AN EXAMINATION OF SOME PAINTING MATERIALS OF SEVERAL 15TH CENTURY POLYCHROME SCULPTURES

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This paper presents the results of a physico-chemical and chemical investigation of the pigments, grounds and other painting materials of six polychrome sculptures from the altar of the Church of Holy Spirit in Tallin (Esthonian SSR) performed by the craftsman Bert-Notke in 1483. Samples were taken off the following sculptures: St Olaf, St Anne - figures of the left side shutter; a group with Apostle Peter, St Dorothy - figures of the central composition; St Victor, St Elizabeth - figures of the right-hand shutter.

The principal methods used included an X-ray diffraction analysis and infrared spectroscopy. X-ray diffraction patterns were obtained with "Mars" diffractometer, infrared spectra were recorded with a "Perkin-Elmer 257" (4000-625 cm^{-1}). In the latter case 1,5 mg of sample substance was pressed with 300 mg KBr into pellets.

The paint palette of polychrome sculptures is represented by four colours: white, red, blue, green.

White paint. Lead was discovered in samples by microchemical and emission spectral analysis. The data obtained from the X-ray diffraction analysis (Table 1) made it possible to conclude that the white paint on the sculptures is a mixture of basic carbonate lead white $2PbCO_3 \cdot Pb(OH)_2$ and a small amount of cerussite $PbCO_3$.

A similar conclusion can be made concerning the white overpainting of St Anne's figure. IR-spectra of the samples taken off the upper layer which dates from

1815, (Fig. 1,a) and those of the samples of the underlying layer (Fig. 1,b) are very similar. They represent spectra of mixtures of cerussite (bands at ~1405, ~840, shoulder at 676 cm^{-1}) and basic lead white (bands at ~1405, ~1630, 690, 680 cm^{-1}) (1). Basic carbonate content in the first sample is slightly larger than in the second one: the band of stretching vibrations of OH-groups at ~3520 cm^{-1} is more clearly seen as well as the band at 1630 cm^{-1} and, especially, at 680 cm^{-1}. Besides, $CaCO_3$ mas found in the mixtures - bands at 3400, 2520, 1800, ~1430, 877 and 715 cm^{-1} (2).

Table 1. Debye-Scherrer patterus of the white paint sample

d, Å	Intensity	d, Å	Intensity
4.48	low	2.08	high
3.61	very high	1.99	medium
3.34	medium	1.95	high
3.07	high	1.90	very high
2.63	high	1.71	medium
2.49	high	1.64	high
2.33	low	1.60	high

Blue paint. Transparent dark blue crystals of 10-200 μ with a small admixture of transparent green crystals of 50-100 μ and transparent colourless pieces of 30-50 μ could be seen in the samples under a microscope. The X-ray diffraction analysis proved that the blue crystals were azurites $2CuCO_3 \cdot Cu(OH)_2$, and the green crystals were malachite $CuCO_3 \cdot Cu(OH)_2$. The latter is, evidently present as a natural admixture of natural azurite. The colourless pieces of quartz and mica are likely to be a natural admixture just as well.

Red paint. Two layers of different red pigments were distinctly seen on transverse sections of the red paint layer under a microscope: the upper layer being thin, glazed and of crimson colour and the lower layer being thick, more dense and consisting of red grains. X-ray diffraction data showed that the underlying pigment was cinnabar.

There was protein in the red paint sample taken off St Victor's shield (Fig. 1,c): bands of Amid I (1650 cm^{-1}) and Amid II (1550 cm^{-1})were seen in the paint's IR-spectrum. In general, the spectrum is similar to the IR-spectrum of egg white (Fig. 1,d, spectrum of egg white having been aged in ultraviolet rays during 405 hours). It is likely that there is a small amount of admixture of $CaCO_3$ in the paint(bands at 1430 and 875 cm^{-1}), although absorption at 1430 cm^{-1} as well as in the regions of Amid bands and at 1015-1150 cm^{-1} can be explained by the presence of carmino acid (2). The major pigment - cinnabar, identified by means of X-ray diffraction, could not be discovered by IR-spectroscopy (2).

The presence of carmine lake was proved by a solubility reaction (3): the solution turned red when the paint sample was heated with NH_4OH. The presence of protein was also confirmed by thin-layer chromatography on ion-exchange plates "Fixion" (4) of paint hydrolysate (5.7 N HCl, 24 hours, 110°C). The set of amino acids and the intensity of spot colouring were similar to those identified while analysing hydrolysate of egg white.

The data autlined above confirm the conclusion drawn from the investigation of the paint layer's cross-section, namely, that the lower thick layer of the red pigment is cinnabar overlaid with a glazed layer of carmine lake which is probably covered with egg white. Such application of egg white was already recorded in a study of medieval Norwegian icons (5).

