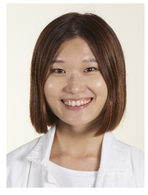

Micro-characterisation of haze and degradation on zinc white oil-based painting, Portrait of a Peranakan gentleman Mr Tan Beng Wan, Singapore

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Introduction

Haze, efflorescence and surface crusts are visual indicators of possible chemical modifications on a painting. Characterization of these degradation areas is important to understand the altered compositions and origins of their formation, which have implications in conservation. A number of advanced studies on such phenomena were recently reported [1-2]. During the examination of "Portrait of Mr Tan Beng Wan", a high value painting from the Peranakan Collection and stored at the Heritage Conservation Centre of Singapore, various forms of whitish haze (S1-S4) were observed on the paint surface.

The haze appeared wide-spread in the dark grey background of the portrait, occurring along selected areas of the blue gown (*chang pao*) and the black jacket (*ma gua*). Craquelure was present throughout the entire surface of the painting as well as paint losses, holes and abrasions were evident. Visually, it was difficult to ascertain if the whitish haze formed in some areas was part of the artist's intention or due to the intrinsic degradation of paint, which would be important information to the conservator's decision in their removal. Preliminary cleaning tests showed that the haze is generally not removable with water swabs. Although mechanical removal alone was possible, it had the risk of damaging the paint layers and was not recommended. More investigation of the haze was deemed necessary to support the conservation treatment.

"Portrait of Mr Tan Beng Wan"
Late 19th century to early 20th century,
Collection of The Peranakan Museum

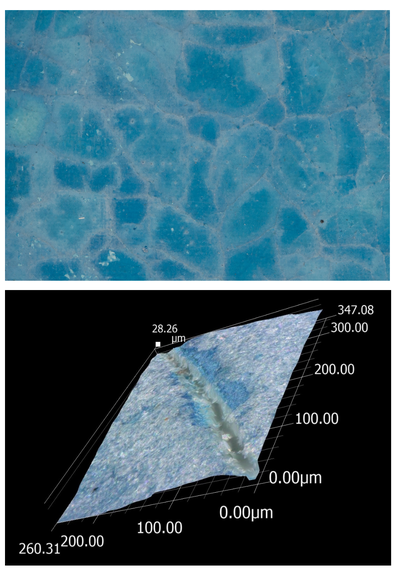
Methods

4 areas of haze were analyzed:

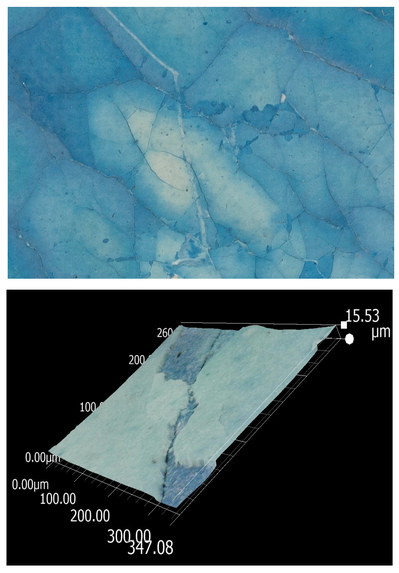
- 3D images were obtained with a Keyence VHX-6000 digital microscope mounted to a portable stand.
- SEM images and elemental analysis were obtained with Hitachi SU5000 SEM coupled to a Bruker EDS.
- Chemical compositions were analyzed with Agilent Cary 670/620 FTIR spectrometer coupled to a microscope fitted with MCT detector, single point transmission. Spectra were compared to the *NIST Standard Reference Database 69* Library.
- A paint cross-section was prepared, polished with successive grades of Micromesh and MOPAS polisher and analyzed with FTIR-FPA imaging using Ge-ATR crystal.

