Paintings in the laboratory: scientific examination for art history and conservation
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Citation for published version (APA):
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ICOM Committee for Conservation
4th Triennial Meeting
Venice 1975
TOWARDS IDENTIFICATION OF BROWN DISCOLOURATION ON GREEN PAINT

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INTRODUCTION

Green areas in paintings often have a brown appearance. This effect varies from what seems a thin brown veil in which no green pigment seems to be present (for instance on the edges of foliage), to a thick brown mass covering the green beneath. Examinations done on paint-samples taken from such areas, show that the reason for this browning is hardly ever due to copper resinate turned brown with time. The difference from copper resinate is also noticed in the restoration of paintings in as much as the brown at issue behaves in cleaning rather more like an oilpaint than a copper resinate would. The latter is a resinous compound and therefore soluble like a varnish (1 and 2). Also, copper resinates found in Flemish paintings are often very well preserved as greens (3). Thus tests performed by Dr. H. Kühn, show, that copper resinate discoulour less than for instance verdigris in oil (4). In the latter darkening may be due to both browning of the oil and of the pigment which, not covered by a varnish, could form black copperoxide. Copper resinate does not need oil as an additional binding medium, hence it is stable.

Since a green glaze was often absent in the paint-samples examined, the question arose whether originally it had been present at all. If it had not, then the brown discoulouration should have had some other cause. Due to the thinness of the brown layer and the irregularity of the opaque paintlayer underneath in samples studied by us, an I.R.-spectrum was sometimes difficult to obtain. Also the analysis of the binding-medium and a test for copper would not always give enough evidence. Copper could have penetrated into the transparent layer from the copper-containing one below. In order to determine the exact location of copper in thin paintlayers we did some experiments with the Scanning Electron Microscope with X-ray Microanalyser Accessory.
MICROSCOPICAL EXAMINATION

1. Green glaze, brown at the uppermost part.
2. Transparent brown layer, no U.V.-fluorescence, contains probably much oil.
3. A thin layer with a few green pigment particles in brown binding medium on top of an opaque paintlayer.
4. Coarse pigment particles are present in the undermost part of the paintlayer, while the uppermost part consists of a transparent brown.
5. a. Yellowed varnish, showing U.V.-fluorescence.
   b. Yellowed varnish, containing much oil, showing no U.V.-fluorescence.
6. Admixture of brown ochre.

POSSIBLE INTERPRETATION

1. a. Copper resinate formed by dissolution of copperacetate or other coppersalt in a resinous solution.
   b. A coppersalt which reacted in the course of time with the medium.
2. a. The same interpretation as under 1b.
   b. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
3. The transparent layer contains much oil and only a little pigment. The oil medium has turned brown.
4. In reference to smalt it has been observed that the pigment particles must be employed in coarse grains in order to preserve the colour. A side-effect is however, that such particles have a tendency to sink down in their binding medium (oil) and that the oil remaining on top will hence darken more visibly (5).
5. a. Copper resinate formed by dissolution of copperacetate or other coppersalt in a resinous solution.
   b. A coppersalt which reacted in the course of time with the medium.
   c. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   d. The same interpretation as under 1b.
   e. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
6. a. Copper resinate formed by dissolution of copperacetate or other coppersalt in a resinous solution.
   b. A coppersalt which reacted in the course of time with the medium.
   c. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   d. The same interpretation as under 1b.
   e. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   f. The same interpretation as under 1b.
   g. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   h. The same interpretation as under 1b.
   i. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   j. The same interpretation as under 1b.
   k. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   l. The same interpretation as under 1b.
   m. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   n. The same interpretation as under 1b.
   o. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   p. The same interpretation as under 1b.
   q. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   r. The same interpretation as under 1b.
   s. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   t. The same interpretation as under 1b.
   u. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   v. The same interpretation as under 1b.
   w. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   x. The same interpretation as under 1b.
   y. Oil, applied by copyists, to get a better image of the picture they wanted to copy.
   z. The same interpretation as under 1b.
   A. Oil, applied by copyists, to get a better image of the picture they wanted to copy.

