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HISTORICAL COATING MATERIALS - EAST ASIAN LACQUER *

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INTRODUCTION

As always when investigating a material hitherto insufficiently analyzed, a suitable method must be found which will answer the relevant historical questions. In the case of East Asian Lacquer which, as is generally known, is a natural polymer, it is therefore essential to cover three basic points:

1) a characterization of East Asian Lacquer
2) the analytical possibilities so far attempted, their short-comings, and some newly applied techniques in this field,
3) a summary of the results obtained by Pyrolysis Mass Spectrometry, a new technique mentioned above and thought to be currently most useful one.

CHARACTERIZATION OF EAST ASIAN LACQUER

The East Asian Lacquer is a tree sap, which has been collected from Rhus verniciflua (Toxicodendron verniciflua) for at least three thousand years. This so-called lacquer tree grows over large areas mainly of China, Japan and Korea. After tapping, the sap is purified and prepared for lacquering. The lacquer can be applied to wood, plant fibers, metal or other materials and this is usually done in thin layers. These layers harden within a short time to lacquer films with a glossy and very durable surface. The lacquering techniques and the character of objects of interest in Archaeometry can vary strongly although the initial product is always the same. This can be demonstrated by comparing an early lacquerpainting of the Han dynasty (figure 1) and a carved lacquer box of the Ming dynasty (figure 2).

The first group of questions to be answered in an archaeometric context has to do with the technology and especially the chemistry of East Asian Lacquer and what additional factors have to be taken into account to obtain relevant results (figure 3)(Burmester 1982a). Figure 4 shows the composition of the raw lacquer. The major component is urushiol, a mixture of substituted catechol derivatives. Further important components are a copper-enzyme (Laccase) and a mixture of polysaccharides. The percentual distribution of these components varies according to the provenance of the lacquer, according to the season and manner of tapping and according to when tapping occured. The last uncertainty factor mentioned is due to long term climatic variations.

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Figure 1: Lacquerpainting, China, Han dynasty (Linden-Museum Stuttgart)

Figure 2: Carved lacquer, China, Ming dynasty (Linden- Museum Stuttgart)

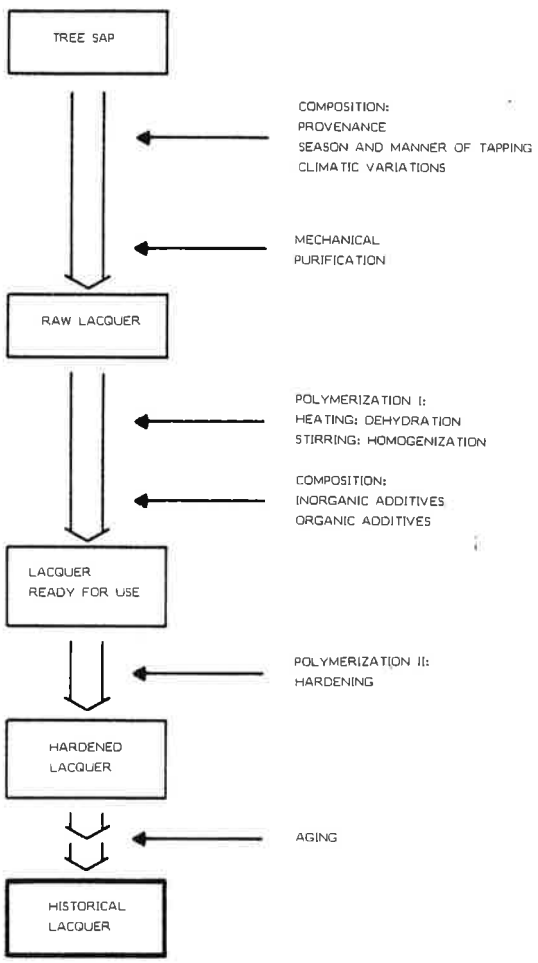
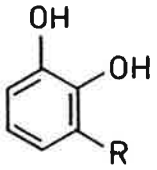