Results

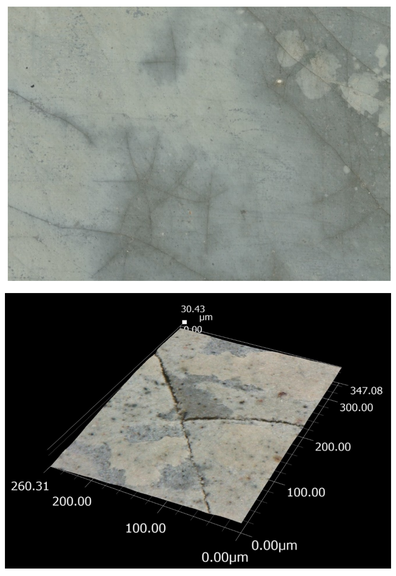
S1. Haze on blue cracks



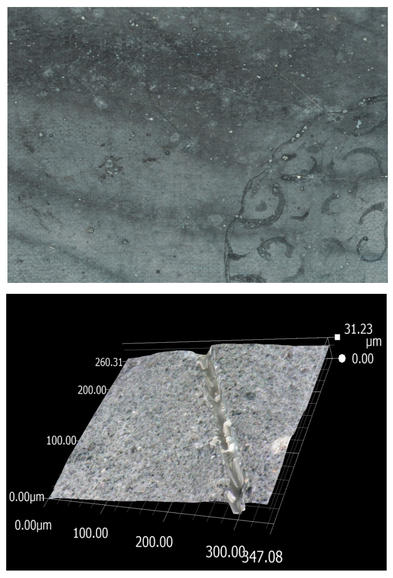
S2. Haze on blue



S3. Haze on grey

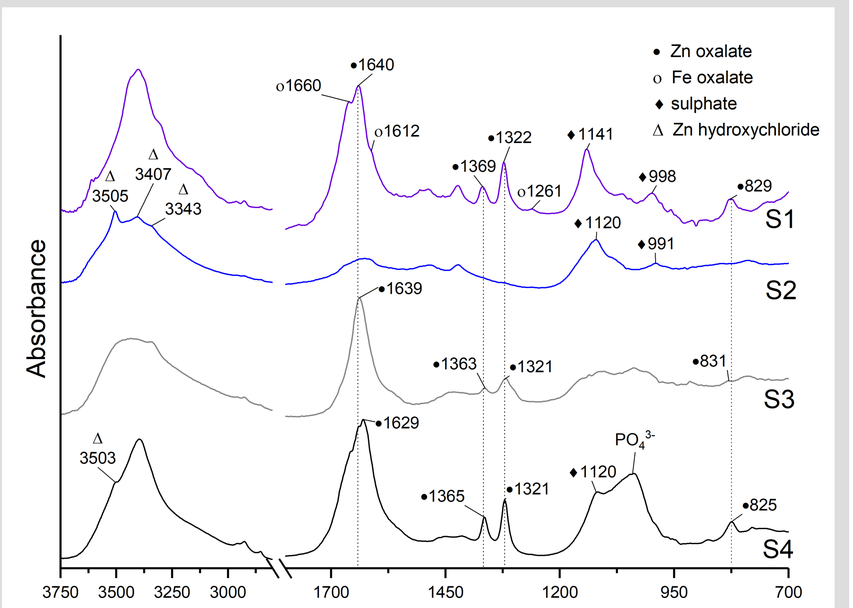


S4. Haze on black



Images of various whitish haze S1-S4- Top tier: 2D visible light images; Middle tier: 3D images at magnification 1000X; and Bottom tier: SEM images at magnifications 3000X (S1), 3000X (S2),11,000X (S3) and 7,000X (S4)

The haze and painted layers were so thin that it was difficult to understand the layering with 2D images. 3D images showed that the conformation of the haze was thinly formed on the paint surface, within 6 µm thickness. SEM images showed the morphology of the haze taking the shapes of polygonal platelet structures, rod-like and needle-like structures, suggesting crystalline growth.