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In this list the occurrence of a dark varnish, purposely applied by the artist, has been omitted because the subject has been fully dealt with by Miss Joyce Plesters and others (8).
In the cross-sections the numbers 3 and 6 can be clearly distinguished and they offer no problem. All the others show either a brownish upperpart of the paintlayer, or a separate transparent brown layer. Distinction can be made by determining whether this layer contains oil or resin and by the presence of copper. Except for copper resinate, oil or resin will give some difficulty, because an oil-medium can contain resin whereas varnish can contain oil. However, microscopically most varnishes clearly show U.V.-fluorescence.

An aspect not mentioned is the possibility that a brown layer may be a later addition. In our laboratory a transparent brown layer which did not show U.V.-fluorescence was found on top of an 18th-century overpainting on verdigris (Pacher-Altar, Skt. Wolfgang, Austria).

METHODS USED

If the transparent brown is thick enough to separate it from the paintlayer beneath, I.R.-spectrometry, thin-layer chromatography or gas-chromatography may be applied.

A test for copper is performed by adding a 5% solution of potassiumferrocyanide to a fraction of the sample. Next to this drop a drop of 3N HCl is placed. As soon as the HCl comes into contact with the sample, a gelatinous envelope of copperferrocyanide is formed if copper is present (9).

Samples used for studying the layer-structure are embedded in polyester resin (10), which hardens into cubes. These are cut and ground on a Knuth Rotor using silicon carbide paper and water as a lubricant. Finally they are polished, using alumina paste. Because of the darkbrown appearance of the particular samples discussed here the paintlayers could hardly be distinguished and therefore thin-sections had to be made. The cubes were glued onto a piece of perspex and ground and polished as before. The same thin-sections were used to detect the exact location of copper by means of SEM with X-ray Microanalyser Accessory.

The apparatus used was a Cambridge Stereoscan MK2A, with wavelength dispersive system. A method which would obtain similar results is the Electron Microprobe, described by Mrs. G. Elzinga-ter Haar (11).

The samples were coated with a layer of approx. 300 Å carbon. Additional 200 Å of gold was provided as a conductive layer. The acceleration voltage of the electron beam was 20 kV. The carbon and goldfilm could afterwards be removed by slight polishing.

The take-off angle of the X-ray beam was 45°, this being a fixed setting in this particular instrument. The diameter of the beam being 0.5 μ, the sample was always placed in the longitudinal axis towards the X-ray beam in order to obtain greater accuracy in the
study of very thin layers. However, due to the fact that the penetration depth is ca 2 μ the information obtained from the edge of a paint layer is inevitably inaccurate. Because many factors were involved (background, irregular surface, lack of homogeneity of the paint layers) no quantitative analysis was made. Results obtained from one sample can thus not be compared with the others. Magnifications used, depending on the sample and on the thicknesses of its layers, ranged from 550 to 1760 x. Polaroid-photographs were made, showing the backscattered electron picture, the X-ray emission picture for copper and a line scan for copper. The X-ray emission picture shows the distribution of copper with bright dots. The exact location of the line scan, as observed on the photographs, is at the straight line.

RESULTS

Three selected cross-sections will be given as an example of the applicability of the above-described technique. All three were prepared from paint samples taken from Lucas van Leyden's "Last Judgment" dated 1526, (Lakenhal, Leiden). Figs. 1 and 2, prepared from sample 672/119 taken from a green dress, show relatively much copper in the brown layer which is about 5 μ thick. (See layer number 2 in both Figs. 1 and 2.)

Layer number 3 is a green glaze; no pigment particles were seen microscopically. Another sample 672/29 taken from the same green dress with an identical layer-structure was analysed by X-ray diffraction. A mixture of basic copper sulfate (Cu₄SO₄(OH)₆.H₂O), lead-tin yellow, leadwhite and azurite was found. Microscopically the green glaze reacted as a copper resinate, being partly soluble and turning yellow with 3N HCl, turning brown with 10% NaOH and slowly turning brown with concentrated HNO₃. The presence of copper resinate (in this case not derived from copperacetate or Verdigris but from basic copper sulfate) may be confirmed by the electron picture which shows a large amount of copper in the brown upperpart of the glaze.

