1621.6 cm^{-1} 1595.9 cm^{-1}
Polysaccharide (glycosidic bond)	1076.8 cm^{-1}	1079.6 cm^{-1}	1078.9 cm^{-1}	1068.6 cm^{-1}	1077 cm^{-1}
Triene (conjugated)	982 cm^{-1}	982 cm^{-1}	981 cm^{-1}	982 cm^{-1}	981 cm^{-1}

Naturally aged lacquer: museum specimens

IR spectra obtained from the Mazarin Chest by Perkin Elmer (Figure 5.15) using Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR; transmittance IR were not carried out as the sample was a solid, non-transparent piece) shows the main absorbance bands occur at 3289 cm^{-1}, 1733 cm^{-1}, 1645 cm^{-1} and 1100 cm^{-1}.

The main difference between this spectrum and that of the artificially aged sample, is the sharpness of the hydroxyl band (3289 $\text{cm}^{-1)}$, the latter samples being less intense and less broad, which indicates the loss of free, or mobile, water molecules over the prolonged ageing period, and therefore, a complete loss of plasticizing molecules. This sample was taken from the border edge of the Mazarin Chest (Figure 5.16).

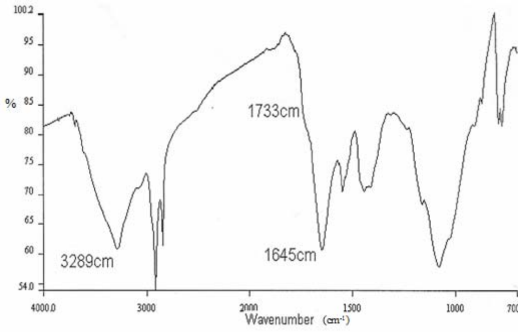


Figure 5.15: Perkin Elmer ATR-FTIR spectra taken from Mazarin Chest sample.


Figure 5.16: Site of sampled lacquer.

FTIR is a useful means of monitoring the change in functional groups of free films, provided the samples are not too thick. Raman spectrometry was attempted but yielded only graphitic peaks - the method is too destructive to the sample. Carbon forms as the polymer degrades in the laser beam, and the effects of fluorescence interference were also problematic.

IR analysis of components extracted from cloths used in the cleaning of the chest and extracted under high humidity, by KBr disc (Perkin Elmer FTIR) gave a strong sharp peak at 3426.0 cm^{-1}, a weak sharp peak at 2934 cm^{-1}, a medium-strong peak at 1636.4 cm^{-1}, medium peak at 1384.5 cm^{-1}, a broad weak-medium peak at 1028.3 cm^{-1} and a short, broad peak at 559.9 cm^{-1} (Appendix F). This indicates that the upper layers of degraded lacquer are partly water-soluble, and this therefore indicates that water cleaning will result in the loss of some of the original, albeit degraded, material. As the lacquer degrades, it is expected that small fragments will be more easily lost from the surface, although LC-MS (positive ion electrospray detection) analysis indicates that large components are present in the water-extracted components of the aged lacquer. One of the spectra obtained (see Appendix G) shows the presence of large fragments (>300) which may correspond to oxidised urushiols, and the fragments seen at >700 may indicate the presence of dimerized urushiol components.

5.9 Discussion

Despite the limitations, results from artificial ageing can aid our understanding of the mechanisms and timescales of naturally aged processes. Preliminary investigations indicate that there are difficulties associated with each acceleration method; however, the use of a mercury-tungsten lamp (HgW) and UV daylight simulation produces significant and measurable changes, albeit at different rates and with different outcomes – neither method produces samples which exactly match the properties seen in a naturally aged specimen. The results are, therefore, useful in determining trends only, and will be regarded as such for application to the solubility experiments, in subsequent chapters.

When focusing on surface topology, only the HgW-arc lamp produces a cracking effect which is subjectively comparable to the cracking seen on long-term, naturally aged specimens. This source generates a reasonably high temperature (~40°C) around the sample, which is likely to contribute to the surface damage and the dehydration. The samples flake on handling due to the loss of plasticizing water and the presence of cracks. The increased crosslinking reduces the flexibility of the films, making the structure more brittle. The shorter wavelength radiation (366 nm being a prominent emission from this source) generated by the HgW lamp creates harsh conditions that also cause breakdown of the surface integrity.

The UV daylight simulation sample surfaces were affected to a lesser extent, as reflected in the SEM analysis, gloss and colour experiments: no cracking was yet visible after 20 weeks of ageing even though the samples were more fragile and discoloured. Infrared spectroscopic analysis of the saturated side-chains showed that the conjugated trienes were reduced after the first 10 weeks of HgW-ageing, after which time a clearer resolution of carbonyl functionalities were observed. However, the side-chain conjugation functionalities seemed to reduce on UV daylight simulator-exposure after only 4 weeks exposure, indicating that rapid changes were taking place with the latter ageing method, despite the absence of cracks after the initial exposure time. The resolution of the carbonyl functionalities is improved for both methods between 10-20 weeks of exposure, indicating the production of more carbonyl groups, in species such as the dibenzofurans, resulting from increased oxidation taking place promoted by both ageing lamps.

UV daylight simulation promotes changes on the molecular level, as shown by IR analysis, and the extensive changes are also observed in the py-GC-MS experiments, which indicate a breakdown of the side-chains as well as formation of long-chain alkanes/alkenes due to photo-oxidation. The brittleness of the previously pliable films, and their colour change on ageing (Figure 5.1) show that a significant change occurs over 20 weeks of UV daylight simulation, at least in the upper 10 microns.

In terms of preparing samples for solubility tests, both UV daylight simulation and HgW sources generate vulnerability in the films, in terms of polymer breakdown, and production of defined crevices, respectively, both of which will make the lacquer more susceptible to solvent uptake and retention.

An important consideration when selecting a suitable ageing method was the availability of the equipment in terms of the space that could be occupied, and the accessibility. Clearly, the diffuse illuminance of the UV daylight simulation source is a less harsh ageing method than the HgW, causing less visible breakdown of the surface, and leaves the surface more or less physically intact. However, since the UV method was more accessible, both the HgW and UV daylight simulation will be used in order to prepare the samples for solvent-polymer interaction analysis, as a large number of samples are required for this investigation. In any case, the use of HgW ageing is limited in terms of space, consistency in terms of intensity of the light source throughout the instrument, and a high temperature that might cause thermal effects in addition to light-source effects.

Drawbacks to other ageing regimes

During this work, other ageing regimes were briefly evaluated. The UVc harsh ageing source displayed a small change in terms of colour and gloss change, however the method displayed too much inter-sample variation, depending on where the samples were put in the lightbox. This was assumed to be due to an uneven emission of light from the tube lamp, and, therefore, this method was not continued with. Thermal ageing was also investigated, using humidity cycling and continuous high temperatures. However, since the experiments were carried out in a sealed oven, and an absence of light, no changes were observed. As previously determined, light is required to initiate the photodegradation of this material. Xenon-arc was attempted for a limited number of experiments; however insufficient data were obtained due to restrictions with the instrument availability.

This work has provided an indication of the degree of exposure to various light sources that is required to produce specific changes in terms of the damage to gloss, colour, molecular changes and cracking of the surface, and these results are compared with damage that has occurred naturally over a prolonged period on a fairly well-protected and well-treated piece. Natural ageing cannot be accelerated; the naturally occurring processes must be compromised in producing damaged materials with which to work, at least within the scope of this project. The accelerated ageing of lacquers is an on-going project at the Victoria and Albert museum at this time; the results of their study are anticipated with interest.

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Chapter 6

The use of solvents as surface cleaning agents

The accumulation of dirt, dust and non-original materials within the top layers of a light-damaged, cracked surface can contribute to its impaired condition over the years. The damage it contributes to the aesthetic of the piece means that it is usually considered necessary to attempt removal of the debris. Current treatment strategies for removing aged, discoloured and non-soluble varnishes or oils, which have altered chemical composition over time, involve the use of a range of solvent types. Several obvious difficulties surround the use of some organic solvents on vulnerable surfaces, including the potential endangering of the original material beneath, and the practicality of using harmful substances in the conservation studio. The careful selection of a suitable solvent for the cleaning a specific material is, therefore, required.

6.1 Historical use of solvents

Three main solvent types stand out in the historical literature involving the cleaning of objects: water (usually with detergent), alcohol and turpentine. Experimental cleaning of oil paintings and textiles was reported from 17th century, and included the use of soapy water, alcohol (warm beer) and 'oyle of turpentine'.[1] A study of solvent use in varnish production reveals that non-water based chemicals were increasingly used throughout the 18th and 19th centuries in the field of art conservation and materials preparation, being refined around the time of the Industrial Revolution, for the dissolution and dilution of a range of substances to create protective and decorative coating materials. A brief historical background to solvent use and availability with particular regard to surface preparation and cleaning is discussed here. This chapter will also discuss why solvents are potentially useful in conservation cleaning, and the disadvantages associated with their use.

The value and utility of solvents was appreciated by artists developing new techniques and preparations during the late 18th century. According to Tingry (1804) "every real solvent changes the form and modifies the nature of the substance which it lays hold of".[2] Their uses were wide-ranging and a variety of solvents were available to 18th century varnish makers, including alcohol, known as rectified spirits of wine, ether, essence or oil of turpentine, ethereous essence of rectified spirit of turpentine, oils of spike and oil of lavender. Such solvents have been used historically to prepare varnishes from resins and gum materials as discussed in Chapter 2. These solvents have also been used in the conservation cleaning of surfaces, and some conservators have even claimed that they can be used in the successful discrimination between aged materials, for example *urushi* and japanning (European lacquer).[3]

Historical use of solvents: the preparation of varnishes

Alcohol: In the 1300s alcohol was referred to, in the literature, as 'burning water', since it was literally viewed as a water that burned, or 'water of life' due to its preservative qualities.[4] High quality alcohol was an essential component of the thriving French perfume industry from the 16th century, and the purity of alcohol was also crucial in the varnish-making process, requiring repeated distillation – an important alchemic process at the time. Wine was used as the starting material; the first distillation yielded brandy, a weak alcohol, although repeating the process several times gives purer alcohol, referred to in Tingry's text as 'rectified spirit of wine'. The strength of alcohol could be altered depending on the volume of water added. Weak alcohol was useless for varnish preparation and repeated distillation was necessary.

The 'Gunpowder test' was a widely employed method used in the preparation of alcohol to determine its purity. Alcohol was added to a metallic vessel containing a small amount of gunpowder, and heated; high water content prevented the ignition of the gunpowder. This test, which signals an excess of water, seems to have been common-practice and is referred to by Bickham (1747),[5] Watin (1772),[6] and Tingry (1804).[2] Bickham's general advice for making the best japanning materials in the Economy of Arts[5] stresses the importance of preparing varnishes with the best spirits of wine being of 'utmost importance', as failure to do this will spoil the varnish, preventing the gums dissolving and causing them to lie unevenly on the surface of the piece.

Ether: The synthetically produced ether solvent was described by Tingry as being superior to alcohol, particularly when used with pure resins, and this was the preferred solvent of choice for French chemists during the late 18th century. Tingry describes the preparation of ether as the treatment of alcohol with 'oil of vitriol', i.e. sulphuric acid, which yields a solvent having characteristics "which seem to assign to it an intermediate place between alcohol itself and the lightest essential oil". This solvent did not make enormous progress with artists as it was not an affordable material and required a relatively skilled chemist to prepare it, but nonetheless, Tingry's writing highlights the importance of such a rapidly evaporating solvent in aspects of varnish applications and cleaning processes, for example in the repair of fractured articles, using a resin such as copal. The synthesis mechanism of ether is formally credited to Williamson (1850), although it was clearly synthesised many years previously.

Turpentine: The solvent used in the Vernis Martin recipe, described in Chapter 2, is turpentine, a resinous fluid of which there are several types.[7] Removal of volatile components from pine resin through evaporation produces a glutinous matter that was sold on as white incense. Turpentine of chio has a firm consistency and is the rarest type, whereas Venice turpentine is fluid, viscous and transparent. Common turpentine is less valuable and is produced from wild pine and its essential oil is highly volatile. Rosin is a by-product of the distillation of oil of turpentine, and is composed of diterpenoids, mainly abietic acid which oxidize to hydroabietic acid (Figure 6.1) and then 7-oxodehydroabietic acid (Figure 6.2). The composition of turpentine is dependent on its geographical origin, containing varying compositions of pimaradiene acids and abietadiene/triene acids. Venice turpentine, from larches, was used as a wax plasticizer, and is frequently mentioned in historical recipes for varnishes and other glazes. It dries slowly, resulting in a fairly brittle film and contains no polymerizable components, unlike drying oils. It does, however, produce clear, glossy films and is soluble in a range of solvents. Venice turpentine was used in large quantities in less expensive products, although it contributes notably to darkening and cracking of varnishes or paints.[8] Oxidation processes cause the dulling of the surface prepared with this material, and it becomes very sensitive to moisture.

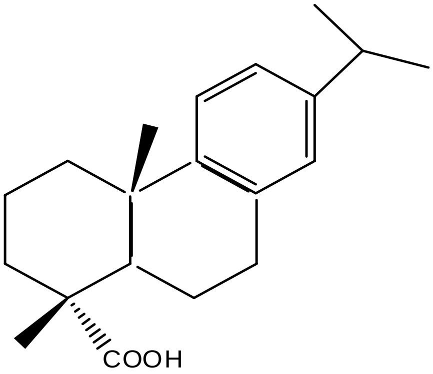


Figure 6.1: The structure of dehydroabietic acid.

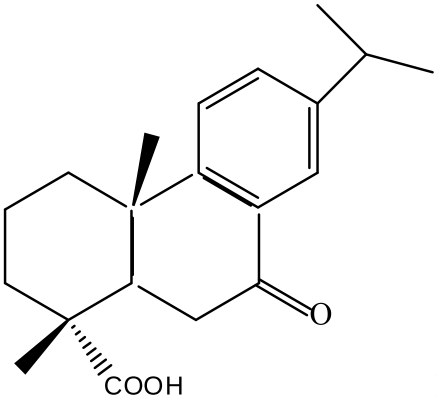


Figure 6.2: The structure of 7-oxodehydroabietic acid.

Tingry has described two methods of rectifying essence of turpentine. The essence (i.e. the essential oil part) is extracted from turpentine by distillation, and used for its lightness of colour for varnish preparation. The essence must be unadulterated by weak alcohol or oils, which may affect the varnish's ability to dry. Essential oils, such as aromatic oils extracted from lavender plants, were also used as solvents, often adulterated with turpentine since they resembled this closely.

Oils: Drying oils harden to a solid film after a period of exposure to air and do not rely on solvent evaporation for film formation. Oxygen is absorbed from the air and autoxidation takes place. Common examples of these types of oil include linseed oil, poppy oil, walnut oil and tung oil which contain high levels of polyunsaturated fatty acids. Oxygen from the air attacks the hydrocarbon chain which leads to a crosslinked polymerization of the oil.

Linseed oil was commonly used as a surface coating component – it was cheap and widely available, although it was not very durable and not resistant to water or alcohols. There was also significant darkening of the films as they aged. This oil does, however, feature in some of the well-known recipes such as the Vernis Martin, Evelyn's grounding materials and timber paint,[9] and Stalker and Parker[10] declared that it produces the 'best drying oil'. Both linseed oil and turpentine were of particular importance in the formulations used in the thriving japanning industry.

6.2 Safety considerations in the use of organic solvents

In this day and age, safety is always an important consideration when using solvents for a particular task. In the 18th century, as craftsmen became more familiar and knowledgeable about the substances they were using, the more they understood about the dangers involved. The literature does not show much evidence of any serious consideration regarding the potentially harmful toxic effects of the materials used in preparing solvents or spirit varnishes, but there is considerable concern shown for the flammability and fire risk involved.

As commercial manufacturers of varnishes and paints began to appear around the time of the Industrial Revolution, along with the favouring of cold processes over the dangerous hot processes, the fire risk was an issue which began to emerge as significant in the literature. Industrial workers generally were not protected until the mid-19th century when laws were introduced to increase safety, to some extent. Before this time, safety in the workplace was not deemed an important issue, although the flammable nature of the solvents was frequently mentioned, and authors advised cautioned in their literature. In Boyle's early 18th century writings he advised his readers on the dangers of setting their homes on fire when using highly flammable turpentine oil.[11] In Williams' 1787 publication of varnish preparation,[12] he too warns of the flammable nature of the solvent used (turpentine) and specifically instructs the reader to contain the substances in an earthen pot, and, for safety, all boiling of the mixtures should be done in a large, open space.

Whilst flammability was considered worth warning the reader about, it is very unfortunate that the toxicity of materials or the effects of inhalation were generally ignored or unknown. Tingry's description of the isolation of turpentine essence hints at a possible danger to human organs saying that the 'oil ... of a penetrating smell ... has a singular influence on our organs ... if a person touch it or inspire air impregnated with its effluvia, the urine acquires a strong smell of violets'. Turpentine oil is well known to cause extreme irritation to the kidneys and intestines, but this was not well known during the 19th century, and so Tingry is sharing his observations as a point of interest rather than a health warning. Specific syndromes as a result of organic solvents exposure to industrial workers in the mid-19th century have been studied by Spurgeon[13] in which Parisian physician Delpech reports the effect of solvents on those working in Indian rubber production. Similar to intoxication by alcohol, the symptoms included confusion, impaired memory and restlessness and were caused by inhalation of carbon disulfide in large quantities due to poor ventilation. Indeed poor ventilation combined with the use of organic solvents was hazardous in industrial environments.

The production of aromatic industrial solvents began with the discovery of benzene by Faraday which was a by-product of the coke carbonisation process. Because of its sweet smell benzene was added to aftershave, but by the later part of the 19th century it had been identified as causing severe conditions including anemia and leukemia after continuous exposure – it is now known to affect the bone marrow.

Whilst effective, rapid swelling or solubility can be achieved for unwanted materials, many organic solvents are unlikely to be useful in general cleaning due to their toxicities and harmful effects.

6.3 Historical solvent cleaning

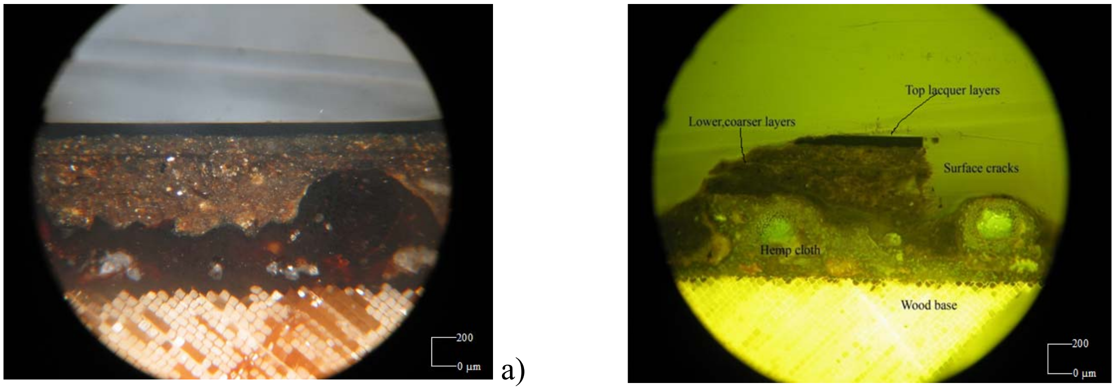
The use of solvents was clearly very important in the production of varnished surfaces as discussed in Chapter 2; however these substances could also be used to clean contaminated surfaces. Some 18th and 19th century literature[1] is concerned with the cleaning of surfaces – mainly paintings − using chemical reagents, as well as the fundamental causes of staining. Environmental damage was considered the main cause of discoloration and deposition of debris onto the surfaces. The chemist Tingry explained in his treatise that the atmosphere contains 'gases' which have an effect on the pigments contained in coating materials (or in paint),[2] specifically 'sulphuretted hydrogen' whose vapour causes white lead to turn black, unless protected by a layer of varnish. On removal or decay and flaking of the varnish, the surface once again is vulnerable. The polluted city atmosphere causes white lead pigments to turn yellow, whereas such a pigment in white paint, however, may become even whiter on exposure to clean country air. Tingry concludes that the effects of sulphuretted hydrogen, present in polluted environments, can be reversed using aqueous cleaning processes, specifically 'highly oxygenated water'. He reports on the success of this method citing the efficient removal of black staining from a Raphael picture, whilst having no effect on the intensity or quality of the other coloured components of the piece.

The attempted cleaning and restoration of valuable artefacts whose surfaces are vulnerable and delicate caused some concern to the experts at this time. Dossie[14] noted that the process of cleaning, specifically referring to paintings in his example, is barely understood even by those who carry it out. Recognising that the incorrect use of solvents could have major, negative effects to the piece undergoing treatment, he cautions against the bad practice of using them without understanding the possible outcomes. He is also reluctant to advise on removing layers of varnish when not absolutely necessary if the original surface may be put in danger, although the careful removal of dirt and dust – the 'foulness' should be approached using water, olive oil, soap, spirits of wine, turpentine oil and lemon essence, in this order: a 'weak' to 'strong' solvent effect.

Aqueous solvents are most commonly mentioned as cleaning materials in the 18-19th century literature. Some artefact surfaces are suitable for solvent cleaning applications, and clearly there are benefits in using aqueous or organic solvents for regenerating historical surfaces. Much is known about the effects of solvents on oil paint films[15-17] and they have been successfully used to clean these surfaces; however, their effects on East Asian lacquers are undocumented. It is necessary, therefore, to investigate the effect of solvents on the light damaged surfaces of this material, and to firstly determine the associated problems with damaged lacquers that will affect the way it can be treated.

6.4 The vulnerability of light-damaged lacquer

The photodegradation processes which occur in the light-damaged, top lacquer layers have been discussed in previous chapters. The resulting breakdown of the structure owing to loss of 'grains' and micro-cracking of the top layers leads to a dulling effect and surface roughening. Additionally, the cracks and uneven surface (Figure 6.3b) attract and retain particles of dirt and dust. The light damaged areas are also very sensitive to moisture, and any subsequent contact causes discoloration of the damaged site. Lower layers (Figure 6.3a-b) become exposed and more susceptible to damage by cleaning attempts and even the use of swabs or gel-pads loaded with solvent, which are generally used to prevent saturation of the surface, may pose a risk to a highly damaged surface.



a) b)

Figure 6.3: Cross-section showing lacquer layers on a) an unaged piece, b) naturally aged 19th century piece of lacquer.

In order to restore the surface to its original even and shiny state, the use of polishing techniques may be applicable, as the original *urushi* application required several polishing stages, as discussed in Chapter 4, followed by application of a new coating of *Ki urushi* with the excess rubbed off. However, in the case of aged and damaged *urushi* layers, whilst the process may remove the top damaged layer, it is inevitable that much more lacquer will be removed than is desired. The lower layers need to be preserved, and polishing may disrupt the stability of these layers. In very fine pieces of lacquer work it is possible to observe numerous thin layers of applied lacquer. Inlay pieces of metal such as gold or silver, and other materials such as mother of pearl are often set into the decorative surface and polishing may disrupt these components if the damage has gone deeper than the surface layer. In any case, these polishing techniques cannot be carried out on a surface that has not yet been cleaned.

6.5 Considering the treatment of a light-damaged lacquer surface

The treatment of the lacquer depends on the conditions that it has been subjected to. Unless detailed records are available, which is not very likely, the treatment processes, or lack of, which the surface has undergone will be unknown. If the lacquer has been damaged by light and no attempt has been made at restoring it, an obvious approach might be to attempt to restore the gloss by the immediate addition of a layer of *urushi*. The insolubility of the *urushi* system means that any additional materials added to the surface of the damaged lacquer will not bond with the original structure. The process, known as *urushi gatame* uses small amounts of fresh *urushi*, sometimes diluted, which is wiped over the surface impregnating the tiny cracks. The excess *urushi* is wiped away to ensure that only the smallest amounts of non-original *urushi* are present. There are dangers involved in the use of such a process on a surface which has not yet been stabilised by cleaning. A vigorous polish is required to finish the process, described above, and if this is done on an unstable structure, there is a high risk of separating layers and causing surface distortion.[18] A moderate cleaning method is therefore required in this scenario.

Alternatively, the dulled lacquer may have been restored in the past by the addition of layers of other materials. These materials may include waxes, oils or spirit varnishes, such as those discussed in Chapter 2, which were also used in the imitation of Japanese lacquer. More than likely the material used is not easily identifiable without destructive analysis of the surface. Varnish materials could potentially offer some improvement of the overall glossy appearance of the surface; however these materials are prone to rapid oxidation and yellowing rendering them insoluble and posing a further threat to the original lacquer, particularly if the unfamiliar material has infiltrated deep into the structure.

In addition, the removal of materials added at a later stage is a subject of controversy amongst conservators. Of primary importance is that the original part must not be damaged during the removal of the subsequently added layer, if the decision is made to remove it. According to Horie there is no method for the removal of a crosslinked polymer from a porous object, as we would expect, the latter being similar to a light-damaged lacquer piece.[19] The use of chemical solvents on such an unstable surface is likely to have a swelling or leaching effect, the swelling is likely to cause some degree of disruption to the original layer. The effects of swelling in oil paints has been studied extensively, but not for lacquer. Phoenix and Sutherland's[16] research follows on from the solvent leaching and swelling of oil film investigations by Stolow[20] in the 1960s. The potential use of solvents as cleaning agents prior to consolidation will be explored later in this work.

6.6 Solvents as cleaning agents

The extensive use of lacquer imitation materials, and the combinations of oriental lacquer panels with new furniture pieces can cause difficulties in identifying the coating material prior to cleaning. Sometimes identification can be carried out by experienced curators and conservators simply by visual inspection. Solubility tests in inconspicuous areas may help in determining whether the piece is a European or East Asian 'lacquer', since different coatings are soluble in different solvent types.[21] For aged pieces, however, this is neither a reliable or safe measure; more specific and structural information on the coating type requires chemical analysis. The difficulties associated with such analysis include the insolubility of aged and oxidized polymeric material which was discussed in the previous chapter.

Good cleaning solvents must have a strong interaction with the dirt or materials they are attempting to remove; the process begins with the diffusion of solvents between the polymer chains and swelling occurs. The outer layer of the polymer swells rapidly as it is in contact with the solvent and can be removed as a rubbery gel-like substance.[19] Crosslinked systems do not dissolve but will swell to a greater or lesser extent. It is unlikely that solvents can effectively be used to swell crosslinked systems from porous systems.

East Asian lacquers have traditionally been cleaned, or their surfaces rejuvenated, by water treatments. Effective removal of discoloration was demonstrated to the Asian Art Museum by Mutsumi and Misako Suzuki[22] who, following dusting to remove free particles, applied a small amount of vegetable oil to a piece of cotton cloth and the Japanese lacquer was polished causing the removal of a dark grey discoloration. Following this stage, water was used for polishing in the same way and this was observed to remove reddish grey discoloration. Gilder's whiteing was finally used to polish up the lacquer, removing a light grey colour as it did. The results obtained from this technique were said to be good.

Another successful aqueous clean is reported by Minney[23] in the conservation of a dry Burmese lacquer statue. He describes his use of solvent tests applied by rolling a soaked cotton wool swab across the surface: the results show that the surface was unaffected by distilled water, xylene and white spirit but softened by acetone, which caused the removal of a yellow trace on to the swab. The cleaning of the entire piece was done with a solution of distilled water containing 0.1% synperonic N non-ionic detergent.

However, Figure 6.4 shows the result of water cleaning of an area of light damage on a piece from the early 1600s, and, in this case, the technique has removed layers of degraded lacquer. The contrasting result to the previous two examples can be explained by a lesser degree of damage on the surface compared to that seen on Figure 6.4, or alternatively that perhaps the first two examples of lacquer had been periodically re-coated with *suri urushi* in order to keep the original *urushi* layers protected, a process usually carried out in Japan for maintaining lacquered pieces. The latter, more damaged piece would not have had such a process carried out, having been prepared for export to Europe.

Figure 6.4: The damaging effects of water cleaning on naturally aged lacquer.

The swelling and distortion observed when the lacquer comes into contact with some solvents also causes it to lose some of its mass through leaching of small fragments. Although the swell-leach effect has been studied extensively for oil paint films, no documented findings are available for this effect on East Asian lacquers. Although the effect of a water balance shift on the shrinkage of lacquer is well known (Chapter 3), however, the effects of organic solvents are unknown. Aqueous cleaning of surfaces is a traditional method in East Asia, but only with lacquer that is appropriate for this treatment.

Additionally, the pH of water used in cleaning moisture-sensitive aged lacquer has implications in these processes since the degraded lacquer surface has increased acidity. In studies of the effects of water pH in aqueous cleaning of aged Chinese lacquer[24] alkaline solutions, whilst being effective in removal of organic debris, will also react with an acidic surface. Gloss and colour changes have been used to quantitatively monitor the effects of pH of water cleaning on the whitening effect on the naturally aged surface, and cleaning solutions of higher pH than the surface's own pH are reported to reduce the gloss of the aged lacquer whereas those solutions having lower pH than the surface enhance the gloss.[24] The pH of the aged surface appears to play a significant part in the effect of cleaning solutions on gloss. Light-damaged lacquers, obtained by short-term exposure to filtered UV daylight simulation, exhibit low pH and this consequently makes them very sensitive to cleaning with water. The effect of varying the pH of water is shown for free films in Figure 6.5, where the mass increase of slightly light-damaged lacquer films immersed in water are observed.

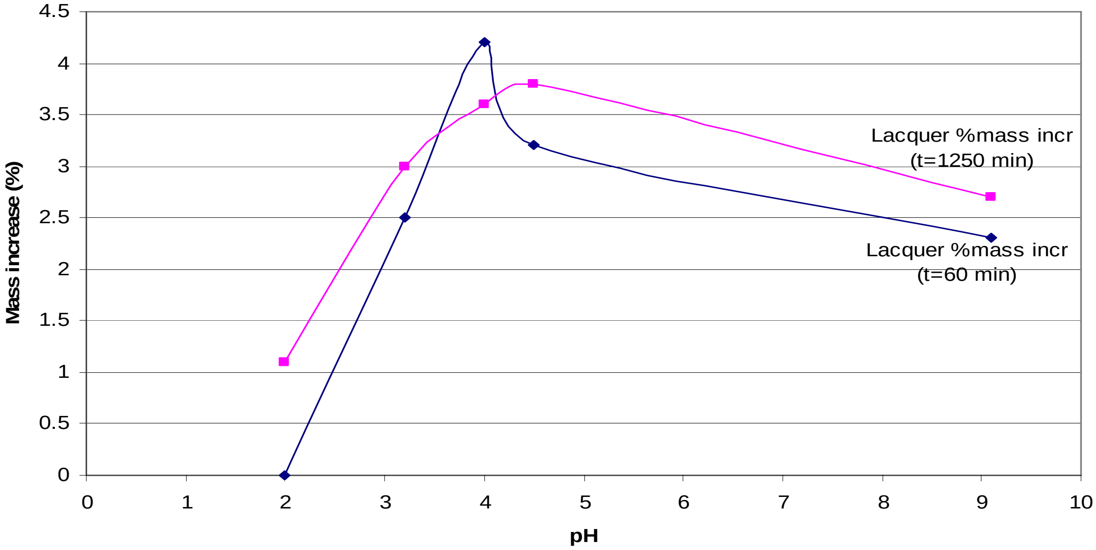


Figure 6.5: The effect of water pH on aged lacquer swelling (t= 60 minutes, and t=1250 minutes).