Green paint. Microscopie investigation of the paint layer's cross-section made it possible to determine that it consists of two sub-layers: the lower thin one (~10 μ), directly overlaying the ground and consisting of pale-yellow grains, and the upper one (~50 μ) - with identical pale-yellow grains and greenish-blue crystals (3-10 μ).

Microchemical and emission spectral analysis helped to determine copper, lead and tin in the green paint. The results of X-ray diffraction analysis are given in Table 2; the d spacings of the pigment lead-tin yellow are also given there (6). A comparison of these values makes it possible to conclude that the described pale yellow grains are particles of lead-tin yellow that had been frequently used in mixture with verdigris (7). X-ray diffraction failed to reveal the structure of the copper green pigment.

Table 2. Debye-Scherrer patterns of green paint and lead-tin yellow.

Green paint d, Å	Green paint Intensity	Pb_2SnO_4 (6) d, Å	Pb_2SnO_4 (6) Intensity
3.35	very high	3.35	100
2.78	high	2.77	40
2.55	medium	2.55	15
2.26	low	2.25	20
2.01	low	2.01	50
1.86	high	1.86	70
1.81	medium	1.80	70
1.72	high	1.73	80
1.58	medium	1.57	65

IR-spectrum of the green paint sample taken off St Anne's figure is shown in Fig. 1,e. It is almost identical to that of the green paint from A.Altdorfer's painting published by H.Kühn (7). It may be assumed that the paint consists of verdigris (bands of stretching vibrations of ionized carboxyl groups at 1550-1620 cm^{-1} are present in the spectrum) and dried-up oil (bands at 1715-1735, 1160, 1245, 1100 cm^{-1}). The band at 1410 cm^{-1} should be attributed to deformation vibrations of CH_2-groups of both verdigris and oil. IR-spectroscopy failed to distinguish lead-tin yellow (6).

It was established that the green paint covers the ground apparently glued with egg white. Thus, a dark layer between the ground and the paint layer was seen on the cross sections of painting samples. A dark film remained after the remoral of paint layer from a small painting fragment taken with the ground and the dissolving of the ground in 1 N HCl. Amid bands at 1640 (Amid I) and 1530 cm^{-1} (Amid II) were clearly seen in the IR-spectrum of this substance while bands of vibrations of carboxyl groups were missing. The distribution of amino acids of the film's hydrolizate on "Fixion" plates and the intensity of amino acids spots were similar to that of egg white hydrolizate. A similar ground treatment by egg white was determined in the case of Norwegian icons (5).

In can be assumed, therefore, that colouring with the green paint was performed by stages. At First painters coated the ground with egg white overlaid by lead-tin yellow which, in its turn, was covered by a layer of verdigris mixed with a small quantity of lead-tin yellow. Verdigris was usually mixed with an oil medium.

For comparison a sample of green pigment from the pedestal of the "Group with Apostle Peter" was investigated. In a microscope it was seen that the paint consisted of large crystals (100-150 μ) of turquoise colour. These crystals dissolved in HCl and HNO_3 without foaming. Copper was distinguished by means of microchemical reactions. An attempt to identify this pigment on the basis of data obtained by X-ray diffraction analysis was not a success (Table 3). The paint's IR-spectrum (Fig. 1,f) was found to be similar to that of the green paint from Norwegian icons (5). The authors who investigated pigments of Norwegian icons came to the conclusion based on spectrum analysis that the icons' paint consisted of verdigris and an oil medium.

A comparative analysis of the spectra obtained shows that if the pigment of overpainting is verdigris it is different from the verdigris found in the original decoration.

Table 3. Debye-Scherrer patterns of the green paint sample

d, Å	Intensity	d, Å	Intensity
6.80	very high	2.28	medium
5.22	low	2.10	low
4.35	very low	2.02	medium
3.46	high	1.93	low
2.88	low	1.86	high
2.67	high	1.81	low
2.43	hight		

<u>The layer</u> covering the gilding on St Victor's shield. The IR-spectrum of this substance (Fig. 1,g) in many ways resembles some of the previons spectra (Fig. 1,c,d) making it possible to conclude that egg white is present in the covering layer. It was also confirmed by chromatography of the sample's hydrolyzate. The covering layer, however, also contains vegetable oil: the IR-spectrum of a compound extracted from the sample by chloroform was absolutely identical to that of a substance extracted from the paint layer of an eighteenth century oil painting (Fig. 1,h). It is difficult to tell whether oil had been added initially while

covering the sculpture with egg white or it was brought in while renovating the altar figures.

Grounds. It was found by means of X-ray diffraction analysis and IR-spectroscopy investigations that calcite was the main component of the ground in all the sculptures. Gelatin was applied as a medium besides, traces of oil were discerned in the ground (8). As in the previous cases it is difficult to tell whether the ground had been saturated with oil initially or the oil penetrated into the ground during renovations.

Conclusions

The investigations undertaken helped to determine the composition of pigments and some other painting materials applied in the 15th century polychrome wood sculpture.

