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Copper resinate: an XPS study of degradation

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ABSTRACT In this paper, we describe an X-ray photoelectron spectroscopy (XPS) study of copper resinate, a transparent green glaze that is coloured by copper salts of resin acids. This pigment was used in Europe in the fifteenth and sixteenth centuries, but it does not seem to be a usual feature of the palette anywhere after the end of the sixteenth century, because its tendency to discolour was already widely known by artists. An essential prerequisite for the restoration of works of art is the understanding of the effects of various climatic parameters on the deterioration process. For this reason, pictorial models of copper resinate in linseed oil, capable of simulating the ancient paintings on mobile supports, were prepared and aged in a climatic chamber, under different conditions such as exposure to UV radiations, humidity and different concentration of chemical pollutants (NO_2 and SO_2).

All the samples were investigated by XPS and the data obtained were evaluated in order to estimate aging effects as well as mechanisms of degradation. On these paint layers damage induced by X-ray irradiation was also verified.

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1 Introduction

Copper resinate is the name commonly given to the transparent green glazes that are coloured by copper salts of resin acids. This pigment was most commonly used in Europe in the fifteenth and sixteenth centuries, but it does not seem to be a usual feature of the palette anywhere after the end of sixteenth century, because its tendency to discolour was already widely known by artists of the time [1]. Degradation very often leads to profound changes in the chemical species that form pigments and binders, causing modifications in the chromatic properties of the paint film. Since the products formed in the early stage of degradation involve a very thin layer (only a few nanometers thick), the analytical techniques usually employed for the characterization of materials, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), or electron-probe microanalysis (EPMA), often do not supply exhaustive information. In this context, as we have reported

and demonstrated in previous works [2, 3], X-ray photoelectron spectroscopy (XPS) is a surface technique with great potential to investigate the degradation phenomena of art objects. In fact, one of the major strengths of the XPS technique is the ability to discriminate between different oxidation states and chemical environments of elements that make up a surface, with a maximum depth of a few nanometers [4]. In many cases it is also possible to study the paint coating in a non-destructive manner, following XPS analysis samples may be further used in other tests.

In order to understand and to describe the modification of copper resinate in linseed oil, as a consequence of the action of different climatic parameters, four kinds of samples were analysed by XPS: pure pigments, freshly prepared oil paint layers; samples that had been aged naturally for two years in the city centre of Florence; and samples that underwent aging in a climatic chamber under different conditions capable of simulating the ancient paintings natural degradation.


2 Experimental

Venice turpentine and turpentine essence were purchased from Zecchi (Florence, Italy), verdigris from Kremer (Aichstetten, Germany).

Copper resinate was prepared by restorers in the Opificio delle Pietre Dure (Florence). This was carried out by interpreting ancient recipes following a scientific approach [5]. The preparation was based on mixing of Venice turpentine, of basic verdigris and turpentine essence using the following procedure: 6 g of Venetian turpentine and 4 g of finely ground basic verdigris were mixed and stirred at 80–90 °C for 25 min. 2 ml of turpentine essence was added at 80–90 °C and stirred for 15 min.; 8 ml of turpentine essence was added to the mixture at room temperature. The final product was a green glaze that was reduced to a powder by grinding. To prepare the copper resinate samples, an amount of linseed oil was finally added to the pure pigment, in order to obtain the appropriate viscosity of painting paste. The obtained mixture was laid in a thin film (approximately 200 μm thick) on glass slides.

2.1 Artificial ageing

All the samples were naturally aged for a period of two years in the laboratory environment of the Opificio delle Pietre Dure. Some samples underwent an additional aging

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period of four weeks during which water condensation in the presence of SO_2 and NO_2 was alternated with short periods of UV (365 nm) exposure to avoid possible biological attacks. The aging process was carried out in an HC 4030 Heraeus Vötsch climatic chamber. The weekly ageing cycle scheme is shown in Table 1.

2.2 XPS measurements

XPS measurements were carried out using a PE-PHI ESCA/SAM5600 monochromator system spectrometer with an analysis chamber base pressure of 5×10^{-10} Torr. X-ray photoemission measurements were performed using a standard Al K_α ($h\nu = 1486.6$ eV) source. The energy scale of the spectrometer was calibrated with reference to the Ag $3d_{3/2} = 368.3$ eV photoelectron line. Binding energies were calculated with respect to the C $1s$ ionization at 285.00 eV from adventitious carbon, coming from pollutant hydrocarbons in the atmosphere, that is generally accepted to be independent of the chemical state of the sample under investigation. The pure pigment samples were mechanically applied to an indium foil and then fixed onto the spectrometer holder. The paint-layer samples were removed from the glass substrates using a lancet, and were loaded onto the holder, and analysed on both sides corresponding to interfaces of air–film and film–substrate. In all the cases the samples to be analysed were subjected to 2 h of ultra-high vacuum (10^{-7} Torr)

in a suitable pre-chamber to reduce degassing processes during the measurement period.

