

# A study of zinc soap aggregates in a late 19th century painting by R.G. Rivers at the Queensland Art Gallery

Gillian Osmond<sup>a\*</sup>, Katrien Keune<sup>b</sup> and Jaap Boon<sup>c</sup>

*a* Conservation Department, Queensland Art Gallery, PO Box 3686, South Brisbane, Qld 4101

*b* Molecular Paintings Research Group, University of Amsterdam

*c* Department of Analytical Mass Spectrometry, University of Amsterdam

\*Corresponding author email address <gillian.osmond@qag.qld.gov.au>

## Abstract

*Metal soap formation in paintings has been implicated in a serious deterioration phenomenon. The present study documents zinc soap aggregates observed in a late 19th century painting by R. Godfrey Rivers. Optical microscopy and scanning electron microscopy with energy dispersive X-ray analysis of paint cross-sections are used to describe the appearance and elemental composition of affected paint layers. Fourier Transform Infrared Spectroscopy (FTIR) is used to confirm the presence of zinc carboxylates and static secondary ion mass spectrometry (SIMS) results are given for one sample. Scanning electron microscopy energy dispersive X-ray (SEM-EDX) maps and spot analyses are used to examine aggregates in detail. In addition to zinc, carbon and oxygen, magnesium is frequently present. Paint composition and environment are discussed in terms of their potential to influence soap formation.*

## Introduction

A serious deterioration phenomenon in lead-pigmented paint layers has been recognised in an increasing number of paintings worldwide. Research has developed in response to surface defects identified in paintings spanning the 13th–20th centuries. Most published material to date has concentrated on the phenomenology and mechanistic aspects of lead soap formation in old master paintings. Rembrandt's *The anatomy lesson of Dr Nicolaes Tulp* was among the first to be studied because of the disfiguring lumps and craters apparent across its surface (Noble et al 1998). Boon et al (2002) discussed the phenomenon of lead soaps at the International Council of Museums Conservation Committee (ICOM-CC) Triennial Meeting in Rio de Janeiro and a detailed questionnaire for international distribution was prepared by Noble [1]. Higgitt et al (2003) comprehensively discussed soap formation in paintings where red lead and lead-tin yellow are the cause of deterioration. Boon et al (2004) propose a mechanism of lead soap aggregation in lead-tin yellow paints. A comparable process of deterioration has also been identified in zinc-containing lead chromate paint layers in paintings by Vincent van Gogh (van der Weerd et al 2003, Keune 2005). These studies prompted the investigation of an Australian painting by R. Godfrey Rivers, which exhibits similar phe-

nomena related to zinc-containing paint.

Metal soaps, metal salts of fatty acids, are commonly formed as part of the normal ageing of oil paint. Depending on the paint composition, fatty acids present in the oil might form metal carboxylates with pigments or other metal containing components (van den Berg 2002). An excess of fatty acids in paint can lead to aggregation or efflorescence. Palmitate and stearic acids are two characteristic fatty acids in oil paint which appear to preferentially separate from the oil network and are most frequently associated with surface 'bloom' (eg. Williams 1988, Koller and Burmester 1990, Ordonez and Twilley 1997, Rimer et al 1999). Palmitic and stearate are similarly significant in soap aggregation (Higgitt et al 2003).

Inorganic material is also often observed at the centre of soap masses, sometimes with a structure suggesting formation via precipitation reactions (Boon et al 2002, Higgitt et al 2003). Studies into lead soaps show this material varies according to paint composition, with lead carbonate the most common mineral phase (Boon et al 2002, Higgitt et al 2003). Zinc oxide was postulated in soap formations in Van Gogh's *Falling leaves (Les Alyscamps)* (van der Weerd 2003), but subsequent research has identified zinc carbonate as the mineral fraction (Keune 2005). In industry it is known that zinc white reacts readily with fatty acids in drying oils and the soaps which

form contribute to the characteristic hardness of zinc paints (Kuhn 1986). So it is not simply the formation of soaps which leads to deterioration, but more the extent to which soaps form and the way they aggregate and ultimately distort the surrounding paint.