There is a clear need to determine whether aqueous or organic solvent use is appropriate in the cleaning of light damaged lacquers. Since the aim of this work is to determine whether an appropriate solvent system can be identified for the cleaning of a photodegraded lacquer surface, a study of solvent behaviour and their interaction with polymeric films in conservation environments is required here. Solubility parameters provide a quantitative method of predicting the interaction between substances, such as solvents and polymers. They are also useful in preparing formulations of solvent mixtures for a specific purpose. In conservation, the Tea's fractional solubility parameters system is a popular guidance model for selecting an appropriate solvent for the removal of aged coatings or cleaning, and its advantages and limitations will be discussed here.

6.7 The molecular basis of solubility theories

Solubility theories are based on the three main types of interactions, which are the dispersion forces, the polar forces and the hydrogen bonding forces.

Weak forces - Non-polar liquids possess weak intermolecular attractions, but no dipole moment, and the source of these intermolecular interactions is related to the random movement of the electron cloud around the molecules which cause fluctuations around the molecular surface. Temporary dipoles are constantly created, as described later in the section.

Two molecules in close proximity can induce polarities in each other; these are induced dipole forces. This is caused by the electron cloud distortion of part of a molecule by the charged part of its adjacent molecule, causing the opposite charge to occur in the area of interaction. These temporary dipoles have a polarity which is related to the surface area of the molecule involved; larger surface areas have larger temporary dipoles and consequently higher intermolecular attractions occur. Dispersion forces are greater in straight chained molecules, since there is more surface area than their corresponding branched isomers. Such forces are present in all molecules, even if they are only weak.

Stronger forces - Polar molecules also interact by dispersion interactions; however they also exhibit much stronger forces. Permanent dipoles are found where there is an unequal distribution of electrons between atoms in a molecule, which are cancelled out if the molecule is symmetrical since no part of it holds more of the negative charge distribution.

The fluctuating dipoles occur for a longer time and therefore correspond to a permanent dipole. Examples of strongly polar substances are water and alcohols, a slightly polar substance is toluene, and an example of a non-polar solvent is hexane.

Further increases in the intermolecular attractions in polar molecules arise from their spatial arrangement, positive to negative. These temperature dependent dipole-dipole forces, Keesom interactions, correlate with the molecular arrangements. Increasing the temperature increases molecular movements, and the net effect is a decrease of the dipole-dipole forces. However, any molecule will be polarized momentarily in the immediate presence of a polar molecule, and the dipoles will be attracted, thereby generating dipole induced dipole forces.

Hydrogen bonding – A very strong polar interaction occurs between hydrogen atoms and strongly electronegative atoms, such as oxygen, nitrogen, or fluorine, and non-bonding electron pairs.[25] The hydrogen atom next to an electronegative atom in the molecule draws its electron, and exposes a positive centre. This then interacts with an area of negative charge on the neighbouring molecule; a protonic bridge is formed that is much stronger than most other types of dipole-dipole interactions.

Atkins[26] describes the formation of a hydrogen bond as a contact-like interaction, due to orbital overlap, arising when AH contacts B, (where A and B are strongly electronegative elements, and B possesses a lone-pair of electrons). In the delocalized molecular orbital formation of three molecular orbitals, A, H and B have all supplied one atomic orbital each. Hydrogen-bonding is a relatively strong force, having a considerable impact on solubility behaviour. The hydrogen bonds can vary significantly in strength, however some typical values are: O—H···:O (21 kJ/mol) and N—H···:N (13 kJ/mol), which are relatively weak in comparison to the covalent bonds such as H-H (436 kJ/mol), H-O (366 kJ/mol) and C=C (614 kJ/mol).

‘Like-dissolves-like’

Intermolecular interactions, known as Van der Waals forces, London forces or dispersion forces,[25] occur between molecules in liquids, and these forces must be overcome by the solvent molecules for dissolution to occur. This is achieved when the solvent molecules position themselves around the solute molecules, whilst the solvent molecules separate, and is most probable when the attractive forces of both components are of a similar order – hence the expression ‘like dissolves like’. If they differ too greatly, the strongly attracted molecules are not separable and weakly attracted molecules are left out, leading to immiscibility. Depending on its structure, a molecule might display van der Waals forces generated by two or more polar contributions. In order for a substance to successfully dissolve another, their intermolecular forces must be similar, and their composite forces must be of equal formation.

In a non-polar molecule the average charge distribution over a specific amount of time is uniform.[25] However, because of electron movement, at any one time the charge may not be uniform and therefore a temporary dipole occurs (Figure 6.6).

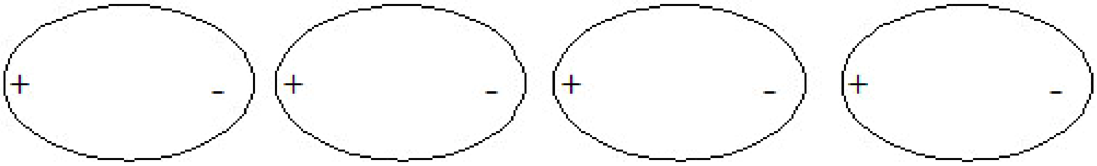


Figure 6.6: Distribution of charge in a temporary dipole.

Geometric properties of the molecule tend to dictate the extent of polarity, and therefore the strength of intermolecular forces. Substances of similar polarities are soluble in each other, although solvation becomes more difficult as deviations in polarity increase.

6.8 Solubility behaviours

Dissolving a solid in solvent is similar to melting a solid since: the ordered crystal structure is broken up to form a more chaotic arrangement of molecules/ions in the solvent as the molecules/ions detach from each other. The lattice energy and intermolecular attractions are overcome by the attractive forces created between the solvent and the solute. When considering an ionic substance, with considerable lattice energy and inter-ionic attractions, solvation of the ions can only be achieved by very polar solvents or water.

The simplest solubility parameter is the Hildebrand solubility parameter, δ, which provides a numerical value to indicate the solvency behaviour of a solvent. This is derived from the cohesive energy density (equation 6.1), a numerical value indicating the energy of vaporization in calories/cm^3, and the overall attractive forces between the molecules in a solvent. Cohesive energy density can be derived from the heat of vaporization, the energy required to vaporize a liquid, after the onset of boiling. Solvents with similar cohesive energy density values are miscible.

$$\delta = \sqrt{(\Delta E_\upsilon / V)} \qquad \text{Equation 6.1}$$

where ΔE_υ is the heat of vaporization, and V is the molar volume of material under analysis.[27]

Hildebrand values of a solvent mixture are obtained by averaging the values of individual solvents by volume, and consequently we are able to predict the properties of a mixture from the solubility parameters of its component solvents.

Other systems have been developed, but can often be correlated with the Hildebrand parameter. A solvent spectrum can be accumulated listing solvents with increasing trend as regards Hildebrand parameter, in order to determine the solubility of polymers,[28] and to list the solvent's hydrogen-bonding behaviour. By experiment, the trend in solubility range can be determined, although cohesion parameters consisting of more components may offer more accurate figures, since they take into account the separate variables from polar and hydrogen-bonding aspects.

6.9 Three-component parameters and practical application in conservation

As previously mentioned, Hildebrand parameters can be used to describe solubility behaviour sufficiently; however more accurate and reliable predictions can be made if this is combined with a polar value, such as a hydrogen bonding number. Improvement in the reliability of the results can be further seen when three parameters are known.

Hansen Parameters

As an extension of the Hildebrand solubility parameter, Charles Hansen developed a three parameter system in 1966, and this has become a widely accepted system. The Hansen parameters divide the Hildebrand value into three components: dispersion force (d), polar (p), and hydrogen bonding (h), denoted in equation 6.2:

$$\delta = \delta_d + \delta_p + \delta_h \qquad \text{Equation 6.2}$$

The theory is based on the assumption that on evaporation, all physical bonds are broken.[29]

The dispersion force of a solvent is determined using the homomorph method (a homomorph of a polar molecule is the nonpolar molecule which is most similar in size and structure). The Hildebrand value for the nonpolar homomorph, since it only has dispersion interactions, is assigned to the polar molecule as its dispersion component value. After squaring this value, and subtracting it from the squared Hildebrand value, the resulting value is assigned to the total polar interaction of the molecule. After extensive work on different solvents, Hansen was able to split this value into the polar component and the hydrogen bonding component, and therefore a three-parameter model is possible.

Polymer solubility and the Hansen model

The Hansen Model is a 3D model on which polymer solubilities can be plotted. To construct this model, Hansen doubled the dispersion parameter axis which formed an approximately spherical volume of solubility for the polymer. This volume is described using the co-ordinates at the centre of this sphere (d,p,h) as the component parameters, and the sphere radius is termed the interaction radius (R). Therefore, the solubility of a polymer in a solvent can be predicted using the Hansen model – specifically if the Hansen parameters for the solvent lie within the solubility sphere for the polymer, then the polymer will be soluble. In determining whether the distance of the solvent from the centre of the polymer solubility sphere is less than the interaction radius of interaction for the polymer, equation 6.3 is used.

$$D_{(S\text{-}P)} = [4(\delta_d S - \delta_d P)^2 + (\delta_p S - \delta_p P)^2 + (\delta_h S - \delta_h P)^2]^{1/2} \qquad \text{Equation 6.3}$$

where $D_{(S\text{-}P)}$ = distance between solvent and centre of solubility sphere, $\delta_x S$ = Hansen component parameter for solvent, and $\delta_x P$ = Hansen component parameter for the polymer.[30] If $D_{(S\text{-}P)}$ is less than the interaction radius for the polymer, the polymer is soluble in the solvent.

This is not the most convenient way of predicting behaviour however, and so the Hansen's 3D method can be illustrated graphically by plotting a cross-section through the centre of the solubility sphere on a graph representing two parameters, usually p and h. The accuracy of this method in predicting the solubility behaviour of a polymer is approximately 90%, and it can be applied for practical use.

6.9.1 Practical application of solubility parameters in conservation: The Teas Chart

A planar graph is required for practical application, on which polymer solubility areas can be drawn on in 2D. Teas introduced a solution to this in 1968 – a triangular graph using a set of fractional parameters mathematically derived from the three Hansen parameters. The third parameter however requires the data to be displayed in a way that is different to a 2D graph, for it to be useful. 3D models are therefore required at this stage.

The first three-component system was developed by Crowley, Teague, and Lowe[31] of Eastman Chemical, in 1966 and utilized the Hildebrand parameter, hydrogen bonding number, and the dipole moment of the solvent to acquire three values. On the Teas chart illustrated in Figure 6.7, solvent families are grouped in specific locations, for example, the hydrocarbons are seen at the right-hand corner, whereas the alcohols are located left of the middle of the chart. The solvents positioned close to each other display similar behaviours. Furthermore, the chart enables the prediction of the outcome of combining two solvents.

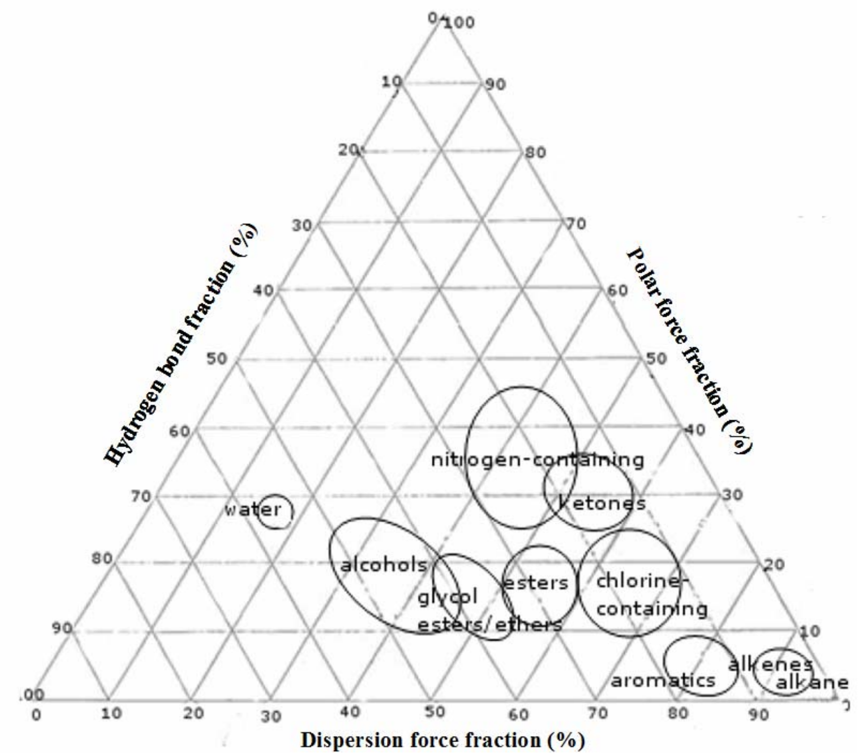


Figure 6.7: The Teas Chart (adapted from Phoenix).[32]

Since it is not usually possible to assign a range of parameter values to a solid, determining its position on the Teas chart requires the systematic testing of the material with a range of solvents in order to define the region of solubility.[15] In this project, determination of the regions of soluble and insoluble activities for aged lacquers and varnishes is required through a series of tests on the aged materials in order that the region of solubility (or swelling) will become apparent. Used in conjunction with tables showing three parameters for solvents, Solubility maps provide useful information regarding the interactions between solvents and polymers. It facilitates the rapid prediction of solubility behaviour. The Tea's chart is an example of such a guidance model, although it has been greatly simplified.

6.9.2 Limitations associated with the Teas Chart

In constructing the Teas graph some assumptions are made. These are that all materials have the same Hildebrand value; therefore solubility behaviour is determined by relative amounts of the three component forces that contribute to the Hildebrand value, and not the differences in total Hildebrand value. This enables us to use percentages rather than unrelated figures.

In the case of Hansen parameters, if all three squared values are added up, the total will equal the square of the Hildebrand value for the solvent in question. The fractional parameters derived by Teas from Hansen parameters, show the contribution made by each parameter, as a percentage, to the whole Hildebrand parameter. All three fractional parameters when added together will always total 100. The Teas chart is therefore only an empirical system, since Hildebrand values are not the same for all solvents. However, it still remains a useful tool for obtaining information on solubility.

Reviewing the data from various researchers in order to determine a physical model of the removal of varnishes from oil paintings, Michalski[17] has determined that the data on equilibrium swelling of linseed oil films from most of the research can be fitted to a three-dimensional system – the data does not fit the two-dimensional Teas chart. In his model he has applied a third dimension, a vertical axis on the Teas chart; this dimension represents Hansen's total solubility parameters.

6.10 Solvent-induced swelling in polymers

In terms of amorphous polymer-solvent interactions, whereby the substance is not seen to dissolve as it structure remains intact, swelling occurs. Polymer solubility can be estimated using a similar method to Crowley *et al.*'s mentioned earlier, by investigating the degree to which the polymer swells in a selection of diverse solvents and comparing these to the Teas graph.

The solubility parameter of a polymer is equal to the solvent which causes maximum swelling, where complete solubility would have occurred had it not been for the polymer's structure keeping it together. By selecting two solvents which are close to the edge of the polymer solubility window, swelling of the polymer is tested in a range of mixtures using these two solvents until a solubilising mixture is determined. The use of fractional dispersion values is a valuable means for designating relative solvent strengths concisely, and can be less limiting than other scales.

The solubility parameters of an unknown polymer might, therefore, be determined by studying its swelling behaviour in a range of solvents. According to Feller, Stolow and Jones,[20] when studying the action of solvents in leaching and swelling, solvent penetration into the film will cause swelling to the outer parts first, followed by the rest of the film. Their experiments were carried out on linseed oil films, which were supported on glass slides, therefore causing the film to expand only in thickness, whereas a free film will expand in all three dimensions. Any soluble components are leachable by diffusion. In these cases, on removal of the solvent, de-swelling occurs and the remaining film would be of a lower volume than it was prior to swelling, and will also have changed physical properties, for example it may be more brittle, denser, and deformed in shape.

Using pre-leached, aged, white lead/stand oil films, the investigators plotted the molecular volume of the solvents against the equilibrium degree of swelling (the volume of solvent taken up per film volume under equilibrium conditions). They did not take into consideration the effect of geometry of the molecule, however their conclusions are as follows: swelling increases with increasing size of alcohols, as with ketones, however aromatic hydrocarbons behave conversely. High degrees of swelling are observed for chlorinated hydrocarbons, whereas aliphatic hydrocarbons show no swelling.

Studies on the rates of swelling and diffusion interactions of solvents with linseed oil films show that the evaporation of the solvents from the films following diffusion and swelling occurs at a generally lower rate than the penetration of the solvents: some of the solvent is held persistently by the film. Leaching is inevitable where solvents are brought into contact with the films, however it can be kept to a minimum by limiting exposure time and solvent quantities. For minimum damage, therefore, a solvent with the ability to dissolve aged varnishes on a surface must have low-swelling and diffusion action towards the aged, original coating, such as *urushi* lacquer, and a rapidly diffusing, high-swelling behaviour towards the unwanted, non-original layer, such as the varnish.

6.11 Use of solvents in conservation

Stolow's work in the 1960s focused on producing a model for the swelling effects of organic solvents on paint films, which were prone to pigment leaching when cleaning with solvents.[20] The work used a non-contact method - a jet to impinge the swelling solvent onto the surface of the film, which retracts as the swelling advances, as discussed by Phoenix and Sutherland[16] to determine the change in film thickness, and consequently follow the swelling and leaching processes over time. The after-effects of swelling and leaching were denser, more brittle films. Stolow found that on repeating the solvent exposure for the same film he found that there was swelling but no leaching. The equilibrium swelling reached was found to be proportional to the Hildebrand solubility parameter. Solvents with low viscosity such as acetone caused rapid swelling compared to solvents of higher viscosity such as iso-butyl alcohol.[20]

Stolow's data has been presented more recently in a more usable form such as the Teas chart. Hedley[15] has plotted this data to illustrate regions of peak swelling for oil films. He also demonstrates the effect of using solvent mixtures which may both individually lie outside this region, but when used in combination they lie within the area. Varnishes were observed to have a larger region of solubility than the oil films, which is useful when the varnish is being removed, although this depends on the resin type.

In approaching conservation cleaning, the solubility of the varnish that is to be removed must be identified, and compared with the region of solubility of the material it is in contact with – whether it be an oil paint or lacquer film, and to determine areas in which the two do not overlap. Figure 6.8 demonstrates the way in which the Teas chart can be used to illustrate the differing regions of solubility of a new linseed oil film and one that has been aged for a prolonged period of time.[19] In their work with oil paints, Phoenix and Sutherland have concluded that the varnish solubility boundary lying on the non-polar side of the chart can indicate suitable solvents for varnish removal whilst acting as a low-swelling solvent towards the oil film.

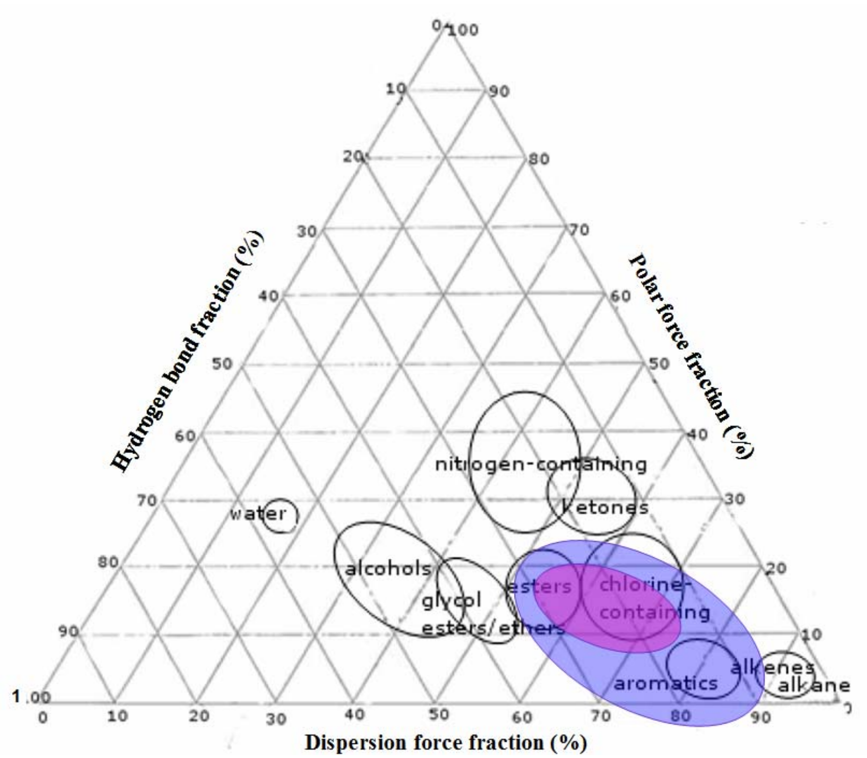


Figure 6.8: The region of solubility for a new linseed oil film (purple, inner ellipse), and an aged, crosslinked oil film (blue, outer ellipse).[19]

However, the limitations to these conclusions are that Stolow's data were acquired using films that were all less than 15 years old, which therefore does not take into account the behaviours of older films. He also prepared his samples using linseed stand oil, and so the behaviour of non-stand oils is not considered.

Capillary action through cracks in aged lacquer will speed up the swelling that will occur; therefore a slow diffusing solvent with high volatility rates is required. The solvent must be able to dissolve the varnish rapidly whilst also being fast drying and rapidly de-swelling. Some solvents have a higher affinity to components of the polymer material it is swelling. This solvent retention has been measured by methods such as isotopic labeling and gravimetric analysis, in order to determine a more suitable solvent that will have a low retention.

The effect of solvent diffusion into *urushi* lacquer samples also needs to be investigated. Prolonged exposure of aged films to solvents, and their effect on the lacquer's increased brittleness or leaching of fragments is important in understanding the solvent-lacquer interaction, which must be known before a decision can be made regarding the safe and practical use of any solvents on a light-damaged and vulnerable lacquer surface. Determining the solubility parameters of aged *urushi*, and their position on the conservators' Teas chart may be a starting point in making such a decision.

6.12 Summary

Over time, lacquer surfaces become dull due to cracking of the surface, trapping dust particles and, more problematically, may have had 'restorative' materials added, which are now insoluble and therefore non-removable through simple cleaning. One of the main detrimental consequences of this is the discoloration that occurs due to the additional (aged) layers. In conservation work, water cleaning and the use of alcohol-based solvent is common, but are these solvents suitable for this purpose? The solvent type and 'strength' that are required to remove persistent fragments might also be responsible for causing damage to the original surface, extending down through its many layers. Before solvents are used in the conservation of valuable artifacts, the risks and suitability must first be verified. Some layers of contamination require 'stronger' solvents to dissolve and remove the layer; however these harsher solutions are potentially dangerous to the original material. There is a need to investigate the degree of solubility/high-swelling for aged lacquers in a range of solvents that include the polar protic solvents such as methanol and water, dipolar aprotic such as acetone, and the non-polar solvents such as hexane. The aim of such an investigation is to enable careful selection of a solvent that will remove the appropriate materials with minimal swelling or leaching of the original material.

Identifying the areas of solubility for the *urushi* materials and the shifts of these areas on a model representing solubility, such as the Teas Chart, as ageing takes place will be discussed in the following chapter using artificially aged lacquer models that were discussed in Chapter 5. A low-swelling solvent with regards to the *urushi* lacquer now needs to be identified which lies in the region of solubility or high-swelling for any potential restorative coatings that may have been applied, and for any other debris that now requires safe removal. Identification of this solvent, or solvent system, will be a key step in answering the question: is it feasible to remove contaminants such as aged varnish using a solvent whilst ensuring that no further damage will be inflicted on the light-damaged surface?

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Chapter 7

Solubility parameters of East Asian lacquers

In this chapter, the interaction of organic solvents with photodegraded lacquer is characterized; the lacquer's response is determined quantitatively by measuring its solubility parameters. The effect of solvent sorption on the lacquer was determined using gravimetric and optical methods. Despite the insolubility of the damaged lacquer, solvents are able to permeate the lacquer structure causing softening and swelling, although the extent of the effect depends on the solvent type.

7.1 Solvent uptake by damaged lacquer: immersion and vapour sorption tests

Experimental details: immersion tests

The uptake of solvents by lacquer films was determined using methods adapted from Zellers *et al.*[1,2] in order to determine the solubility parameters of the lacquer at various degrees of damage. Lacquer films of approximately 25mm x 5.5mm x 0.01mm were weighed (W_1) and immersed in a range of solvents, as shown in Table 7.1, for 24 hours. After this time, they were removed from the solvent and dried for 6 hours. The films were re-weighed (W_2) before being returned to the solvent for a further 72 hours. The films were re-weighed (W_3). The first immersion stage allowed for leaching from the damaged lacquer. The lowest weight from W_1 and W_2 was subtracted from the final weight to determine overall swelling. Each film type was repeated six times.

Four ageing methods were used to prepare lacquer samples: 500 hours daylight ageing (light/dark cycling), 3,500 hours UV daylight simulator with polycarbonate filter ageing, 2000 hours mercury-tungsten (HgW) lamp source exposure without filter, and a freshly cured standard. The overall immersion swelling and/or leaching results for each lacquer type are shown in Table 7.1, where the δd, δp and δh values represent those of the dispersion force, polar and hydrogen bonding parameters, respectively.

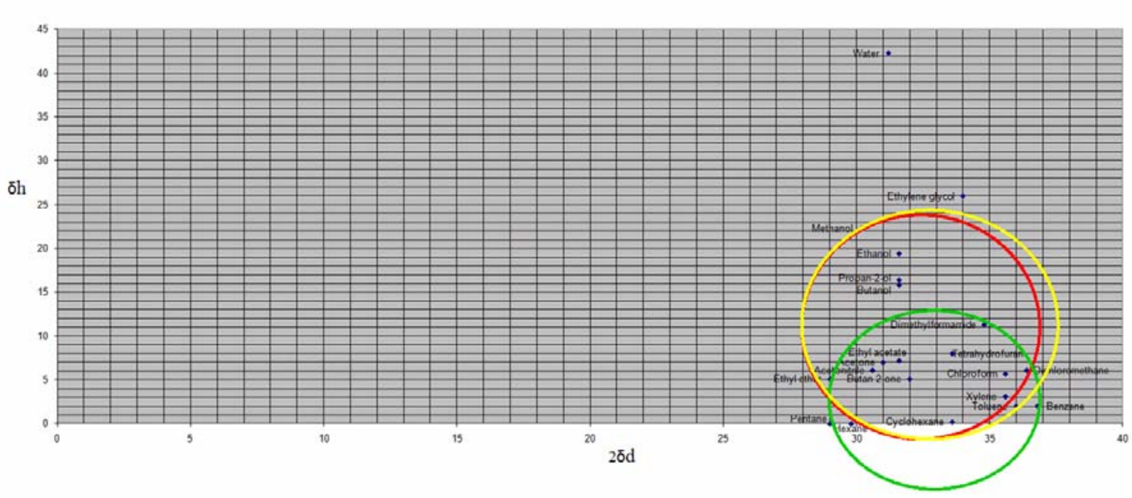
Table 7.1: A summary of leaching and swelling effects of a range of solvents, the grey boxes indicate a minimum of 5% weight increase (standard error in parenthesis)

				Unaged		UV 3,500 h		Daylight 500 h		HgW 2,000 h	
Solvent	δd	δp	δh	Leach (%)	Swell (%)	Leach (%)	Swell (%)	Leach (%)	Swell (%)	Leach (%)	Swell (%)
Hexane	14.9	0	0	0	2.9 (0.01)	0	0 (0.00)	0	1.4 (0.02)	0	0 (0.01)
Benzene	18.4	0	2	0	2 (0.08)	0	1.3 (0.09)	0	5.1 (0.13)	1.4	6.7 (0.17)
Tetrahydrofuran	16.8	5.7	8	2.6	0.5 (0.20)	2.8	6.7 (0.13)	3.1	5.6 (0.14)	4.3	7.3 (0.25)
Ethanol	15.8	8.8	19.4	0	3 (0.10)	0	9.2 (0.56)	0	2.4 (0.50)	0	11.7 (0.71)
Chloroform	17.8	3.1	5.7	2.3	1.9 (0.40)	2.7	8.3 (0.44)	2.5	6.2 (0.35)	3	13.2 (0.41)
Diethyl ether	14.5	2.9	5.1	0	2 (0.90)	1.9	5.3 (0.70)	0	6.4 (0.70)	0.9	6.5 (0.80)
Ethyl acetate	15.8	5.3	7.2	0	2.3 (0.65)	0	7.7 (0.13)	0	7.2 (0.20)	0	8.9 (0.23)
Xylene	17.8	1	3.1	0	3.1 (0.93)	0	3.2 (0.87)	0	3.6 (0.66)	0	5.4 (0.09)
Butan-2-one	16	9	5.1	3.1	2.4 (0.07)	2.9	5.8 (0.08)	3.2	6.3 (0.07)	5.6	6.7 (0.07)
Water	15.6	16	42.3	0	2.9 (0.07)	0	4.2 (0.05)	0	3.2 (0.06)	0	4.4 (0.09)
Pentane	14.5	0	0	0	3.2 (0.04)	0	1 (0.04)	0	2.1 (0.06)	0	0 (0.01)
Acetone	15.5	10	7	0	2.5 (0.50)	1.2	5 (0.70)	0	3.9 (0.45)	1.3	7.6 (0.80)
Toluene	18	1.4	2	0	2.1 (0.20)	0	2.2 (0.15)	0	5 (0.30)	1.9	4.3 (0.42)
Dichloromethane	18.2	6.3	6.1	0	2.5 (0.03)	2	6 (0.05)	0	5.9 (0.13)	2.1	6.2 (0.08)
Acetonitrile	15.3	18	6.1	0	0.9 (0.24)	0	0.3 (0.30)	0	0.5 (0.39)	1.5	1.3 (0.41)
Propan-2-ol	15.8	6.1	16.4	0	0.3 (0.30)	0	5.1 (0.19)	0	1 (0.56)	0	5.7 (0.29)
Methanol	15.1	12	22.3	0	0.4 (0.51)	0	5.2 (0.66)	0	0.7 (0.60)	0	5.6 (0.70)
Butanol	15.8	5.7	15.8	0	0.8 (0.24)	0	3.4 (0.44)	0	1.1 (0.30)	0	5.4 (0.40)
Cyclohexane	16.8	0	0.2	0	1.7 (0.18)	0	1.3 (0.15)	0	1 (0.20)	0	0 (0.09)
Dimethylformamide	17.4	14	11.3	3	0.3 (0.12)	3.7	0.9 (0.20)	6.7	1.3 (0.25)	14	2.1 (0.20)
Ethylene glycol	17	11	26	0	0 (0.01)	0	4.4 (0.03)	0	0 (0.01)	0	3.6 (0.01)

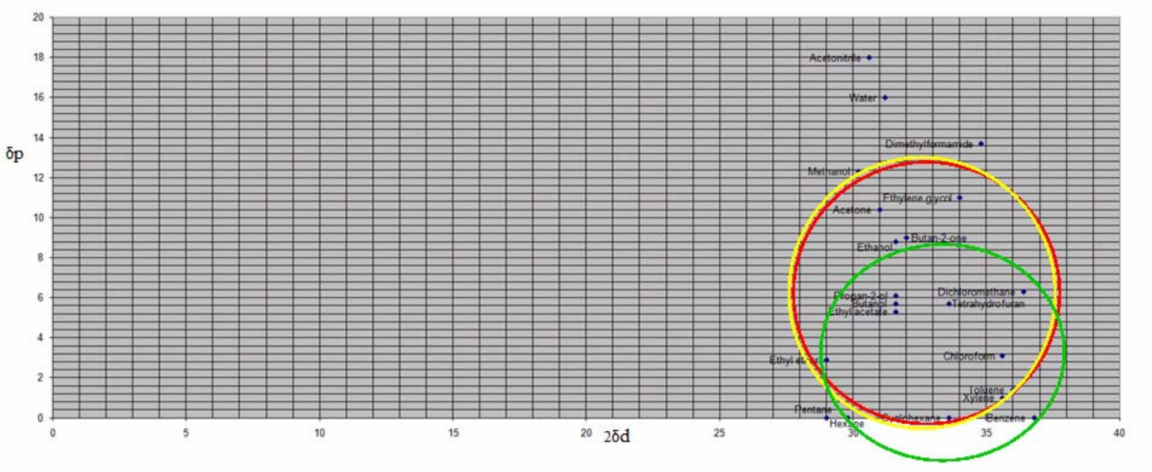
Swelling data

The overall swelling data was used to determine solubility parameters using Hansen's graphical estimation method, the suitability of which is discussed in the previous chapter. This method has been used by Zellers *et al.*[1] in the determination of solubility parameters for lightly crosslinked polymers when assessing the properties and responses to solvents of materials used in laboratory gloves.