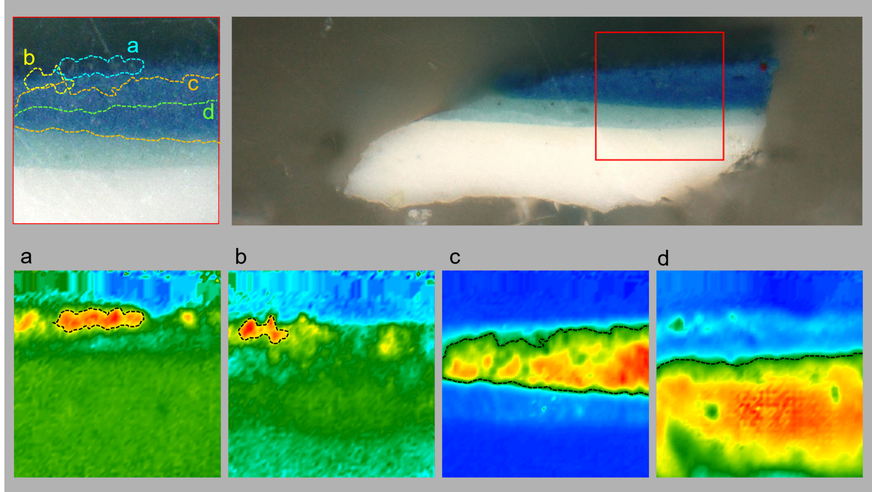


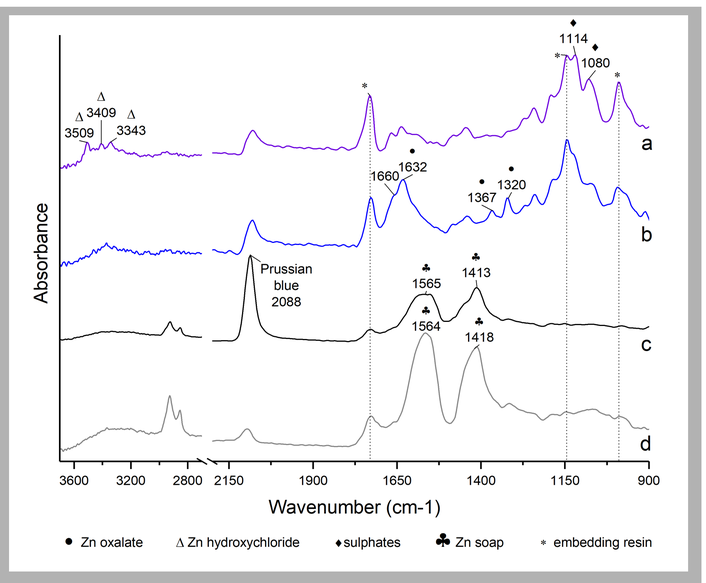
FTIR spectra of four micro-areas of haze: S1- Zn oxalate, sulphate and Fe oxalate; S2- Zn hydroxychlorides (possibly simonkolleite), sulphate; S3- Zn oxalate; S4- Zn oxalate, Zn hydroxychloride (possibly simonkolleite), sulphates

HAZE	FTIR	SEM-EDS
1	zinc oxalate, ferric oxalate, sulphate	Zn, S, Cl, (Fe)
2	zinc hydroxychlorides, sulphate	Zn, S, Cl, (Fe)
3	zinc oxalate	Zn, S, Cl
4	zinc oxalate, calcium oxalate, zinc hydroxychlorides	Zn, S, Cl, (Ca)

FTIR and SEM-EDS results showed that the haze formed on the paint matrix (oil-based binder containing zinc white, Prussian blue, bone black) was mainly composed of zinc-related efflorescence containing hydroxychlorides, sulphates and oxalates.

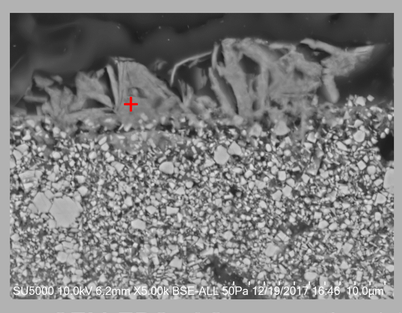
Seeing through the paint layers

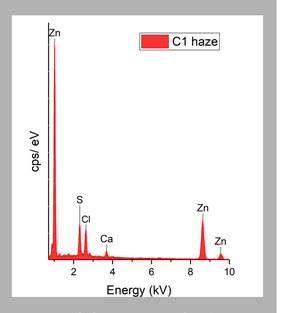




FPA-FTIR images (70 x 70 µm) of cross-section from haze on blue cracks (S1) with integrated absorbance: a – (1114 cm^{-1}) zinc hydroxychlorides, sulphates; b – (1320 cm^{-1}) zinc oxalates; c – (2088 cm^{-1}) Prussian blue; and d – (1564 cm^{-1}) zinc soaps.

The SEM image of cross-section 1 showed that the thin haze (about 2-6 µm thickness) was formed on the surface of the blue paint and aggregates were present in the paint layers and the zinc white ground. From the FPA-FTIR images, these aggregates were identified as zinc soaps (d), whereas the occurrences of zinc oxalates (b) and zinc hydroxychlorides, sulphates (a) were localised at the paint surface.





SEM-EDS of Cross-section 1 (haze on blue cracks)

Conclusion and future work

- The results suggests that the haze was due to intrinsic degradation of the painting and not intended by the artist.
- The formation of hydroxychlorides and sulphates is likely due to migration of zinc soaps from the ground and the paint layers, which subsequently interacted at the paint surface with the environment (e.g. dirt, pollution) [3]. The source of oxalates was postulated to arise from oxidative degradation of the organic binder or resinous coating to oxalic acid, catalyzed by the zinc white pigment [3, 4].
- For future conservation work, the removal of the haze using different cleaning systems such as chelating agents shall be investigated.

Acknowledgements

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