### Investigation of paintings at the Queensland Art Gallery

A significant number of British and Australian paintings from the late 19th and early 20th century in the Queensland Art Gallery collection are suspected to contain zinc soap aggregates based on light microscopic examination of paint cross-sections. An initial survey of archived cross-sections from fourteen paintings of this general oeuvre has been undertaken. Table 1 details nine that appear to contain soaps; all are catalogued as oil on canvas; however, no medium analysis has been undertaken.

The present study describes analytical imaging techniques used to examine the appearance and composition of zinc soap inclusions found in one of the listed paintings, *Woolshed, NSW* (1890) by R. Godfrey Rivers.

R. Godfrey Rivers was born in England and stud-

ied at London's Slade School from 1877 to 1883. He arrived in Australia in 1889 and in 1891 moved to Brisbane to become Art Master at Brisbane School of the Arts. In 1895, he became the Queensland Art Gallery's inaugural Curator. Despite being a 'Slade' man, Rivers maintained a strong association with the Royal Academy and its more traditional painters. During return visits to England, he visited the studios of many Academicians, including Frederick Leighton (Strumpf 1996).

*Woolshed, NSW* is conventionally painted on a commercially primed canvas. It portrays the interior of a sheep-shearing shed, with glimpses of the Australian landscape beyond (Figure 1). This painting was acquired by the Gallery within a few years of being painted and showed little evidence of conservation intervention prior to its cleaning and varnish removal in the early 1990s. Fine, mechanical cracking is widespread. Localised drying cracks are also apparent. Under magnification, small, translucent spots are distributed through some passages of paint. In lighter paint these inclusions appear dark, sometimes with a defined centre (Figure 2). In darker (brown) paints, they give the surface a globular,



Figure 1. R Godfrey Rivers, *Woolshed, New South Wales* 1890. Gift of the artist 1895. Numbers denote sites from which paint samples derive.



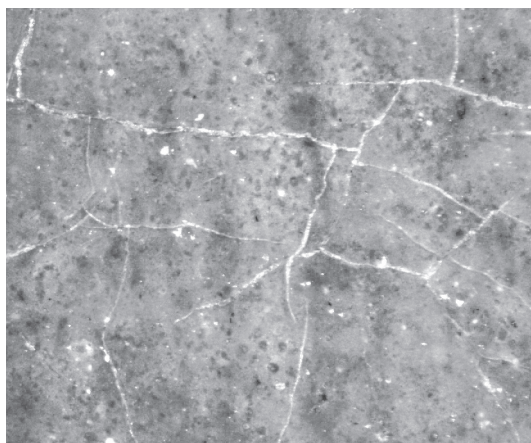


Figure 2. Surface detail from passage of flesh (photographed at 50× magnification). Soap aggregates appear as dark spots or small craters with defined centres.

bubbly texture. Soap formation has subtly altered the appearance of the painting.

### Sample preparation and examination techniques

Three paint samples from Rivers, *Woolshed, NSW* (1890) were selected for detailed study to characterise their inclusions. RWS5 was sampled from blue-grey paint in the iron roofing of the shearing shed, RWS4 contains yellow green paint from the background landscape and RWS3 is from a shearer's dark brown trouser (Figure 1).

Paint samples were embedded in a polyester resin, and microtomed with a tungsten blade to expose a cross-section. Final (dry) polishing where necessary was undertaken with Micro-Mesh™ cloth-backed abrasive sheet (12 000 grit). Cross-sections were documented using optical microscopy with visible and ultraviolet (UV) light sources. RWS3 and 4 were then carbon coated to enable scanning electron microscopy (SEM) imaging with energy dispersive X-ray (EDX) analysis at the University of Queensland Centre for Microscopy and Microanalysis, using either a Philips LaB6 XL30 [2] or JEOL JSM-6460 LA [3] scanning electron microscope. Samples were examined in high vacuum mode at 20 kV accelerating voltage. Points of interest on the specimen were acquired in spot mode. Larger regions of the sample were full spectrum X-ray mapped to elucidate elemental distribution.

RWS5 was examined separately at the Foundation for Fundamental Research on Matter, Institute for Atomic and Molecular Physics (FOM-AMOLF). Preliminary data have been summarised in the PhD thesis of Keune (2005). In addition to SEM-EDX, FTIR imaging was undertaken using a Bio-Rad Stingray [4], and static-SIMS experiments were performed on a Physical Electronics TRIFT-II time-of-flight secondary ion mass spectrometer (TOF-SIMS)

[5]. In all samples, optical and fluorescence characteristics in cross-section and elemental composition have been used to infer the likely presence of pigments. Organic pigments have not been identified due to the limitations of SEM-EDX.

