Experimentation Manufacturing Zinc Orange Pigment

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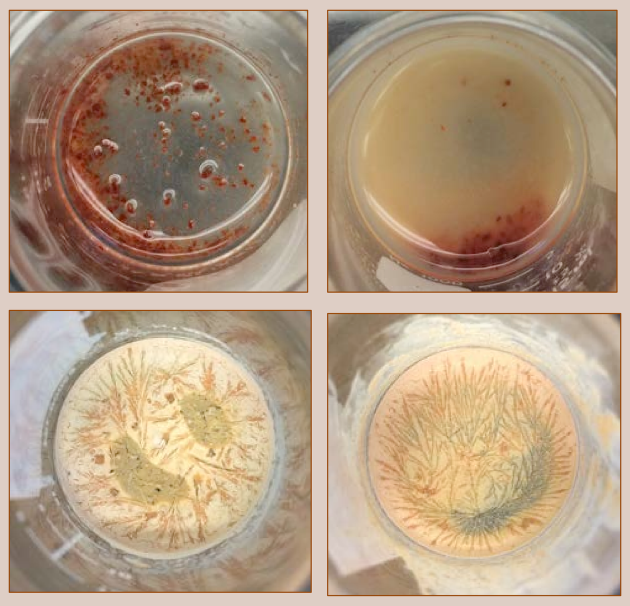
Introduction:

Zinc orange is a rare and generally undocumented artists' pigment lost in the history. Only one sentence is devoted to it in George Field's 1869 *Chromatography*: "…when hydrochloric acid and zinc are made to act on nitro-prusside of sodium, a corresponding zinc compound is formed of a deep orange colour, slightly soluble in water, and not permanent"[1]. The focus of this project was to investigate how zinc orange was manufactured, as described by Field's *Chromatography.* Various ratios of the listed ingredients metallic zinc, hydrochloric acid, and sodium nitroprusside were attempted. Different methods of processing the resulting pigments were tested, including heating, grinding, and washing. Additionally, artificial aging was performed to test the light stability of the pigment.

Mixtures:

A number of mixture were compared, varying the ratio of $ZnCl_2$ to $Na_2[Fe(CN)_5NO]$. The results produced either a waxy non-viable pigment, or a fine pale orange precipitate.



Sample	Ratio	Result
1	1:1	Slow-drying waxy
2	2:1	Waxy, non-drying
3	1:2	Fine, pale powder

Figure 1: Samples 1 (left) wet and dry, sample 3 (right) wet and dry

Figure 2: Preparing sample 3

Sample 3 was produced in a larger volume and washed with deionized water prior to the preparation of paint-outs in linseed oil and gum Arabic.

Washing was an effective method to remove the chlorine (Cl), as can be seen in the XRF spectra to the right.