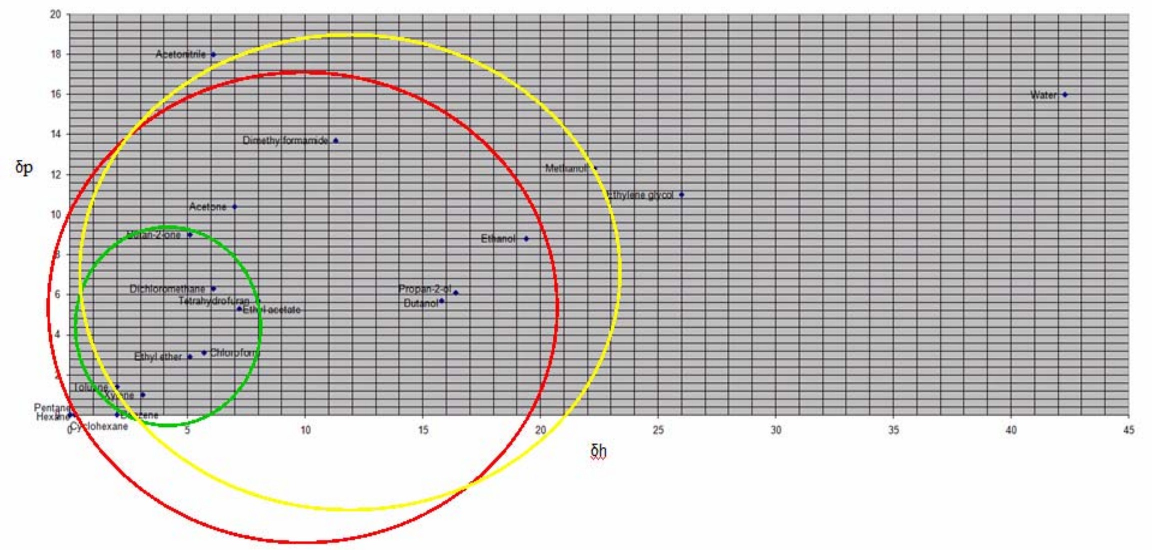
The graphical method is an estimation of Hansen's 3d solubility parameters (3DSPs) that uses the high swelling solvent data only. Unaged lacquer films did not swell more than 2.9% weight (wt.) for any of the organic solvents and, therefore, the graphical estimation of partial solubility parameters was not possible for this type. In the determination of lacquer 3DSPs for UV-aged (3,500 h), mercury tungsten (2,000 h) and daylight aged (500 h), the minimum solvent swelling criteria was >5% wt. The results for these immersion tests are shown in Graphs 7.1-7.3, and the partial solubility parameters are assigned according to the centre of the 3D spherical region obtained from the graphs, where the smallest circle possible that encloses all solvents meeting the minimum % weight criterion of 5% is drawn.



Graph 7.1: Plot of partial solubility parameters 2δd *vs* δh of solvents with minimum swelling criteria (5% wt.) for UV-aged (red circle), daylight aged (green circle) and mercury tungsten aged (yellow circle).



Graph 7.2: Plot of partial solubility parameters 2δd *vs* δp of solvents with minimum swelling criteria (5% wt.) for UV-aged (red circle), daylight aged (green circle) and mercury tungsten aged (yellow circle).



Graph 7.3: Plot of partial solubility parameters δh *vs* δp of solvents with minimum swelling criteria (5% wt.) for UV-aged (red circle), daylight aged (green circle) and mercury tungsten aged (yellow circle).

Since an arbitrary value (>5%) is assigned to the data used for the calculations, not all the data obtained in the immersion experiments are used. Graphs 7.1-7.3 also show that some of the solvents which do not display any swelling above the minimum criterion are present within the region of swelling illustrated by the red (UV-aged), green (daylight-aged) and yellow (mercury tungsten-aged) circles. A more accurate analysis of the results would take into account the effects of molar volume and use all of the swelling measurements. To calculate the partial solubility parameters in this way, a weight-averaged calculation was used with weight-averaging factors as described by Zeller,[2]

$$\delta_{(d2,\ p2,\ h2)} = \sum u_i V^z \delta_{(d2,\ p2,\ h2)} / \sum u_i V^z \qquad \text{Equation 1}$$

where partial solubility parameters $\delta_{(d2,\ p2,\ h2)}$ are determined from the fractional uptake (u_i) of the solvent, and the molar volume (V) of the solvent, taking into account the effect of molar volume by using z, which is an exponential factor (z = 0, 1, 0.5) varied to adjust the effect of molar volume, since molar volume will influence the uptake of solvents in terms of rate of diffusion or capacity of the polymer.

The 3D solubility parameters were calculated using the immersion test results for each lacquer type, and are shown in Table 7.2.

Table 7.2: 3D solubility parameters obtained for immersed lacquers by graphical estimation and weight-averaged methods

Lacquer type	Method used	δd (MPa$^{1/2}$)	δp (MPa$^{1/2}$)	δh (MPa$^{1/2}$)
Unaged	Graphical estimate	n/a	n/a	n/a
	Weight averaged	16.30	5.72	8.07
UV aged 3500 h	Graphical estimate	16.2	7.2	12.9
	Weight averaged	16.47	6.50	8.04
Daylight aged 500 h	Graphical estimate	16.2	4.1	4
	Weight averaged	16.6	6.19	7.42
HgW aged 2000 h	Graphical estimate	16.4	6.4	11.4
	Weight averaged	16.61	6.52	7.54

There are limitations in studying the responses of free films using immersion. In particular, the mass increase is very small and, therefore, difficult to measure with any accuracy. The high standard errors, which range from 0.05 for water uptake, to 0.7 and 0.66 for the faster evaporating solvents acetone and methanol, respectively, reflect the problems associated with this method of analysis, where non-swelling solvents fall within the circle enclosing the solvents of significance. The free films also tend to curl, split and stick to the glass vessel surface, causing further breakage and loss of sample. The most damaged films disintegrate very easily once placed in the solvent reservoir, and consequently another method for quantifying solvent uptake is required. The experiments were therefore repeated using a technique whereby the lacquer was suspended in a sealed vessel containing a saturated atmosphere of solvent. No actual contact was made between the solvent reservoir and the film.

Experimental details – vapour sorption:

A list of solvents used in this study is shown in Table 7.3. The lacquer films were suspended on a perforated aluminium stage in a saturated solvent atmosphere for 24 hours, after which time the mass increase was determined immediately on removal from the vessel. The films were then exposed to ambient laboratory conditions in an open container for a further 24 hours, and desorption of the solvent from the film after this time was also measured. 24 hours was determined as the optimal time for exposure through trial and error, and no further uptake was observed after this time. The sorption cycle was repeated and measured. The 3D solubility parameters were determined as for the immersion tests, and the results are shown in Table 7.4.

Table 7.3: Solvent uptake in vapour sorption experiments

		% wt.uptake of solvents, standard error in parenthesis			
Solvent	Molar volume (cm^3/mol)	Unaged	Daylight-aged	UV-aged	HgW-aged
Water	18.07	5 (0.06)	2.8 (0.09)	5.7 (0.07)	7.3 (0.07)
Ethanol	58.52	15.3 (0.09)	22.1 (0.13)	15.4 (0.20)	16.6 (0.45)
Ethyl acetate	98.54	79 (0.39)	29.1 (0.61)	76.1 (0.35)	76 (0.30)
Acetone	73.93	13.3 (0.15)	33 (0.13)	29.2 (0.50)	33.3 (0.60)
Hexane	131.31	2.7 (0.01)	0 (0.01)	2 (0.00)	2.9 (0.02)
Toluene	106.56	12.6 (0.19)	62.9 (0.15)	33.6 (0.09)	39.4 (0.18)
THF	82.44	47.2 (0.08)	68.4 (0.05)	48 (0.09)	92 (0.09)
Chloroform	80.66	40.3 (0.50)	83.1 (0.46)	51.3 (0.34)	78 (0.60)
Benzene	89.48	4.9 (0.20)	10.9 (0.34)	4.3 (0.23)	9.7 (0.19)
Butan-2-one	90.1	12.8 (0.10)	26.1 (0.09)	45.6 (0.07)	51 (0.09)
Acetonitrile	52.68	4.3 (0.20)	6.3 (0.40)	5.2 (0.29)	16.7 (0.35)
Diethyl ether	105.5	4.2 (0.23)	13 (0.19)	22.4 (0.20)	9.1 (0.17)
Pentane	111	1.3 (0.03)	0.5 (0.06)	0 (0.02)	1.3 (0.05)

Since the films are allowed to swell and contract with little damage as a result of their movement, they are less likely to disintegrate, and gravimetric results are obtained more easily and accurately. For this method, standard errors for the UV-aged lacquer vapour sorption results were, as a general trend, better than those for the immersions tests, as a result of the limitations of the latter method. The exceptions are water, ethyl acetate and benzene – the standard errors for the UV-aged lacquers were higher for the manual vapour sorption tests than the immersion tests. Although this method is a good measure of 3DSP values, the response is not comparable to a real, multi-layer lacquer surface (Figure 7.1) since the swelling and desorption of solvents would cause problematic movement within the degraded structure. A high-swelling solvent which permeates into the cracked structure and is held within the layers will cause delamination of the coating, leading to problems beyond simply a dull surface.

Table 7.4: 3D solubility parameters obtained for lacquers exposed to vapour sorption by graphical estimation and weight-averaged methods

Lacquer type	Method used	δd ($MPa^{1/2}$)	δp ($MPa^{1/2}$)	δh ($MPa^{1/2}$)
Unaged	Graphical estimate	17.3	4.3	6.5
	Weight averaged	16.53	5.56	7.85
	Weight averaged (V)	16.53	5.05	6.76
	Weight averaged ($V^{1/2}$)	16.54	5.26	7.19
UV aged 3500 h	Graphical estimate	16.7	5.7	4.8
	Weight averaged	16.47	6.50	8.04
	Weight averaged (V)	16.62	5.20	5.79
	Weight averaged ($V^{1/2}$)	16.56	5.76	6.66
Daylight aged 500 h	Graphical estimate	16.7	5.5	8.5
	Weight averaged	16.6	6.19	7.42
	Weight averaged (V)	16.67	5.64	6.68
	Weight averaged ($V^{1/2}$)	16.64	5.89	6.99
HgW aged 2000 h	Graphical estimate	16.6	5.8	6
	Weight averaged	16.61	6.52	7.54
	Weight averaged (V)	16.71	5.64	6.20
	Weight averaged ($V^{1/2}$)	16.67	6.03	6.72

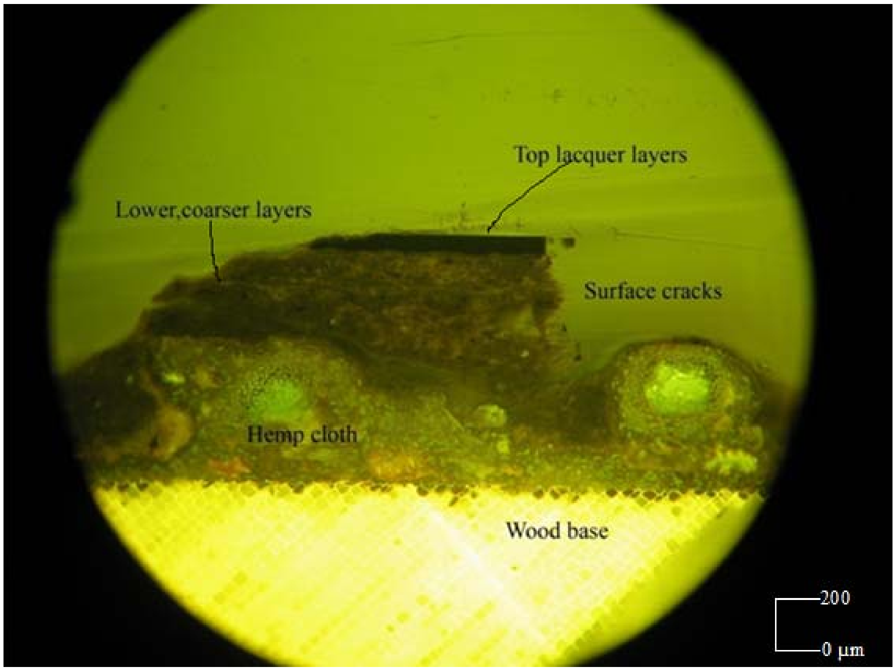


Figure 7.1: A damaged lacquer layer, from a 19th c. naturally aged Japanese screen frame, in a fixed position in the layered system (note the areas of surface cracking, which expose the lower layers to further damage).

7.2 Relevance to conservation – the Teas chart

Since conservators consult the Teas chart when selecting solvents for cleaning purposes, it is useful to apply the results from these experiments here. The Teas chart is a simple chart which uses a set of fractional parameters derived from Hansen's parameters, and the solvents are assigned values according to their relative strength of dispersion, hydrogen-bonding and polarity, allowing three-component solvent data to be plotted on a 2D graph, and grouped according to their solvent class.

The chart makes the assumption that all materials have the same Hildebrand value, and therefore, solubility behaviour is shown by relative contributions of the three forces. Despite its limitations, the chart is useful in aiding the selection of a suitable solvent or blend of solvents to demonstrate a specific behaviour, for example, dissolving one material but not another. It is also important to point out that this chart has been used extensively since the 1960s in the coatings industry as an effective tool.

For example, Figure 7.2 shows the region of solubility for an unaged and aged dammar varnish, frequently used on oil paintings, taken from the literature.[3] Figure 7.3 shows the effect of ageing of linseed oil on its solubility region.[3] Figure 7.4 shows the regions of high swelling on an aged Japanese lacquer as determined using the data obtained in section 7.1, and Figure 7.5 shows the region of high swelling lacquer (from data) in comparison to the solubility region of a varnish (from literature).

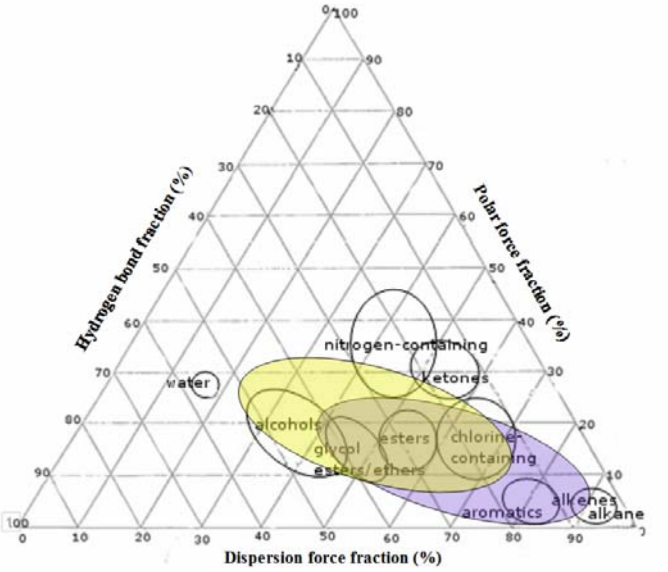


Figure 7.2: Region of solubility for an unaged (blue) and aged (yellow) dammar varnish.[3]

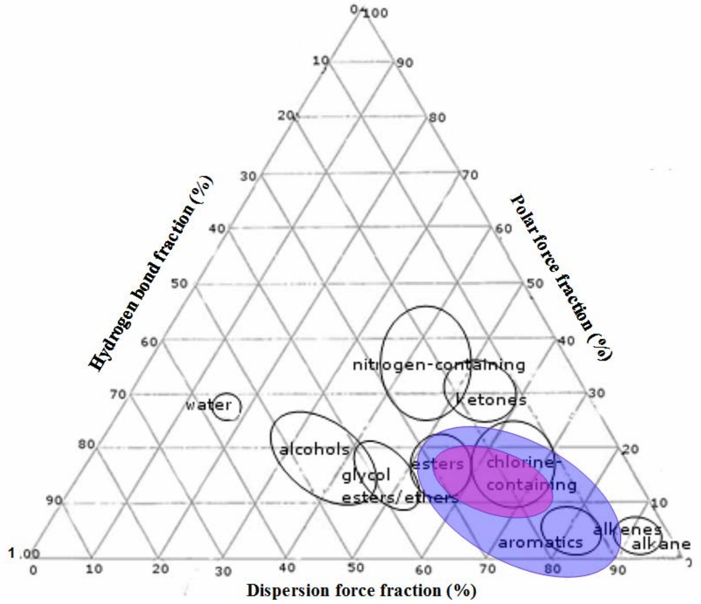


Figure 7.3: Region of solubility for an unaged linseed oil ("purple" inner ellipse), and aged crosslinked oil film (blue, outer ellipse).[3]

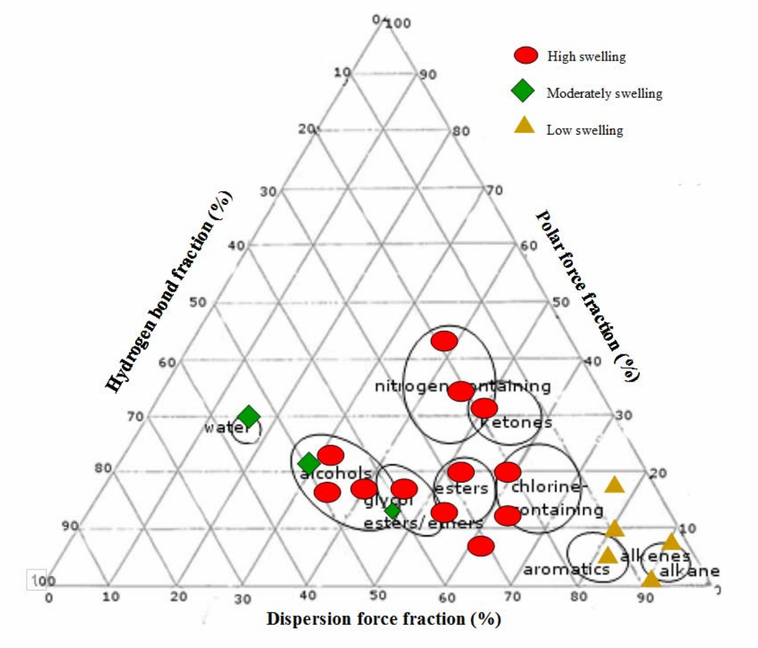


Figure 7.4: Region of high (>10%), low (<3%) and moderate (3-10%) swelling for an HgW-aged lacquer film.

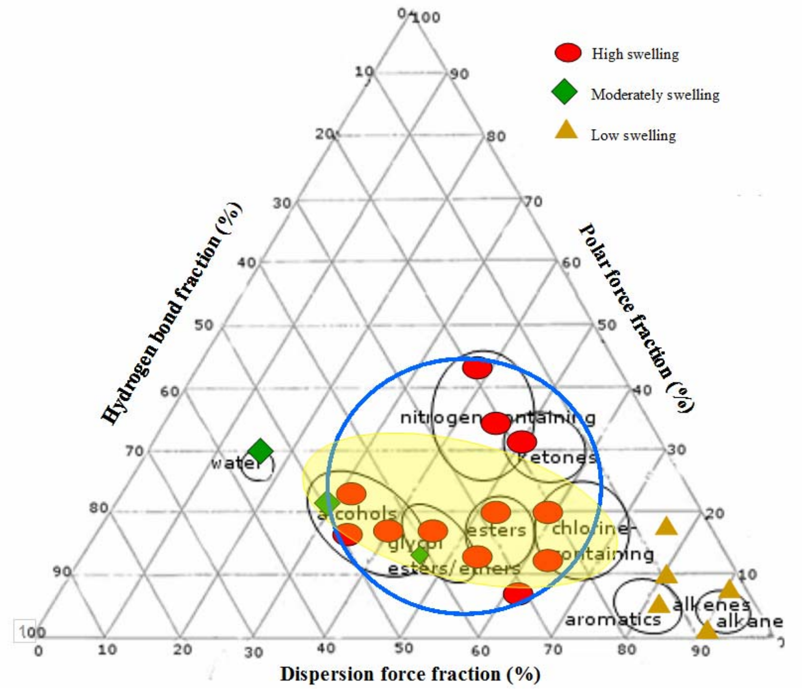


Figure 7.5: Region of solubility of an aged dammar[3] varnish (yellow ellipse) compared with region of high swelling of HgW-damaged lacquer (contained within the blue circle).

In the case of Japanese lacquer, a large area of the Teas chart is covered by high swelling solvent effects, but a general idea of the most dangerous areas can be seen. Only the non-polar alkane and aromatic solvents exhibit minimal swelling, and whilst they may be used to clean contaminants such as grease and fingerprints, they are unlikely to have any effect in the removal of aged oxidised varnishes.

The 3DSPs determined by vapour sorption uptake, and calculated using the contribution of molar volume by the weight averaged model, are plotted in Figure 7.6. The Teas fractional solubility parameters are derived from the 3DSPs and calculated using the relationship:[4] $f_d + f_p + f_h = 100$

where :

$$f_d = \delta_d / (\delta_d + \delta_p + \delta_h)$$

$$f_p = \delta_p / (\delta_d + \delta_p + \delta_h)$$

$$f_h = \delta_h / (\delta_d + \delta_p + \delta_h)$$

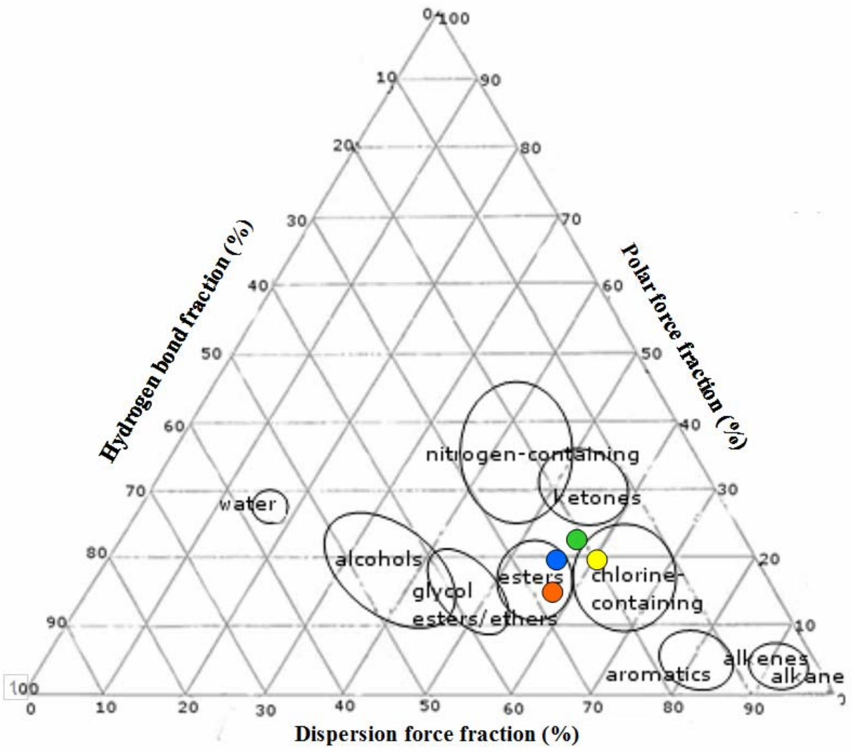


Figure 7.6: Teas chart showing the position of the regions of solubility of the unaged (red), daylight aged (blue), UV aged (yellow) and mercury tungsten aged (green) films as determined by calculated solubility parameters from vapour sorption data.

The calculated values are displayed on the Teas chart in Figure 7.6. The chart shows that the unaged lacquer's region of 'solubility' lies within the ester family of solvents, and as ageing processes are applied, the regions of 'solubility' move towards the chlorinated solvent group, with the most aggressively aged lacquer lying in the most polar region of this particular class of solvents according to the chart.

Other solubility parameter scales, such as the Kamlet-Taft scale, are useful in predicting the surface properties of an aged polymer, and therefore, the interactions between the lacquer and solvents, based on the swelling data from the vapour sorption analysis. The Kamlet-Taft solubility scale's parameters measure the hydrogen bond donating/acidity (α), hydrogen bond acceptor or basicity (β) and polarizability (π^*) component of the test solvents used. A regression analysis applied to the swelling data indicated that the π^* component was significant for the unaged lacquer ($P = 0.0022$, where P indicates the likelihood that random sampling would give a correlation coefficient as extreme as that observed), whereas for the harshly aged HgW lacquer, the π^* ($P = 0.00026$) and α ($P = 0.03$) components had a significant correlation. Therefore, on ageing, the lacquer exhibits a higher interaction with hydrogen-bond donating solvents and polar solvents. Therefore, the unaged lacquer exhibits effects from the π^* components of the solvents, and, theoretically shows a negative swelling behaviour towards the lacquer with hydrogen-bond donor solvents, such as alcohols. However, in the case of the damaged lacquer, hydrogen bond acceptors, basicity, have no influence on the swelling of the damaged lacquer, which implies that the lacquer aged to this extent does not exhibit acidic protons in its damaged top layers.

7.3 Dynamic Vapour Sorption analysis

Improving on the gravimetric analysis approach, lacquers were exposed to a range of solvent vapours and their uptake was measured by Dynamic Vapour Sorption (DVS). This is a highly accurate and reproducible technique, although it has a restricted range of useable solvents. Unlike the manual vapour sorption experiment described in section 7.1, the mass change was measured whilst the sample was inside the solvent-saturated atmosphere, thereby eliminating the error introduced on removal from the saturated atmosphere for weighing, and allowing observations of absorption kinetics. The DVS also provides controlled vapour pressure leading to determination of isotherms. The determination of vapour sorption and diffusion rates of organic solvents or water are useful in a range of applications such as in the food industry, pharmaceuticals and polymers.[5-7] DVS methods are more accurate means of measuring organic solvent uptake, but moreover it can be used to study the kinetics of solvent uptake.

In DVS the vapour partial pressure surrounding the lacquer film is controlled by combining saturated and dry carrier-gas streams. The temperature within the sample chamber is kept constant to +/- 0.1^{o}C, since it is enclosed by a temperature-controlled chamber; the following experiments were carried out at 30^{o}C. These experiments were possible thanks to Surface Measurement Systems Ltd, Alperton, London, who designed the DVS-HT High Throughput system. The system has 10 stainless steel sample pans (10 mm dimension).

The DVS provides a very good indication of the response, and, therefore, susceptibility to damage, of the lacquer, to a particular solvent type. For example, 0.1 g of aged lacquer (9 micron thick) shows a 24% uptake of ethanol in a saturated atmosphere (Figure 7.7), but a negligible uptake (less than 0.2%) of octane (Figure 7.8). In these two figures, two sorption cycles are shown. The predicted (target) %P/P_0 (where P represents pressure) is illustrated by the blue lines showing the individual programmed steps. The red lines indicate the actual changes occurring. The closer the actual change in mass lies to the target mass, the better equilibrated the experiment. The desorption cycle (shown by the decrease in target %P/P_0) shows the release of solvent from the film; Figure 7.7 shows that not all of the solvent is released after the first cycle. The second sorption cycle shows a better adherence to the target cycle.

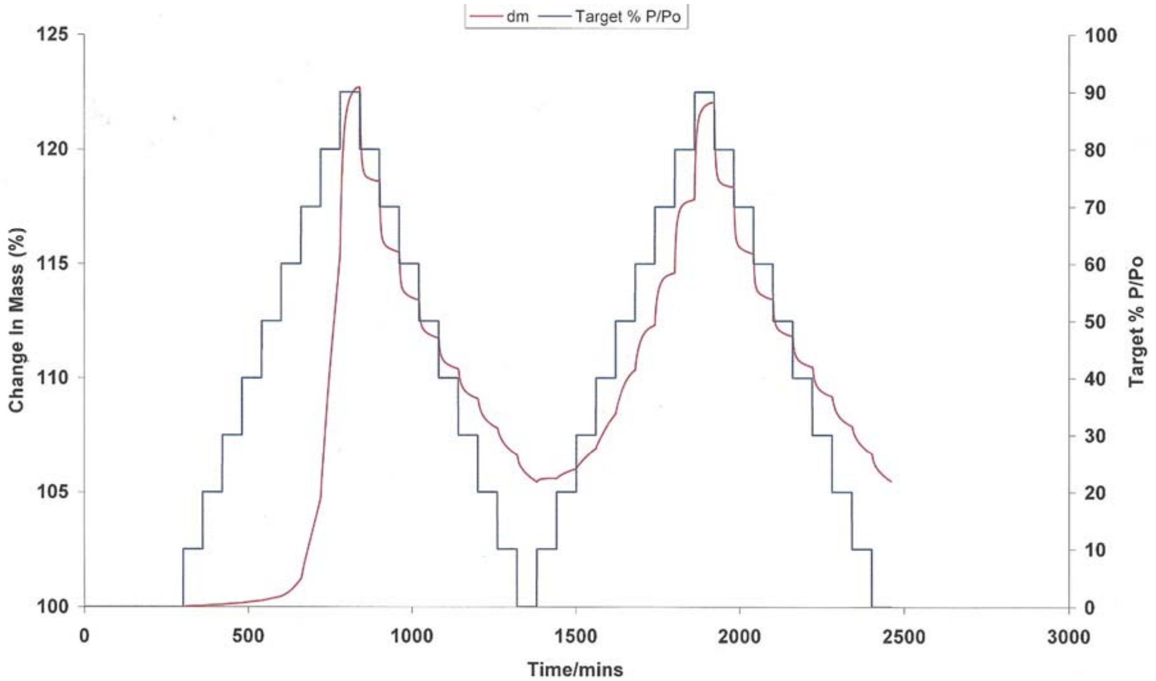


Figure 7.7: Uptake of ethanol by aged lacquer aged for 2,000 h, measured by DVS.