Table 1. Paintings with zinc soap inclusions

Painting
RIVERS, R. Godfrey England/Australia b.1859 d.1925 <i>Woolshed, New South Wales</i> 1890 Gift of the artist 1895
RIVERS, R. Godfrey England/Australia b.1859 d.1925 <i>Under the jacaranda</i> 1903 Purchased 1903
RIVERS, R. Godfrey England/Australia b.1859 d.1925 <i>An alien in Australia</i> 1904, reworked later Gift of the Godfrey Rivers Trust 1940
HOBBDAY, Percy Stanhope Australia b.1879 d.1951 <i>The western sky</i> c.1909 Purchased 1909
FOX, E. Phillips Australia/France b.1865 d.1915 <i>Bathing hour (L'Heure de Bain)</i> c.1909 Purchased 1946
LISTER, W. Lister Australia b.1859 d.1943 <i>Sydney Harbour, overlooking Taylor's Bay</i> c.1912 Purchased 1949
HEMY, C. Napier England b.1841 d.1917 <i>The home wind</i> 1901 Purchased 1903
CALDERON, W. Frank England b.1865 d.1943 <i>Crest of the hill</i> 1898 Purchased 1899
LISTER, W. Lister Australia b.1859 d.1943 <i>Sea breeze</i> AGNSW collection

### Results

Paint visible in cross-section is characteristic of commercially prepared paint with typically small and uniform particle size. The three samples have complex pigmentation and distinctive inclusions are distributed through certain layers of paint. Consistent with the results described previously by others, inclusions comprise a gel-like phase quite distinct from the granularity of surrounding paint. The gel is highly UV-fluorescent. Backscatter electron images (BSI) are dramatic because of contrast between the elements of high atomic mass dominant in the paint

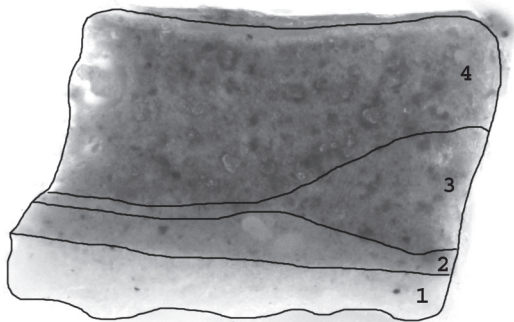


Figure 3. Rivers WS5 visible light microscopic image with outline denoting layers. Soap aggregates are concentrated in layer 4 and appear as dark, transparent voids, many with defined, refractive centres.

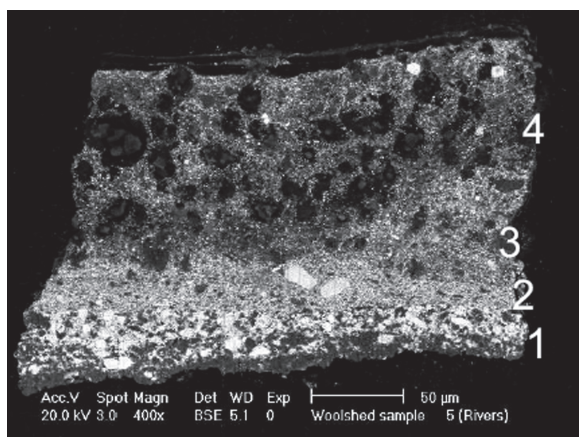


Figure 5. Rivers WS5 backscatter electron image. Soaps are most prevalent in the upper paint layer (4), visible as rounded dark regions with brighter centres.

and the organic nature of the soap phase. Inorganic centres within soapy inclusions are clearly resolved in the SEM. EDX mapping illustrates the alignment of elements within samples and allows more confident pigment attribution. Subtle variations in size and distribution of pigment particles between layers are also revealed; the significance of these differences is unknown and beyond the scope of the present study.

