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TG-MS CHARACTERIZATION OF THE REACTION PRODUCTS OF CADMIUM YELLOW AND MALACHITE ARTIST'S PIGMENTS

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The deleterious interaction of some traditional sulphide artists pigments and copper ions results in the formation of black copper sulphides, in particular, covellite (CuS), and, hence, the discolouration of valuable artworks. In this paper the interaction of malachite, a source of copper(II) ions, with the pigment cadmium yellow, a sulphide pigment comprising of a solid solution of cadmium and zinc sulphides, is investigated by XRD and TG-MS. XRD showed the presence of the copper sulphide and cadmium carbonate phases, produced by a simple ion exchange mechanism. TG-MS showed the complexity of the range of metastable phases produced. The identification of these phases, however, requires further work.

Keywords: *cadmium yellow, malachite, thermogravimetric analysis*

Introduction

The deleterious interaction of some traditional sulphide artists pigments and copper ions results in the formation of black copper sulphides, in particular, covellite (CuS), and, hence, the discolouration of the artwork [1–3]. This is a particular problem for paintings produced in the 18th and 19th Centuries where sulphide pigments were commonly applied and remains a problem for conservators who conserve and repair these artworks. In order to understand the mechanisms involved in these deleterious processes, and, hence, aid the conservation of valuable artworks, characterisation of the reaction products is a first step. As the reaction between the pigments is heterogenous, occurring most likely through the transport of copper ions to the sulphide pigment surface, characterisation of the reaction products and extent of reaction is difficult and requires multiple analysis techniques. This study, therefore, combines X-ray diffraction (XRD) and thermogravimetric analysis coupled with mass spectroscopy (TG-MS) for evolved gas analysis in the characterisation of the interaction between copper ions, using malachite as the source, and cadmium yellow, a solid solution of cadmium and zinc sulphides, as the sulphide pigment.

Experimental

The system chosen for study was the interaction between cadmium yellow (CdS containing approximately 10% ZnS as an isomorphous solid solution) and malachite (a basic copper carbonate ($Cu(OH)_2{\cdot}CuCO_3$)). Both pigments were supplied by Kremer Pigments (NY, USA). Artists usually blend the pigments in drying oils, such as linseed oil, for application. Although the transport of copper ions is easily facilitated by these oils, the rate of reaction is slow and can take years to occur. In order to accelerate the reaction, the medium selected in this study was water. Malachite and cadmium yellow pigments were blended together and mixed with an excess of water. Samples prepared for analysis in this manner were: 100% malachite and 100% cadmium yellow and blends of malachite and cadmium yellow in the ratios 10:1, 1:1 and 1:10 by mass. The blend samples are identified as C1:M10, C1:M1 and C10:M1, respectively, in the text. Each suspension was left at room temperature for two months before the water was removed and the sediments dried for analysis. XRD experiments were carried out on Siemens D5000 X-ray Diffractometer with CuK_α radiation from 15 to 80° 2θ at 0.02° 2θ s^{-1}. TG/MS measurements were carried out using a Setaram Setsys 16/18 thermobalance coupled with a Balzers ThermoStar mass spectrometer for evolved gas analysis. All experiments were carried out in alumina (Al_2O_3) crucibles at a heating rate of 10°C min^{-1} from ambient temperature to 800°C under flowing (20 mL min^{-1}) high purity argon gas.

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Results and discussion

The as received pigments were identified as malachite ($Cu(OH)_2 \cdot CuCO_3$) and cadmium sulphide (CdS) by X-ray diffraction (XRD) [3]. Blending the pigments in water resulted in significant visible change with the production of a dark reaction product. The reaction products identified by XRD for each blend were copper(II) sulphide (CuS) and cadmium carbonate ($CdCO_3$) indicating that a simple ion exchange is occurring based on the relative solubilities of the reactants and products.

$$Cu^{2+}+CdS \rightarrow CuS+Cd^{2+} \quad (1)$$

In addition to these products, the reactants were also observed to be present after the reaction mixture was dried. In the 1:1 blend, both malachite and cadmium yellow were observed. Although the 1 to 1 blend by mass was not a stoichiometric ratio (approximately a 1 Cd to 1.4 Cu mole ratio), this slight excess of copper ions was not enough to take the reaction to completion. In both the 1:10 and 10:1 blends, only the reactant in excess remained (i.e. CdS was observed in the C10:M1 specimen and malachite was observed in the C1:M10 specimen).

