Characterisation of the artist John Opie's pigments, dated 1806.

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ABSTRACT: This paper discusses the contents of an artist's paint box currently in the possession of St. Agnes Museum, Cornwall, UK, containing a selection of historic pigments. On its lid is a metal plaque that reads 'John Opie 1806'. Very little is known about this paint box, so this piece of research aims to uncover some of the hidden information stored within it through identification of some of the pigments it contains.

The main body of this research shows the first results obtained by the identification of a selection of the pigments from the paint box, using Fourier Transform Infra Red spectroscopy (FTIR) and optical microscopy techniques. These findings will be considered in relation to what this tells us about the artist John Opie, the authenticity of the pigments within the paint box, and the use of pigments in the early nineteenth century.

1. THE ENGLISH ARTIST JOHN OPIE AND HIS PAINTBOX

In St Agnes Museum, Cornwall, is a paintbox that is believed to have belonged to the artist John Opie (Fig. 1a). There is very little known about the paintbox, but it is thought it was presented by the Royal Academy of Art after Opie was granted the position of Professor of Painting in 1805 (Earland 1911, 213), as a metal plaque on the top of the box states 'John Opie 1806'. Opie was a highly regarded painter during his lifetime, producing mainly portraits and historical scenes in oils. However more recently his work has been overlooked and is very little studied (Hendra, 2007). After his election as professor by the Royal Academy, John Opie gave a series of four lectures. The first commenced on 16th February 1807, and the fourth and final lecture was delivered on the 9th March 1807, just one month before his untimely death at the age of 45 (Rogers 1878, 42).

The paintbox contains fourteen different pigments, three bottles (labelled turpentine, linseed oil and varnish), plus a glass pestle and mortar and measuring flask. This paper discusses the analysis of four pigments from the paintbox, using Infrared spectroscopy (FTIR) and Optical Microscopy.

The study of the pigments in this box (Fig. 1b) could help add information about the kind of paints used in this particular English artistic period, and those used by this artist in particular. Understanding the chemical composition of the pigments allows studies of pigments deterioration processes, and aids in decision making for conservation and restoration. Increasing the knowledge of pigments used in this era is of great value to researchers working in this area in general. This is also of benefit for detecting possible forgeries. In addition, it is of interest to art historians to increase knowledge of historic pigments, particularly with the potential link to the Royal Academy.

Figure 1. a) Opie´s paint box from the front. b) The fourteen pigments from the box.

2. METHODOLOGY

The methodology used for sampling the pigments took the well-being of the object into consideration. It was important to consider the delicate nature of the corks and the necks of the glass pigment bottles, some of which were already damaged. Samples were therefore taken carefully from bottles, removing corks without undue pressure being applied to the object, thus preventing damage. A small amount of pigment was removed using a cocktail stick, placed in a small glass vial and sealed with a plastic stopper. Samples were taken from the bottles labelled with F. White, Bt. Sienna, Indian Red and also from an unlabelled black pigment.

FTIR analysis was undertaken using a Perkin Elmer Spectrum 100 FTIR Spectrometer with attenuated total reflectance (ATR). The scan range was 4000–450 cm^{-1} with a scan number of 32, a resolution of 4 cm^{-1} and a scan speed of 0.5 cm s^{-1}. FTIR-ATR analysis of the samples produced infrared spectra which were compared to a combination of in-house libraries using the Euclidean algorithm (processing software: Perkin Elmer Spectrum, version 6.1.0.0038). Correlations were assessed and a match above 95% was deemed conclusive. Where no match was obtained, comparison pigments were obtained from Cornelissen (London) and assessed for match using the FTIR software. All FTIR graphs shown depict wavenumber in cm^{-1} on the x axis and absorbance on the y axis.

Once the samples had been analysed using the FTIR, small amounts were then mounted onto glass slides using Histomount and cover slips. The samples were then viewed under high magnification using visible light and polarising light (PLM). PLM images were taking using a digital Dino-Eye and a Microtec RM-1 polarising microscope. Visible light images were obtained through a Basic Dino-Lite digital microscope.