### RWS5

A double ground is evident in cross-sections taken from *Woolshed*. The lower layer contains calcium carbonate with a small amount of lead white. The upper ground is consistent with lead white and a minor chalk component. Three paint layers can be discerned: a light brown paint (layer 2), a blue-grey layer (3), and a purple-grey layer (4) (Figure 3). Iron and earth-based pigments are present in all paint layers. Cobalt blue is evident in layers 2 and 4. Pigment with fluorescence typical of madder is prevalent in layer 4. All paint layers appear to be mixtures with white. Two areas of unmixed lead white paint can be discerned in layer 2 (carbonates are confirmed

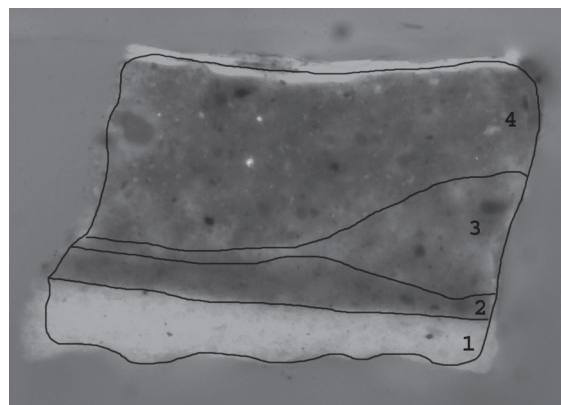


Figure 4. Rivers WS5 ultraviolet fluorescence image. Soap centres appear dark with a fluorescent surround.

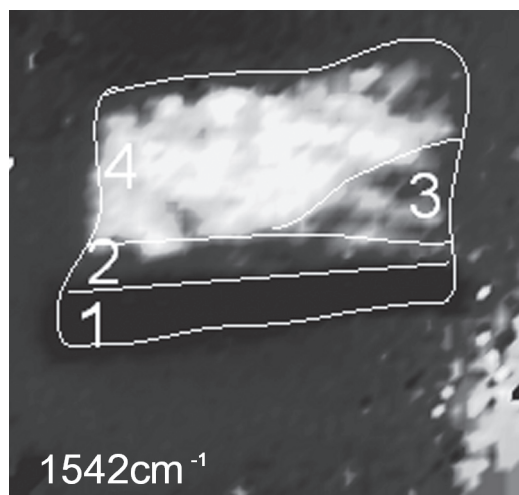


Figure 6. Rivers WS5 FTIR image. Zinc carboxylate distribution is illustrated by absorbance intensity at  $1542\text{cm}^{-1}$  (peaking in layer 4).

with FTIR). A few isolated spots of bright UV-fluorescence in layer 4 suggest zinc oxide is also present. Lead, zinc, carbon, oxygen, aluminium, silicon, magnesium, and chlorine are widely detected with EDX analysis of the paint matrix in each layer.

Layers 3 and 4 are affected by many small aggregates (approximately  $10\ \mu\text{m}$ ) with a greenish core and a transparent, UV-fluorescent halo (Figure 4). The small aggregates are finely distributed within the paint matrix of both layers, although are more prevalent and slightly larger in layer 4. The aggregates are clearly visible in BSI; all aggregates consist of a brighter centre and a dark rim (Figure 5). EDX analysis shows only the presence of carbon, oxygen, zinc, and magnesium (low) inside the aggregates. Zinc is predominant in the core of the aggregate, while carbon is predominant in the rim. A very small amount of magnesium is found inside the aggregate.

FTIR imaging of RWS5 detects metal soaps at  $1542\ \text{cm}^{-1}$  in paint layers 3 and 4 (Figure 6). The dark circular areas observed in layers 3 and 4 in BSI are interpreted as zinc soap aggregates. Although the aggregates are too small in size to identify them



with imaging FTIR (spatial resolution limit approximately  $7\ \mu\text{m}$ ), the position of the asymmetric metal carboxylate vibration peak is very informative. The position of this absorption peak is dependent on the type of metal attached. The peak at  $1542\ \text{cm}^{-1}$  in the spectrum of layers 3 and 4 is indicative for zinc carboxylates (Robinet and Corbeil 2003).