Figure 3: Technology of East Asian Lacquer

Urushiol		65 - 70 %
Laccase (Cu - enzyme)		1 %
Water		20 - 25 %
Polysaccharides		5 - 7 %

R $(CH_2)_{14}-CH_3$

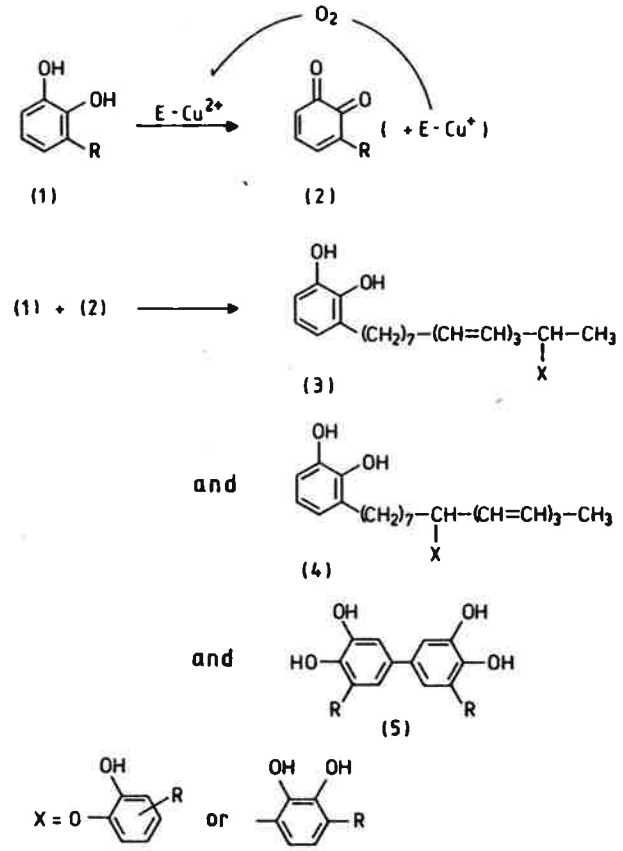
$(CH_2)_7-CH=CH-(CH_2)_5-CH_3$

$(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_2-CH_3$

$(CH_2)_7-CH=CH-CH_2-CH=CH-CH=CH-CH_3$

(Kumanotani 1979)

Figure 4: Composition of the raw lacquer



(Kumanotani 1979)

Figure 5: Polymerization of the lacquer, R see figure 4

To reduce the high percentage of water content the raw lacquer is heated to 40°C. During steady stirring the lacquer is homogenized and a polymerization takes place (figure 5) (Kumanotani 1976, 1979). In the first step of polymerization an urushiol monomer is enzymaticly oxidized and then the benzoquinone formed reacts immediately with a further urushiol. Different dimeric molecules have been found. The following steps of polymerization have not as yet been sufficiently enlightened, but it is supposed that the presence of the polysaccharides and high humidity play an important part in the hardening process. In fact the knowledge of East Asian Lacquer as a naturally occuring polymer is really rather incomplete. Even more so for historical lacquer films! Further complications are created by inorganic and especially organic additives, introduced during preparation of the lacquer, which alter the chemical composition and render analysis much more difficult. There is no certainty that the method of the preparation of the lacquer has not changed in the past. And last but not least the aging process of the hardened lacquer films is completely unknown.

ANALYSIS OF EAST ASIAN LACQUER

Several attempts have been already made to analyze the hardened, aged and insoluble lacquer films (figure 6). Kenjo propagates the use of conventional Infra Red Spectrometry (figure 7a). Insufficient additional information was gained by using Fourier Transform Infra Red Spectrometry (figure 7b). The same is true for CP/MAS FT carbon-13 Nuclear Magnetic Resonance on the solid lacquer sample (figure 7c). The main disadvantage seems to be that all analytical methods presented and carried out on the intact and solid polymer do not take into account the complex situation of the natural polymer illustrated above.