3. RESULTS AND DISCUSSION

3.1 Flake white

The FTIR spectra produced by the Opie sample from the pigment labelled F. White was compared with the data in the FTIR library, giving a 97% match to Flake White. Further comparisons to zinc oxide and titanium white FTIR spectra showed no significant correlation (data not shown). This pigment (also known by the name white lead) was first manufactured by the Ancient Greeks, and remained the most commonly used white available to artists until the late 18th century, when zinc oxide was introduced (Eastaugh 2008, 419). It is still regarded as the whitest of the white pigments, and consists of a basic lead carbonate ($2Pb(CO_3)_2.Pb(OH)_2$) (Barnett et al., 2006).

The results from the FTIR analysis were further confirmed using light microscopy. Figure 2 shows a sample of the Opie F. White pigment at x220 magnification. Gettens and Stout state that under magnification lead white is highly birefracting and that individual grains can be tubular or twice as broad as thick and hexagonal in outline (1966, 174-5). When viewed using a polarising filter, the pigment showed clear birefringence (Fig 2, right).

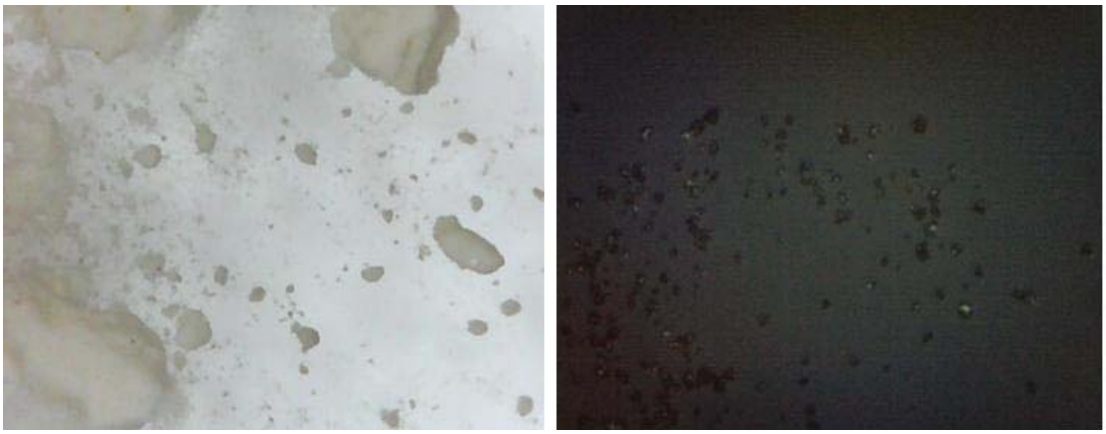

Figure 2. F. White pigment at x220 magnification using light microscopy (left); F. White pigment at x400 magnification under polarised light (right) showing birefringence.

3.2 Bt. Sienna

The FTIR spectrum produced by the Bt. Sienna sample was run comparatively against the FTIR library and produced no strong matches. In addition to this two modern samples of burnt sienna were also run through the FTIR. The spectra produced by these are shown in comparison to the Opie Bt. Sienna sample in figure 3. Although there was only a 39% and 55% match to the modern samples when compared to the Opie sample, it is clear there are strong similarities when comparing peak positions. Burnt Sienna is a prepared by calcining (a heating process which brings about thermal decomposition) raw sienna. It is hydrated ferric oxide (goethite, $Fe_2O_2.H_2O$), with alumina and silica. A good sienna should contain at least 50% of iron oxide (Fe_2O_3), while some of the best quality contain 70% or over. It generally also has a small amount of manganese dioxide (0.6 to 1.5%) (Gettens & Stout, 1966, 156). This demonstrates that the sienna pigment itself exists in a number of different grades, made up of a number of different combinations of components.