The paint cross-section was also analysed with static-SIMS. Figure 7 shows the positive secondary ion images of lead ( $m/z\ 208$ ) and zinc ( $m/z\ 65$ ), and the negative ion image of deprotonated palmitic acid ( $m/z\ 255$ ). The deprotonated palmitic acid ion image represents the distribution of oil in the paint. Lead is present in all the layers, but absent in areas corresponding to the aggregates in layers 3 and 4. Zinc is present in the aggregates (mainly in layer 4) and in lower intensity in the other parts of layer 4. Palmitic acid observed with SIMS is present in all four paint layers, but the intensities are too low to correlate its distribution to the light microscopic or backscatter images. The P/S ratios determined with SIMS give a reliable indication to distinguish the types of oil in the paint (Keune et al 2005). The P/S ratio of layer 1 is 1.7, layer 3 is 2 and layer 4 is 3. The ratio of palmitic to stearic acid varies between layers, indicating differences in the types of oil or possibly mixtures of oils in these layers (Mills and White 1994).

#### RWS4

Ground layers are consistent with RWS5. Two paint layers are present: light purple underlying a yellow-green. Pigments considered present in both layers include green earth, barium chromate, and a fluorescent aluminium-based red assumed to be madder. The lower layer also contains cobalt blue and a second red pigment. Colours in both layers are mixtures with white.

Characteristic features of soap aggregation are present in both layers. UV-fluorescent masses are concentrated in the lower layer (Figure 8). Inclusions in the top layer appear darker with a narrow fluorescent halo. BSI (Figure 9) distinguishes large regions dominated by elements of low atomic mass in the bottom layer, whereas the top has smaller dark regions, many with bright centres; zinc is concentrated in these areas (Figure 10). Cobalt and magnesium occur in alignment with zinc concentrations. Lead dominates in the surrounding matrix. Carbon concentration is low in the top layer, higher in the bottom.

#### RWS3

Ground layers are consistent with RWS5. Paint appears very dark with a translucent central band; blue, red, and brown pigmentation was observed at the time of sampling. UV fluorescence distin-