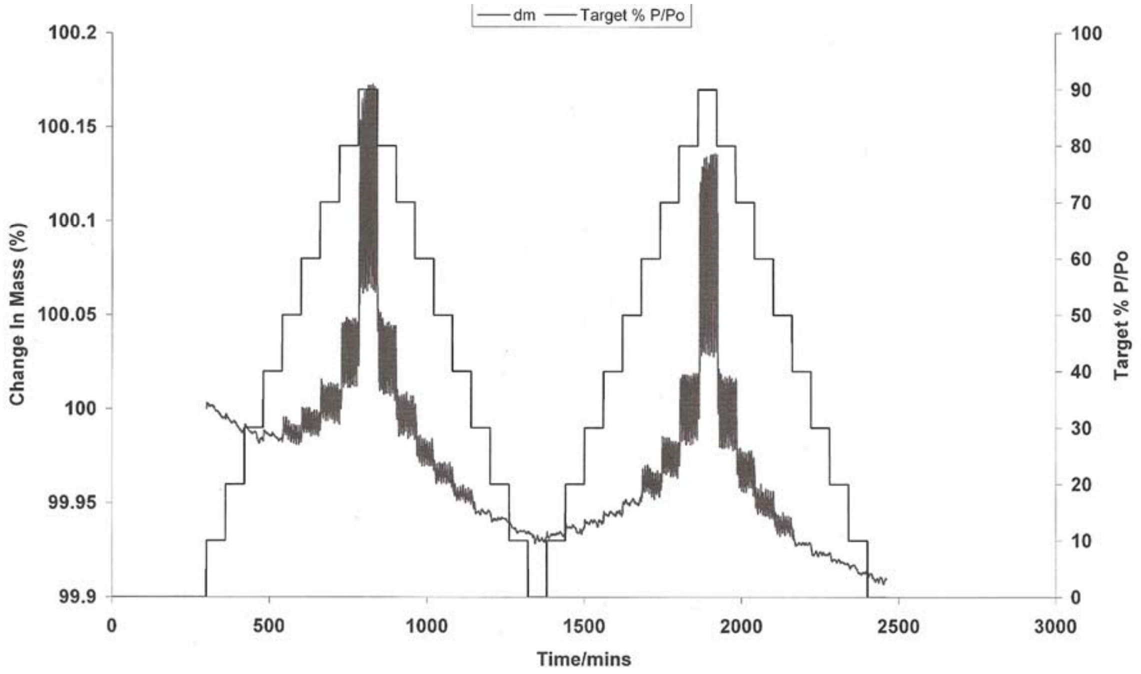
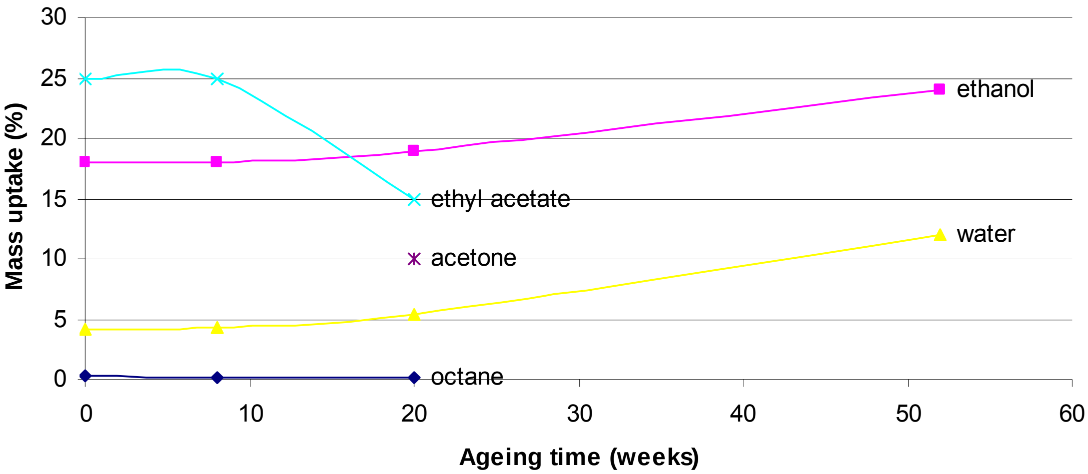


Figure 7.8: Uptake of octane by UV-aged lacquer for 2,000 h, measured by DVS.

This method shows the increasing susceptibility of the ageing lacquers to some solvent types. Graph 7.4 shows the uptake of octane, ethanol, ethyl acetate, acetone and water measured for lacquer exposed to filtered UV daylight simulator for 0 to 20(+) weeks.



Graph 7.4 Summary of mass changes of UV-aged lacquers on exposure to a range of solvents over increasing ageing time measured by DVS.

DVS isotherms show the equilibrium vapour uptake as a function of vapour partial pressure. The isotherms for five different solvents were obtained for a range of damaged lacquers, and the sorption properties, including desorption and re-sorption cycles, of the films determined.

Discussion of results from DVS measurements

a) Non-polar solvents: alkanes

The first test solvent used was octane (vapour pressure 1.5 kPa, 30^{o}C). The uptake of the alkane solvent for each lacquer-aged type is negligible (see Figure 7.8). For a lacquer film aged for 20 weeks under UV daylight simulation there is a maximum uptake of 0.17% octane. This mass is lost completely during desorption and the second sorption cycle shows an increase in mass of 0.14%. The negligible uptake of alkane by the lacquers, including aged samples, is consistent with the previous immersion and vapour sorption measurements where hexane, cyclohexane and pentane uptakes were measured in saturated atmospheres and/or immersion tests. Limited swelling of the crosslinked lacquer is seen in the case of long-chain, non-polar alkane solvents, since these have a low affinity for the saturated and polar constituents of the urushiol molecule or the other water-soluble components. These solvent types are potentially useful for cleaning dust and some dirt from the surfaces without causing swelling, however, non-soluble, oxidised substances, such as aged varnish, bonded to the original layer would not be dissolved or swelled by the solvent either.

b) Alkenes/aromatics

The DVS experiment was not appropriate for these solvents; health and safety restricts the use of an aromatic such as xylene, and experimentation with conservation gatame solvents such as HAN8070, would involve a mixture of aromatic vapours which would not involve an accurate uniform mixture. The initial immersion and vapour-sorption experiments, however, included representative solvents, including benzene and xylene.

c) Alcohol

DVS experiments were carried out with ethanol (vapour pressure 14kPa, 30°C) as a test solvent. Alcohols are often used for surface cleaning during conservation or restoration work. The uptake of ethanol is presented in Table 7.5 for different lacquer types.

Table 7.5: Ethanol uptake by aged lacquers for two cycles and retention of solvent following desorption (Abbreviation: n/d, none determined)

Lacquer type	1st sorption cycle mass uptake (%)	Retention after desorption cycle (%)	2nd sorption cycle mass uptake (%)
Unaged	18	3	18
UV-aged (20 weeks)	19	4	13.5
HgW-aged (12 weeks)	20	4	14
UV-aged (52 weeks)	24	4.5	n/d

The change in mass of an unaged, dried lacquer film after one sorption cycle was substantial at 18%, and, notably, 3% of the solvent entering the film during this stage did not leave following desorption, although the same amount was then resorbed during the second cycle. The isotherm plot for these events is shown in Figure 7.9. The mass uptake for standard aged samples (20 weeks by UV daylight simulation and 12 weeks by mercury tungsten) was not substantially increased at 19% and 20%, respectively, although when ageing was significantly prolonged, for example ageing for 12 months by UV, the mass increase was 24%, with 4.5% being retained after the first exposure.

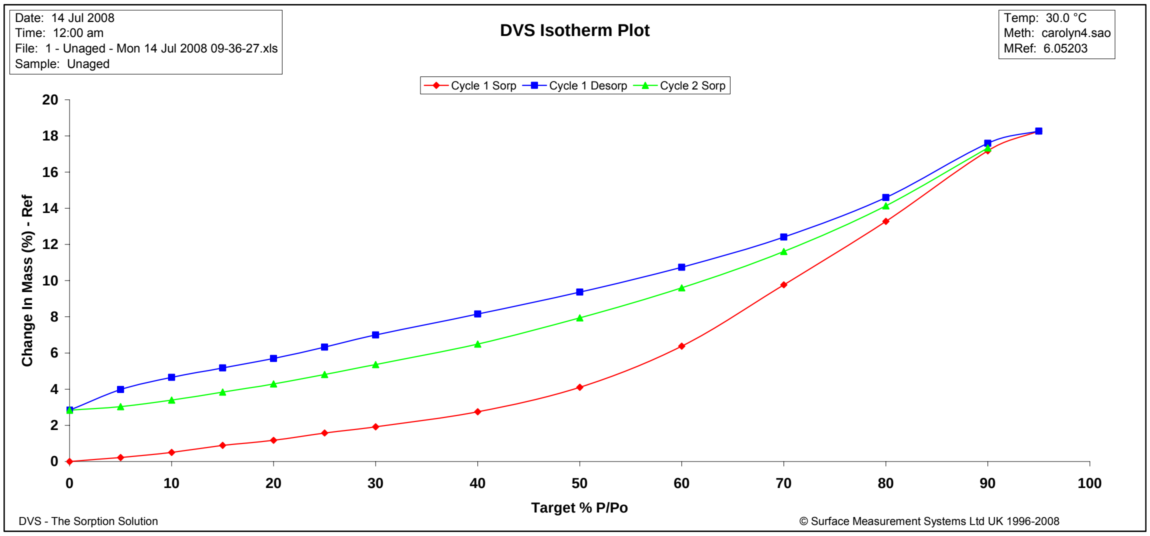


Figure 7.9: DVS isotherm plot for unaged lacquer ethanol uptake; first sorption cycle in red, desorption cycle in blue, and second sorption cycle in green.

d) Water

DVS experiments were carried out using water at pH 5.5 (vapour pressure 4.3 kPa, 30^{o}C). The unaged lacquer exhibited a varied uptake of between 2-4.1% water throughout these experiments. UV-aged lacquer had an increased mass of water, as shown in Table 7.6.

Table 7.6: Uptake of % mass of water by UV-aged lacquers measured by DVS

Length of ageing time (weeks)	Uptake of water (%)
0	2 – 4.1
8	4.3
20	5.4
52	12

The mercury tungsten samples for these experiments were damaged and readings could not be taken. In all cases the desorption and re-sorption cycles followed a similar pattern to the first cycle, that is to say that there was no water held in the lacquer film following desorption and the same amount of water was reabsorbed on the second exposure to the solvent, as demonstrated in Figure 7.10.

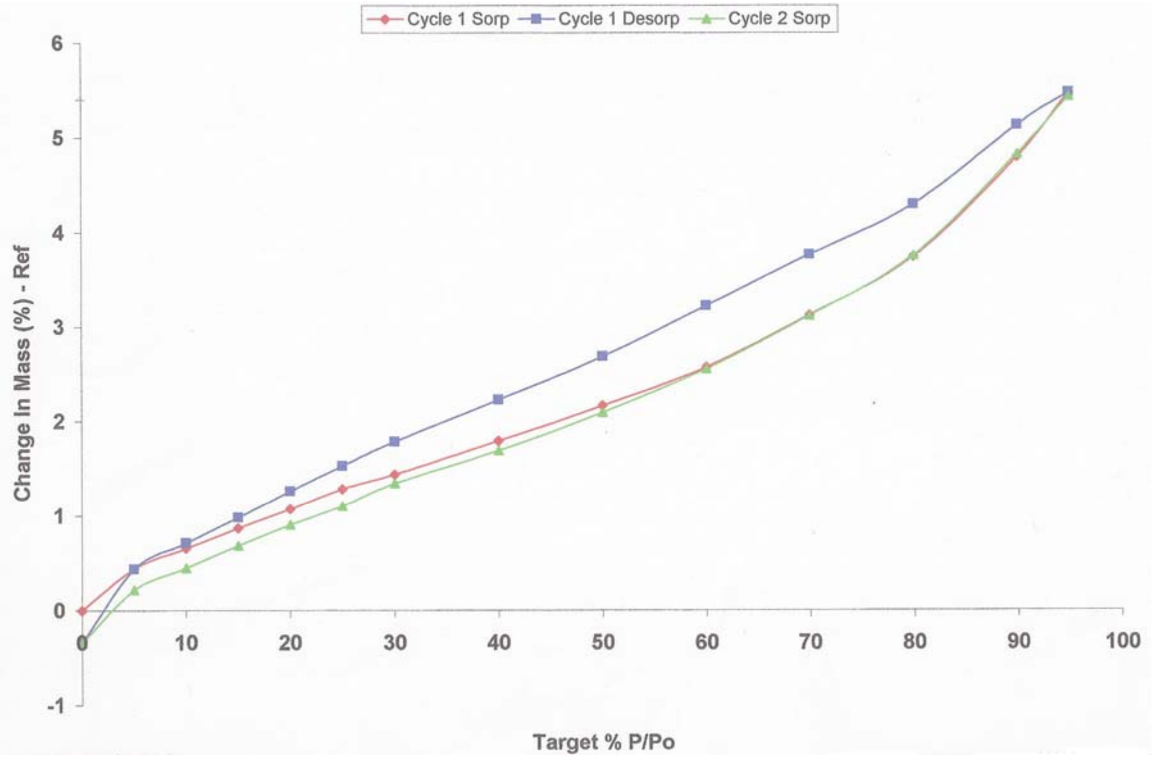


Figure 7.10 DVS isotherm for water sorption, desorption and resorption cycles on UV aged lacquer (20 weeks).

e) Polar solvents with carbonyl groups

Acetone

Acetone is also used as a cleaning agent during conservation and restoration work,[8-10] and its effects on lacquer were monitored by DVS. The results, however, were unsatisfactory, given that the test could only be carried out once on a sample that was not predried, due to instrument availability. This solvent is suspected of having a corrosive behaviour towards the DVS instrument and is, therefore, not carried out frequently. After the initial mass loss, attributed to water loss, the damaged lacquer was increased in mass by 10% on the first cycle and also on the second cycle for lacquer damaged by HgW. Lacquer aged by UV daylight simulation (20 weeks) absorbed approximately 8% on a sorption cycle, and desorbed the same amount, once the instrumentation had been stabilised. These initial results give much lower uptakes than the manual vapour sorption experiments

(29.2-33.3% uptake for damaged lacquer, the data is shown in Table 7.3), although they do indicate that whilst a significant amount of solvent is taken up by the lacquer, none of it is retained.

Ethyl acetate

A member of the ester solvent group, ethyl acetate, was chosen to confirm the results of the vapour sorption tests which showed a greater response of the ester solvents towards non-lacquers than those which were aged. An unaged sample absorbed 25% wt., the highest increase seen from any of the test solvents; the desorption cycle ended with the lacquer retaining 5% wt. solvent. Upon artificially ageing the lacquers, the uptake for UV 20 weeks was 15%. The desorption cycle again did not see all of the solvent lost; after desorption had taken place, the lacquer had a mass increase of 6% on the original, and the second cycle saw an increase of another 15% mass (Figure 7.11).

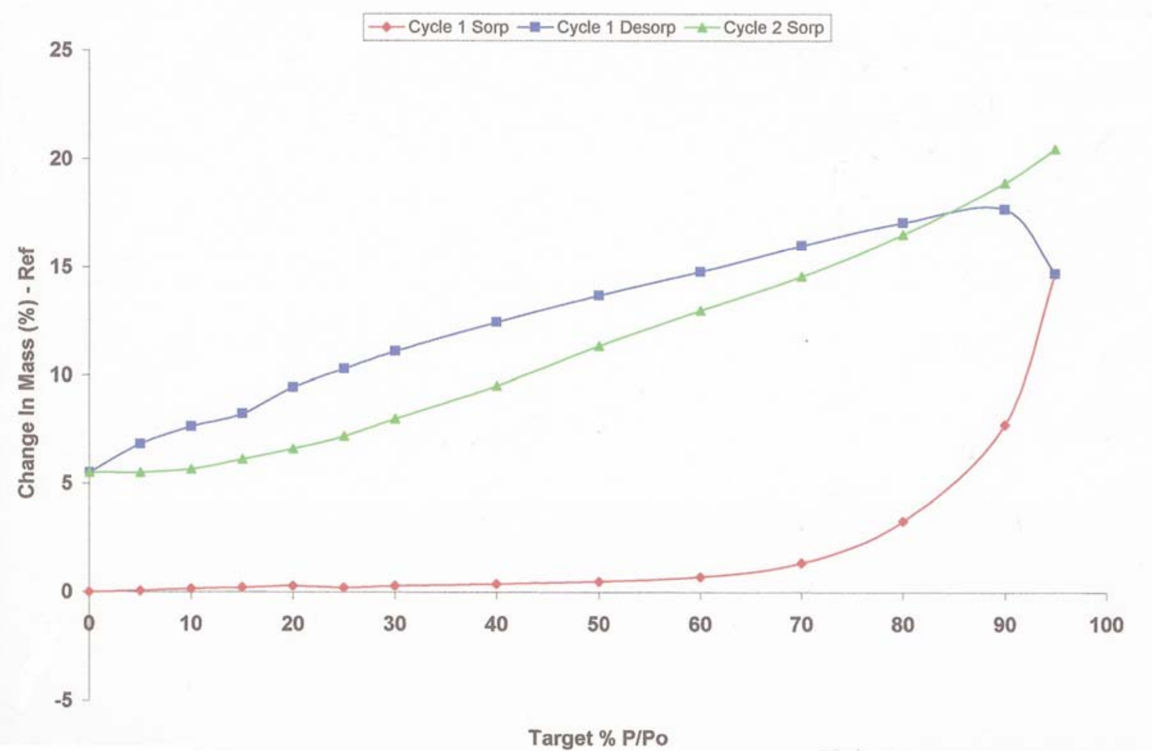


Figure 7.11 DVS isotherm showing sorption, desorption and re-sorption cycles for ethyl acetate on UV aged lacquer (20 weeks).

The mercury tungsten sample followed a very similar pattern to the UV-aged – a mass increase of 16% was observed, 5% was retained after desorption, and a further 12% was absorbed in the second cycle.

Table 7.7 A comparison of methods for solvent uptake measurement by UV-aged lacquer (20 weeks)

Solvent group	Solvent name	Immersion uptake	Vapour sorption (manual) uptake	DVS uptake (%)
Alkane	Octane	n/d	n/d	0.17
	Hexane	0	2	n/d
	Pentane	1	0	n/d
Alkene/aromatic	Benzene	1.3	4.3	n/d
	Xylene	3.2	n/d	n/d
	Toluene	2.2	33.6	n/d
Aqueous	Water	4.2	5.7	5.4
Alcohol	Ethanol	9.2	15.4	19
	Methanol	5.2	n/d	n/d
	Propan-2-ol	5.1	n/d	n/d
	Butanol	3.4	n/d	n/d
Polar with carbonyl groups	Acetone	5	29.2	8
	Ethyl acetate	7.7	76.1	15
	Diethyl ether	5.3	22.4	n/d

Abbreviation: n/d, not determined.

The results of the uptake of the limited range of solvents that were available for DVS analysis are compared to the uptakes measured by the manual methods in Table 7.7 for UV-aged lacquer (20 weeks). The DVS analysis confirms the data obtained in the manual tests for water (data range, 4.2-5.7%) and the alkane solvents (~negligible uptake-2%), however, there are substantial differences between the solvent-sorption measurements for the alcohols and polar solvents with carbonyl groups, highlighting the inaccuracies of the manual (immersion and vapour uptake) methods. DVS is the only method with a controlled solvent atmosphere – the manual methods required the brief removal of the sample from a saturated atmosphere, which had a significant effect on the accuracy of the results obtained. A greater range of solvents available for the DVS analysis would be advantageous for further work.

7.4 Scanning electron microscopy

In addition to the solvent-swelling tests, lacquers were examined using SEM to determine observable surface changes. Samples were taken from an unaged board, Xenon-arc- and HgW-lamp damaged boards, and a naturally aged piece taken from a 19th century lacquered screen. A small area of the initial lacquer piece was imaged under SEM. A set of each lacquer types (2 mm^2) were swabbed with 0.2 ml solvent and allowed to dry for 24 hours after which time they were re-swabbed and the samples were left to sit for 7 days in the dark in ambient r.h. and temperature. After this time, the samples were re-examined under SEM, and the same region of the sample was photographed, where recognisable. Images taken at x1000 magnification before and after solvent application are included in the results below.

Solvent-lacquer interaction experiments: discussion of SEM results

a) Non-polar solvents: alkanes

The SEM images (Figure 7.12) confirm that the alkane had little effect on the physical structure of the surface in terms of the larger cracks; the images show the artificially aged lacquer before and after swabbing with hexane solvent.

Exxsol DSP80/110 is a solvent which has been used in *urushi* gatame trials at the Victoria and Albert Museum for dilution of *urushi*. It is a petroleum-derived industrial substance composed of *n*-hexane (2%), heptane and isomers (71%), cyclohexane (8%), methylcyclohexane (14%), hexane isomers (2%) and octane isomers (3%). Its behaviour ought to be similar to the pure octane or hexane, but, due to the practical relevance, swab tests on a naturally aged sample were examined under SEM (Figure 7.13).

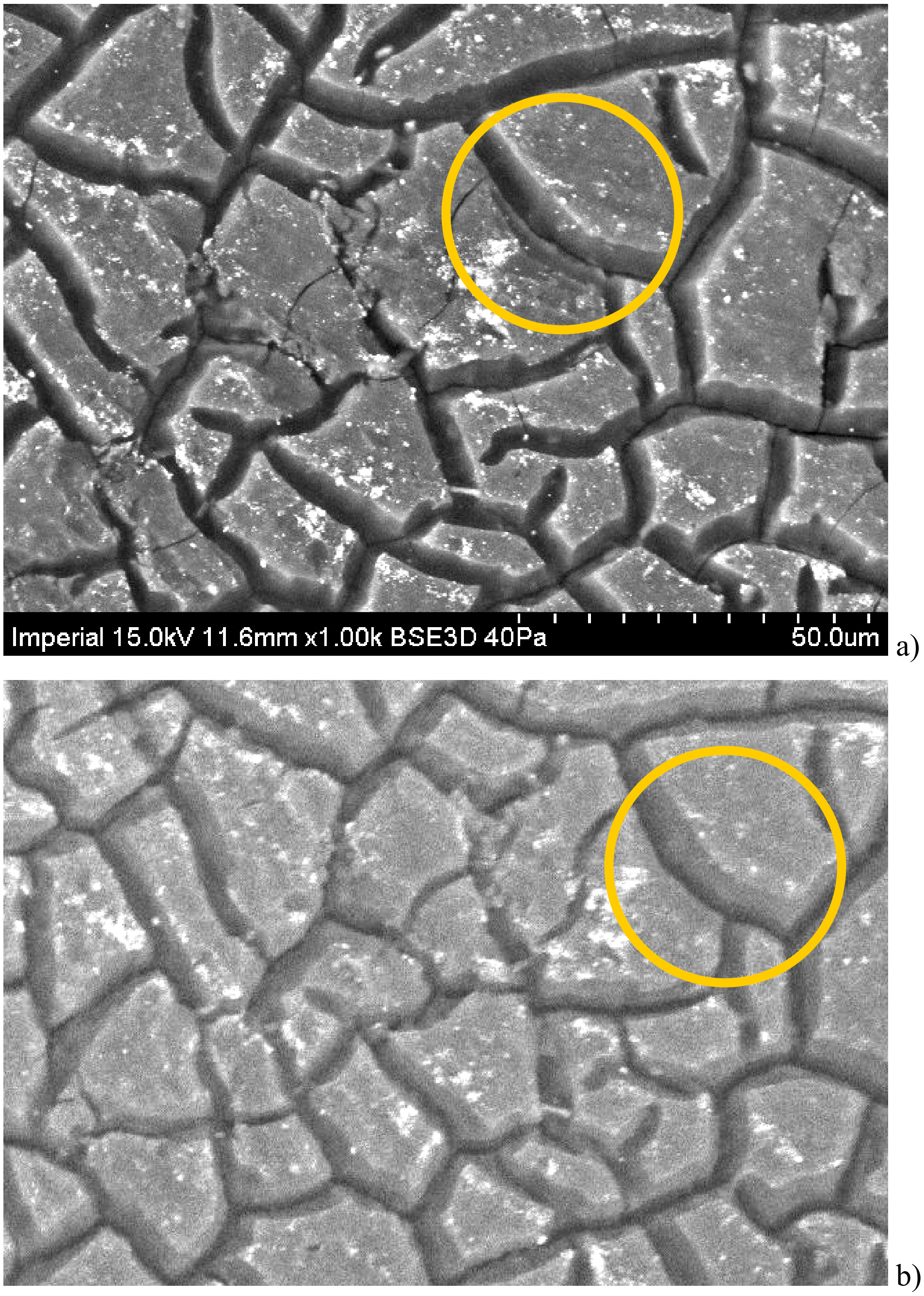


Figure 7.12 Lacquer aged by HgW for 12 weeks a) before and b) after swabbing with hexane.

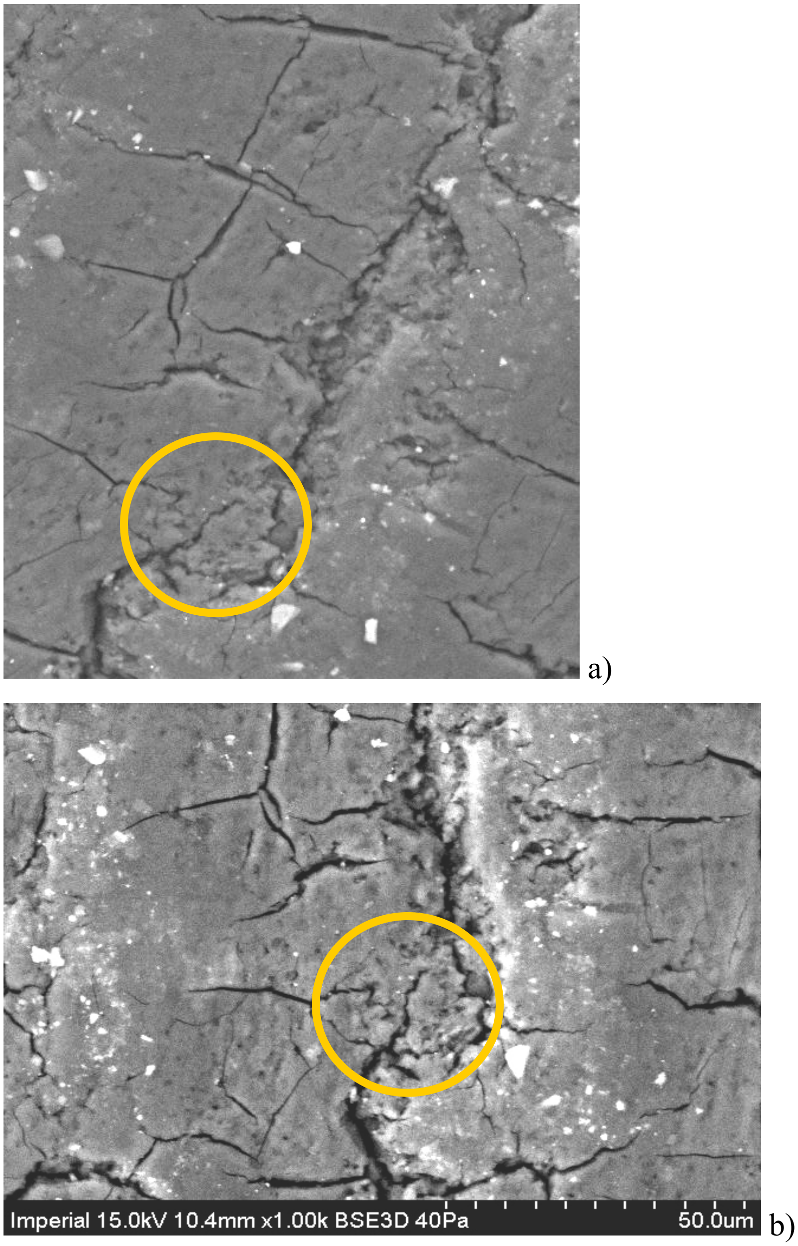


Figure 7.13 Naturally aged lacquer from a 19th century Japanese screen a) before and b) after swabbing with Exxsol; yellow circle shows a common point between the images.

No exacerbation of larger pre-existing cracks was observed using either hexane (Figure 7.12b) or Exxsol (Figure 7.13b) on the aged lacquers; however, the finer areas of cracking show increased definition. The surface debris seen on the Exxsol before-swabbing image of the artificially aged lacquer (Figure 7.14a) has been washed away but the original surface appears largely unchanged with the exception of the short, hairline cracks. The bright, white areas are present on the surfaces of the lacquer in Figure 7.14, both before and after swabbing, and are likely to be caused by scratching during the polishing stage of preparation. The white regions present in the lacquer in Figure 7.13b, are not present in the pre-swabbed lacquer, and therefore are possibly indicative of residual material charged in the SEM. No leaching effects indicated by weight loss of the film after immersion were observed during the immersion tests of hexane. It is not clear whether the more defined fine cracks are due to damage by the alkane solvents or by the conditions they are exposed to whilst under analysis in the scanning electron microscope.

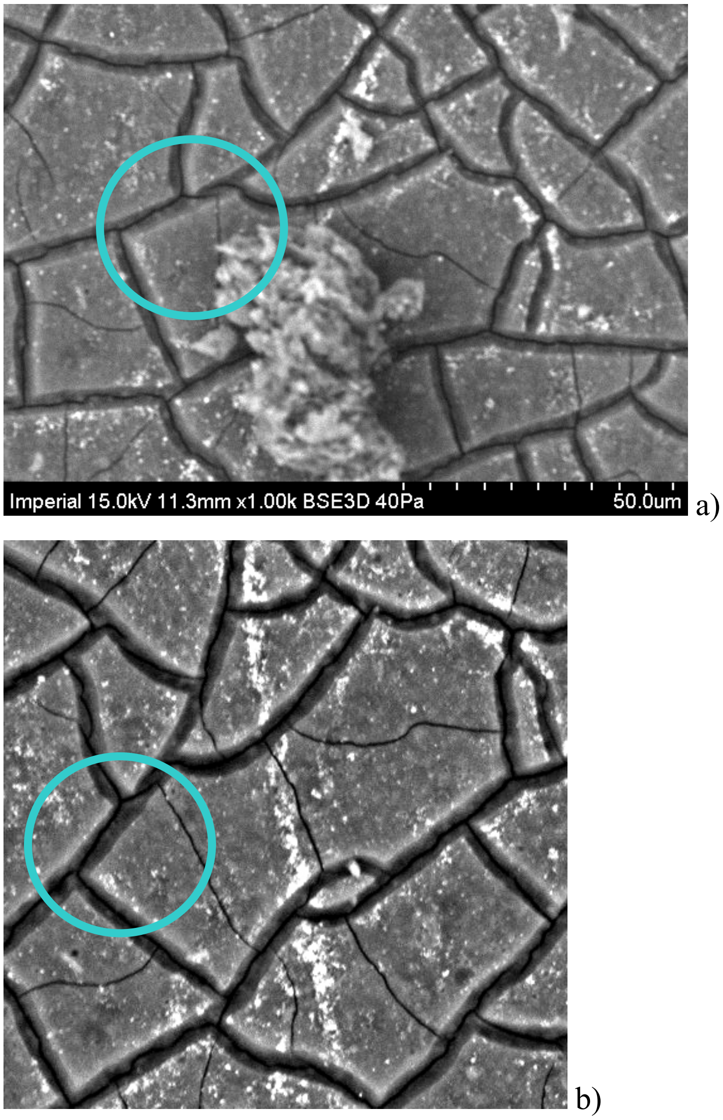


Figure 7.14 HgW aged lacquer a) before and b) after swabbing with Exxsol solvent, with blue circle indicating common point.

b) Alkenes/aromatics

The effects of alkene/aromatic-based solvents were also examined under SEM, by swabbing with Han 8070 industrial solvent or xylene. The HAN8070 solvent, also used in gatame processes, is an aromatic hydrocarbon mixture, consisting of kerosene (20-30%), naphtha (70-80%), trimethylbenzene (1-5%), mesitylene (0.1-15) and naphthalene (5-10%). The before- and after-swabbing images taken for light damaged lacquers (natural and artificially-obtained) for Han 8070 and xylene are shown in Figure 7.15 and Figure 7.16, respectively.