The TG and DTG curves for the five specimens are shown in Figs 1 and 2. A limit of 800°C was used as cadmium sulphide is known to sublime at 980°C. MS curves for 18 (attributed to H_2O), 44 (CO_2) and 64 amu (SO_2) ions are shown in Figs 3 to 5, respectively. 64 (rather than 32 or 34) amu was chosen for investigation as some of the sulphur evolved in the furnace would be oxidised by the small amount of oxygen (<10 ppm) present in the purge gas.

The cadmium sulphide was observed to be fairly stable up to 800°C, however some mass loss was observed with approximately 3.2% mass loss observed at 800°C. The mass loss may be attributed to dehydration (≈1.0%) and to sulphide removal (≈2.2%). The XRD showed the presence of cadmium sulphate hydrate ($CdSO_4 \cdot nH_2O$) after conditioning the cadmium yellow in water and drying. This suggests that the cadmium sulphide has been oxidised by atmospheric oxygen dissolved in the deionised water. Peaks in the 18 amu curve suggest that water is lost up to 550°C and is

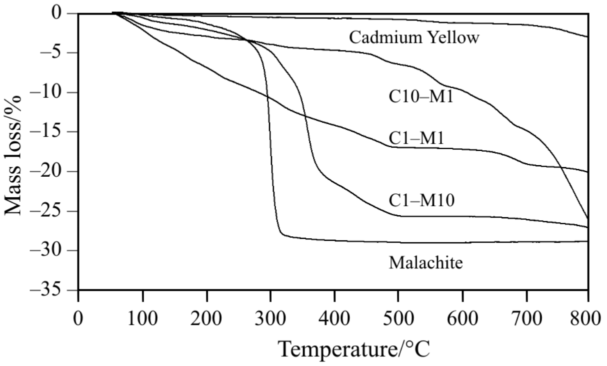

Fig. 1 TG curves of the five systems studied: cadmium yellow, malachite and reaction blends of 10:1, 1:1 and 1:10 by mass

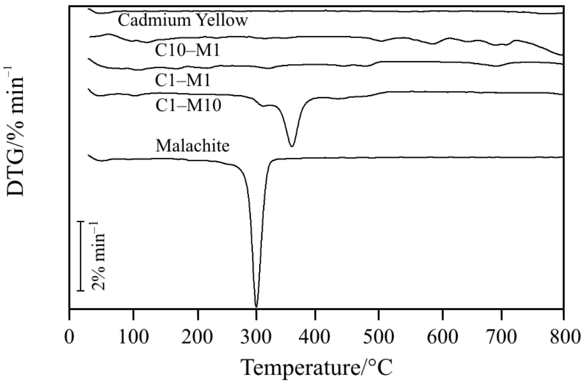

Fig. 2 DTG curves of the five systems studied: cadmium yellow, malachite and reaction blends of 10:1, 1:1 and 1:10 by mass

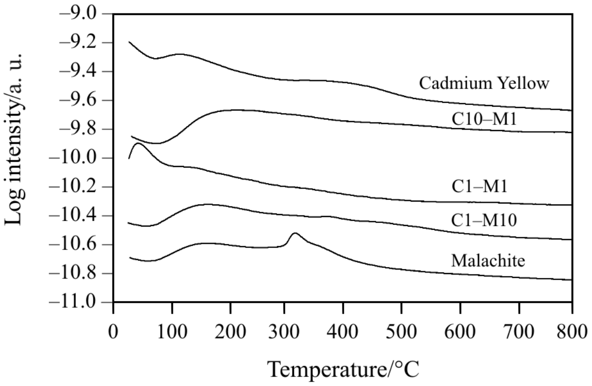

Fig. 3 Mass spectra response curves (in arbitrary units as intensity is non-quantitative) for 18 amu for the five systems studied: cadmium yellow, malachite and reaction blends of 10:1, 1:1 and 1:10 by mass