Some efforts have also been made to analyze modern lacquer films by Thermal Analysis. More information is to be obtained with the Pyrolysis Mass Spectrometry (Py-MS)(Burmester 1981a). As opposed to Thermal Analysis the information gained with Py-MS is not limited to pyrolysis behaviour. Finally it should be added that the use of Laser Microanalysis gives excellent results when analyzing pigments and inorganic additives embedded in the polymeric matrix.

During the Py-MS experiment 300 micrograms of lacquer are pyrolized with an external temperature input and control of a special characteristic (figure 8). The pyrolysis products are ionized in an electron impact ion source and the fragmentation products analized by a quadrupole mass filter. The result is a mass spectrum shown in figure 9: it shows ions of every molecular weight over and above 250. The procedure yields 1000 data points per sample. The only way to deal with this abundance of figures was the use of Multivariate Data Analysis discussed elsewhere (Burmester 1981a). The procedures supplied by SPSS and Wishart's CLUSTAN served as multivariate statistical and clustering routines. The dissimilarity measure used was the 'error sum of squares'. In this connection data transfer, data pretreatment and reduction as well as the destination of the real number of clusters were problematic.

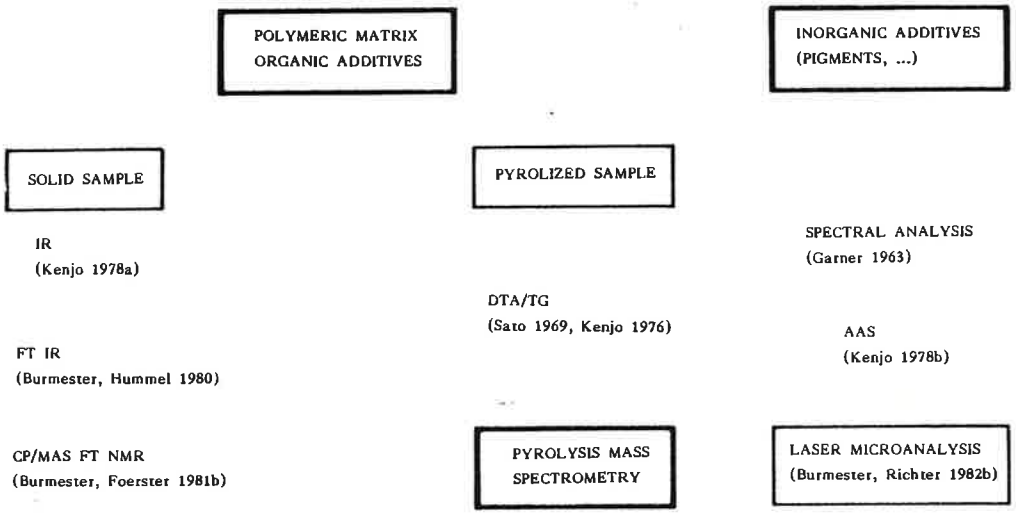
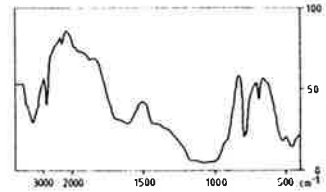


Figure 6: Analytical methods applied

7a

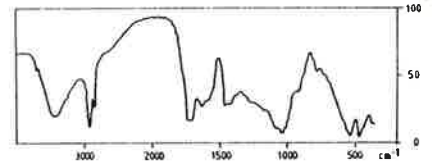
Infra Red Spectrometry (Kenjo 1978a)



7b

FT Infra Red Spectrometry

(Burmester, Hummel 1980)



7c

Cross Polarization / Magic Angle Spinning
^{13}C FT Nuclear Magnetic Resonance

(Burmester, Förster 1981b)