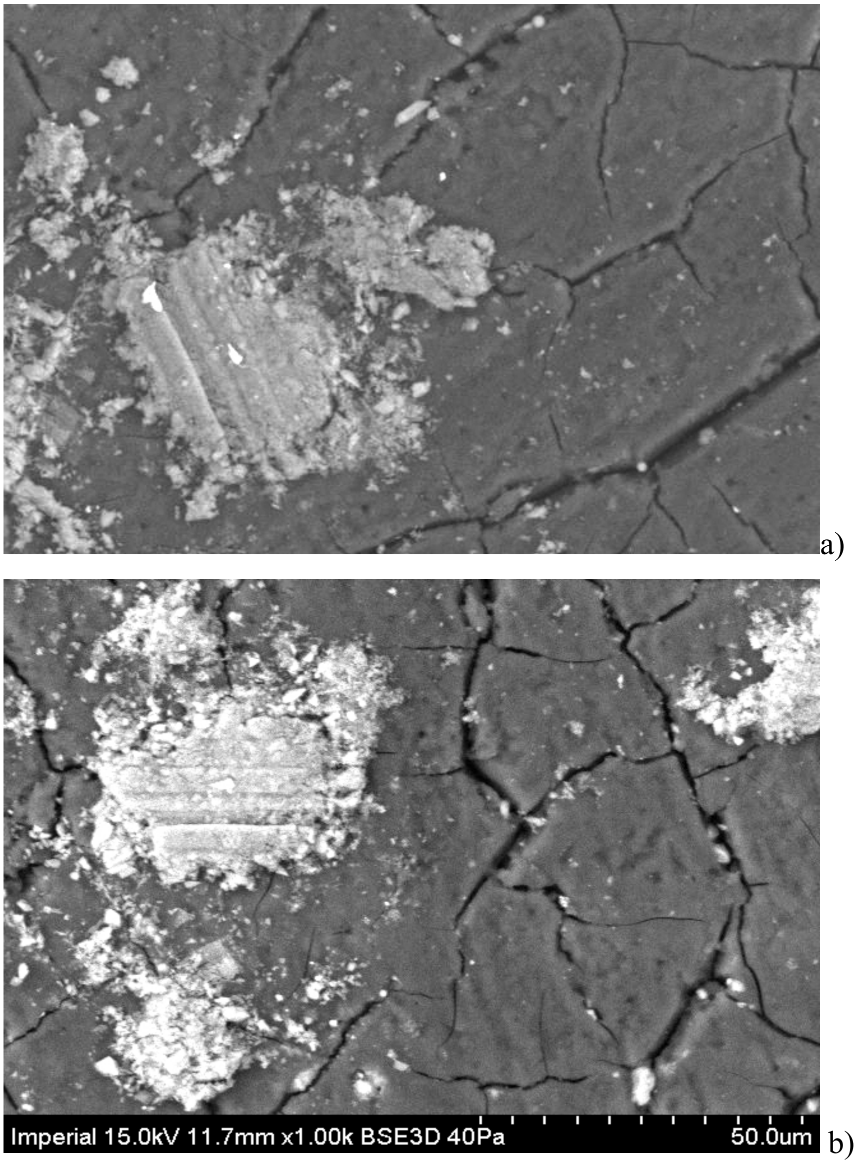
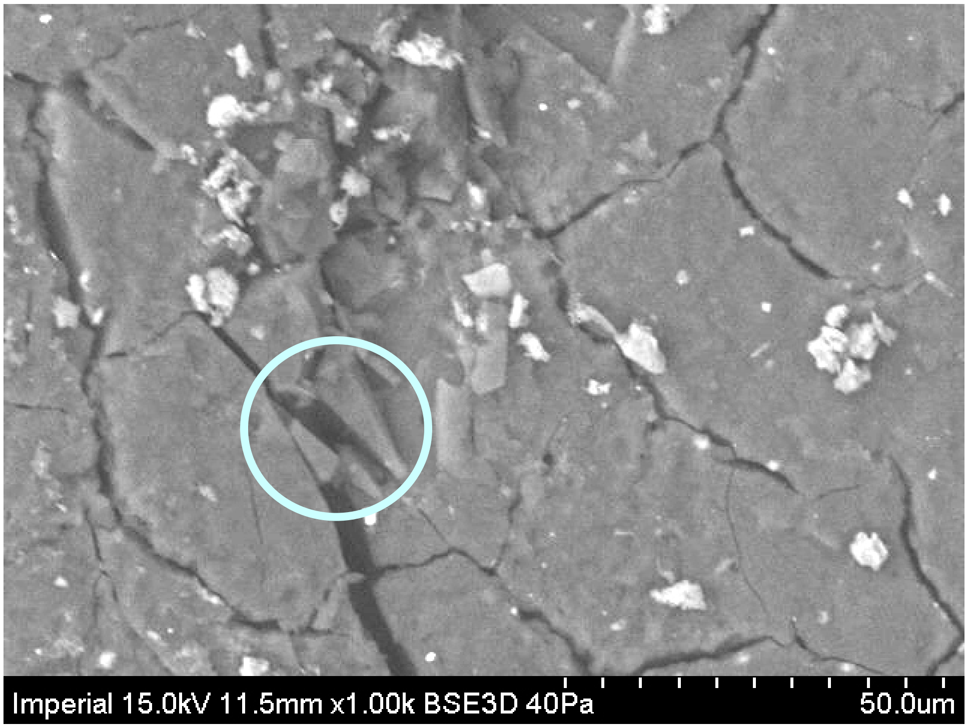
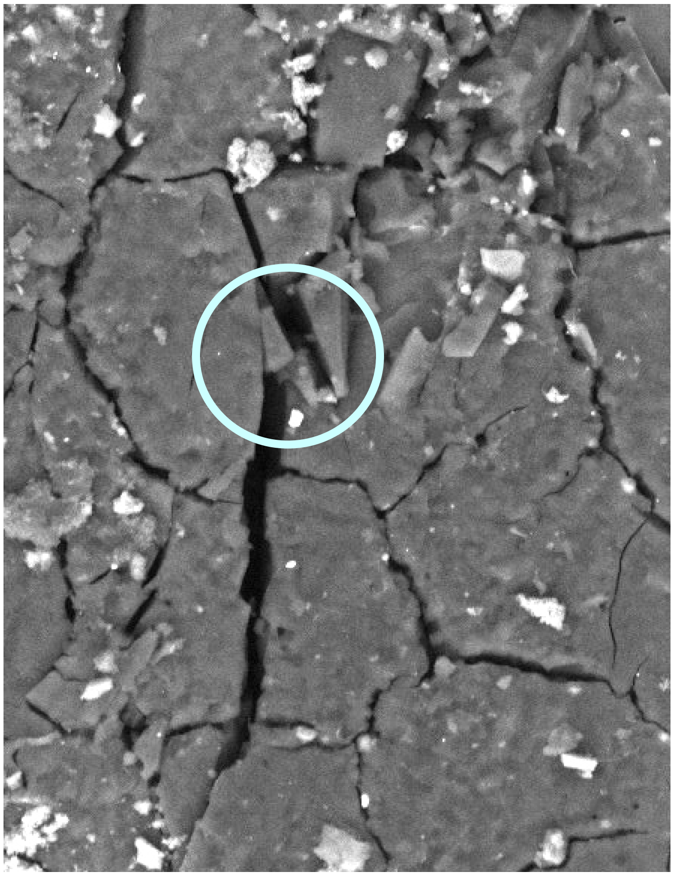


Figure 7.15 Naturally aged lacquer a) before and b) after swabbing with Han8070



a)



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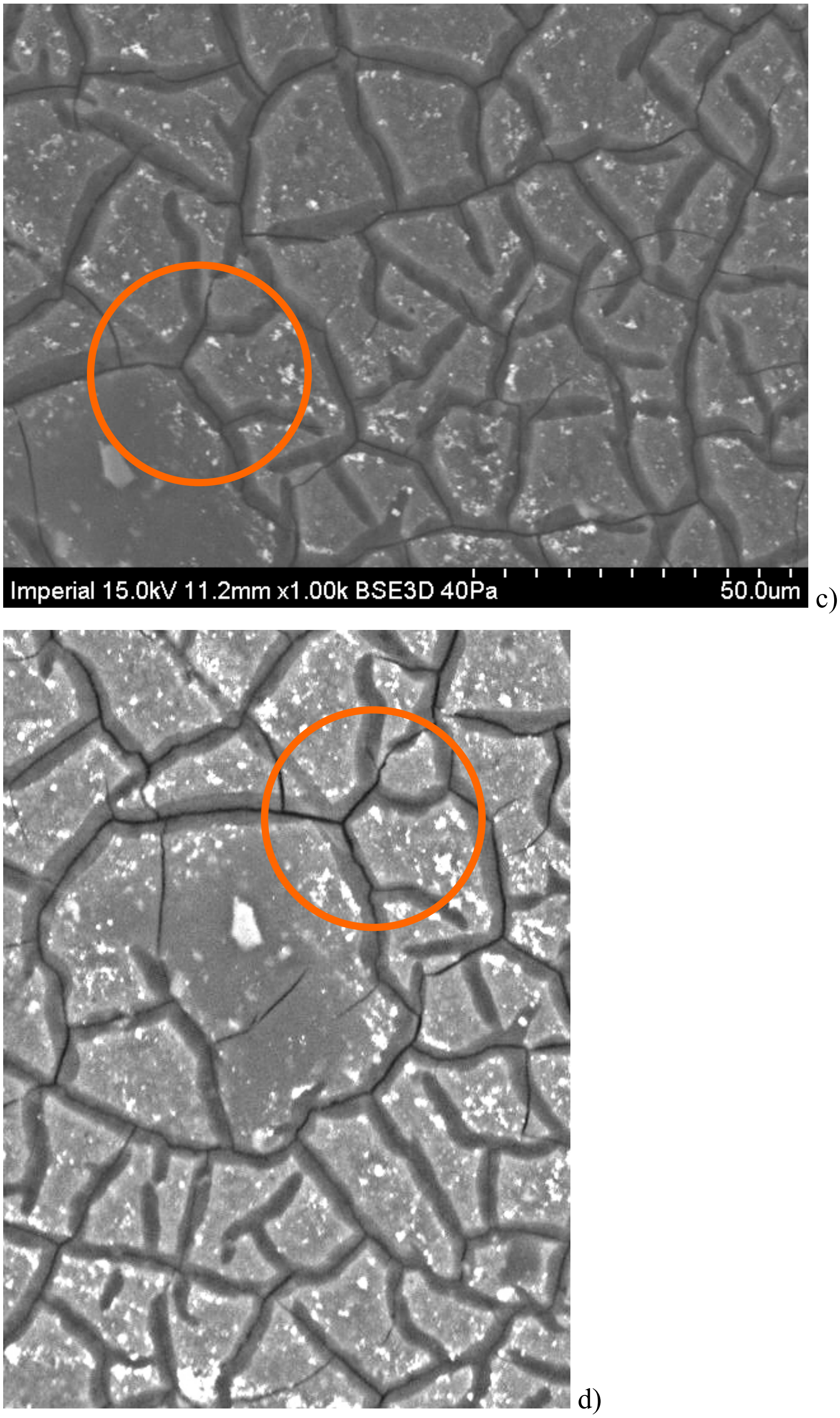


Figure 7.16: Naturally aged lacquer a) before and b) after swabbing with xylene, common points indicated by turquoise circle, and artificially aged lacquer c) before and d) after xylene swabbing over the surface, common points indicated by an orange circle.

As with the alkanes, these solvents have minimal impact on the surfaces, leaving cracking patterns undisturbed and looser fragments in place. Toluene uptake, however, was considerable in the aged lacquers for the vapour sorption tests indicating that the aromatic solvents would be more prone to interacting with the surface, but over limited exposure times no problems occurred. No leaching effects were observed during immersion tests.

c) Alcohol

Unsurprisingly, when aged lacquer surfaces are observed under SEM after swabbing with ethanol, the cracks are seen to have grown on the naturally aged surface (Figure 7.17). The image taken for the mercury tungsten-damaged surface shows an interesting change for some of the cracked areas (Figure 7.18): the area highlighted in green seems to have decreased the sharpness of the crack that had been visible before swabbing. A possible explanation for this is that the solvent has dissolved some fragments of the aged lacquer in this area or dirt and other debris, causing a redeposition of this material within the large crack, seemingly ‘filling’ it in. This effect may also result from deposited impurities in the solvent. Further cracking occurs over the top of the filled areas showing a substantial change to the damaged surface on swabbing with ethanol.

Clearly, the alcohol solvents have an effect on the surface of the vulnerable lacquer, and whilst these solvents might have the ability to dissolve or swell additional oxidised materials, the safety associated with their application to the surface of a vulnerable piece is questionable. No measurable leaching effects were observed for ethanol during the immersion tests.

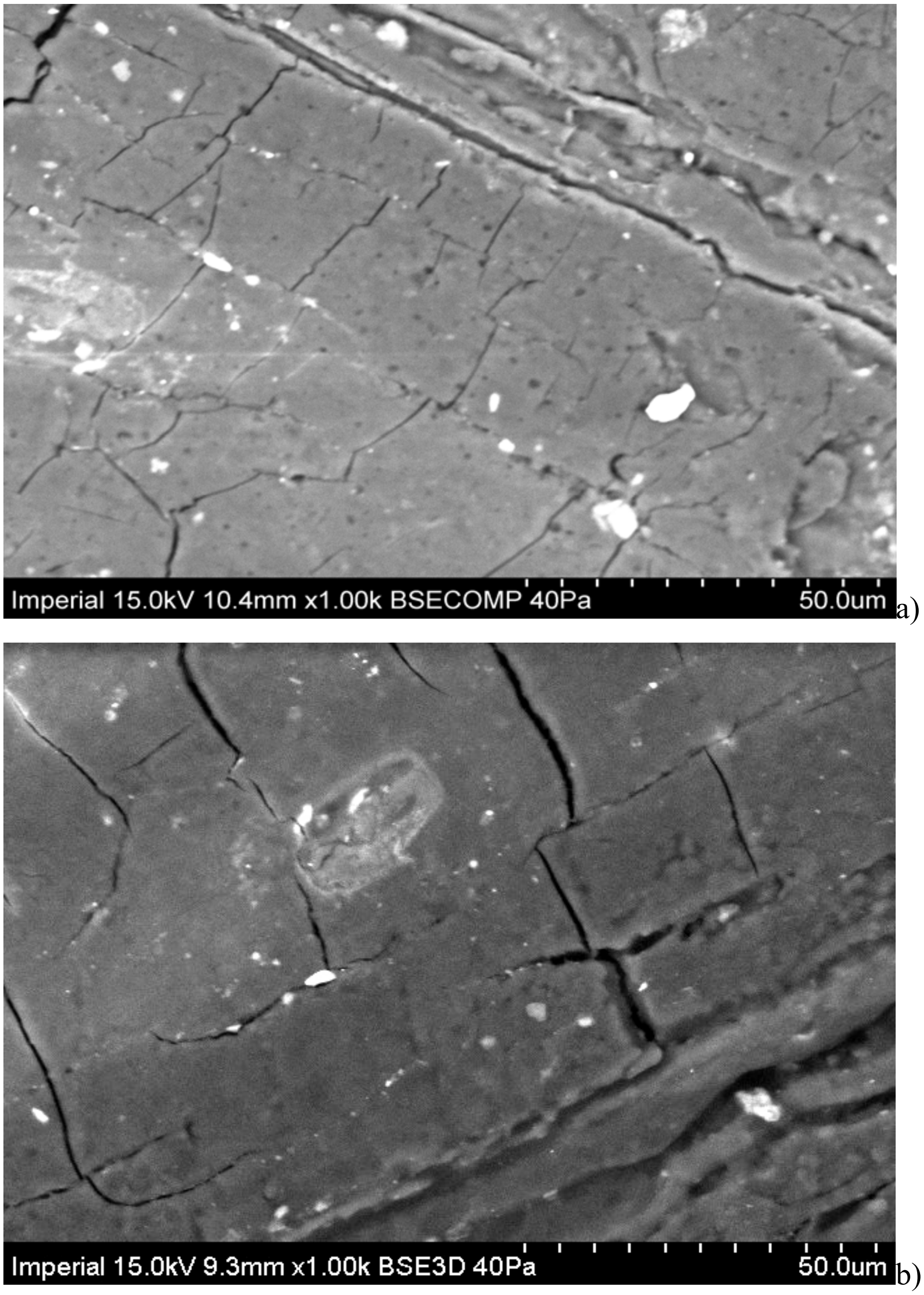


Figure 7.17 Naturally aged lacquer a) before and b) after swabbing with ethanol.

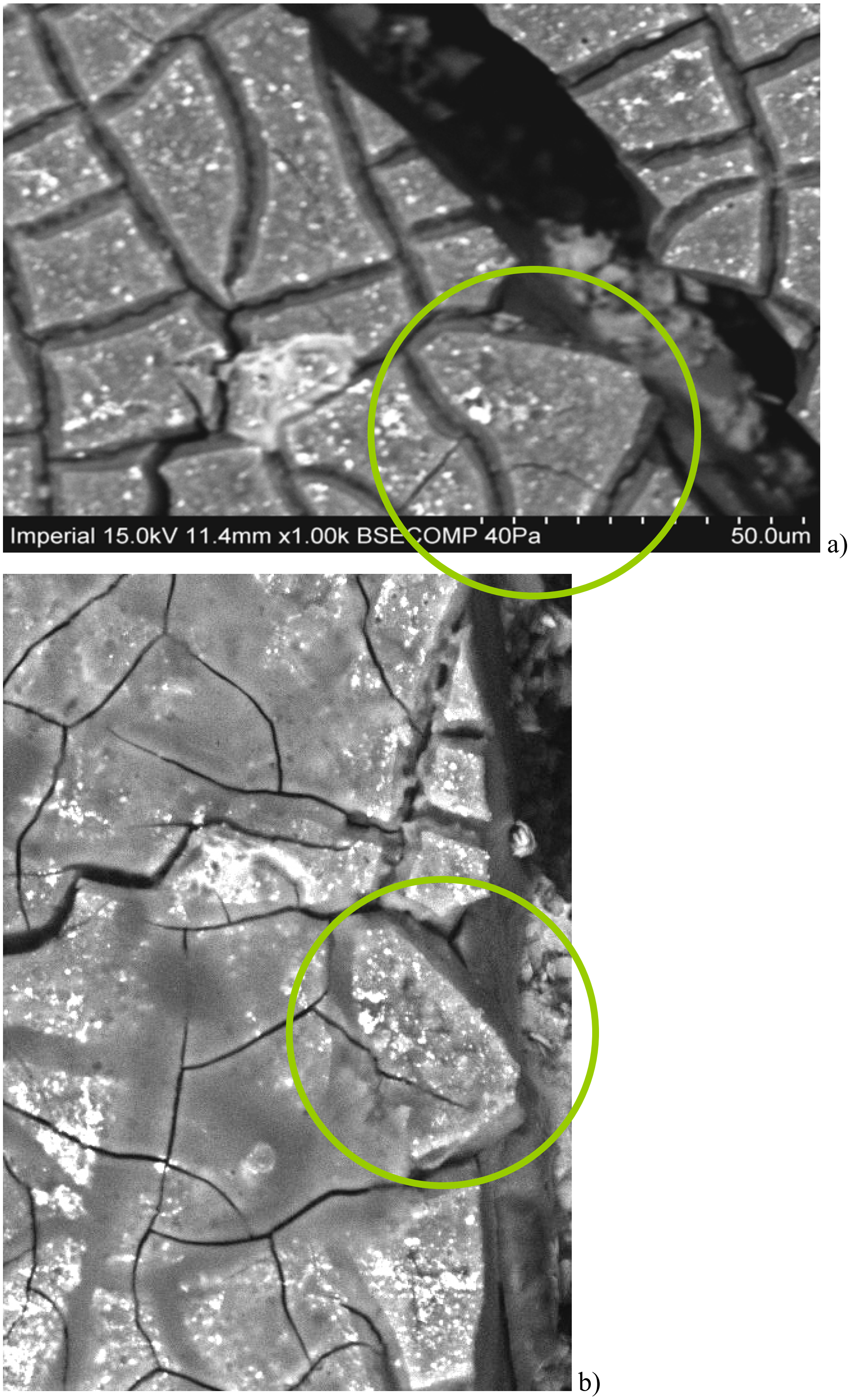


Figure 7.18: Artificially aged lacquer a) before and b) after swabbing with ethanol.

d) Water

As mentioned in the previous chapter, the pH of water seems to have a significant effect on the swelling of lacquer. Whilst it is not possible to alter the pH of water in the DVS or vapour sorption experiments, the pH of water that was swabbed over the surface of the light-aged lacquer was varied using pH values of 3, 5.5 and 8. The pinprick areas are increased in number and size following swabbing at these pHs (Figures 7.19-7.22) for the artificially aged lacquers.

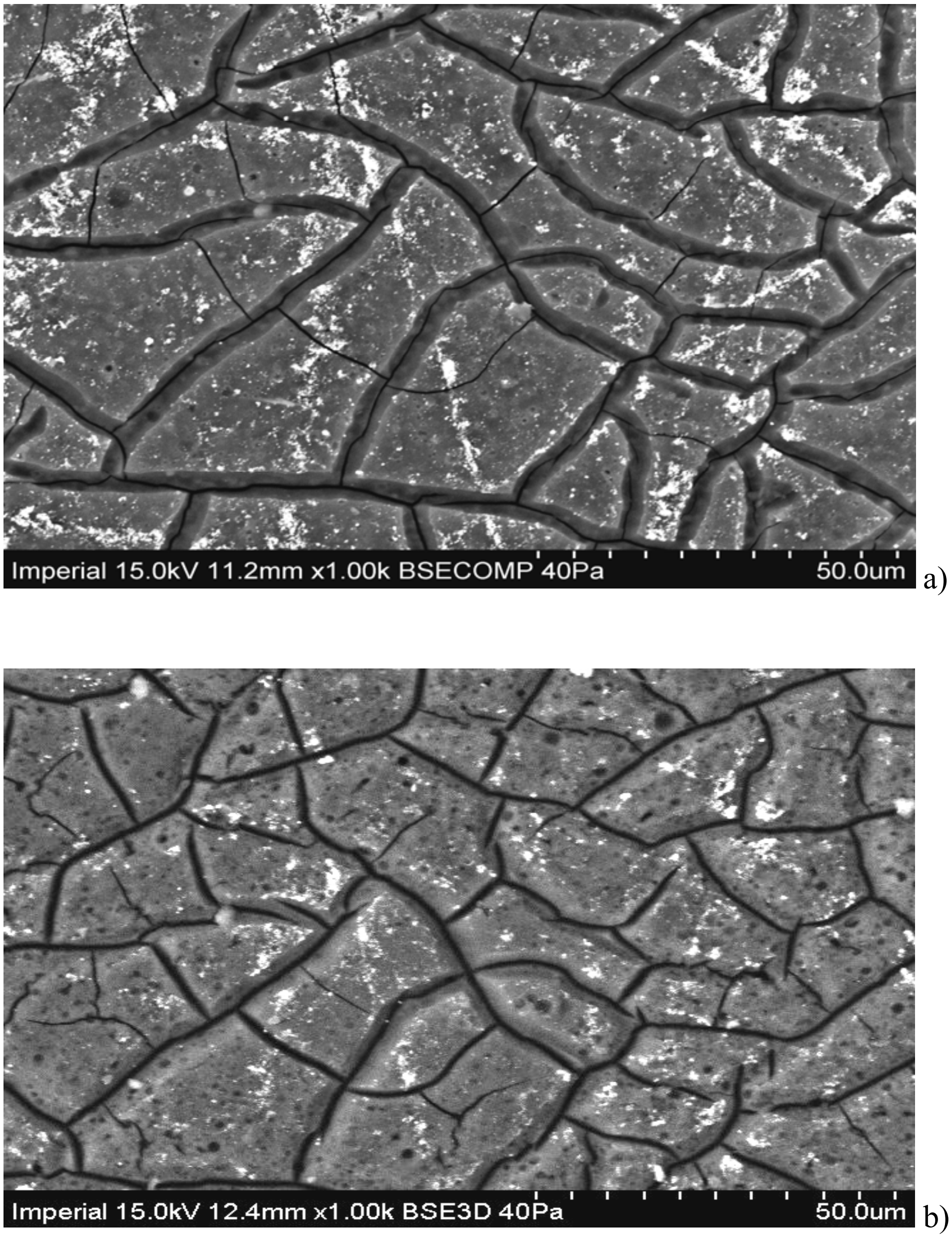


Figure 7.19: Artificially aged lacquer a) before and b) after swabbing with water of pH 3.

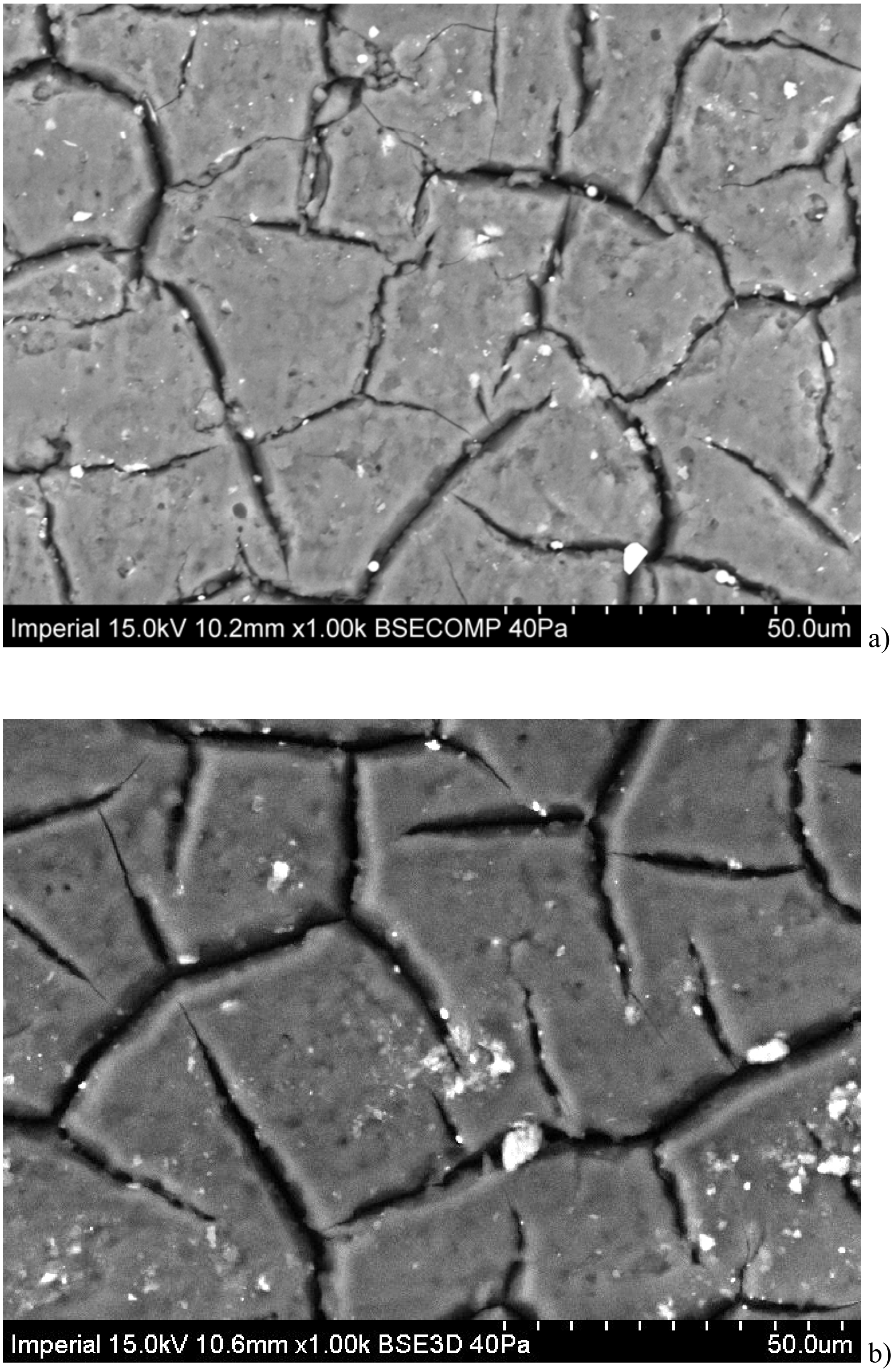


Figure 7.20: Naturally aged lacquer screen a) before and b) after swabbing with water at pH 3.

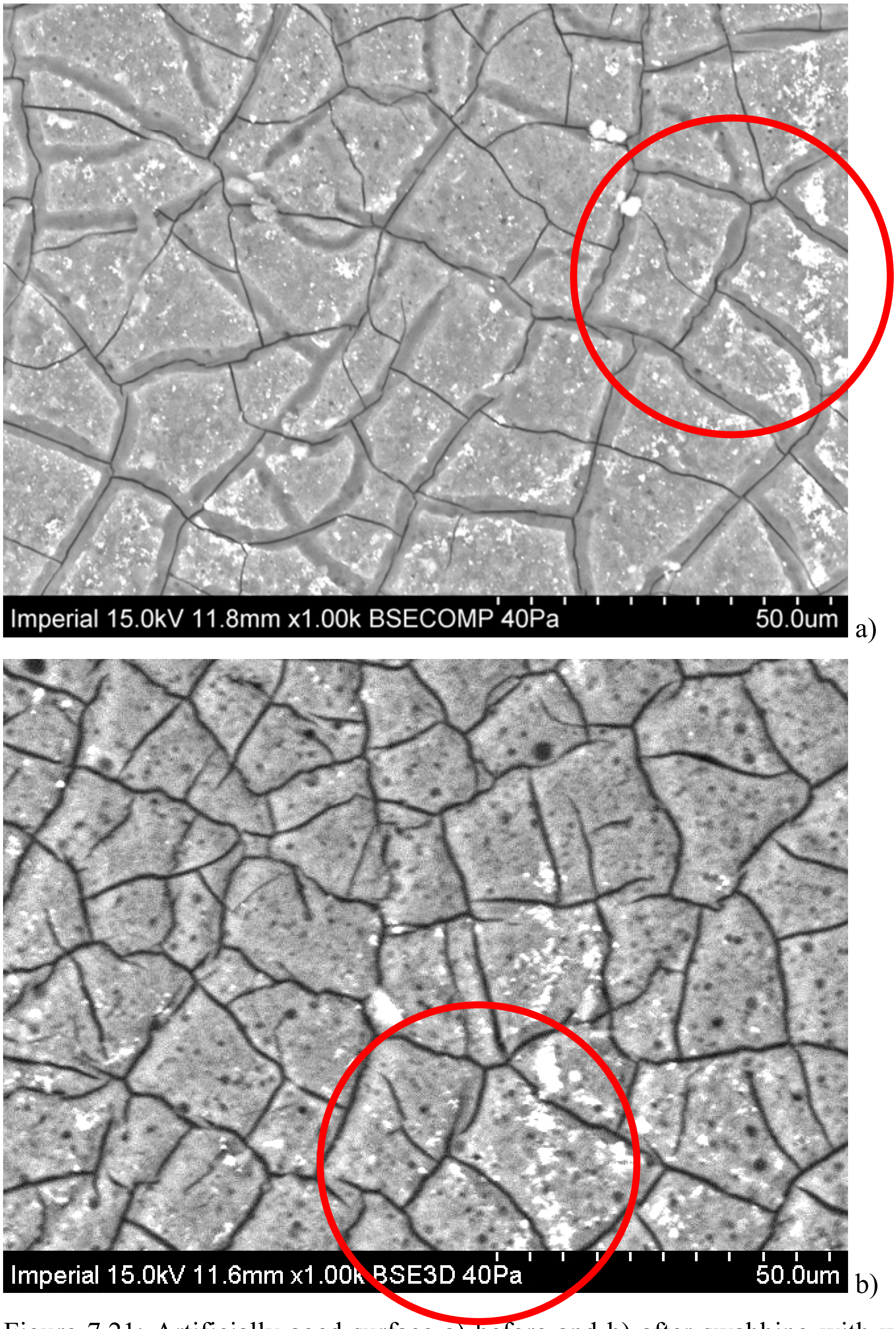


Figure 7.21: Artificially aged surface a) before and b) after swabbing with water at pH 5.5.