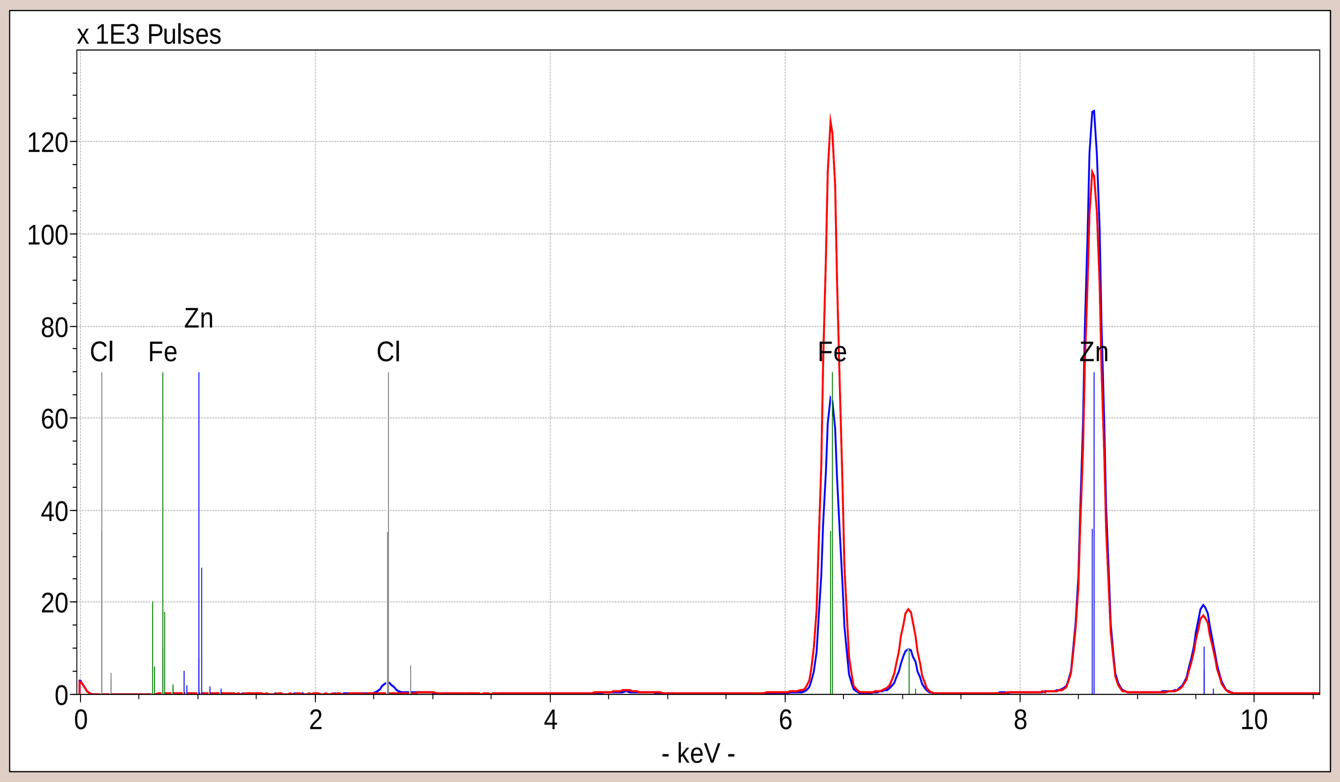


Figure 3: XRF spectra showing sample 3 prior to washing (blue) and after washing (red) indicating the removal of chlorine

Making Paint:

The pigment samples were dispersed into two types of paint media, a 3% Gum Arabic and a cold-pressed linseed oil.

Figure 4: Dispersed in linseed oil

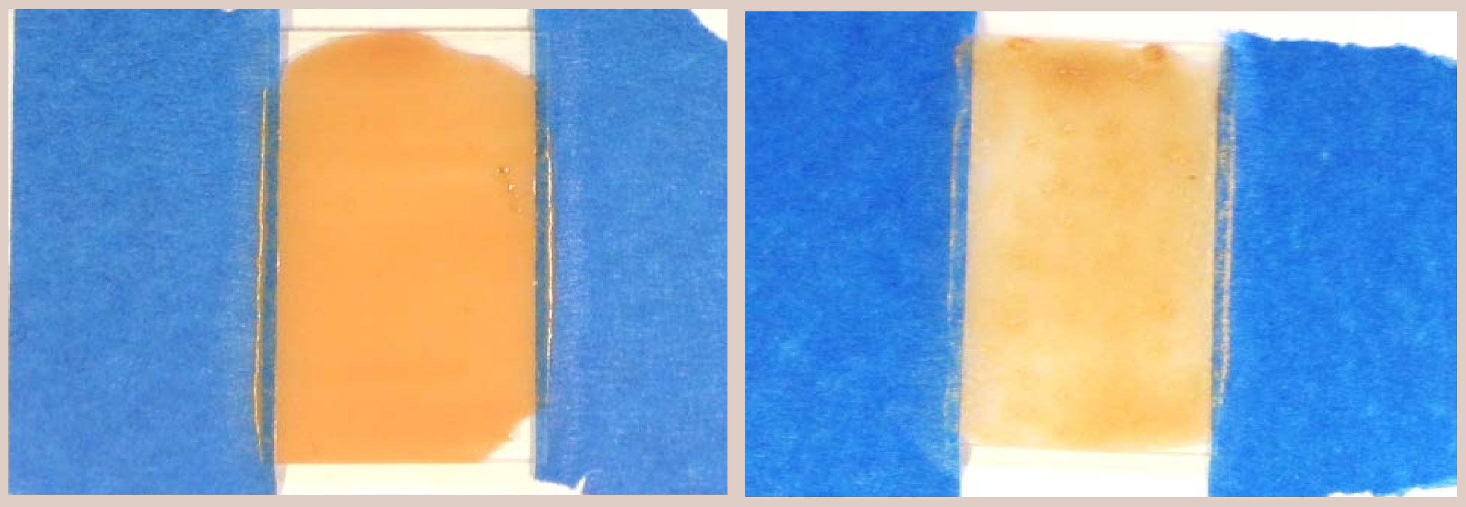


Figure 5: Sample paint-out in linseed oil (left) and gum Arabic (right)on glass slides