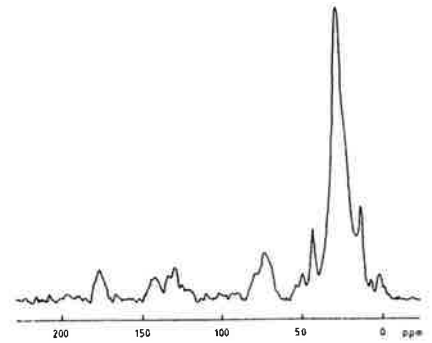


Figure 7: Analytical results on historical lacquer films

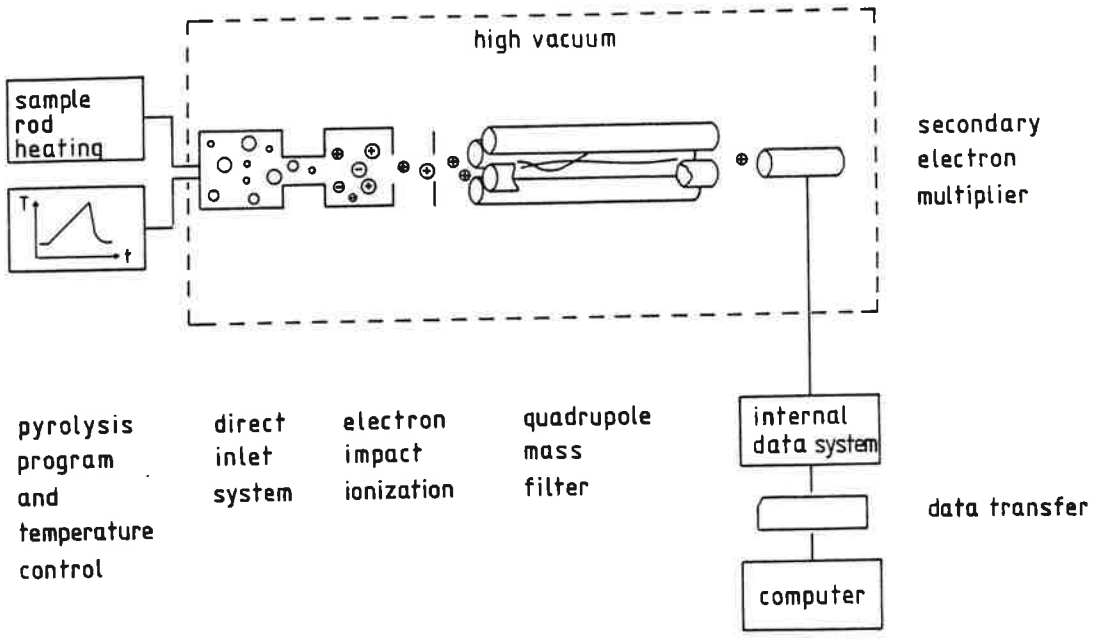


Figure 8: Py-MS experiment

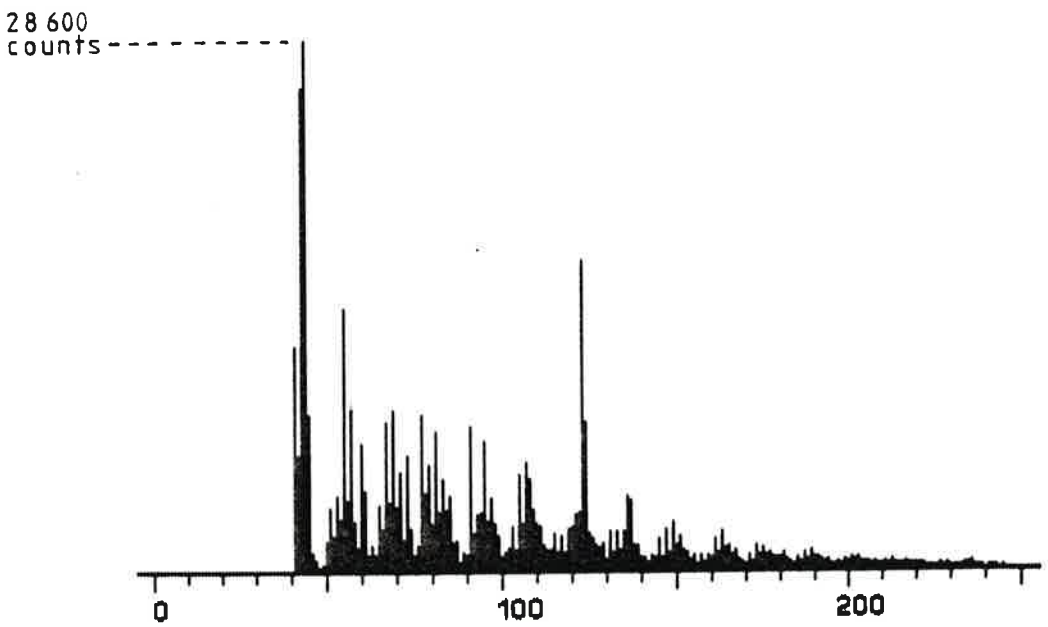


Figure 9: Py-MS spectrum of East Asian Lacquer m/e 41 to m/e 249 (Varian MAT 44, 70eV, direct, source 220°C, probe 200°C)

RESULTS

For the sake of clarity a dendrogram has been chosen as presentation of the classification carried out on 47 lacquer samples (figure 10). A subsequent relocation procedure reveals that the classification result is almost stable. Only two samples are fused to another group. A distinct separation of clusters can be observed.

Preliminary experiments showed a good reproducibility of Py-MS measurements. This reproducibility is yet further confirmed by the high similarity of repetitive measurements, marked by characters A to C (figure 10).

Different samples prepared from the same object show mostly high similarity: for instance the samples marked by characters D to G were prepared from directly superposed layers. The