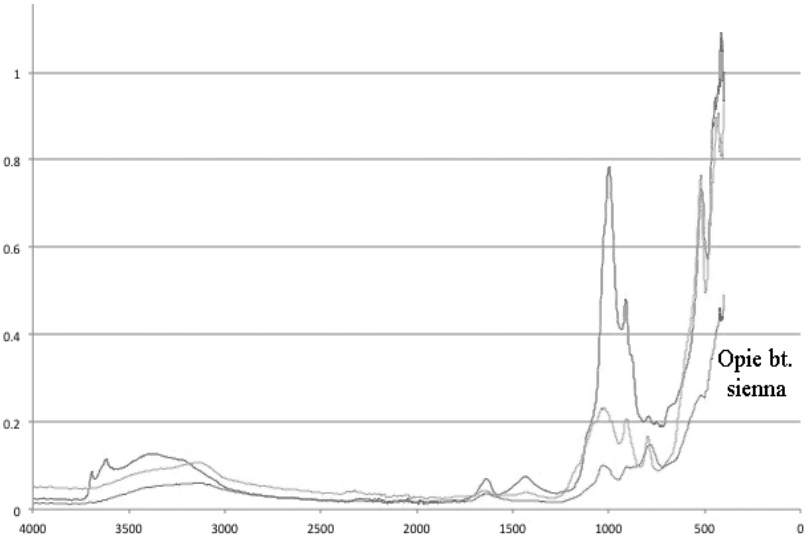

Figure 3. FTIR data showing a comparison of the Opie pigment sample 'Bt. Sienna' (lower line) and two samples of Burnt Sienna pigment.

Microscopically, sienna should be quite heterogeneous; it is a mixture of transparent, colourless, yellow and brown-red particles, along with opaque brown particles and a few scattered pink ones. Burnt Sienna however, after the calcination process (which changes it from the ferric hydrate of raw earth to ferric oxide), becomes warm reddish brown. Microscopically,

it becomes more even in colour and the grains are reddish brown by transmitted light (Gettens & Stout, 1966, 156). This description is a good fit with the microscope image shown in Figure 4, where the diverse components of the sienna are visible.

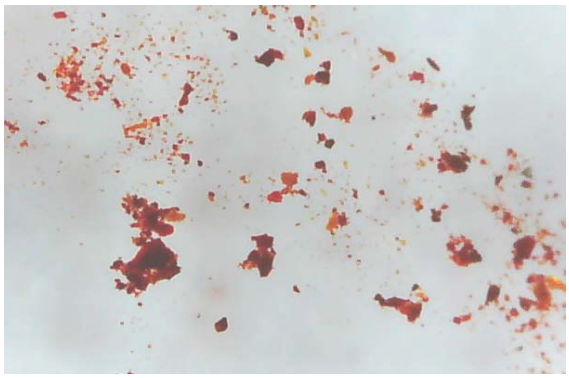

Figure 4. Bt Sienna pigment, transmitted light microscopy at x230 magnification.

The above observations therefore concur with the results from the FTIR that the Opie Bt. Sienna sample is a form of burnt sienna pigment. Causes for the variation in FTIR spectrums may be accounted for by differing percentages of the components making up the pigments tested.

3.3 Indian Red

The spectrum produced by the FTIR for the Opie Indian Red sample is shown in figure 5. When compared to the FTIR library no match was produced. For this reason a sample of modern Indian Red was run through the FTIR. This produced a spectrum with a 46% match and a comparison of these can be seen in figure 6. Although these spectra are similar, the match is less than 0.95 and visually they are not identical. Again it appears likely that the Opie sample of Indian Red pigment is in fact Indian Red as labelled on its bottle. This is a form of iron oxide red, also known as red ochre, Venetian red, light red, haematite or Mars red among others, that could be natural or created artificially. The chemical composition is Fe_2O_3 (anhydrous) or $Fe_2O_3.nH_2O$ (Plesters, 1956). The FTIR results did not produce an exact match to the sample of Opie Indian Red pigment; as with the burnt sienna this is likely to be due to the varying chemical compositions and impurities that relate to the colour and grade of the pigment, and the original source.