1. White pigment of the author's painting and overpainting is a mixture of basic carbonate lead white with a small amount of cerussite.

2. Blue pigment is azurite with an insignificant, possibly natural, admixture of malachite.

3. The main red pigment is cinnabar. The red paint consists of two-layers: a thick layer of cinnabar is overlaid with a thin glazed layer of carmine lake and, later, with egg white.

4. The main green pigment is verdigris. Painting with green colour performed was also by stages: First the ground was saturated with egg white and then covered with a layer of lead tin yellow, followed by a layer of verdigris with a small admixture of the same pigment.

5. The ground was made of $CaCO_3$ and gelatin.

6. Initially, the decoration was possibly covered with egg white for the latter was identified in the covering layer of gilt and red paint.

References

1. Kühn H. - "Farbe und Lack", B. 73 (1967), s. 99-105, 209-213.
2. Birstein V.J. - In Grenberg Yu.I. (Ed.) "Methods of analysis and the pigment identification problem", M., 1975, pp. 22-34.
3. Kühn H., "Reports and Studies in the History of Art, National Gallery, Washington", 1968, pp. 155-202.
4. Deveni T., Gergei Ya. "Amino acids, peptides, proteins", M. 1976, pp. 242-264.
5. Plahter L.E., Slang E., Plahter U. Gothic painted alter frontals from the church of Tingelstad. 1974, pp. 91-95.
6. Kühn H., "Studies in Conservation", 13 (1968), pp.7-33.
7. Kühn H., "Studies in Conservation", 15 (1970), pp. 12-36.
8. Birstein V.J., "Comparison of gelatins isolated from grounds of polychrome painting of wood sculptures and easel tempera paintings of the 15th-18th century", Report at ICOM Conference, Belgrade, 1978.

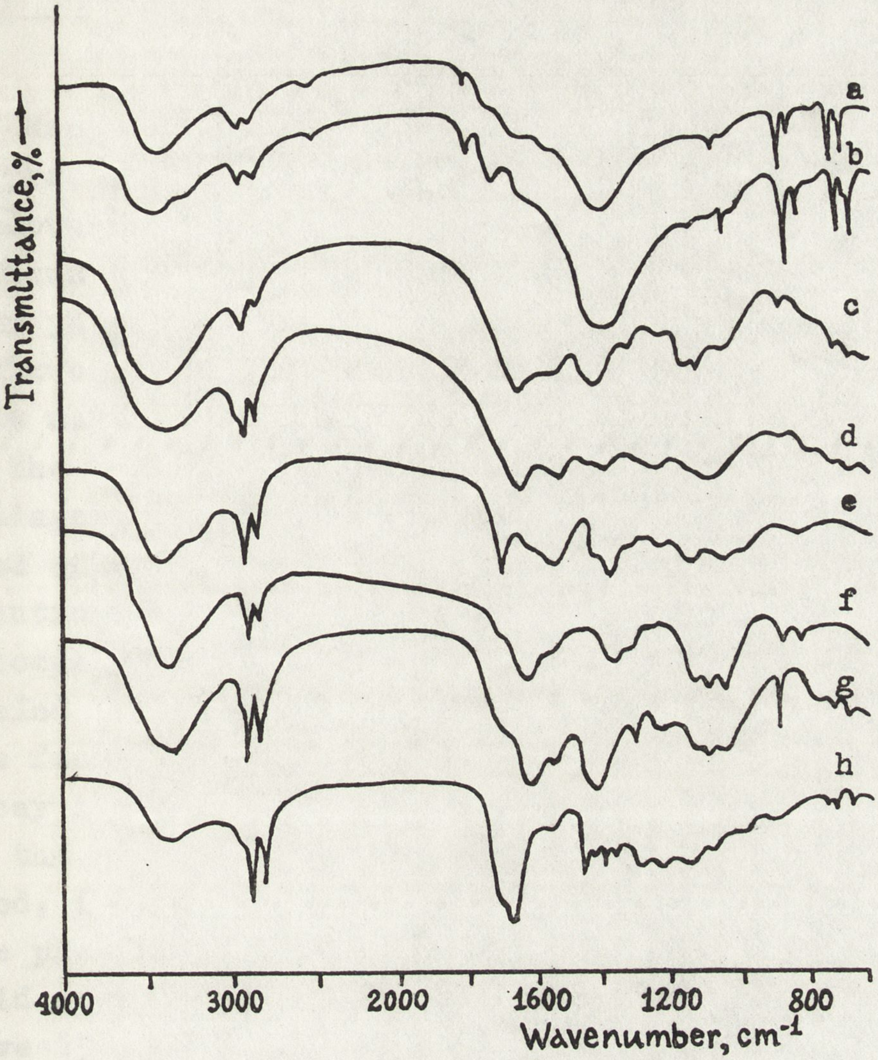

Fig. 1. IR-spectra of painting materials