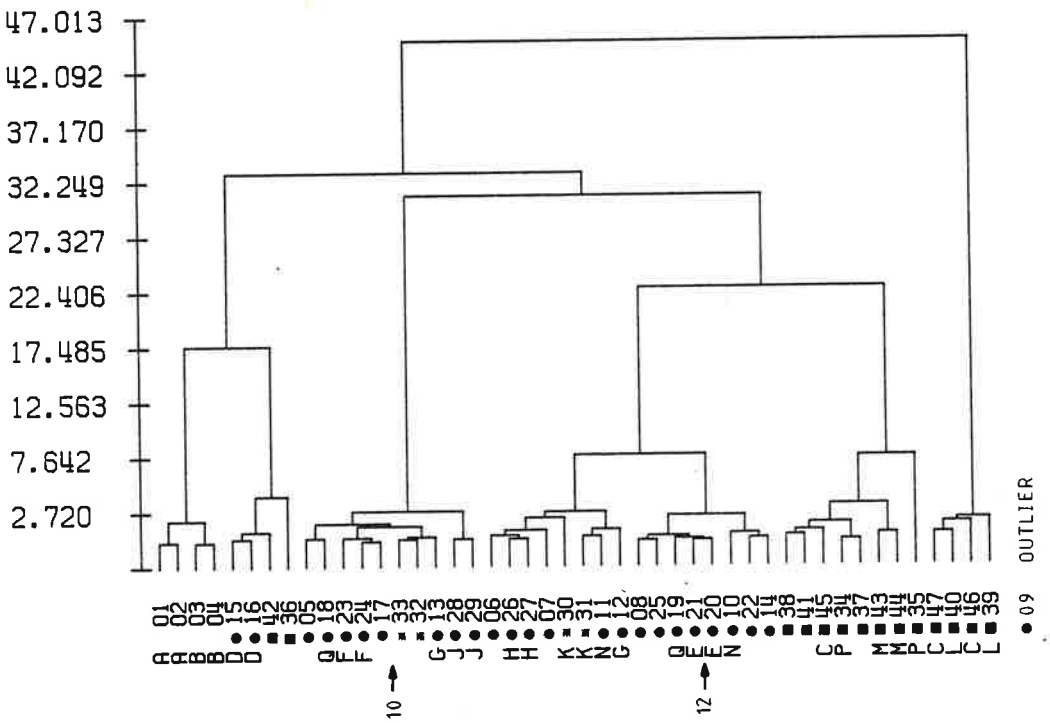


Figure 10: Dendrogram, Ward's method.
Sample specification: repetitive measurements A - C; same object, superposed layers D - G; same object, different samplings H - P; non-lacquer material No. 9; laboratory hardened lacquers No. 1 - 4; conserved lacquers No. 39, 40, 46 and 47.
Periods (China): ■ Zhou (before 222 B.C.), Qin (221 - 206 B.C.), Han (206 B.C. - 222 A.D.);
✱ Tang (618 - 906), Song (960 - 1279);
● Yuan (1279 - 1368), Ming (1368 - 1644), Qing (1644 - 1912).
All samples (excl No. 1 - 4) from Chinese lacquerwares of the Linden-Museum Stuttgart.

samples marked by H to P are those from different locations, for example from the inside and outside of the same bowl. Exceptions were only observed in four cases (G, N, O and P).

The grouping result can be summarized as follows:
- Sample No. 9 is obviously an outlier. It was however taken from a damaged edge of a Chinese table. A closer examination showed that the edge had been restored with a non-lacquer material. That explains the behaviour observed, and emphasizes the importance of careful sampling.
- Some early lacquers of the Han dynasty (No. 39, 40, 46 and 47) form a separate group. During sample preparation these lacquers showed unusual characteristics. A conservation of the objects in our times with a low molecular polyethylene glycol, proven by chemical analysis, causes the separation of this group.
- A further distinct group is formed by unpigmented (No. 1 and 2) and pigmented (no. 3 and 4) 'modern' lacquers which were hardened under laboratories conditions.
- The grouping of the remainder of the samples corresponds approximately with the dates proposed by historians. As can be seen all the early lacquers of the Zhou, Qin and Han dynasties have been grouped together with only two exceptions. Because of some facts not discussed here it can be assumed that the conserved lacquers would have shown a high similarity with the group of early lacquers had they not been treated with a conservation agent. The remaining groups are formed by later lacquers from the Ming to Qing dynasties, however fused together with lacquers of the Tang and Yuan dynasties.

DISCUSSION