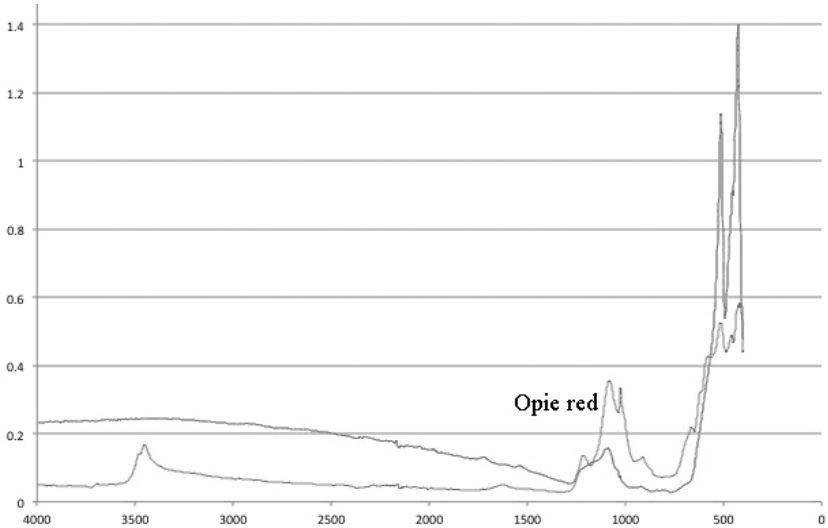

Figure 5. FTIR data showing a comparison of the Opie pigment sample ‘Indian Red’ (labelled) and a sample of Indian Red pigment.

According to Berrie (2007, 74), red iron oxide pigments are coloured primarily by hematite. In transmitted light, small particles appear almost black, while larger particles are deep red to orange. Gettens and Stout (1966, 122), state that the natural forms are heterogeneous in composition and in particle size, and that in the darker varieties, elongated and splintery, dark brown, lustrous particles of haematite can be seen. They also state that in some varieties, the smaller particles are ruby-red by transmitted light, similar to vermillion, but that they are usually opaque and dense. This is consistent with the microscope image shown in figure 6, which appears to be a natural form of the pigment due to the heterogeneous composition.

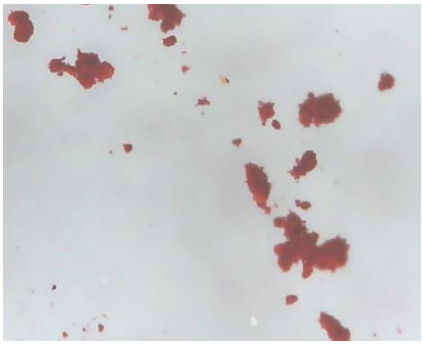

Figure 6. Indian Red pigment viewed at x225 magnification, transmitted light.

3.4 Unlabelled black pigment

The FTIR spectrum produced by the Opie sample of unlabelled black is shown in figure 7. When this data was compared with the data in the FTIR library, a significant 95% match with Ivory Black ($Ca_3(PO_4)_2$) was produced.

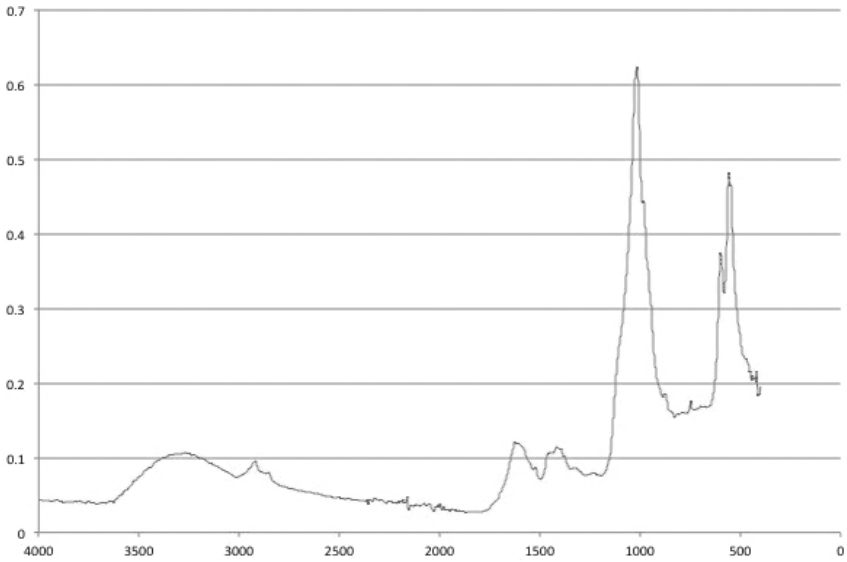

Figure 7. FTIR data for the black Opie pigment sample.