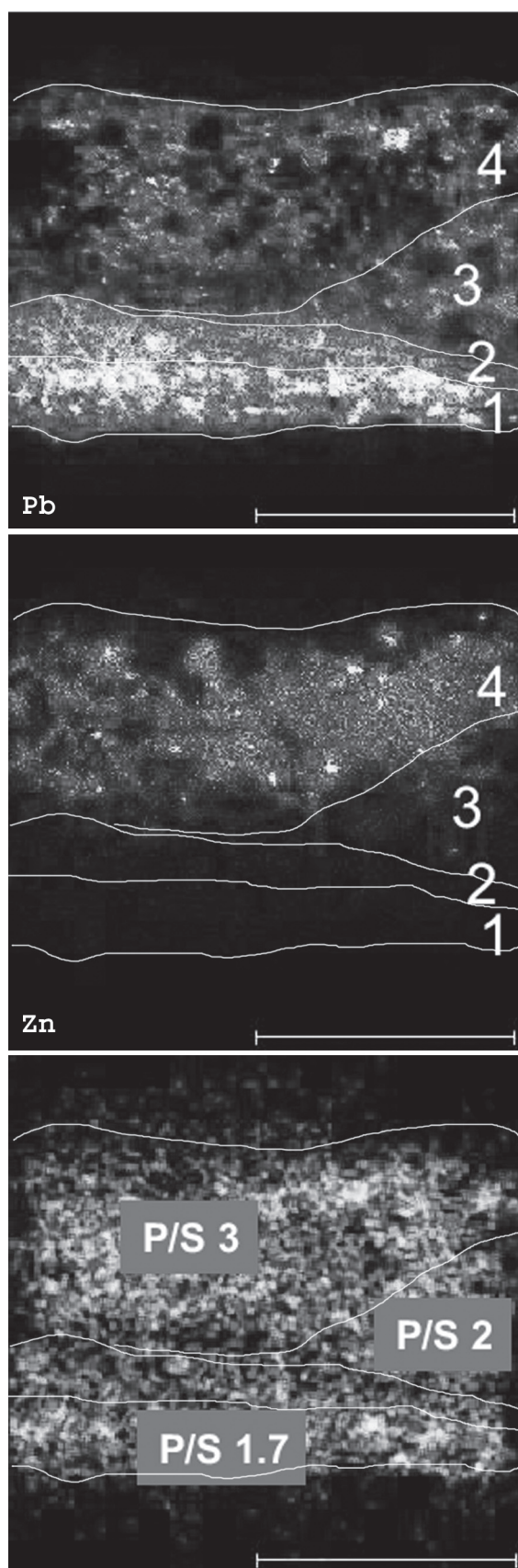


Figure 7. Rivers WS5 SIMS images representing lead (+; $m/z\ 208$ ), zinc (+; $m/z\ 65$ ) and deprotonated palmitic acid (-; $m/z\ 255$ ). The three palmitic/stearic acid ratios (P:S) representative for layer 1 (P:S 1.7), layer 3 (P:S 2) and layer 4 (P:S 3) are shown in the ion image of deprotonated palmitic acid.

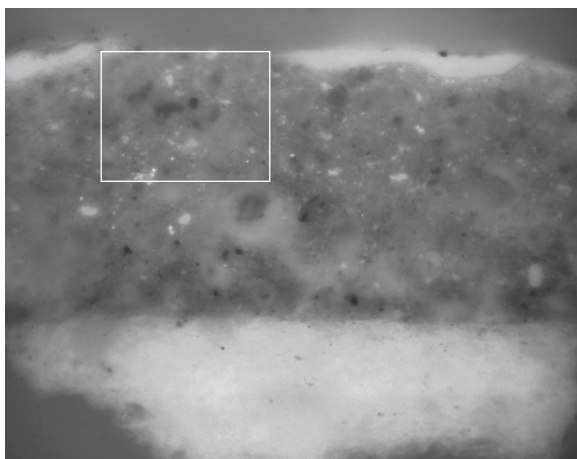


Figure 8. Rivers WS4 ultraviolet fluorescence microscopic image. Sample consists of (double) ground and two paint layers. Soaps are present in both paint layers with those in the lower layer visible as round, fluorescent masses. Box denotes region detailed in Figure 10.

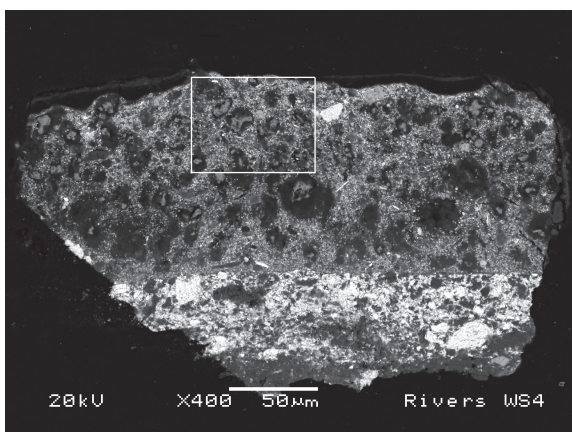


Figure 9. Rivers WS4 backscatter electron image. Soaps in the lower paint layer are visible as round, dark regions. Soaps in the top layer have defined centres. Box denotes region detailed in Figure 10.

guishes three ‘layers’, the central band containing a mass of fluorescent soap (Figure 11). Madder, vermilion, cobalt blue and green earth occur throughout the paint.

Paint layers appear dark and have low contrast in BSI (Figure 12), indicating a predominance of elements of low atomic mass. Zinc corresponds with soap aggregation through the central band of the sample (Figure 13). Cobalt is not observed within fluorescent masses. Although the colour of the sample and BSI suggest little use of lead white, mapping indicates some lead is present through the central layer, in the regions not dominated by zinc. Magnesium follows a pattern similar to lead. Carbon is closely aligned with zinc.

### Inclusions

BSI is particularly useful for distinguishing features of samples at high magnification. Variations in image density across small areas confirm the complexity of inclusions.