The discussion of the results must be based on the analysis by Py-MS and Multivariate Data Analysis as the currently only suitable tool to solve practical problems. The areas to be considered are mainly questions of authenticity, technology and dating.

The first three points of figure 11 - the identification of non-lacquer material, synthetic and modern lacquers - can be solved by Py-MS with high probability. It should therefore be possible to identify modern restorations, copies or forgeries.

The high similarity of samples prepared from the same object suggests that the lacquerware was manufactured from 'one pot of lacquer'. This is an observation of high technological significance and will in future permit the identification of restorations as well as, and this is of exceptional importance, whether or not all parts of a lacquerware form a creative unity.

But how is one to explain the separation of the early lacquers from the later ones? It might be caused by a change in technology, or by natural aging. Furthermore several groups of later lacquer objects can be observed, all sampled from carved lacquerwares. At present these results cannot be definitively explained but it is likely that various factors mentioned earlier on would play their part, as for example provenance of lacquer, time and manner of tapping, preparation of lacquer and especially the change in composition by organic additives.

An absolute dating is not yet possible. A further development of radiocarbon dating might make this feasible, but a comparison to lacquerwares dated by inscription might allow a relative dating or even an attribution.

EAST ASIAN LACQUER : POSSIBLE APPLICATIONS FOR Py-MS

PROBLEM 1 : NON - LACQUER MATERIAL	+
PROBLEM 2 : SYNTHETIC LACQUER	+
PROBLEM 3 : MODERN LACQUER	+ - ?
PROBLEM 4 : FORMER RESTORATIONS	+
PROBLEM 5 : UNITY OF A LACQUERWARE	+
PROBLEM 6 : ABSOLUTE DATING	-
PROBLEM 7 : RELATIVE DATING	?
PROBLEM 8 : ATTRIBUTION	?

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Figure 11: Results

All photographs by U. Didoni (Linden-Museum Stuttgart)(figures 1 and 2) and V. Strauß (TU Berlin)(figures 3 to 11).

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