3 Results and discussion

The wide-scan X-ray photoelectron spectrum of the pure copper resinate sample is shown in Fig. 1. The core-level lines, Cu $3p$, Cu $3s$, C $1s$, O $1s$, Cu $2p$ and the Auger lines Cu LMM and O KVV can be clearly seen. The high intensity of the C $1s$ signal is due to the organic components of the green pigment: Venice turpentine and turpentine essence. These diterpenic resins were commonly used by the artists for their excellent optical, adhesive and protective properties that conferred to copper resinate the characteristic glassy transparency [6]. Core ionisation signals Cu $3p$, Cu $3s$, Cu $2p$ and the Auger line Cu LMM obviously referred to copper-based species contained in the pigment.

3.1 Stability of Cu(II) ions during XPS measurements

As we mentioned above, the XPS technique permits discrimination between different oxidation states and chemical environments of elements. In our study we were able to evaluate the oxidation state of copper ions. In fact, it has been reported that the combination of Cu $2p_{3/2}$ and $L_3M_{45}M_{45}$ Auger emission induced by X-rays offers this possibility. Cu(II), with its characteristic shake-up satellite structure and the higher B.E. value of Cu $2p_{3/2}$ is easily discriminated from Cu(I) and Cu(0) where the shake-up structure disappears. On the contrary, the $L_3M_{45}M_{45}$ Auger transition and the corresponding Auger parameter allow distinguishing between Cu(I) and Cu(0) [7]. Moreover, it is well known that pronounced surface reduction of some $3d$ transition ions in many compounds has been observed during XPS measurement. In particular, the reduction of Cu(II) to Cu(I) during XPS analysis has been widely reported in the literature and has been attributed to the integrated X-ray dose [8], heating from the X-ray gun [9], outgassing in a vacuum [10] and/or slow electrons emanating from X-ray windows during analysis [11]. In Fig. 2, XPS Cu $2p$ spectra of pure copper resinate acquired at different times of X-ray irradiation are reported. Marked changes in the Cu $2p$ core level structure and in the corresponding shape of the Cu $L_3M_{45}M_{45}$ Auger (see Fig. 3) occurred with increasing analysis time. In fact after 35 minutes of X-ray bombardment Cu(II) appears to be completely reduced to Cu(I).

This phenomenon was imposed to maintain the XPS acquisition time under 10 min. This suggests however, that the possible damage produced by X-rays on real paintings should have been evaluated in all diagnostic techniques commonly used to study and to investigate the paint layers of masterpieces, employing X-ray sources [12].

3.2 XPS analysis of copper resinate in linseed oil

Samples of oil paint layers containing copper resinate, both freshly prepared, and naturally and artificially aged, were also characterized. In particular, for each sample we investigated the paint layer–air interface and the paint layer–substrate interface, to evaluate if the possible chemical

Day	Pollutants	Temperature (°C)	Relative Humidity (%)	Time(h)
Mon	NO_x (10 ppm) + SO_2 (10 ppm)	Condense(18°)	75	24
Tue	UV(365 nm)	30	75	24
Wed	NO_x (10 ppm) + SO_2 (10 ppm)	Condense(18°)	75	24
Thu	UV(365 nm)	30	75	24
Fri	NO_x (10 ppm) + SO_2 (10 ppm)	Condense(18°)	75	24
Sat/Sun	UV(365 nm)	30	75	48

TABLE 1 Week ageing cycle scheme (repeated for 4 weeks)