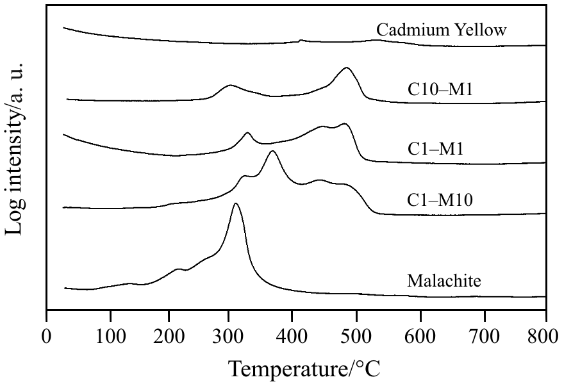

Fig. 4 Mass spectra response curves (in arbitrary units as intensity is non-quantitative) for 44 amu for the five systems studied: cadmium yellow, malachite and reaction blends of 10:1, 1:1 and 1:10 by mass

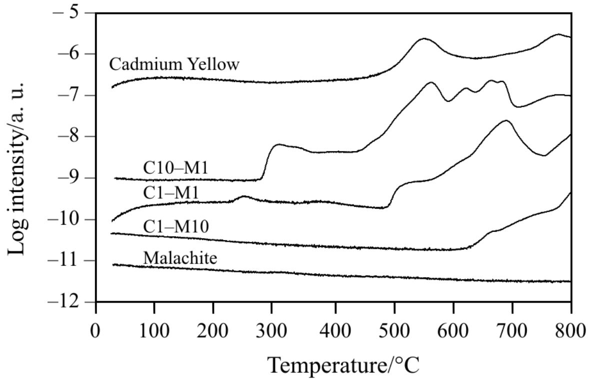

Fig. 5 Mass spectra response curves (in arbitrary units as intensity is non-quantitative) for 64 amu for the five systems studied: cadmium yellow, malachite and reaction blends of 10:1, 1:1 and 1:10 by mass

consistent with the dehydration of cadmium sulphate hydrates reported elsewhere [4]. Sulphates formed at heterogenous interfaces are known to decompose at temperatures lower than the bulk crystalline phase [5]. The peaks at 556 and 782°C, observed in both the DTG and the 64 amu curves, may, therefore, be attributed to sulphate decomposition.

The malachite was observed to decompose through a single step with a peak in the DTG curve at 302°C as has been reported in the literature [6, 7]. This single sharp peak is accompanied by a complex series of peaks in the 44 amu (CO_2) curve at 137, 214, 261 and 306°C (Fig. 4). 18 amu curve also showed a wide temperature range for decomposition attributable to adsorbed water with a broad peak at 170°C and a sharp dehydroxylation peak at 320°C with a shoulder at 370°C. The MS curves suggest a more complex decomposition process than the TG/DTG as has been reported elsewhere [8]. The mass loss for the thermal decomposition of malachite was 29.0% which is a little lower than the expected 30.8% theoretical loss based on a stoichiometric reaction of Eq. (2) in thermal decomposition [6–8].

$$CuCO_3{\cdot}Cu(OH)_2 \rightarrow 2CuO+CO_2+H_2O \qquad (2)$$

The decomposition of each pigment blend is observed to be quite complex and through a number of steps in each case suggesting significant change in composition in each sample. From the XRD the major species present were the reactants, malachite and cadmium yellow, CuS and $CdCO_3$. In the temperature range studied, CdS is expected to be stable, malachite is reported to decompose according to Eq. (2), CuS is expected to decompose at 507°C [9]:

$$2CuS \rightarrow Cu_2S+S \qquad (3)$$

and $CdCO_3$ is expected to decompose with a peak in the DTG curve at 445°C [10].