Ivory black is produced by charring ivory in closed vessels and then grinding, washing, and drying the black residue. Gettens and Stout state that this term is now commonly used for the black from animal bones known as bone black (1966, 122). Ivory black or bone black, generally contain about 10% carbon, 84% calcium phosphate and 6% calcium carbonate (Gettens & Stout 1966, 99). Because of their similar chemical make-ups it is not possible to differentiate between the two pigments using the FTIR.

The results from the FTIR analysis were further confirmed using light microscopy. Gettens and Stout (1966, 99) state that microscopically ivory / bone black particles are coarse and

irregular in shape and size. This is concurrent with the image of the Opie unlabelled black sample (data not shown), with no fluorescence visible under PPL.

4. CONCLUSION

We have successfully identified four of the pigments from the Opie paint box using a combination of light microscopy, polarising light and FTIR. F. White is conclusively identified as white lead. Lead white was manufactured on a fairly large scale in England from the seventeenth century onwards (Harley 1982, 167), so it is unsurprising this was included in the paintbox. Flake white was generally accepted to be the highest quality form of the lead white pigments (Eastaugh 2008, 163).

Two earth pigments have been identified, the Burnt Sienna and Indian Red. Burnt Sienna contains iron oxide, with other impurities. The term burnt sienna appeared in English usage by the end of the eighteenth century, denoting a pigment obtained in the region of the city of Siena (Berrie 2007, 45; Gettins & Stout 1966, 156). Indian red is a red ochre originating from India, where the iron oxide rich soils were used to form the pigments (Gettens & Stout 1966, 119). Certainly the term Indian Red was in use by 1738 (Eastaugh 2008, 193). The unlabelled black is ivory black or bone black. Bone black was a less expensive version of the pigment, available on a large scale during the nineteenth century (Harley 1982, 158-159). The presence of Flake White suggests that the box may have contained quite high grade pigments, which would suggest a black composed of ivory rather than bone. However using FTIR and microscopy it is not possible to distinguish between these pigment types.

All these pigments found are consistent with pigments which were freely available during the early nineteenth century. Although this does not prove that the pigments are Opie's originals, there is no evidence to suggest any later alterations or additions. The pigments had all been opened and partially used. An examination of the pigments found in Opie's paintings from this period would provide further evidence to support this, by looking for clear matches to the existing FTIR information.

If we assume that the box is original to the period, it is clear that it was considered a valuable and lavish gift when presented to Opie. The red felt lining, inclusion of artists tools and varnishes alongside the selection of pigments, shows that the Royal Academy held the recipient in high regard.

5. ACKNOWLEDGMENTS

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REFERENCES

Barnett, J., Miller, S. & Pearce, E. 2006. Colour and art: A brief history of pigments. *Optics & Laser Technology* 38: 445-453.

Berrie, B.H. (ed). 2007. *Artists's Pigments; A Handbook of Their History and Characteristics (Vol 4)*. London: Archetype Publications.

Church, A.H. 1915. *The Chemistry of Paints and Painting* 4th ed. Seeley, Service & Co., 38 Great Russell Street, London.

Earland, A. 1911. *John Opie and His Circle.* London: Huchinson & Co.

Eaastaugh, N. 2008. *The Pigment Compendium; A Dictionary and Optical Microscopy of Historical Pigments.* Oxford: Elsevier Butterworth-Heinemann.

Gettens, R. J. & Stout, G.L. 1966. *Painting Materials. A Short Encyclopaedia* Dover: New York.

Harley, R.D. 1982. *Artists' Pigments; c. 1600-1835*. London: Butterworth-Heinemann.

Hendra, V. 2007. *The Cornish Wonder; A Portrait of John Opie.* Truro: Truran.

Plesters, J. 1956. Cross-sections and Chemical Analysis of Paint Samples. *Studies in Conservation* 2: 110-157.

Rogers, J.J. 1878. *Opie and His Works; Being a Catalogue of 760 Pictures by John Opie, R. A., Preceded by a Biographical Sketch.* London: P&D Colnaghi and Co.