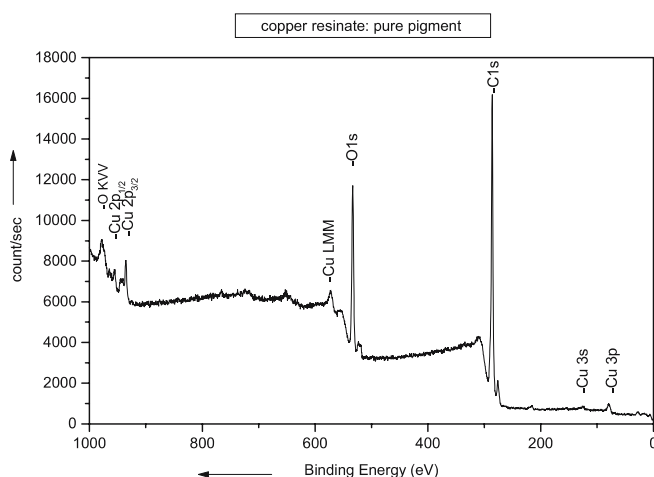


FIGURE 1 XPS wide-scan spectrum of pure copper resinate

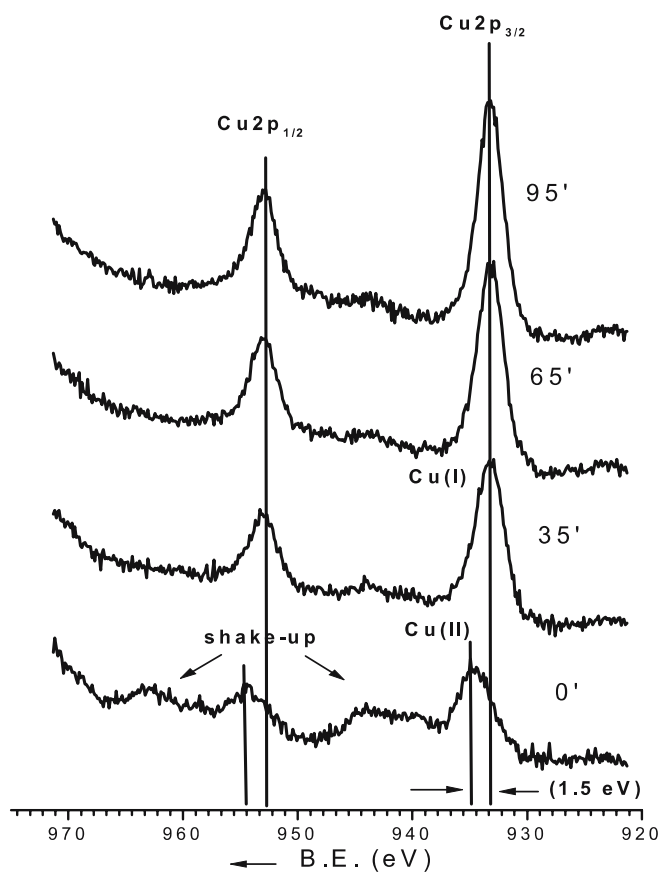


FIGURE 2 Cu 2*p* spectra from sample of pure copper resinate acquired at different X-ray irradiation times

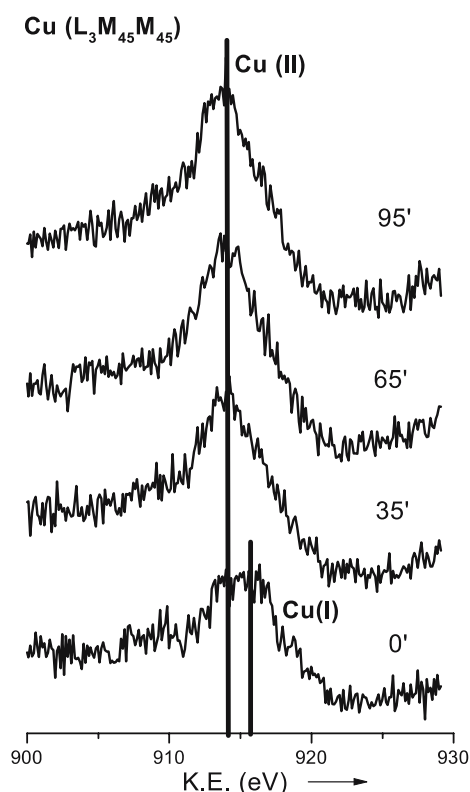


FIGURE 3 The Cu LMM Auger spectra from a sample of pure copper resinate acquired at different X-ray irradiation times