Acknowledgements:
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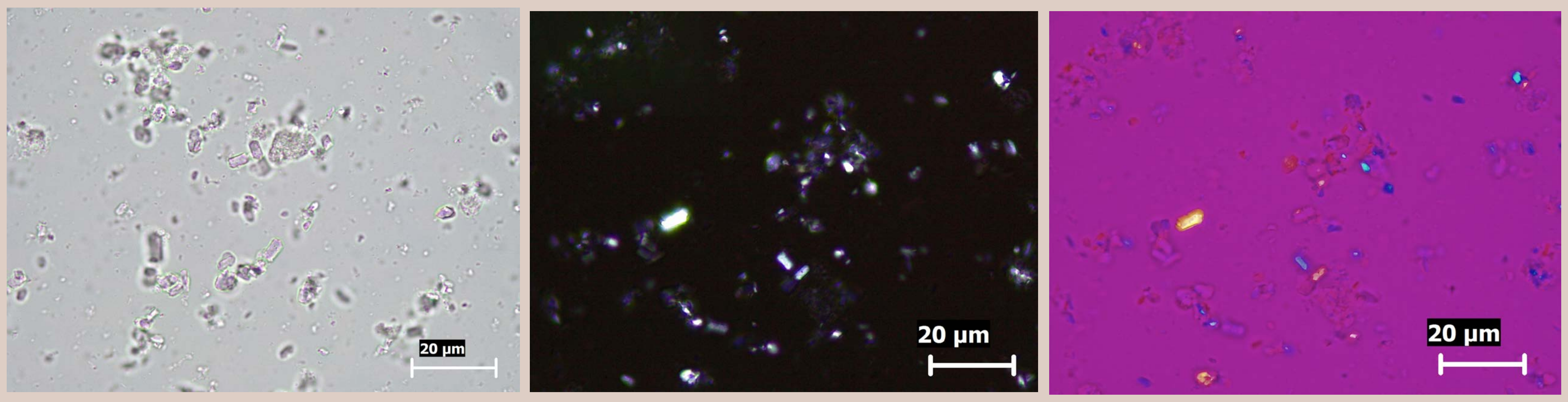
References:

1. G. Field, and T. W. Salter. *Chromatography*. (Windsor and Newton, London, 1869) p. 261.

Under the Microscope:

The washed pigment samples were dispersed on glass slides in Cargille MeltMount™ (n_D=1.662) and observed under both plane polarized light (PPL) and cross-polarized light (XPL).



Figures 6-8: Optical micrographs of the pigment in PPL, XPL and XPL with a λ compensator

The particles have a transparent/translucent pink colour under PPL. They are rhomboid, prismatic, acicular and irregular in habit and have a lower refractive index than the media. The prisims are approximately 5x1 µm. They are anisotropic, showing high birefringent and a negative sign of elongation.

Vibrational Spectroscopy:

µ-transmission FTIR and Raman spectroscopies were used to investigate the molecular structure of the resulting pigment. Both techniques showed good matches for cyanide (2130-2010 cm^{-1} and 610-580 cm^{-1}) and nitrosyl groups (~1945 cm^{-1}). Characterization is still in progress.