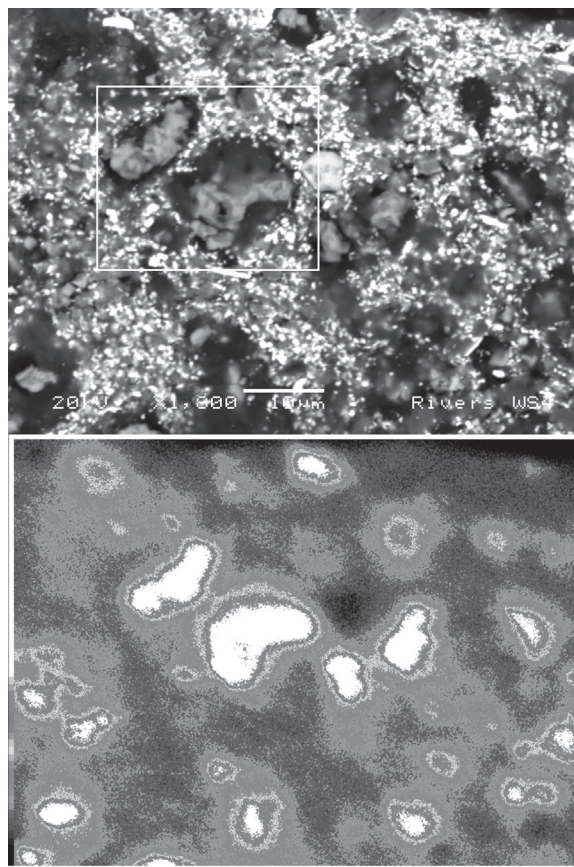


Figure 10. Rivers WS4 (detail) Backscatter electron image (top) and false colour zinc map (bottom) show correlation between soaps and zinc concentration. Zinc is most abundant at the centre of inclusions. Box denotes region detailed in Figures 14 and 15.

Areas with characteristic soap aggregation were selected from samples for more detailed study using SEM-EDX. The centres of a variety of inclusions were analysed in spot mode.

The defined centres contained in soaps from samples RWS4 and RWS5 comprise mostly zinc, oxygen, and carbon together with minor components from the surrounding paint (Figure 14). Magnesium is represented in every spectrum (including those from RWS3) and is associated with higher oxygen intensity (Figure 15). Spot analyses coupled with stronger back scattering confirm a higher density of zinc at soap centres, possibly in mineral form. Clear zinc-based crystals have been identified in soap aggregates of another Australian painting in the Queensland Art Gallery’s collection (*Lister Sydney Harbour ... c 1912*) (see Table 1) (Keune 2005). Heavily mineralised aggregates examined by Keune (2005) in Van Gogh’s painting, *Falling leaves*, were demonstrated to be zinc carbonate crystals.

In *Woolshed*, the phenomenon of mineralisation of soap aggregates is not uniformly present. Soap aggregates in RWS3 have no discernible centre and spot analyses consistently detected carbon in amounts exceeding 70 atomic percent. Together with zinc, this result appears consistent with the presence



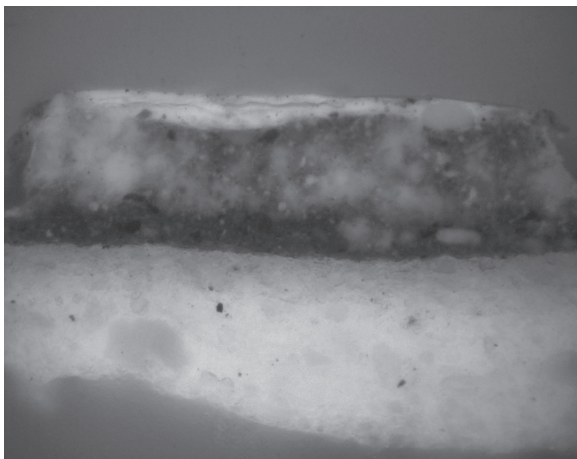


Figure 11. Rivers WS3 ultraviolet fluorescence microscopic image. Sample consists of (double) ground and three paint layers. Strongly fluorescent soaps are distributed through the central layer. Their gel-like appearance contrasts with surrounding paint.

of zinc carboxylates identified in a similar sample using FTIR [6]. In a number of cases, zinc is again concentrated in the centre of the zinc soap aggregate but crystal formation cannot be observed. The presence of an organic layer surrounding the zinc mineral may be difficult to discern at 20kV accelerating voltage in BSI mode, but would make a significant contribution to the X-ray signal. The process of mineralisation is typically underway in the Rivers paintings and may become more pronounced over time.

Further investigation is required to confirm the composition of inclusions from this and other paintings.