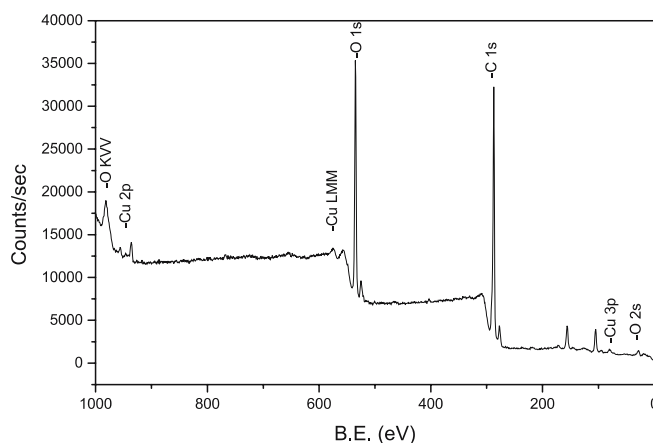


FIGURE 4 XPS Wide-scan spectrum of copper resinate in linseed oil (external surface)

changes induced by ageing were limited to the external surface or affected the layer taken as a whole. In Fig. 4 the XPS spectrum of copper resinate in oil, freshly prepared, is shown.

The C 1*s* signal due to the oil medium and diterpenic resins is distinctly visible as well as signals generated by copper (Cu 3*p*, Cu 3*s*, Cu 2*p* and the Auger lines Cu LMM). Other pollutant signals are absent.

We have also evaluated the concentration of chromophore elements on the surface. This data could, in principle, give information about the pigment grains exposed to air that emerge from the paint layer. The high atomic concentration of copper ions on the surface (46%) strongly suggests that copper resinate is soluble in linseed oil. In a previous work we have compared the concentration of grains in the paint surface for different pigments and binders. Zinc white and lead white in linseed oil gave values of chromophore surface concentration of one order of magnitude lower than copper resinate, the two white pigments having a good chemical inertia in oil media [4].

The film naturally aged for two years did not indicate any significant differences with respect to the freshly prepared layer. On the contrary, XPS analysed of artificially aged models showed interesting chemical modifications. The wide spectrum of the external interface (paint layer–air) showed the presence of pollutant signals (S 2*s*, S 2*p*, N 1*s*) that were absent in the analogous spectrum recorded on the internal interface (paint layer–glass substrate) of the same sample. This result suggests that only the external surface of the layer is affected by deterioration processes and that the oil medium protects the enclosed pigment better than the protein binders. Tempera paintings in fact, are permeable to air pollutants and their deterioration involves the paint layer in its entirety as we reported in previous works [2, 4].

In Fig. 5 the S 2*p* and N 1*s* expanded regions acquired on external and internal surfaces are reported.

The corresponding B.E. values clearly indicate that nitrogen and sulphur possess oxidation numbers of +2 and +6 respectively. This evidence strongly suggests that a red–ox reaction between SO₂ and NO₂ occurred at the layer surface. Moreover the N 1*s* signal totally disappeared after a few hours of UHV exposure. So probably NO species is only physisorbed to the surface. On the contrary, sulphur species