$$CdCO_3 \rightarrow CdO+CO_2 \qquad (4)$$

The specimen C1:M10 was observed to contain $CdCO_3$, malachite and CuS as the phases present after the reaction. Four peaks are observed at 315, 360, 439 and 481°C in the DTG curve (Fig. 2). These peaks correspond well with the peaks in the 44 amu curve (CO_2) at 320, 362, 438 and 482°C (Fig. 3). This suggests a complex series of carbonate phases present which includes both the basic copper carbonate and the cadmium carbonate. It is likely that (basic) zinc carbonate is also present, although basic zinc carbonate has been observed to decompose with a peak rate at 250°C [7], a temperature lower than the CO_2 evolution observed here. For the C1:M10 specimen SO_2 is not observed until 630°C, a much higher temperature than expected for the decomposition of CuS despite the fact that the XRD indicated complete consumption of the cadmium yellow in the reaction.

The C1:M1 sample loses mass throughout the temperature range studied. A series of small peaks are observed in the DTG at 116, 177, 226, 324, 446, 483 and 694°C (Fig. 2). It is likely that the lower temperature steps are associated with the removal of water of hydration. CO_2 is evolved from approximately 220°C with peaks in the 44 amu curve at 324, 444 and 479°C (Fig. 4) suggesting the presence of malachite, cadmium carbonate and possibly other phases such as zinc carbonate. The 64 amu curve (Fig. 5), indicating sulphur evolution, has an onset of 495°C and is fairly close to the decomposition temperature of the CuS in accordance with Eq. (3). Further loss of sulphur is likely to be associated with the decomposition of the cadmium yellow remaining.

The C10:M1 sample contained approximately 5% water which was removed by 200°C. Further mass loss is associated with the decomposition of the reaction species present. The 44 amu curve (Fig. 4) has peaks at 298 and 482°C. Neither of these carbonate species are likely to be malachite as no malachite was observed in the XRD. Identification is again difficult, however, these peaks are probably associated with zinc and cadmium carbonates. For this specimen, the onset of the 64 amu evolution is at 282°C (Fig. 5), the lowest of all the systems studied. Additionally, the peaks in both the 44 and the 64 amu curves in the low temperature region (<450°C) coincide indicating that it is the decomposition of partially reacted cadmium yellow that is occurring. Higher temperature peaks in the DTG curve are observed at 507, 590, 645, 690 and 708°C with the onset of a larger mass loss process above 730°C (Fig. 2). All of these peaks coincide well the peaks in the 64 amu curve indicating sulphur loss from the specimen. The total mass loss for this blend ratio is greater than its counterparts suggesting significant disruption to the cadmium yellow phase.

Examination of the phases produced by reacting malachite with cadmium yellow in an aqueous medium by XRD indicated that the reaction produced reaction products based on an ion exchange mechanism where copper(II) sulphide and cadmium carbonate were the products. The TG-MS data suggests that the phases present in the reaction products are much more complex with a variety of products being produced with a range of thermal stabilities. The C10:M1 specimen, in particular, demonstrated the extent of the effect that copper ions have on sulphide pigments. Although this study has demonstrated the complexity of the reaction and the range of reaction products produced, further investigation is required to identify these reaction products.

Conclusions

The interaction of malachite, a source of copper(II) ions, with the cadmium yellow, a sulphide pigment comprising of a solid solution of cadmium and zinc sulphides, resulted in the production of the pigment discolouring copper sulphide as a reaction product. The reaction was observed to be rapid in its initial stage, although completion only occurred when one or other reactant was in vast excess under the conditions studied. The reaction products, identified by XRD, were copper sulphide and cadmium carbonate. TG-MS, however, showed the complexity of the range of phases produced by the simple ion exchange mechanism proposed. The identification of these phases, however, requires further work.

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