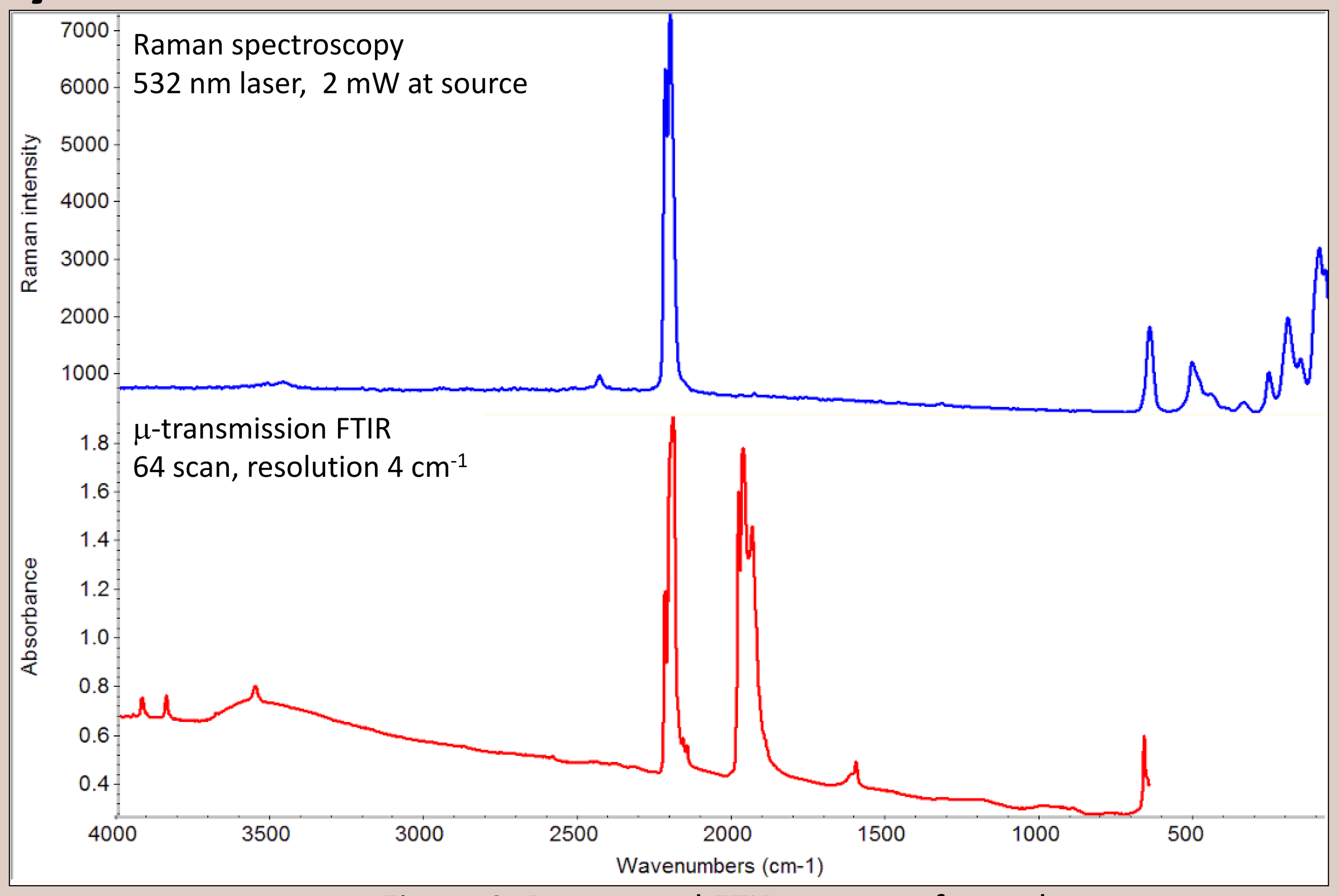


Figure 9: Raman and FTIR spectra of sample

Artificial Ageing:

Cast samples in linseed oil (left) and gum Arabic (right) artificially aged according to ASTM 4303-06. exposure was set for 411 hours reaching a total radiant of 517.8 kJ/m^2 in a Q-Sun Xenon Xe-1 Test Chamber. This exposure resulted in extreme darkening of the pigment exceeding acceptable standards.

Figure 10: Paint-outs after artificial ageing

Conclusions:

A weight ratio of 2:1 sodium nitroprusside to zinc produced the most viable pigment. Washing with deionized water greatly improves the quality of the product. The pigment in media is unstable and darkens upon exposure to light and heat (~62°C). This supports the reported instability of zinc orange.

Presenter Information:

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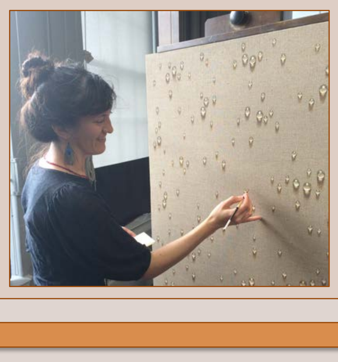

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