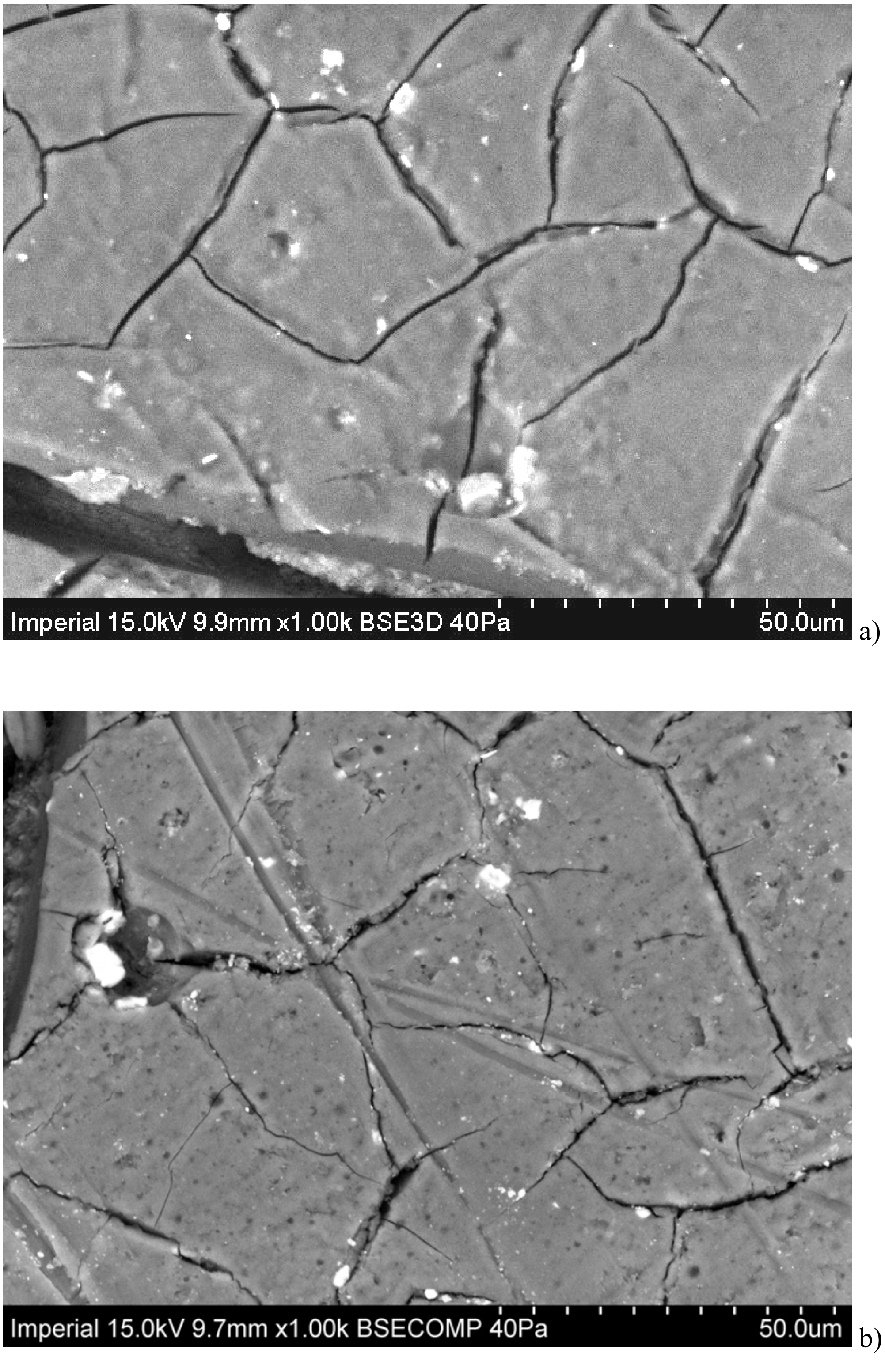


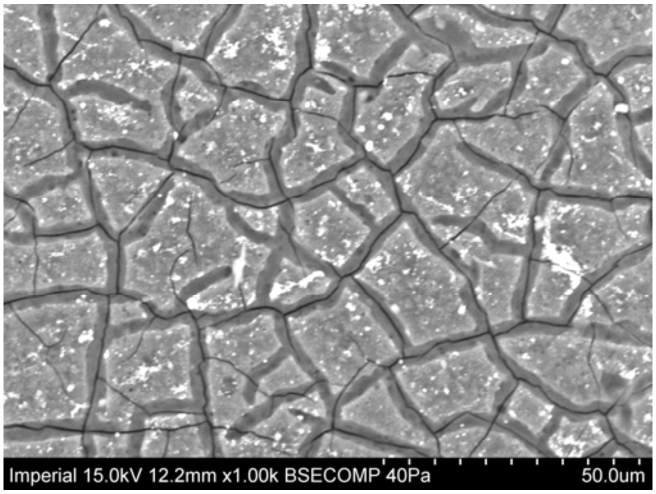
Figure 7.22: Naturally aged lacquer a) before and b) after swabbing with water at pH 8.

The main cracking patterns do not alter substantially; however, hairline cracks are exacerbated and extended on the artificially aged surfaces swabbed with the lower pH aqueous solvents, pH 3 and pH 5.5. For the naturally aged surfaces, the effect of swabbing with water of lower pH shows no obvious pinprick increases or changes in cracks or hairline cracks, compared to that seen in the artificially aged samples, although the pitting is seen after swabbing with pH 8 water. No measurable leaching effects were observed for water during the immersion tests.

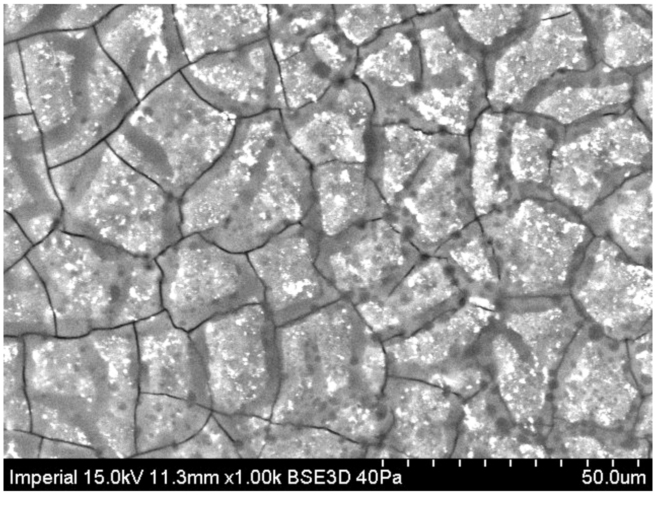
e) Polar solvents with carbonyl groups

Acetone

SEM-imaging of acetone-swabbed lacquer (Figure 7.23) show that debris is removed from the surface of the naturally aged piece, and cracks seem more defined.



a)



b)

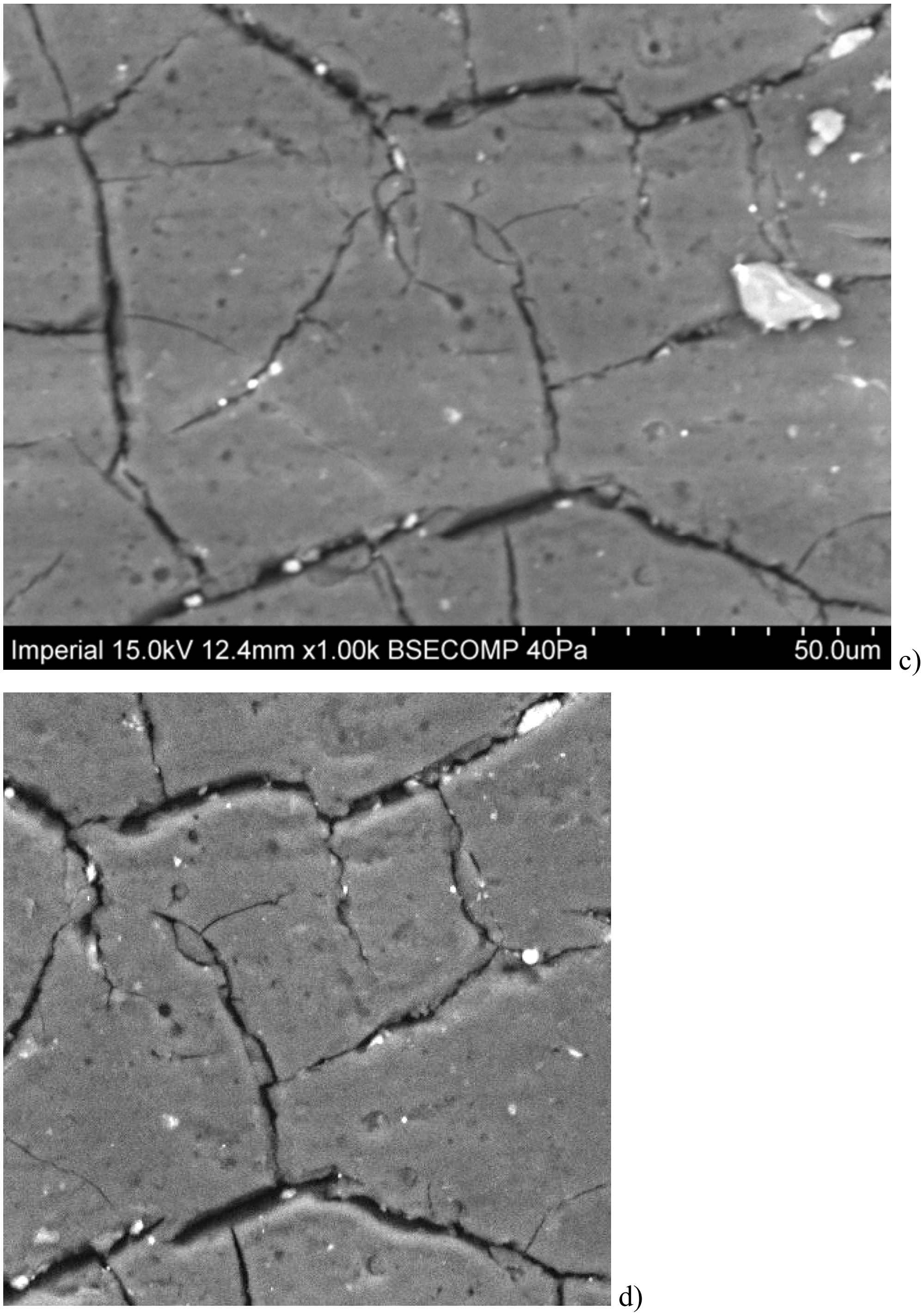
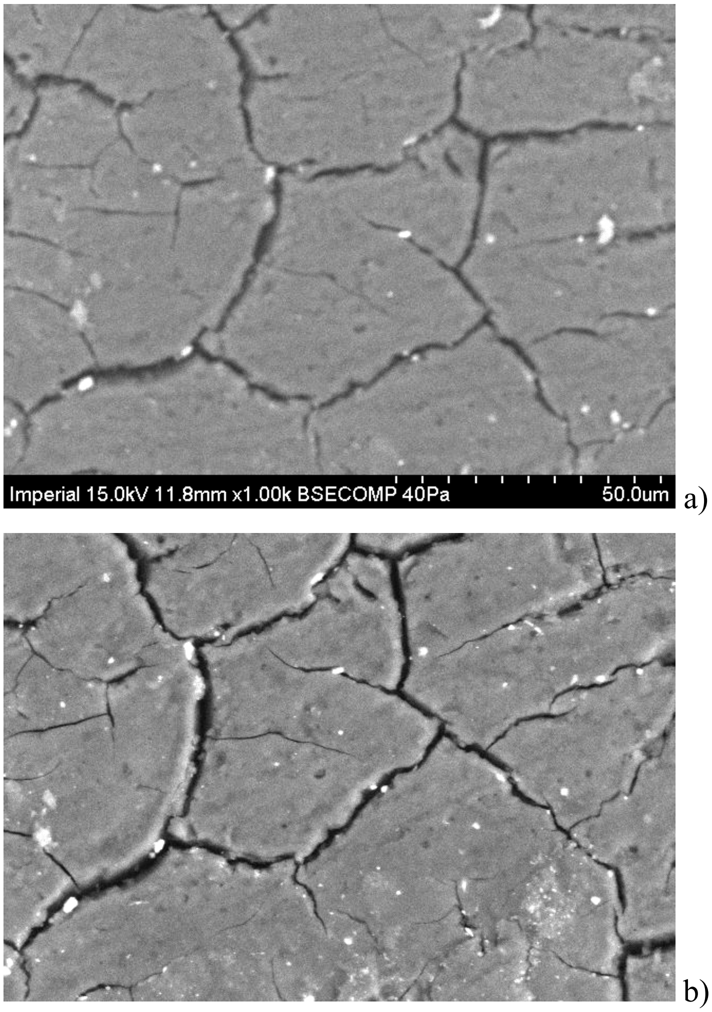


Figure 7.23: Artificially aged lacquer a) before and b) after swabbing with acetone, and naturally aged lacquer surface c) before and d) after acetone swabbing.

The artificially damaged piece displays a similar effect to that seen in the ethanol experiment – redeposition or recrystallisation of small molecule fragments appear to have ‘softened’ the large cracks to some extent, although this does not prevent new, fine cracks from appearing (also seen in the artificially aged, ethanol-swabbed samples). The pinprick regions are more defined also. During the immersion tests, leaching effects were observed for acetone on the artificially aged films were negligible (maximum 1.3%).

Ethyl acetate

The swabbing of the solvents accentuated the hairline cracks on the artificially aged surface (Figure 7.24c-d), but seemed to have minimal effects on the naturally aged piece (Figure 7.24a-b). The results from the vapour sorption tests also indicated, when plotted on the Teas chart, that an unaged lacquer had a higher swelling activity in the esters region, and on ageing the results move away from this region and towards chlorinated and more-polar solvents. No leaching effects were observed through immersion tests for this solvent on any lacquer type.



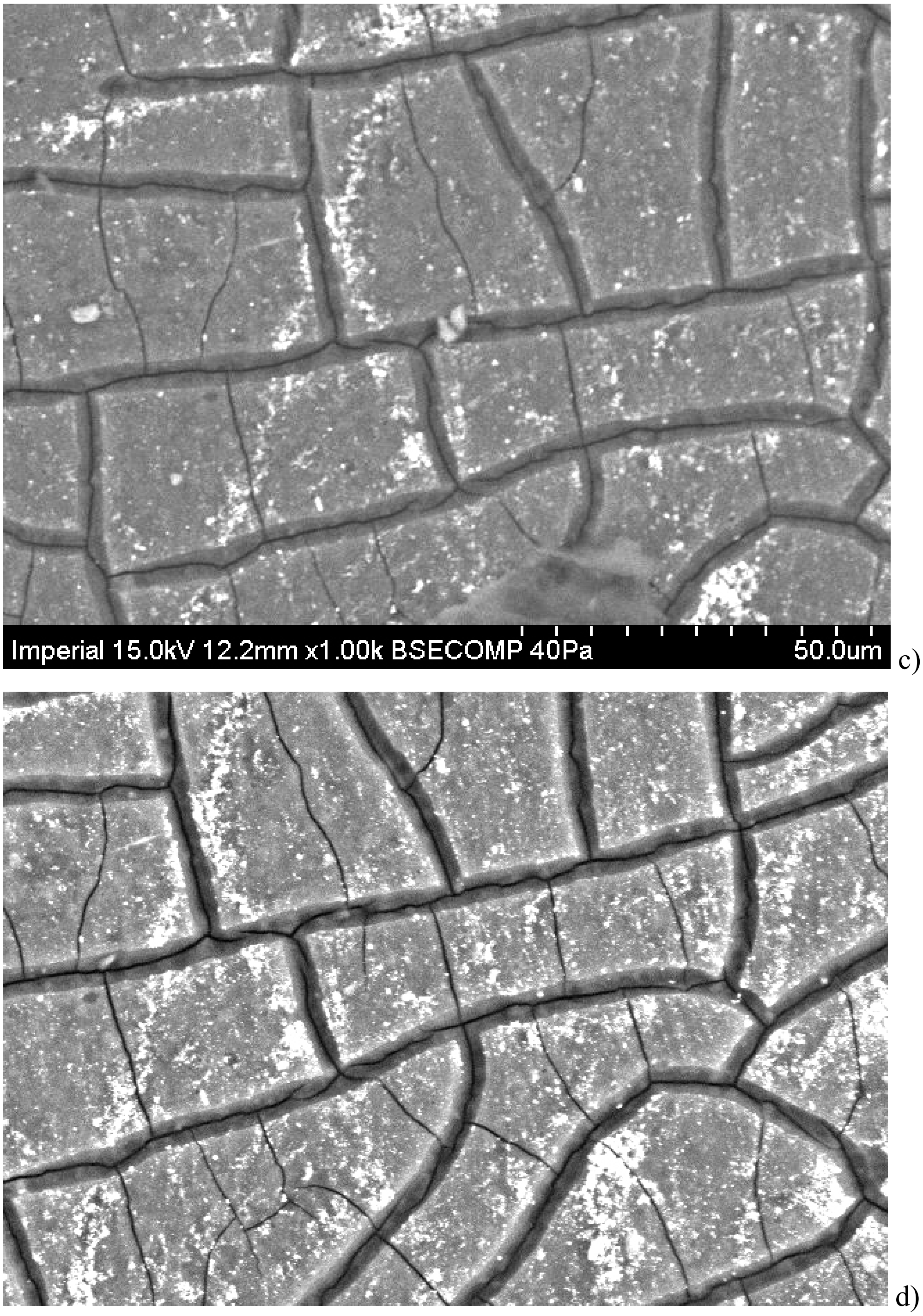


Figure 7.24 Naturally aged lacquer a) before and b) after swabbing with ethyl acetate, and artificially aged lacquer c) before and d) after swabbing with ethyl acetate.

7.5 Discussion

The purpose of these investigations was to determine whether a solvent or solvent mixture can be used safely to dissolve or swell unwanted materials from a photodegraded surface without affecting the original layers or leaving behind any damaging residue. The behaviour of damaged lacquer exposed to individual solvents has been studied here.

Solvents interact with *urushi* lacquer by diffusing into the extensively crosslinked system and swelling it to some degree. Some fragments, low-molecular weight components, may be leached or dissolved away. The extent of swelling or dissolution is dependent on the solvent type, its molecular size, and the functional groups it contains, as well as the degree of crosslinking within the lacquer, scission of lacquer and other components present. As discussed in Chapter 3, *urushi* lacquer becomes more acidic as it degrades, and contains increasingly more polar groups within the surface as a result of oxidation processes that cause the formation of ketone groups and acids. The use of polar solvents would, therefore, be expected to cause most swelling of the top lacquer layers after ageing.

To investigate the effects of a range of solvent types on aged lacquers, solubility experiments were conducted on aged films (including unaged, HgW-, UV- and natural daylight-aged lacquers) in two parts: first, by complete immersion of a free film, and second, by exposing the film to a solvent-saturated atmosphere. In these tests, the solvent uptake was not restricted in any direction as the film was not mounted on any substrate, which allowed solvent-induced movements (i.e. curling). The effect of brief solvent exposure to the damaged surface was also studied by SEM. The combined results from the immersion and vapour sorption and SEM tests show that damaged surfaces are most heavily affected by ethanol, acetone and ethyl acetate, as shown by the large uptake of solvent by mass; SEM images indicate disturbances on the surface after only brief exposure, whilst immersion and vapour sorption tests also demonstrate significant uptake of these solvents, as well as chlorinated solvents (chloroform, dichloromethane) and ketones. Interestingly, acetone/alcohols are commonly used as cleaning agents, since they show effective removal power when applied to layers of dirt, grease and other unwanted materials,[8,9] however, these investigations indicate that even a short exposure time has a noticeable effect on the damaged lacquer by these solvents. Some of the solvent volume remains after removal from the solvent basin or atmosphere in the immersion and vapour sorption tests - indicating that the damaged top layers do retain a proportion of these solvents. Following swabbing with these solvents, SEM images show that even a brief exposure by the high-risk solvents promotes the exacerbation of the cracks already present and, in some cases, initiates the generation of hairline cracks that spread from the original cracks.

Solubility tests carried out by complete immersion of the lacquer films do give an indication of the leaching and swelling effects of each solvent, although errors occur particularly during the process of removing the lacquer from the vessel, where an unmeasured proportion of the solvent absorbed is lost prior to the gravimetric measurement of uptake. The use of DVS, with uptake measured under continuous environmental/atmospheric conditions, provides a much more accurate indication of the lacquer films' tendencies to respond to different solvent types, under conditions where evaporation is not permissible. DVS gave reproducible and accurate measurements that show minimal impact on the lacquer by an alkane, a moderate impact by water, and a significant impact by ethanol and ethyl acetate (and acetone).

Unfortunately, the DVS experiment was limited to these solvents. A simple laboratory-based experiment, however, enabled the use of a wider range of solvents using a saturated atmosphere in which the samples were contained over a period of time, and weighed instantly. Although there is a high risk that a proportion of the solvents would be lost during the brief period in which it was removed from its saturated environment, the drying/blotting stage required for the immersion tests is not required here, and the results are fairy comparable with those obtained by DVS. For example, unaged lacquer exhibited an uptake of 18% and 15.3% by DVS and the lab-based vapour uptake, respectively, for ethanol, and 4.1% and 5%, respectively, for water. There are limitations involved with the methods used for calculating the 3D solubility parameters, which have been discussed earlier; however, the solubility parameters determined using a graphical estimation and weight-averaged method were comparable, although these calculations are limited by the small number of solvents used on the limited lacquer available.

The solubility parameters calculated from vapour sorption tests indicate that prolonged or harsh ageing tends to move the solubility region in the direction of an increasingly polar solvent, particularly towards the chlorinated solvent region. The shift from the ester region to more polar solvents as ageing increases is interesting; the unaged lacquer seems to be most responsive to ester-solvents such as ethyl acetate (a result backed up by the DVS experiment) and tetrahydrofuran, and the fresh lacquer does contain ester linkages due to the acid-alcohol reactions during the curing process, which possibly explains this affinity. As the lacquer is aged, it becomes less responsive to the ester class of solvents and more responsive to chlorinated solvents and possibly towards the ketone solvents too.

It is important to note that there are drawbacks associated with some of the methods used here. However, the overall trends observed by the vapour sorption, DVS and SEM give a very good indication of the behaviour of a lacquer of differing states of ageing when exposed to different solvent types. The DVS and vapour sorption experiments saturate the atmosphere around the sample with solvent for prolonged periods, however in the SEM experiments the swabbing action only exposes the lacquer for a brief period, and so the rates of uptake/effect are not comparable.

In addition to swelling, and the consequent movement of the lacquer layers, solvents also pose the risk of leaching smaller fragments of a decayed surface. By observing the SEM surfaces following brief swabbing with a small amount of solvent, as opposed to the immersion or exposure to vapour as excess solvent, some of the solvents are seen to exhibit a leaching or pitting effect. From the immersion tests, leaching steps did demonstrate an initial loss of up to 5% of the mass of the film: these included THF, chloroform, butan-2-one, acetone, DMF, ether, and in the case of the most aggressively damaged lacquer (by mercury tungsten) aromatics such as benzene and toluene both had a leaching effect (<2%). SEM also indicates that some fragments are either being removed, washed away from the surface or dissolved, or possibly re-crystallized into the cracked sections, either of which slightly alters the surface appearance. As the degradation of lacquer becomes more severe, the surface responds increasingly to more polar solvents.

Burke[4] has suggested that the Teas chart of fractional parameters can be useful in predicting the behaviour of a mixture of solvents, an therefore enabling the selection of ‘safe’ solvents in terms of toxicity and evaporation rate, as well as its ability to swell a material and not another. The advantages of using a mathematical or graphical determination of the position on the chart of a particular solvent blend include the reduction of trial and error tests required to determine solvent behaviour.

The changes observable in the solubility parameters of the lacquers studied here give a general indication of the region of solubility of each lacquer, and the direction in which it moves as ageing progresses. Determination of the diffusion rates (diffusion coefficients) could potentially supply useful and practical information, since such values would compare the relative proportion of each solvent type diffusing through the lacquer layer, or other materials, over a period of time. The periods of time during which vapour sorption is monitored here bear no relation to the amount of time a cleaning solvent would be exposed to a surface during conservation and so rate coefficients may prove useful, particularly when measured alongside other materials, such as spirit varnishes for comparison. Other necessary considerations for solvent cleaning in conservation are discussed in the next chapter.

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Chapter 8

Applicability of solvent-cleaning of East Asian lacquer artefacts

In the previous chapter, the responses of damaged lacquer to a range of organic solvents were discussed. Cleaning processes rely on the ability of a solvent to interact with unwanted material, including crosslinked polymers, by swelling the unwanted coating matrix, forming a gel-like layer which can either be dissolved in a liquid solvent or carefully removed as a gel through mechanical action. In doing this, there is the danger of removing more than the unwanted layer, and thereby exposing original surfaces to damaging substances, or actual removal.

The effect of solvents on aged lacquer has been investigated in order to determine how vulnerable, light-damaged lacquer might behave during conservation treatments. Such information is of particular importance if the removal of other materials, debris or coatings is required. Without being able to identity the contaminants - a difficult task requiring invasive and destructive analysis of part of the surface - the selection of a suitable solvent is difficult. The results discussed in the previous chapter show that there are very few solvents that do not interact with aged lacquer to some extent. The aliphatic alkanes show the least tendency to swell a damaged lacquer, however, while these solvents exhibit some solvation effects on beeswax, unaged mastic and dammar, and linseed oil,[1] they are ineffective for the swelling of aged resins, including shellac, dammar and mastic, and have no effect on cellulose nitrate or cellulose acetate (modern lacquers). Aged resins and oils require solvents of increased polarity in order to swell substantially, mainly alcohols, ketones or chlorinated solvents. Since the polar solvents needed for the effective removal of unwanted materials will swell lacquer, it is helpful to consider whether there is a useful difference in the swelling rates between the two classes of material.

8.1 Diffusion coefficients of cleaning solvents

In addition to establishing the solvent isotherms, Dynamic Vapour Sorption (DVS) can be used to assess the rate of solvent diffusion.

Experimental details: In the following experiment two spirit varnishes (shellac and sandarac) were prepared alongside a lacquer sample and aged for 20 weeks under an unfiltered mercury-tungsten source. For comparison, lacquers aged by UV daylight simulation, natural daylight, and also unaged samples were prepared. The sample pieces measured 3 mm x 3 mm x 9-11 μm; from a range of varnish resins cast out, only shellac and sandarac were successfully prepared in these dimensions for DVS analysis. A one-step DVS experiment was carried out with the target pressure programmed from 0% to ~100% with no intermediate levels. Samples were stabilised in situ for 25 hours at 0% at 30°C, and then exposed to saturated ethanol vapour for 25 hours. The method reported in a Surface Measurement Systems Application Note (Number 16)[2] was applied to determine the diffusion coefficients for these materials. The study was carried out in one step using ethanol as the test solvent to represent alcohols, a group of solvents commonly used in cleaning (for example, industrial methylated spirits and rubbing alcohol). Unaged lacquer was compared with lacquer aged by mercury tungsten, UV daylight simulation and natural daylight, and the aged lacquers were compared with the solvent uptake by sandarac and shellac spirit varnish films.

The literature method[2] of determining the diffusion coefficient of a coating material, D, is based on the diffusion equations derived by Crank and Park, reproduced in equation 8.1, which describes the kinetics of solvent sorption into the crosslinked polymer sample, assuming Fickian diffusion behaviour, a negligibly short diffusion time, and a controlled, constant partial pressure within the instrument, where M_t represents the amount of ethanol absorbed at time t, M_∞ represents the amount of ethanol absorbed at thermodynamic equilibrium, and d is the thickness of the lacquer film.

$$M_t / M_\infty = (4 / d) \,.\, \sqrt{(Dt / \pi)} \qquad \text{Equation 8.1}$$

The diffusion coefficient, D, could be derived from equation 8.1, to give equation 8.2:

$$(d / 4) . M_t / M_\infty = \sqrt{(Dt / \pi)}$$

$$d^2 / 16 . (M_t / M_\infty) = Dt / \pi$$

$$D = (\pi / t) . (d^2 / 16) . (M_t / M_\infty)^2 \qquad \text{Equation 8.2}$$

For each material M_t / M_∞ was plotted against $t^{1/2}$/d, and the slope determined, following the step from 0% ethanol to saturated ethanol vapour. An example of the uptake of ethanol by a photodegraded (HgW) lacquer is shown in Figure 8.1. The change in mass(%) plot shows the percentage change in mass with reference to the dry mass i.e. the first 1500 min was at 0% P/P_0 and the sample was drying (decrease in mass).

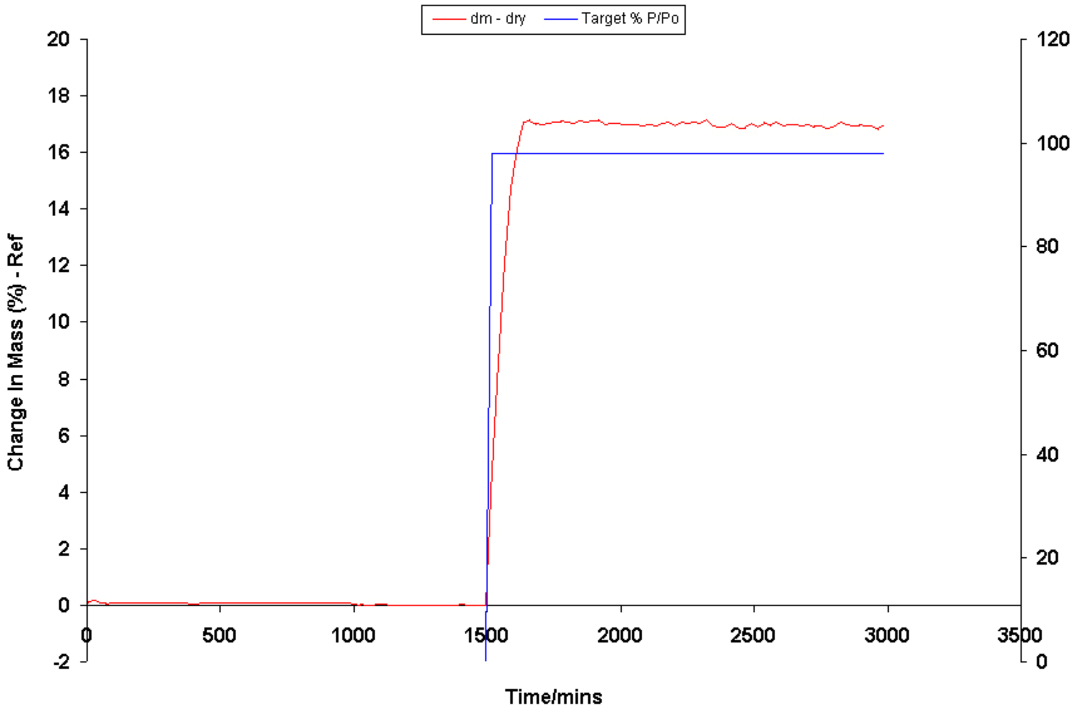

Figure 8.1: DVS change in mass plot for ethanol in HgW aged lacquer (30°C).

Figure 8.2 shows a section of the linear fit to equation 8.1.