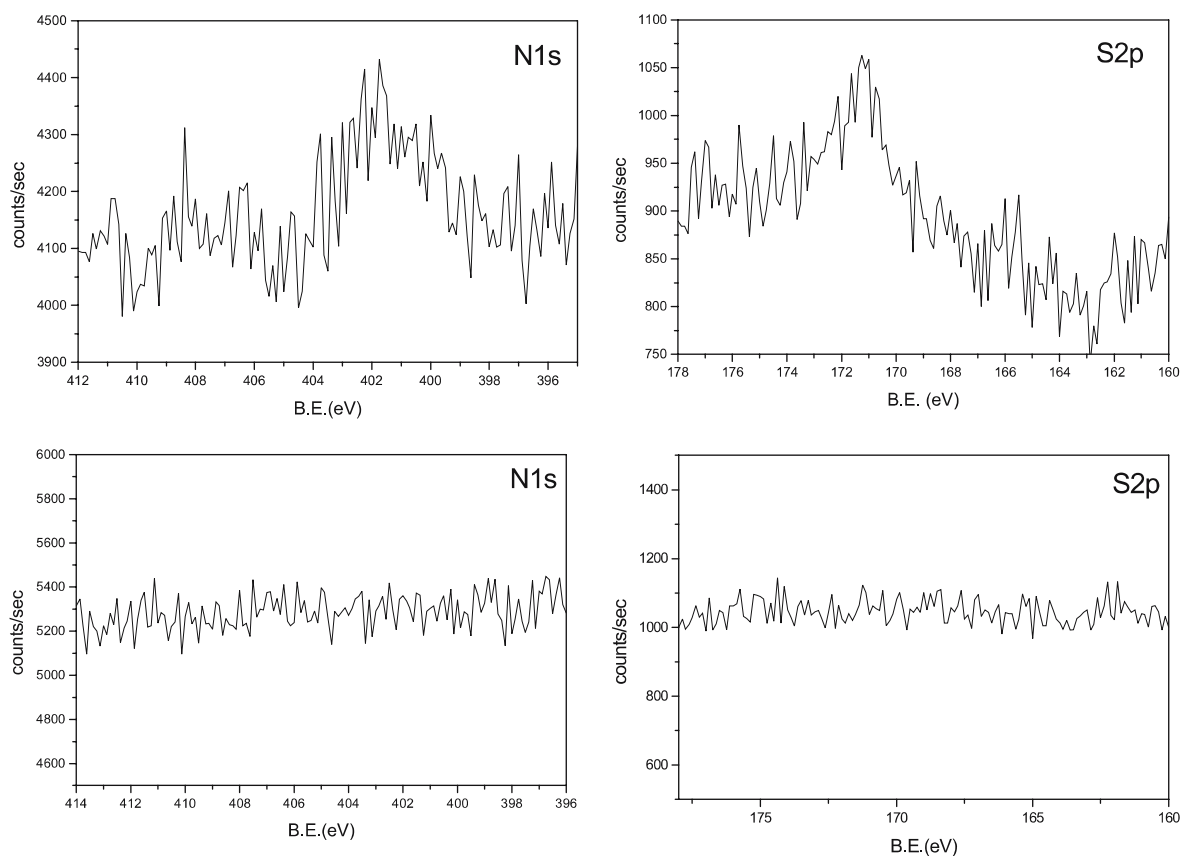


FIGURE 5 S 2p and N 1s expanded regions acquired on the external (*up*) and internal the (*down*) sides of copper resinate in linseed oil film artificially aged

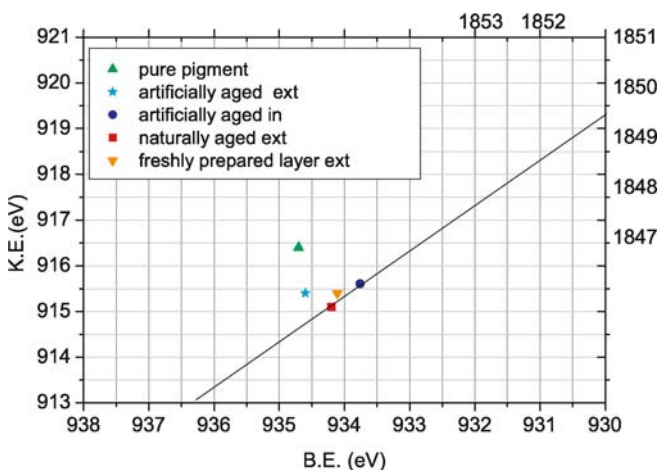


FIGURE 6 Auger parameter of pictorial films models

(probably a SO_4^- ion) is strongly chemisorbed, because the S 2p intensity did not change during exposure at UHV.

Finally, Auger parameters, obtained by adding the B.E. of Cu 2p 3/2 and the K.E. of Cu LMM, reported in Fig. 6, allows gathering of additional information.

The values calculated for both freshly prepared and naturally aged surfaces of and for artificially aged internal surfaces are similar, but differ from pure copper resinate and artificially aged external surfaces.

These results indicate that solubilisation of copper resinate in linseed oil involves a change in the coordination environ-

ment of the metal ions and, on the other hand, that the effects of pollutants on external surfaces result in profound chemical modification of copper.

4 Conclusions

X-ray bombardment performed by an Al K_α source caused Cu(II) reduction to Cu(I). The high atomic concentration of copper ions on the surface (46%) strongly suggests that the green pigment is partially soluble in linseed oil in contrast to a similar investigation performed on a series of different systems in oil. This property could explain the greater reactivity of this pigment with the external environment. Moreover, the different value of Auger parameters of copper in the pure pigment (1851.1 eV) with respect to the oil paint layer (1849.3 eV) shows that the copper chemical environment changes as a consequence of the pigment solubility in linseed oil.

XPS investigations of the external surfaces of artificially aged samples suggest that sulphate species are chemisorbed and NO molecules are only physisorbed. The modification of nitrogen and sulfur oxidation states indicate that a red-ox reaction between SO_2 and NO_2 species occurred at the paint layer surface.

The absence of pollutants on the inner side of the layer strongly suggests that the oil film is a good barrier against the attack of aggressive molecular species and protects the enclosed pigment better than protein binders. Finally, no evi-

dence of Cu(II) reduction has been observed neither in naturally and artificially aged samples.

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