In sample 672/117 taken from a tree, directly under the transparent brown, an opaque paint layer was found (Fig. 3, layer number 3). Microscopically it shows a mixture of a green copper pigment, lead-tin yellow and leadwhite. In comparison with the opaque paint layer and with the background, the brown layers (nr. 1, thickness ca 1 μ and 2, thickness ca 6 μ) show relatively little copper. Microscopical observation suggests the presence of much oil. The opaque paint layers of sample number 672/14, prepared from a sample taken from a tree (Fig. 4, layer numbers 4 and 5), contain a mixture of basic copper sulfate, azurite, lead-tin yellow and leadwhite (X-ray diffraction). The brown layer on top (layer number 3, thickness ca 7 μ) shows no U.V.-fluorescence microscopically and is probably a mixture of oil and resin. The X-ray emission picture shows a relatively large amount of copper in contrast to the uppermost brown layer and the varnish (Layer number 2 and 1).
Fig. 1: Sample 672/119 taken from a green dress. The uppermost part of the green glaze is brown. Backscattered electron picture with line scan for copper. Magnification 550 x. 1. Overpainting; 2. transparent darkbrown; 3. green glaze; 4. leadwhite, some black.

Fig. 2: The sample as shown in Fig. 1. X-ray emission picture. The distribution of copper is shown by the bright dots. Magnification 1760 x.
Fig. 3: sample 672/117, green from a tree. Backscattered electron picture with line scan and X-ray emission picture for copper. Magnification 1760 x. 1. darkbrown layer, contains most probably oil; 2. brownish oil-layer; 3. mixture of green copper pigment, lead-tin yellow and leadwhite (micr.); 4. blue-green copper pigment (micr.).

Fig. 4: sample 672/14, green from a tree. Backscattered electron picture with line scan and X-ray emission picture for copper. Magnification 1760 x. 1. varnish; 2. darkbrown layer containing probably oil and resin; 3. brownish layer, probably oil and resin; 4. basic coppersulfate, azurite, lead-tin yellow, leadwhite; 5. the same mixture as in 4., with the exception that it contains more azurite (analysed with X-ray diffraction).
DISCUSSION

The evidence gathered so far is insufficient and the cause of the brown discolouration could not yet be determined. An attempt has been made to get an indication of the applicability of X-ray microanalysis in solving the problem.

Since the diameter of the electron beam is only 0.5 μ and the thicknesses of the layers to be measured are mostly 5 to 15 μ, it is possible to detect copper in these layers. But the mere detection of copper is not sufficient. The question is whether the concentration throughout the layers is the same, or only the result of absorption from the one below. It should also be considered possible that due to polishing of the samples copper-containing particles have become dislodged from their original locations. The information gathered from the edge of the paintlayers is inevitably inaccurate because the electron beam penetrates into the paintlayers approximately 2 μ. Thus also a paintlayer adjoining the layer which is actually studied may be analysed which then leads to mixed results. A setting of 45° was fixed in this apparatus, whereas a larger take-off angle of the electron beam would give a more accurate result. The line scan gives information about a very narrow line across the sample. The X-ray emission picture which shows the exact location of copper in bright dots and gives an overall-view, is more reliable.

Only a few analyses could be carried out due to the fact that the equipment needed, a Cambridge Stereoscan MK2A with wave-length dispersive system, is not part of our laboratory set-up and the expensive work has had to be put out to contract. It remains to be determined yet whether the method described above is sufficiently useful for the identification of various kinds of brown discolouration in paintings. The intention of this interim-report is to provoke comment from those engaged in finding a solution to the same problem.

ACKNOWLEDGEMENT

The author is grateful to Mr. G.O. Heukels of the firm P.D.O. in Amsterdam for operating the Cambridge Stereoscan and for his cooperation in discussing its applicability to this particular study.

REFERENCES


10. Poly-Pol PS 230, with 0,6 to 1% Mek.p-katalyst. Obtained from Poly-Service, Amsterdam.


ABSTRACT

In studying cross-sections of green paintlayers we sometimes observe that the green is either covered with or embedded in a brown coloured substance. In an attempt to determine whether this is to be attributed to discolouration of the green paint we have tried to detect the eventual presence and the exact location in this brown substance of copper. We used the Scanning Electron Microscope with X-ray Microanalyser Accessory. Some results of preliminary tests are given in order to indicate the possibilities and the limitations of this method for this purpose.