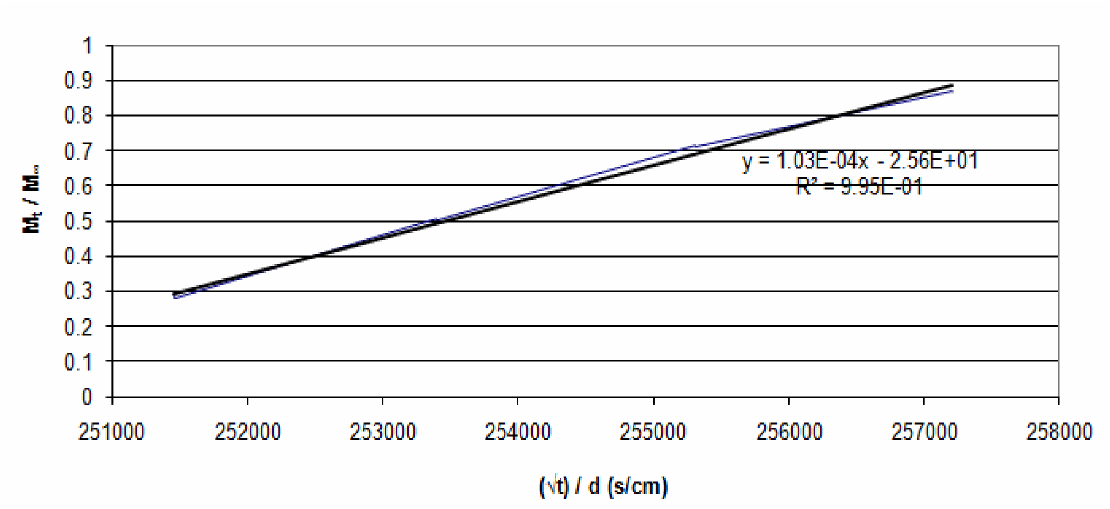

Figure 8.2: Slope fitted on plot of M_t / M_∞ against √t /d for ethanol diffusion into HgW aged lacquer.

D was obtained from the slope of each linear fit, using equation 8.3.

$M_t / M_\infty = (4 / d) \cdot \sqrt{t} \cdot \sqrt{(D / \pi)}$

So,

$M_t / M_\infty = (\sqrt{t} \ / d) \cdot 4 \cdot \sqrt{(D / \pi)}$ Equation 8.3

Where $4 \cdot \sqrt{(D / \pi)}$ is equal to the slope of the linear fit.

The diffusion coefficient, *D*, is therefore determined by equation 8.4.

Slope = $4 \cdot \sqrt{(D / \pi)}$

1/4 slope = $\sqrt{(D / \pi)}$

1/16 (slope)^2 = D / π

Therefore, $D = \pi/16 \cdot (\text{slope})^2$ Equation 8.4

This method was applied to all the aged lacquers and varnishes, and results are summarised in Table 8.1. Owing to restrictions regarding access to this instrumentation, only one test cycle could be obtained, with ethanol being chosen as the test solvent.

Table 8.1: Diffusion coefficients calculated for coating materials using 100% target RH

Coating material	Diffusion coefficient x 10^{-9} (cm^2/s)	R-squared
Unaged lacquer	3.63	0.9500
Lacquer aged HgW	2.08	0.9950
Lacquer aged UV	1.20	0.9998
Lacquer aged daylight	0.28	0.9950
Seedlac unaged	0.32	0.9374
Seedlac aged (HgW)	1.18	0.9741
Sandarac unaged	0.11	0.9439
Sandarac aged (HgW)	0.06	0.9782

The diffusion coefficients calculated show the quantity of solvent moving through the lacquer or varnish film over a unit of time. For example, the diffusion coefficient of unaged lacquer indicates that ethanol diffuses 1.75 times faster than in HgW aged lacquer. The R-squared values have been included in Table 8.1 to indicate the goodness of fit (100% accuracy = 1.000).

Discussion of results

Diffusion is the movement of the solvent molecules from a region of high concentration to a region of low concentration, along a concentration gradient, to achieve a uniform concentration throughout. The diffusion coefficients, *D*, measured here show the same order of magnitude for the aged and unaged lacquers, with the exception of daylight (natural) ageing, which indicates a much slower rate of ethanol diffusion through the lacquer compared with the unaged lacquer. The reduced diffusion rates of ethanol through an increasingly aged lacquer are due to the increased crosslinking within the aged polymer network, which forces the solvent molecules to move along a more tortuous path, thereby reducing the speed at which they can achieve movement.

Diffusion of ethanol is slower for the non-lacquer materials studied here, for both aged and unaged forms of the materials, with the exception of the aged seedlac, whose *D* value is comparable with an aged lacquer, showing the same order of magnitude of diffusion rate, which is not advantageous where the seedlac needs to be removed before the lacquer is swelled. The diffusion of ethanol through the aged sandarac material is much slower than in the damaged lacquers. This is contrary to the required outcome: removal of the unwanted material whilst leaving the lacquer unaffected.

8.2 The effect of crosslinking in aged materials

The solvent molecules flood into the microcavities within the polymer network of the unaged lacquer. These spaces are large enough to allow the ethanol molecules to move rapidly through the matrix, although as ageing progresses, and therefore crosslinking proceeds, these cavities may become reduced either in size or in number, restricting movement of these molecules.

The rapid solvent movement through fresh lacquer film is also possible because of the flexible nature of the polymer chains, indicated by the lower glass transition (T_g) values compared with aged versions of the materials (T_g of *kijiro* is 120^{o}C prior to ageing; following nearly 6 weeks of ageing the T_g was 170^{o}C),[3] which may move to accommodate the solvent molecules. This flexibility can be attributed both to a lower crosslinking density and to plasticizing by the high water content.[4] As discussed in Chapter 3, on ageing, the glass transition temperature is increased, due to the increase in crosslinking which occurs firstly as the lacquer cures from liquid to a solid film, and continues as the film ages.

In the solvent-uptake experiments discussed in the previous chapter, aged polymers allow some degree of uptake of the solvent despite the crosslinking, however there are chemical effects which influence both the uptake and the retention of a proportion of this solvent following desorption cycles. There is a possible interaction with the polymer or restriction of solvent movement within the network. Kamlet-Taft analysis of the HgW aged lacquer showed that the material was mostly affected by the polarity or polarizability of a solvent, rather than its acidic or basic components.

The rate of movement of a solvent molecule through a coating polymer is influenced by the functional groups it contains, as some groups will interact with those of the polymer structure, for example, the acidic protons. Such interaction may result in a clustering of the solvent molecules in one part of the polymer matrix, thereby slowing down the overall movement through the film. Alcohols would exhibit this clustering effect where the aged polymer also contains largely polar groups. The steric effect, that is the size of the alcohol may limit the uptake of the solvent into the film, that is to say that using a longer chain alcohol, such as octanol, may have a much slower effect on the lacquer, or the varnish material.

8.3 The use of solvents in cleaning photodegraded lacquer

The previous chapter showed that solubility parameters of aged lacquers moved slightly towards the direction of increasingly polar solvents such as ketones and chlorinated solvents, and were decreasingly affected by ester solvents, although swelling remained significant. DVS experiments show that the lacquers became only slightly more sensitive towards ethanol after ageing. The only solvent types that displayed negligible swelling were the alkanes. However, SEM experiments did indicate that, whilst the hexane successfully removed particulates from the surface, it also left behind a residue, shown by the charged, white regions on the surface of the lacquer swabbed with the solvent. The source of this residue is unknown, however; it may be a result of impurities in the solvent or other contaminants, or leached material from the lacquer or swab used.

As already discussed in Chapter 7, the diffusion of organic solvents and water into a damaged *urushi* lacquer crosslinked network results in swelling to a greater or lesser extent, depending on the solvent class. The smaller fragments of damaged lacquer, i.e. those of lower molecular weight or volatile species, are at risk of being leached out of the layer. The removal or dissolution of small fragments has been observed through a minimum weight loss of 5% in the lacquer films following immersion in tetrahydrofuran, chloroform, butan-2-one, acetone, dimethylformamide, ether, and a loss of up to 2% by some aromatic solvents. SEM shows the increase in pitting effects on the surfaces following swabbing with water (pH 3-8) and acetone, which have leached out some components of the damaged surface and left voids (see Figures 7.19 and 7.21). There is also the danger that the action of some solvents could facilitate the solvation of surface contaminants, making them increasingly reactive towards the damaged parts of the lacquer surface.

Graphical summary of swelling/solubility regions of materials of interest

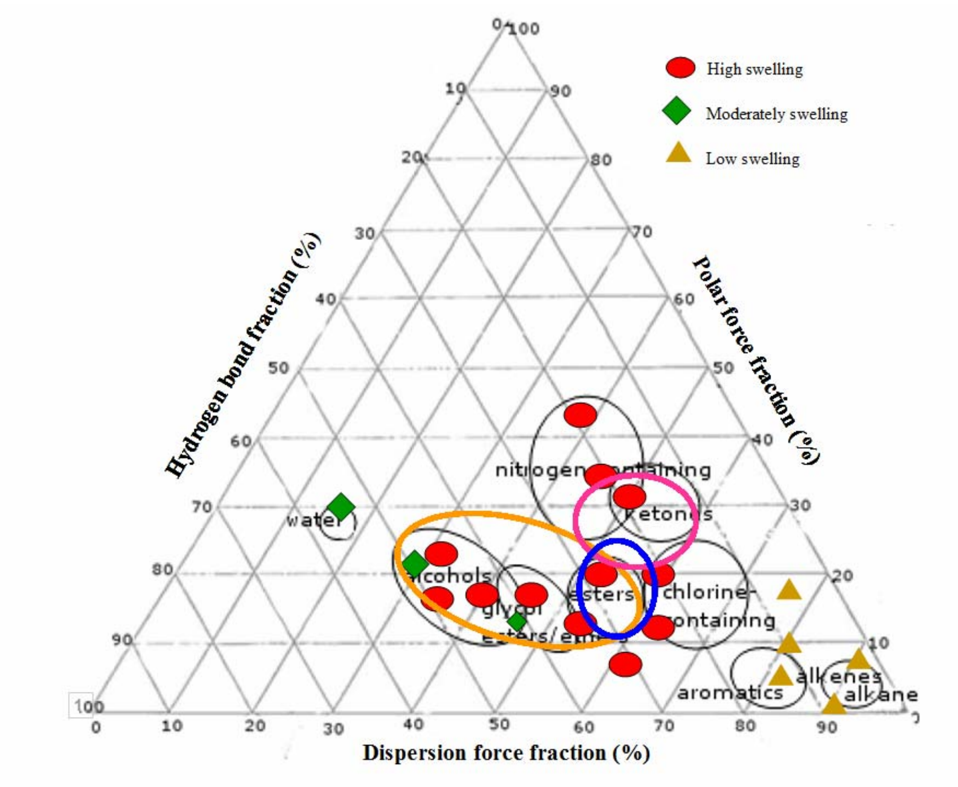

Figure 8.3 Graphical summary of swelling/solubility of HgW artificially aged lacquers and natural resin varnishes, including dammar (orange ellipse), shellac (pink ellipse) and mastic (blue ellipse).

The Teas chart in Figure 8.3 summarises the solubility characteristics as determined in Chapter 7 for harshly aged lacquers, along with the approximate regions of solubility/swelling for aged varnish materials as by Horie.[1] The aged dammar and mastic data are based on 100 years natural ageing (from Feller and Curan, 1975, reported by Horie), and the polymerized shellac is only soluble in some nitrogen-containing compounds such as pyridine and also dichloromethane.[5]

The regions of effective swelling for the three varnish resins indicated here show a general overlap with the high swelling solvents for aged lacquer. The calculated diffusion coefficients show that ethanol swelling is more rapid in the damaged lacquer than in non-lacquer based materials (marginally for the seedlac, and substantially for the sandarac), and so brief exposure to solvents can potentially damage the lacquer first before the non-lacquer is affected. More problematically however, solvent retention by swelled lacquer contributes to a damaging delamination of the layers that make up the artefact's coating.

8.4 Discussion of the considerations involved in solvent-treatment of East Asian lacquer

Whilst a differential rate of swelling might provide a solution, unfortunately the data in section 8.1 shows that uptake rate of the test solvent was higher in lacquers than in varnishes. In that case, the applicability of solvents for the purpose of removing non-lacquer-based materials from lacquer-based materials is questionable when taken alongside the solubility data which indicates that a large range of solvents are highly swelling towards damaged lacquer, and are likely to cause significant harm to the original surface.

However, the classification of certain solvents as high-risk based solely on their high-swelling behaviours could result in unnecessary elimination of a solvent that has applicability in conservation processes. As pointed out by Michalski,[6] the effect of diffusion, capillary action and retention all have an effect on the solvent activity towards oil paint films, and these parameters are also significant for aged lacquers. Other factors must be taken into consideration, including the evaporation rates of the solvents, since these will affect the actual penetration and exposure time of the solvent to the lacquer, and, therefore, the extent to which it will cause it to swell or dissolve. Clearly, there are marked differences between the experimental conditions used in this work and the conditions that would be used in a conservation studio, including the solvent exposure time. The lacquer would not be completely immersed in a liquid or vapour solvent for any length of time, but instead swabbed with gels or wands loaded with solvents for seconds at a time, and this factor must be considered when assessing the data presented.

Evaporation rates of the individual solvents will have a significant effect on the extent to which a solvent will penetrate into the damaged coating. A fast evaporating solvent, such as acetone, will have minimal penetration into the layers, and, therefore, even highly swelling solvents will not, in conservation conditions, be exposed to the damaged material for sufficient time to allow substantial swelling to occur where the evaporation rate is high; this permits a certain amount of 'control' over the solvents' effects on photodegraded lacquer. Table 8.2 presents a range of solvents and their vapour pressures, and where available the evaporation rate as per the ButylAcetate scale, where *n*-butyl acetate (BuAc) is used as the reference material (BuAc=1).

Table 8.2: Vapour pressures and evaporation rates of a range of organic solvents (data from MSDS Safety Sheets)

Solvent	Vapour pressure (kPa) at 20°C	Evaporation rate (BuAc scale))
Pentane	57	28.6
Hexane	17.6	8.3
Water		0.3
Acetone	24.1	5.6
2-butanone	9.5	2.7
Benzene	9.9	~3.0
Toluene	2.9	2.24
THF	17.2	8.0
Methanol	12.9	5.9
Ethanol	5.3	1.4
2-butanol	1.6	1.3
Chloroform	21.2	11.6
o-xylene	6.8	0.6
Acetonitrile	9.7	5.79
Ethyl acetate	10.1	6
Diethyl ether	58.7	37.5
Ethylene glycol	0.0003	<0.001
Dichloromethane	46.7	27.5
Mineral spirits		0.1
Pyridine	2.1	8
Dimethylformamide	0.4	0.17

The swelling data obtained here can be used to enhance the lacquer conservators' awareness of the potential damaging effects of certain solvent classes on the surfaces. There can be no guarantee that no damage will occur with any of the solvents investigated in this work, although where treatment is necessary (e.g. a varnish layer must be removed) the conservators can make a judgment based on a range of available data.

Water

At different pHs water is seen to leach out some components of the aged lacquer by SEM. The leaching effect was not measurable by mass loss in the film upon immersion; however the SEM images in section 7.4 displayed obvious pitting of the surface, indicating removal of some surface components leaving pinprick sites. Water has a slow rate of evaporation, and therefore, even though the swelling effect is only moderate, the obvious damage seen is probably due to the effect of pooling of the water on the surface for a significant period prior to evaporation. These observations indicate that water is unsuitable in the cleaning of lacquers, and, in any case, would be ineffective in dissolving or swelling an aged, oxidized material.

Alcohols

A polar solvent is needed for the removal of a resin-based varnish, as shown in Figure 8.3. In the case of alcohols, ethanol shows a high-swelling behaviour towards damaged lacquer films, whereas other alcohols show a moderate-to-high swelling effect. This solvent class is effective in dissolving triterpenoids, such as dammar; methanol also has a high evaporation rate, and ethanol and 2-butanol have medium evaporation rates, therefore, the damage due to penetration of these solvents would be minimized. Diffusion rates determined by DVS for ethanol, however, show a faster uptake by the photodegraded lacquer in comparison to the diterpenoid (sandarac) and insect (shellac) resins.

Alkanes

In terms of cleaning dirt, grease, fresh fingerprints, alkanes should be considered benign, since little solvent-polymer interaction has been observed in the tests described in Chapter 7. For resin varnish removal, the use of any alkane is, broadly speaking, unlikely to cause damage, and, therefore, poses a negligible risk to the photodegraded lacquer. However, a degraded, resin spirit-varnish will not be dissolved by this class of solvent. Crosslinked, oil-based photodegraded varnish is very insoluble, and, again, the alkanes are likely to be ineffective towards these materials.

Ketones

Acetone is an effective solvent in terms of removal of polar dirt, however, the SEM images indicate that there is (as with water) a small degree of leaching following exposure of the lacquer to the solvent, indicated by pinprick changes on the artificially aged surface. There is no weight loss measured in the immersion experiments, however, this may be explained by the redeposition of minute fragments from one area of the surface to another. Acetone is not retained by the damaged lacquer film after the first vapour/DVS desorption cycle, and the fast evaporation rate of this solvent would minimize the opportunity for any significant volume to penetrate the top lacquer layers, thereby reducing the potential risk of swelling despite this solvent being classed as 'high swelling'. In addition, acetone has low toxicity, which improves its applicability in practical terms. Butan-2-one is a moderate sweller, but a high-leaching solvent, and the slow evaporation rate means that the exposure time is prolonged, thereby exacerbating the potential risk.

Esters

Ethyl acetate is seen to accentuate the existing cracks on an artificially photodegraded lacquer, but does not cause any measureable leaching. A high-swelling effect is observed by this solvent, particularly for unaged, fresh lacquer, and, although the harshly aged lacquers are swelled to a lesser extent, the swelling is still significant. Ethyl acetate is a fast evaporating solvent, minimizing exposure time.

Ethers

Tetrahydrofuran (THF) and ethylene glycol (from immersion only) were observed to have moderate swelling effects towards harshly aged lacquer. The THF was also a moderate-leaching solvent towards immersed films, whereas the ethylene glycol did not display any leaching effects that could be measured by change in weight only. A more accurate determination of leaching is by observing the surfaces under SEM before and after exposure. The ethylene glycol is not appropriate as a cleaning solvent in this capacity, as it was difficult to remove from the surface of the damaged lacquer, and has a very slow evaporation rate at BuAc <0.001. Therefore, despite the moderate swelling effects of this solvent, the prolonged exposure that result from difficulties in its removal are highly likely to cause significant damage in terms of the solvent penetration further down the lacquer strata, specifically delamination. THF has a fast evaporation rate however, and is therefore unlikely to penetrate far into the damaged surface. Diethyl ether is a substantial swelling solvent of aged lacquer, however, it has a very fast evaporation rate and exhibits low-leaching during immersion tests, as determined by weight changes. This solvent, which is found in paint and varnish strippers, would potentially be useful in removal of triterpenoids, due to its rapid evaporation from the damaged surface, and its effective dissolution or swelling of dammar or mastic-based materials. Having said that, diethyl ether should be used with great care in a conservation studio, since it is classified as both harmful and highly flammable.

Aromatics

The aromatic solvents are generally low-to-moderately swelling, do not leach components from the lacquer surface, and do not have any obvious effects on the surface morphology of the photodegraded lacquer surface. These solvents, particularly xylene, are effective in the removal of dirt and some debris from the lacquer surface, although xylene has a slow evaporation rate, and could therefore pool on the surface and collect in the cracks, intensifying the swelling effects and contributing to delamination. Toluene has a medium evaporation rate which may decrease this risk to some extent, although the retention of this solvent by harshly aged lacquer after the 24-hour desorption cycle was high (10%), and this could contribute to destabilisation of the lacquer structure due to the stress applied by such a large, persistent volume.

Nitrogen-containing compounds

The effect of nitrogen-containing compounds has been observed in limited solvents, since, although these substances are known to swell resin varnishes, and also swell some crosslinked oil varnishes, they are also highly destructive towards lacquer, even fresh films. Dimethyl formamide, for example, was difficult to use in the experiments described in Chapter 7, since it ripped the films apart quickly upon immersion, and notable leaching of the HgW-aged lacquer components was observed both through mass loss measurements (14%), and discolouration of the solvent. Most significantly, however, members of this class of solvents are not generally applicable in conservation cleaning due to their highly toxic and harmful properties. Dimethylformamide, for example, is classified as ‘harmful’ and is known to cause damage to the internal organs on ingestion, inhalation or through skin contact. Similarly, pyridine, whilst known to dissolve aged shellac, is a toxic and corrosive substance, which irritates and burns the skin, causes organ damage at low levels, and is known to affect fertility. Acetonitrile has a moderate-to-high swelling effect on photodegraded lacquer, but a fast evaporation rate and no measured leaching effects.

Chlorinated solvents

Dichloromethane is a high-swelling solvent; however, it also has a high evaporation rate, which would reduce the extent to which it penetrates into the photodegraded lacquer. This solvent, however, is also classified as 'harmful' and a possible carcinogen, making it an unsuitable choice for use in a conservation studio.

The swelling, retention, evaporation and diffusion effects must be considered together (Table 8.3), by the conservator, and the least-damaging solvents towards the vulnerable lacquer surface must be based on one of the three categories:

1. Fast evaporating, low swelling, low retention
2. Slow evaporating, low swelling, low retention
3. Fast evaporating, high swelling, low retention

To summarise, high- or low-swelling solvents cannot be the main criterion used in determining its suitability or applicability in conservation cleaning. Water, for example, has exhibited a moderate-swelling effect on aged lacquer, and a low-to-medium retention after removal from the solvent, however, it has displayed leaching effects on artificially aged samples (pH 3-8), and, therefore, is an inappropriate solvent for cleaning degraded lacquer, where its exposure time is prolonged due to the low evaporation rate.

Table 8.3: Summary of solvent characteristics

Solvent	Swelling	Evaporation rate	Retention	Safety
Pentane	Low	Fast	n/a	HF, H
Hexane	Low	Fast	n/a	H, F, Env
Water	Moderate	Slow	5%	n/a
Acetone	High	Fast	n/a	F
2-butanone	Low	Medium	n/a	HF
Benzene	Low	Medium/Fast	2%	T, HR
Toluene	Low/Moderate	Medium	10%	HF, T
Tetrahydrofuran	Moderate	Fast	n/a	HF
Ethanol	High	Medium	4%	F
2-butanol	Moderate/High	Medium	n/a	H
Chloroform	High	Fast	6%	T, Env
o-xylene	Low/Medium	Slow	n/a	H
Acetonitrile	Medium/High	Fast	n/a	T, HF
Ethyl acetate	High	Fast	5%	HF
Diethyl ether	High	Fast	n/a	H, HF
Dichloromethane	High	Fast	n/a	H
Mineral spirits		Slow	n/a	F
Dimethyl formamide	High	Slow	n/a	H
Methanol	Moderate	Fast	n/a	T, HF
Ethylene glycol	Moderate	Slow	n/a	H

Swelling of lacquer high=>10%, moderate=3-10%, low=<3%; Evaporation rate fast=>3.0, medium=0.8-3.0, slow=<0.8 (based on MSDS classification); Retention of solvent from DVS/vapour sorption tests; Safety data: T=toxic, F=flammable, HF=highly flammable, H=harmful, Corr=corrosive, Env=dangerous to the environment

Diffusion coefficients are useful data to have in predicting solvent behaviour. Due to restrictions in the use of instrumentation, obtaining diffusion coefficients using the method described in section 8.1 for other solvents was not possible. In future work, obtaining the diffusion coefficients for the photodegraded lacquers using a range of solvents would add significantly to a workable conservation solvent model.

The evaporation rate of each solvent is an important consideration when selecting a solvent, as it affects the rate at which the solvent will leave the surface undergoing treatment once it has been applied, and can indicate to the conservator whether the volume or application method being used is suitable. Solvents that have the opportunity to pool on surfaces displaying microcracking are of particular risk to the surface, even when they are only moderate in their swelling behaviour, and leaching of low-molecular weight components, or penetration into deeper layers are possible outcomes. Conservators must take this important factor into consideration when selecting a solvent for cleaning purposes. None of the solvents discussed here can be said to be both safe for use on light-damaged lacquer and effective as a cleaning agent. Whilst selection of a rapidly evaporating alkane, aromatic or ester-based solvent could potentially ensure brief contact with the damaged layers, and therefore minimal disruption to the surface morphology, the success of the solvent as a cleaning agent is dependent on the nature of the surface contaminant.

8.5 Risk assessment

The disruption that may be caused to the surface and the possible removal of original material during solvent cleaning must be carefully considered. Different solvent classes have been shown to behave differently towards aged lacquers in terms of swelling, and when using solvents as cleaning agents, the potential risk of damage must be evaluated against the desired outcome and the ‘acceptable’ level of damage, if any.

One of the main aims of the Mazarin Chest project was to ‘develop an integrated approach to the conservation of *urushi* objects that respects both western conservation ethics … and Japanese conservation values’,[8] and another was to stabilise the condition of the chest, which has experienced a range of treatments in the past, as well as being damaged through natural, environmental processes. Intervention is thought to be required because, following visual inspection, conservators have speculated that there are non-traditional, resin (probably western) materials present on some parts of the chest. The natural degradation processes to which lacquer is susceptible (namely light and humidity) have, over the years, caused a change in its structural stability and the deterioration is evident from the matt texture of the lacquer on light-exposed areas of the chest. A discoloration of the resin component causes an alteration in the overall aesthetic, and is undesirable. In order to conserve such pieces, these layers need to be removed.

As discussed in Chapter 1, records do not describe all of the treatments that the chest received, although the damage since the beginning of the 19th century when the chest was brought over to England from France is recorded briefly. The ‘rubbed’ surface was noted in the sale documents. It is not clear what is meant by this term, although clearly the chest is not in perfect condition by this time (~1800), and it is most likely that it referred to areas of the surface that appear abraded through to the foundation layers. Treatment to counter the discoloration, reduction in gloss, or abrasion may have been attempted in England to repair the ‘rubbed’ surface by its new owner. However, such speculation cannot be backed up with documentation since no records exist recording any restoration attempts, nor the materials used. Destructive, direct chemical analysis of the chest’s coating might identify the substance, but this is not desirable from a preservation point of view.

Solvent cleaning

The problem encountered by the Mazarin Chest has arisen because of the difficulties associated with maintaining the material. On a piece of such high quality lacquer, it can be assumed that materials of the highest quality will have been used for its production. Since the chest was designed for export, its designers would not have anticipated re-lacquering of the surface; this process was applied mainly to outdoor lacquer pieces, to maintain the glossy finish and facilitate water cleaning. However, lacquer that has been allowed to deteriorate for centuries develops a high sensitivity towards water, as well as other solvents. Conservators, or keepers of lacquer collections in Japan, with more knowledge of the material may have re-lacquered valuable objects before they reached a deteriorated state, thereby maintaining their aesthetic with appropriate materials. This would not be possible on exported items, however.

Before re-lacquering the surface, contaminants must be removed in order to stabilise the *urushi* surface, since any additional materials present may hinder the bonding of the original *urushi* to the new *urushi* and, particularly where vigorous polishing is applied, the structure’s integrity could be further compromised, as previously discussed. Other cleaning regimes that have been employed in conservation work involving sensitive materials include detergent application, chelating agents and laser ablation. The applicability of chelating agents, however, is limited since they require water as a solvent, which has been shown to swell and leach components from aged lacquer, and, therefore, these agents are unlikely to be of use. Water-based detergents are, similarly, ruled out; detergents that can be dissolved in alkanes to interact with polar dirt or non-original materials may be of interest, however, in future work.

A sensitive approach to the importance of cross-cultural outlook is important when considering the conservation of this piece, at least in the context of this project. The originally intended aesthetic has already changed – we know this because of the reduction in gloss which is marked compared to the inside of the lid. This object, however, can be traced through an interesting historical journey within France and England. Any subsequent changes, additions or ‘damage’ could therefore be regarded as an important part of its history, particularly since the piece was made for export to Europe and is, therefore, not solely the cultural property of Japan.

The removal of non-original varnish is important for the conservation of this particular object as its intended aesthetic is, in places, being marred by dirt and non-original materials. The removal of discoloured aged varnish is, in general lacquer conservation, desirable since the overall aesthetic is due to photodegradation products of a non-original material as opposed to the photodegradation products of *urushi* lacquer, on some areas of the chest. Re-establishing the gloss on a surface containing degraded products of the original layer only is a separate issue, and is a restorative course of action rather than a conservation process, requiring the addition of a new layer of material. Once the non-original or degraded coatings have been removed, the bare *urushi* surface is likely to exhibit uneven and unattractive damage, and re-coating (gatame) procedures would be required to improve the aesthetic of the surface. The original makers were lacquer artists of several generations experience and knowledge, however, and the characteristics and original condition of the surface cannot necessarily ever be faithfully recreated. A balance should be kept between treating this piece in keeping with Japanese cultural integrity whilst appreciating that the historical value of the piece is closely connected with its journey throughout Europe and the changes which it underwent during that period. Addition of the small, wooden feet was presumably carried out for practical reasons, for example, and the attempted restoration of a dulled surface, using non-*urushi* materials that happened to be widely available in Europe (although these could never match the subtle effect of *urushi*), is a valuable part of its historical function.

8.6 Intervention and remedial action

Conservation and restoration processes are subject to ethical considerations in museum environments. Conservation focuses on object preservation by slowing the progress of deterioration without causing any alterations to the piece, whereas restoration seeks to improve aspects of the artefact, thereby altering the piece. The removal of non-original materials from lacquered pieces has two objectives; firstly, to expose the original surface, and secondly, to stabilise the surface structure by removing the discolouring material. These are the desired outcomes. However, undesirable outcomes would be the removal of original material and the swelling of lacquer layers further down the lacquer strata. The ethics of conservation and restoration is a highly-charged field, and will not be entered upon in this project. However, it is important to note that the aim of removing the dirt and accretions, and any aged varnish that is present, from the original surface is not a restorative exercise that seeks to restore the gloss, but an exercise in conserving the original layer.

Conservation of unstable pieces should also involve careful consideration of the environment and climate at which they are stored or displayed. As discussed in Chapter 3, limited light exposure and closely controlled humidity retards the deterioration of lacquer. The display of lacquer, therefore, presents significant problems as regards its protection, although the presentation of such artefacts is obviously an essential component of the museum function. There is an on-going tension between the preservation of light-sensitive objects, such as lacquer, and the need to provide access, whether by display or loan.

On the other hand, careful consideration should be given to whether interference is absolutely necessary from an aesthetic point of view. Ageing, wear through use or display, and oxidation processes are all part of the historical progress of an artefact. In regarding treatment of a brass metal object, for example, there are two approaches; the first is to polish the metal, thereby maintaining its sheen, as would have been seen originally, the second is to allow the metal to dull over time, remaining untreated and following a natural course of ageing. Child describes the latter as a defence of the 'inherent nature of an object, rather than its restoration to a subjective former state'.[9]

The application of solvents to clean a lacquer surface, to remove the discoloration caused by additional materials, or to prepare it for further treatment, removes a part of the historical aspect of the piece, which may be regarded as acceptable damage. Furthermore, the addition of some solvents adds to the destabilisation of the lacquer layers, which unless disturbed could remain unchanged for many more years, if kept in suitable environmentally-controlled environments.

8.7 An overview of the problem faced by photodegraded lacquer: the approach so far

Prior to discussing the recommended solvents for cleaning valuable and unique pieces such as the Mazarin Chest, it is worthwhile to review the problems faced by these photodegraded coatings and the approaches taken so far. Lacquered pieces made in Japan are rare and valuable, and while made to an excellent standard, their condition now depends on the circumstances surrounding their storage over a lengthy period. Aside from the remarkable decorative style and skills involved, the high gloss and colour saturation achieved through application of *urushi* lacquer is the main characteristic that makes such pieces so unique; they could not be reproduced in the West due to difficulties in handling the material and lack of experience. Their scarcity and highly collectable nature meant that they were very expensive and much effort was devoted to attempted reproduction of the glossy black effect using other materials available in Europe.

Through a great deal of experimentation, recipes were produced which made use of natural resins and oils that could, when coloured and applied carefully, produce a very high gloss. This process was termed 'Japanning', and it is seen not only as the main decoration on many artefacts, but also on *urushi*-decorated pieces where restoration has been carried out, or where an original lacquered panel has been blended into a new piece. When juxtaposed in this way, the differences in the aesthetic of the two materials are evident. The rates at which the materials deteriorate are also very different, due to the unique chemical composition and physical properties of *urushi*.

As highlighted in section 1.7, *urushi* degradation is observed as a dulling of the gloss, whereas the varnish based material shows cracking or blistering on ageing.

The lacquer is obtained as sap from a tree, and the importance of refining this prior to use has been discussed, in section 3.3, in terms of its subsequent stability when dry. The stability of lacquer is largely due to the many layers that are carefully applied to form the surface structure. Deterioration of this remarkably durable material is initiated by light damage of the upper layers, and exacerbated to some degree by humidity fluctuations. Humidity and temperature variations can cause shrinkage or movements that render lower layers vulnerable. Once damage commences, the material becomes very sensitive to the further effects of the environment and by water and solvents. These effects are irreversible, and the studies here show that most types of solvent cause damage to some extent once the lacquer has reached a certain level of deterioration – the potential for damage is high compared to the likely benefits of cleaning, and removal of degraded original material is highly probable.

In East Asia, there are several types of lacquer available to lacquer artists. However, the higher quality Japanese lacquer has been confirmed to contain *urushi* only, despite suggestions that some pieces made in Japan might have used lacquer imported from other parts of Asia due to raw material shortages in Japan during the 17th century. Determining the type of lacquer present on an artefact cannot, therefore, be assumed by where it was made. As discussed in Chapter 4, there are methods to distinguish the botanical source of lacquer; however, this involves irreversible and destructive analysis of a piece of the artefact, such as pyrolysis-GC-MS.

The use of artificial ageing has been applied in this work to produce models of damaged lacquer on which to carry out solubility tests. The limitations of using increased light exposure over short periods of time are often discussed; the general consensus is that there is a limit to how much accelerated damage can be inflicted before the process ceases to have any bearing on a natural ageing process. Useful trends could still be determined with the use of these methods, however, and mercury-tungsten lamps and UV daylight simulation have been shown to produce significant, measurable changes to the stability of the lacquer. The cracking patterns seen on the naturally-aged specimens were mimicked by the mercury-tungsten light exposure, possibly aided by the dehydration from thermal effects of the lamp, whereas the UV daylight simulation did not achieve any cracking.

The HgW methods caused a significant reduction in gloss and change in colour, the UV daylight simulation had a less pronounced effect on the gloss, but a colour change was evident. Marked changes on a chemical level were observed by IR analysis which proved that the side-chains had degraded after similar exposures to UV daylight simulation or HgW lamps. Pyrolysis-GC-MS experiments have also indicated a breakdown of urushiol side-chains as well as formation of long-chain alkanes/alkenes as a result of increased oxidation in the side-chains. Overall, however, changes observed in naturally aged lacquer could not be faithfully achieved by any one method, in terms of cracking, appearance and changes at the molecular level. A compromise is required to rapidly obtain a large number of damaged lacquer samples, displaying as many changes as possible that would occur naturally.

These models are required to determine the outcome of saturating the surface with organic solvents, thereby emulating the cleaning processes required to remove non-original materials and contamination. Persistent, oxidised materials require solvents which pose a risk towards the original lacquer material – the suitability of each solvent type can be roughly determined using the artificially aged models as described is this work. Minimal swelling and leaching of the original lacquer along with maximum swelling of non-original materials is the desired outcome.

Photodegraded lacquer also faces challenges due to its environmental sensitivity. In addition to polar solvents, *urushi* lacquer is highly sensitive to atmospheric pollutants. As discussed in Chapter 3, lacquer gloss is susceptible to irreversible damage by sulfates in acidic atmospheric conditions, which contribute to side-chain degradation of urushiol. A London-based museum should therefore take extra care to protect the pieces in storage or on display from such conditions; in such a case, containment in an inert atmosphere may be required. Particulates that form in the air as a result of fuel combustion contain harmful sulphates, sticky or sooty components, and low pH components. Solvent-related treatment of these surfaces retaining such pollutants could potentially cause more damage if they facilitate the chemical action of such components by placing them into solution, thereby increasing the rate at which chemical interactions occur between pollutants and the lacquer.

As the lacquer degrades, the lower layers are exposed. Small pores, emanating from microcavities and cracking caused by photodegradation, open pathways which may extend all the way down to the wooden carcass. Since excessive fluctuations of moisture, that is humidity cycles, will change the shape and dimension of wood, this, in turn, can potentially shift the position of the coating materials through shrinkage, for example; the stress caused could exacerbate the surface damage, thus challenging the rationale behind the use of liquids on these damaged surfaces. It may be beneficial to attempt removal of polluting dirt accumulated within the many cavities prior to further treatments, such as gatame recoating of the surface, since dust components settling within the microcracks could hinder the binding of the old and new materials.

Important environmental considerations

Balance of humidity

The stability of the lacquer polymer can be affected by humidity, as previously discussed, and it plays a potentially significant role in its degradation. Since water acts as a plasticizer, very dry conditions increase the brittleness of its constitution, whereas moderately-humid atmospheres could, in contrast, contribute to the flexible and durable nature of the film, thereby extending its lifetime. While this assumption may be reasonable for free films, a lacquer coating constrained by the wooden base will experience stress and strain by a change of its dimensions, ultimately causing further damage to the coating. Additionally, the plasticized lacquer could allow faster diffusion of vapours or liquids, leading to an increase in leaching of important components, thereby destabilising the structure further.

Effect of light

Upon exposure to UV/visible light over time, the crosslinking density of lacquer increases, causing film stress and producing microcracks. The overall change in appearance as a result is from gloss to matt, and a decrease in the colour saturation. These changes have been mostly observed in the top layers only, since the lower layers are protected from these effects. In preserving the condition of lacquer, the piece must be kept out of direct sunlight, and filtration of radiation wavelengths below

400 nm must be applied. Inspection of the inner lid of the Mazarin Chest perfectly illustrates the importance of protecting the lacquer from the effects of light, since this surface has been kept in darkness over the years and continues to display an excellent glossy finish. The length of time of light exposure must also be strictly limited, and when not on display the lacquered pieces should be contained in the absence of light.

Heat exposure

Lacquer has been described as being thermochromatically sensitive with colour changes being observed at temperatures as low as 50^{o}C, although only when in combination with exposure to moisture on the surface.[7] The thermal ageing processes discussed in Chapter 5, show that very little change is observed in lacquer films exposed to thermal treatment only for 6-8 weeks.

8.8 Recommendations

From a chemical point of view, there are no solvents that can be definitively identified as being ‘safe’ for use on photodegraded lacquer surfaces. There are various degrees of swelling observed for the different solvent classes, and, when combined with the evaporation rates, estimations on the potential for damage to lacquer layers can be obtained. In practical terms, it is not possible to eliminate solvent use from conservation cleaning, and so conservators must use a combination of the data available to them, in addition to their experience and assessment of the suitability of the treatment, and, finally, trial and error methods are still applicable when approaching such a problem.

When attempting removal of dirt and accretions from an unaged or aged lacquer, aliphatic, non-polar alkane solvents are recommended, since there is negligible interaction between the solvent and the polymer. In the case of removing aged spirit resin-varnishes from photodegraded lacquer, it is useful if the varnish type can be identified in terms of triterpenoid, diterpenoid, or other category, since they exhibit different regions of solubility. However, unless the varnish used has been documented (which may be the case in more recent restorative attempts) it is difficult to select a suitable solvent unless chemical analysis can be used. The triterpenoids may be swelled by a low-molecular weight alcohol such as methanol, which, whilst displaying moderate swelling effects towards the lacquer, has a fast evaporation rate and low retention, thereby minimizing contact with the degraded lacquer layer. Ethyl acetate, from the ester solvent class, also evaporates very rapidly, although the retention in a saturated environment may be as high as 5%, and the solvent is high-swelling towards lacquer at all stages of ageing and degradation.

A diterpenoid, such as sandarac, has lower solubility in the alcohol solvents, and as shown in the DVS results, ethanol diffuses through aged sandarac very slowly when compared to similarly aged lacquer. Similarly, aged shellac (insect resin) requires a more-polar solvent such as dichloromethane or a nitrogen-containing solvent to swell considerably, although dimethylformamide should not be used as it causes considerable damage towards photodegraded lacquer. Acetonitrile shows considerably less damage in terms of swelling the lacquer, and is also a fast evaporating solvent.

Aged, crosslinked oil-based varnishes are prepared with drying oils, such as linseed oil, which, when aged are mostly soluble in mineral spirits, and some aromatics. However, the other components of the varnish are highly crosslinked and insoluble in these solvents, and require chlorinated or nitrogen-containing solvents such as dichloromethane and pyridine (as with aged shellac), and some components are soluble in ketones. These solvents pose a threat to the photodegraded lacquer, requiring more application time due to the extensive crosslinking, and therefore it is unlikely that a solvent system would effectively and safely separate the two crosslinked materials. It is recommended that the removal of an unwanted layer should not be attempted if its identity is unknown.

Definitive answers to a complex problem cannot be given here, but estimations based on some of the data obtained here in combination with the effects of evaporation rates and exposure times can offer conservators more information to improve their judgement regarding the selection of solvents and application times.

8.9 Conclusion: applicability of solvents in conservation

The irreversible damage that appears on the surface of the Mazarin Chest and other lacquered pieces is a discoloration of the surface due to deposition of dirt, or aged, non-original material and/or disruption of the microstructure of the top layer that creates a matt effect. Areas where varnishes have been applied become more evident and contrast with the original surface as ageing progresses, due to differing rates of degradation. The silver-metal features on the surface have become tarnished over time, lacquer has become abraded in places, some mother-of-pearl or gold leaf components have flaked off, and large cracks are seen on the lid of the chest, possibly because of fluctuations in the dimensions of the underlying wooden base.

It is important to consider that the aesthetic beauty of some materials, for example aged wood, are a product of the permanent changes caused by ageing. It would be difficult, however, to view any of the irreversible changes described on this particular piece as contributing beneficially to its aesthetic appeal. This damage, however, is partly a result of the movement from one climate to another – East Asian to European, as was originally intended for the piece. Upkeep was not possible by traditional means, and perhaps was not considered by its European consumers. The gloss and colour are the most significant features of this unique surface, and, now lost, are a permanent change which detracts from the original aesthetic value and intention of the piece. However, the piece is four centuries old, and bearing this in mind, it is in excellent condition. Of note, although the Mazarin Chest was given a functional form - a storage chest - it was unlikely to have been a functional item, and thereby, treated well and not subjected to the wear and tear of everyday use. The discoloration of parts of the surface due to obstruction by aged varnish materials, however, is not an acceptable change, and so the objective of this work was to investigate the applicability of solvent cleaning of such substances.

Identifying solvents with a low-risk of administering damage to photodegraded lacquer, through leaching or delamination, requires the consideration of swelling, retention, evaporation and diffusion behaviours. In addition, the conservators own experience and instinct is essential in determining the appropriate course of action, the solvent used and the means and period of exposure. Most of the solvents investigated here show that they pose a risk of damage to photodegraded lacquer. Dirt and accretions can, in general, be safely removed using alkanes, and this is particularly useful for objects which have a build up of years of polluting dirt.

Crosslinked, oil-based varnishes, prepared with drying oils are not likely to be separated from a crossslinked lacquer material using solvents, and the potential damage that would be caused by the polar solvents necessary for swelling or dissolving these materials is likely to rule out solvent cleaning as a conservation approach.

Rapidly evaporating solvents may be effective in the removal of degraded resin spirit-varnish from photodegraded lacquer, even where the solvents have been classified as high swelling, if the application times are restricted so that the solvents are not able to swell the damaged lacquer layers. Identification of the varnish present would be desirable in the effective cleaning of these surfaces, however. The use of chlorinated or nitrogen-containing solvents might demonstrate effective removal of an unwanted surface, although such chemicals are particularly harmful to health and should be used with great care. Their use outside an equipped laboratory is not really feasible.

An improved understanding of the solvent-lacquer interaction should help conservators in their quest to find suitable solvents for use in conservation cleaning, and further work is required for solving the problem of whether photodegraded lacquer can be separated from other, aged materials. Other approaches that could prove useful include the use of laser ablation, detergents or chelating agents, and there are other substances which are traditionally used as gentle cleaning agents, based on citric acids or ethanoic acid (vinegar), that may have beneficial effects, being less vigorous in their interaction than the organic solvents. Further work on obtaining diffusion coefficients is also necessary in achieving a more complete conservation cleaning model.

A means of quantifying the damage exhibited on a piece of lacquer, perhaps by measurement of cracking, for example, would be useful in guiding the conservator in solvent selection, and could be considered in future work.

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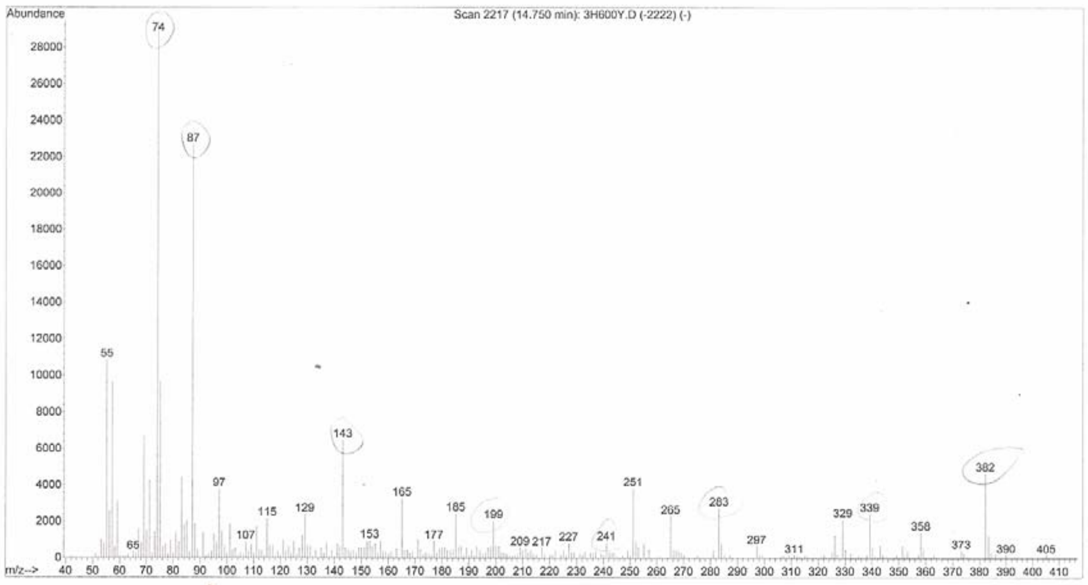
Appendix A

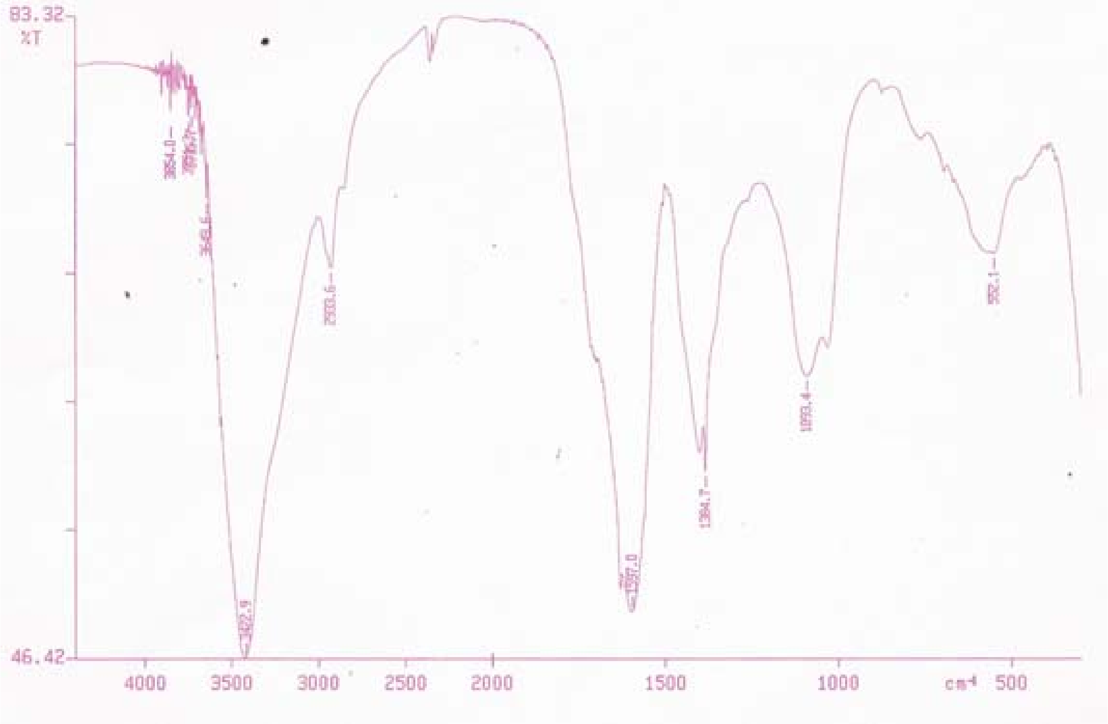


MS fragmentation pattern for peak at 14.750 min of lacquer sample taken from glossy part of a 19th century Japanese lacquer screen frame.

Appendix B

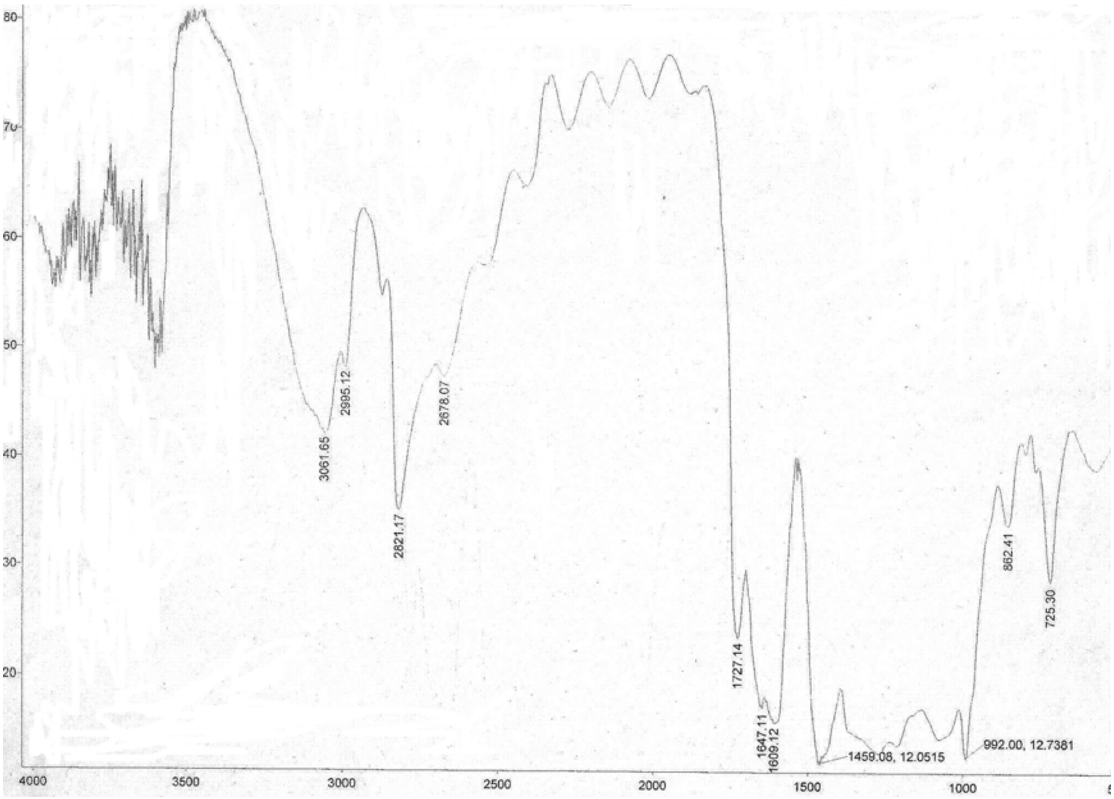
		Gloss measurement (gloss units) - mean value with standard errors in parenthesis		
Ageing time (weeks)	Ageing method	20°	60°	85°
0	Daylight simulation (UV)	20.21 (0.25)	63.54 (2.62)	86.7 (0.22)
	UVc	23.45 (0.24)	62.66 (0.51)	86.84 (0.25)
	Mercury-tungsten arc	23.03 (0.31)	63.4 (0.52)	86.09 (0.39)
	Thermal	20.22 (0.24)	62.88 (0.45)	86.44 (0.96
	Daylight	21.33 (0.27)	63.1 (0.93)	86.45 (0.56)
3	Daylight simulation (UV)	21.66 (0.3)	63.14 (0.69)	84.11 (0.67)
	UVc	21.32 (0.36)	61.24 (0.4)	85.73 (2.88)
	Mercury-tungsten arc	5.24 (0.1)	31.01 (0.18)	74.19 (0.59)
	Thermal	20.03 (0.2)	62.65 (0.16)	86.24 (0.45)
	Daylight	21.10 (0.22)	61.79 (0.29)	86.01 (0.48)
6	Daylight simulation (UV)	19.46 (0.23)	61.36 (0.42)	85.25 (0.84)
	UVc	20.30 (0.5)	61.2 (0.35)	82.84 (0.37)
	Mercury-tungsten arc	0.7 (0)	8.49 (0.12)	61 (0.74)
	Thermal	20.01 (0.29)	62.11 (0.43)	86.11 (0.49)
	Daylight	18.79 (0.4)	60.98 (0.3)	84.98 (0.86)
12	Daylight simulation (UV)	18.89 (0.28)	61.46 (0.79)	80.73 (0.39)
	UVc	21.59 (0.11)	61.07 (0.23)	80.67 (0.74)
	Mercury-tungsten arc	0.4 (0)	6.0 (0.14)	51.85 (0.26)
	Thermal	19.99 (0.34)	61.92 (0.14)	86.12 (0.23)
	Daylight	18.23 (0.18)	59.98 (0.25)	83.11 (0.35)
20	Daylight simulation (UV)	19.51 (0.08)	60.01 (0.25)	77.4 (0.93)
	UVc	21.42 (0.28)	58.01 (3.55)	79.59 (0.98)
	Mercury-tungsten arc	0.1 (0)	3.12 (0.98)	45.6 (0.36)
	Thermal	20.00 (0.19)	61.12 (0.33)	86.03 (0.87)
	Daylight	18.11 (0.26)	58.66 (0.14)	79.22 (0.44)

Appendix C



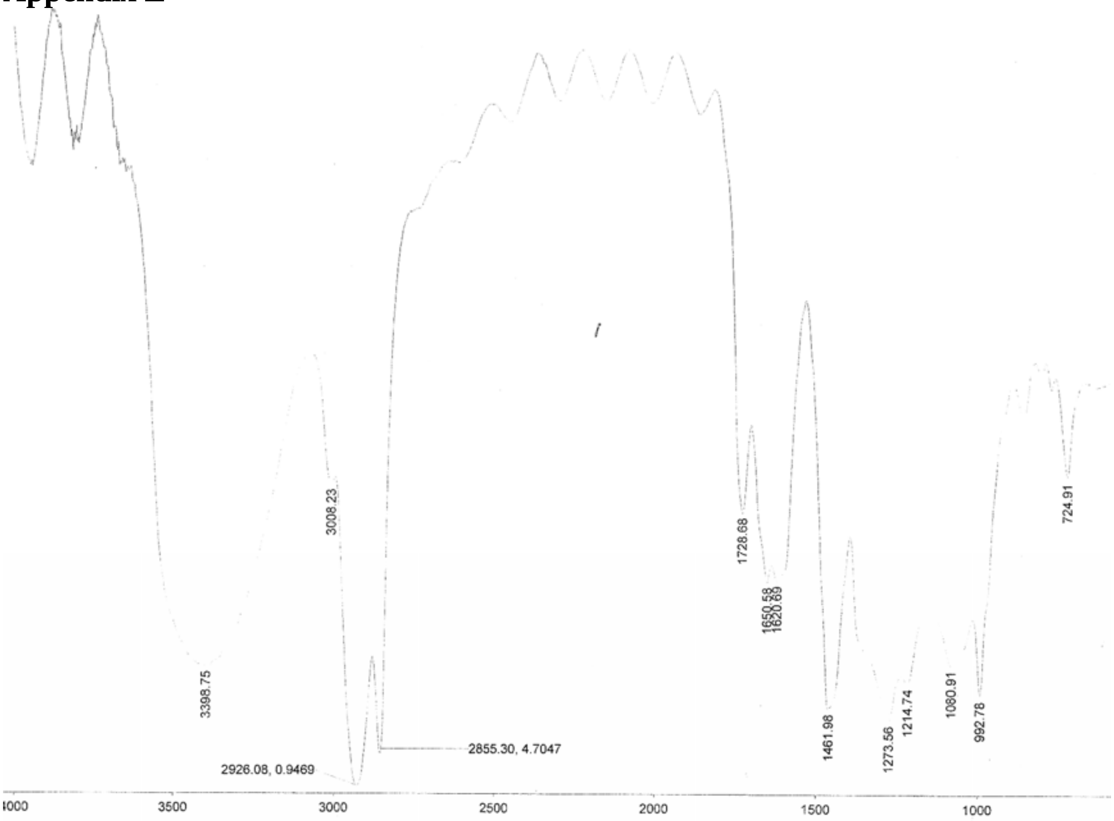
FTIR spectra of *kijiro urushi* lacquer film after 52 weeks natural ageing

Appendix D



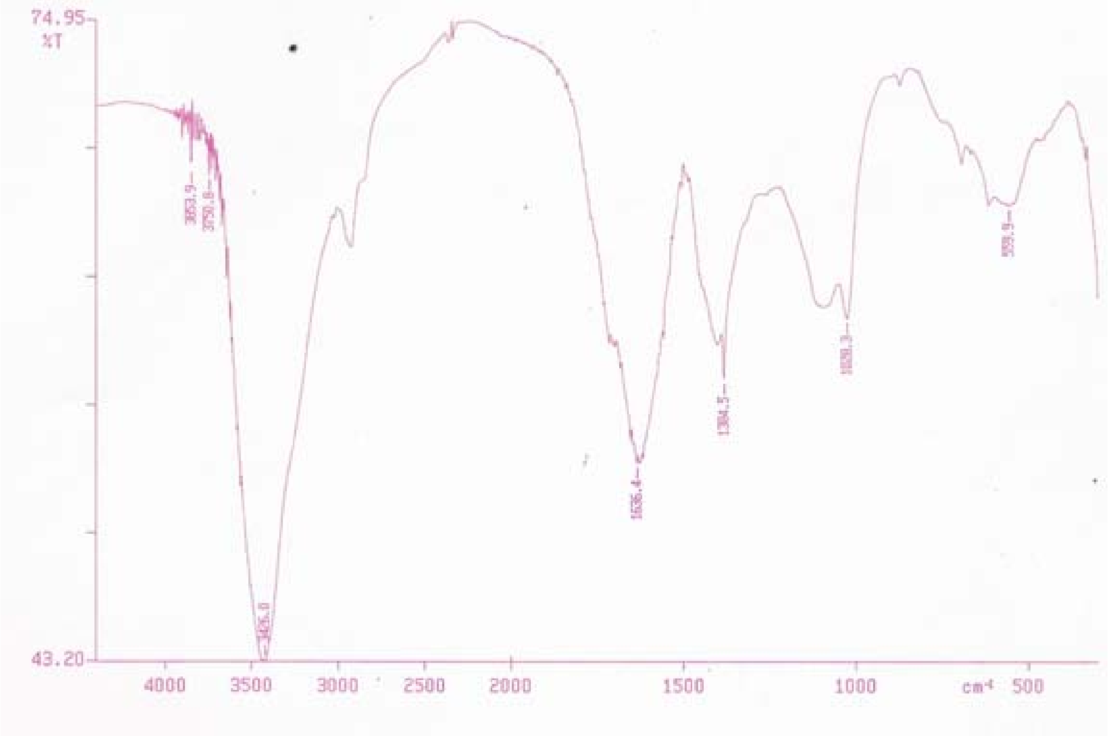
FTIR spectra of fresh lacquer heated for 3 days under vacuum

Appendix E



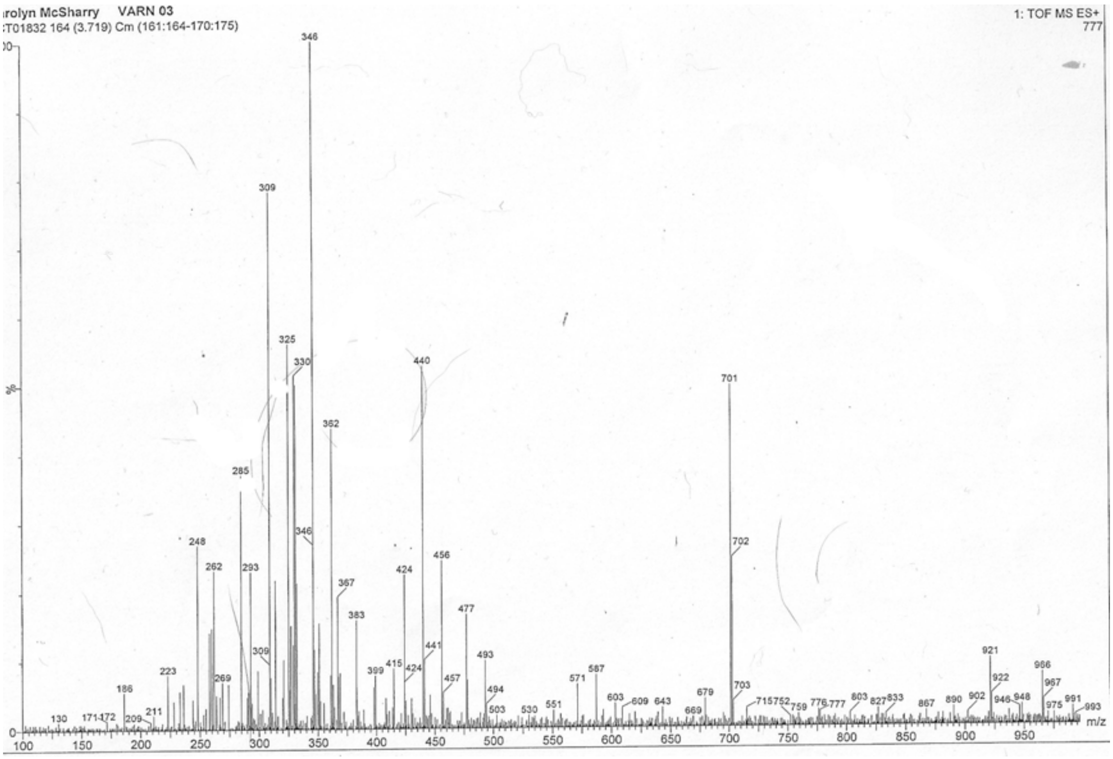
FTIR spectra of fresh lacquer stored in desiccator for 3 days under P_2O_5

Appendix F humid



FTIR spectra of components extracted from the surface of the Mazarin Chest under high humidity

Appendix G



Liquid chromatography- mass spectrometry spectra (positive ion mode) for water-soluble components of naturally aged lacquer