## Discussion

A variety of factors are likely to influence the formation of soap aggregates in paint films and their potential to cause defects. These include the inherent reactivity of zinc in oil, the quality and source of the zinc, the type and preparation of oil, the combination of components in the paint, and the environmental conditions and treatment interventions the painting might have experienced.

Soap aggregates documented here occur in layers with consistently high concentrations of zinc and carbon. Carbon concentration might derive from paint with a high oil to pigment ratio. Slow-drying pigments, and pigments which require high percentages of oil to produce a workable paint, such as madder, cobalt blue, and zinc white, are also often present in affected layers. High oil concentration is likely to produce paint with a significant mobile fraction; this may be particularly pronounced where poorly drying pigments or media are used. Mobile components in paint films have been the subject of considerable research. The initial cross-linked oil in paint has been found to hydrolyse over a period of a century (van den Berg et al 2001) leading to reactive free fatty acids. Normally,

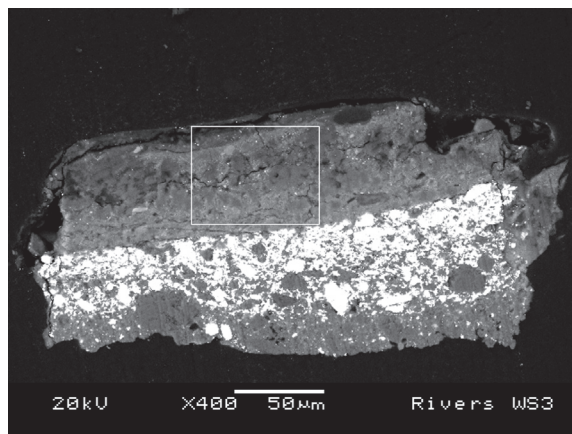


Figure 12. Rivers WS3 backscatter electron image. Soaps aggregated through the central layer lack the granularity of surrounding paint. Box denotes region detailed in Figure 13.

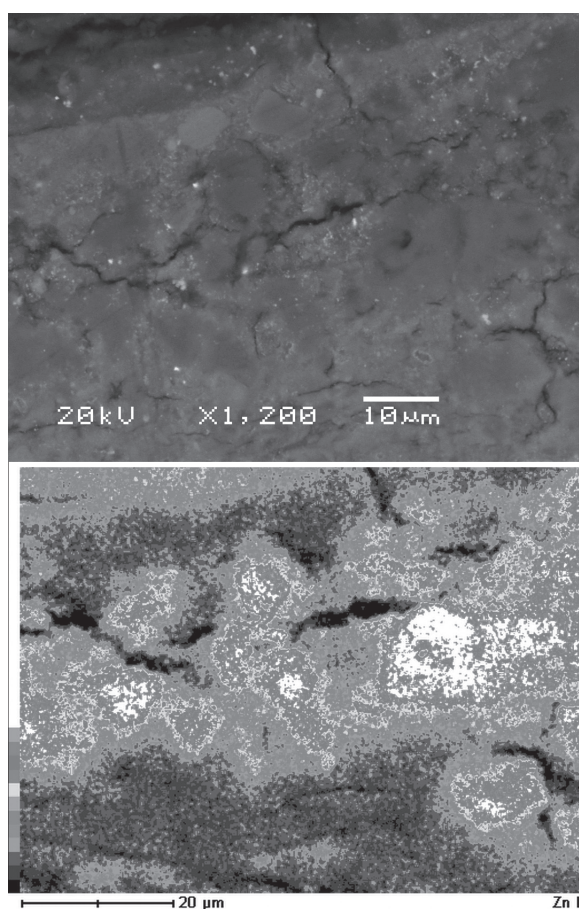


Figure 13. Rivers WS3 (detail). Backscatter electron image (top) and false colour zinc map (bottom) show correlation between soap formation and zinc concentration. Zinc is most abundant through the central layer.

sufficient metal ions are present to form metal carboxylates which stabilise the oil paint. However, in some cases insufficient metal ions are present to trap the acids and blooming may result (Koller and Burmester 1990; Rimer et al 1999). A significant mobile fraction in the paint similarly enhances opportunities for metal carboxylates to form and aggregate. Van der Weerd et al (2003) further describes the

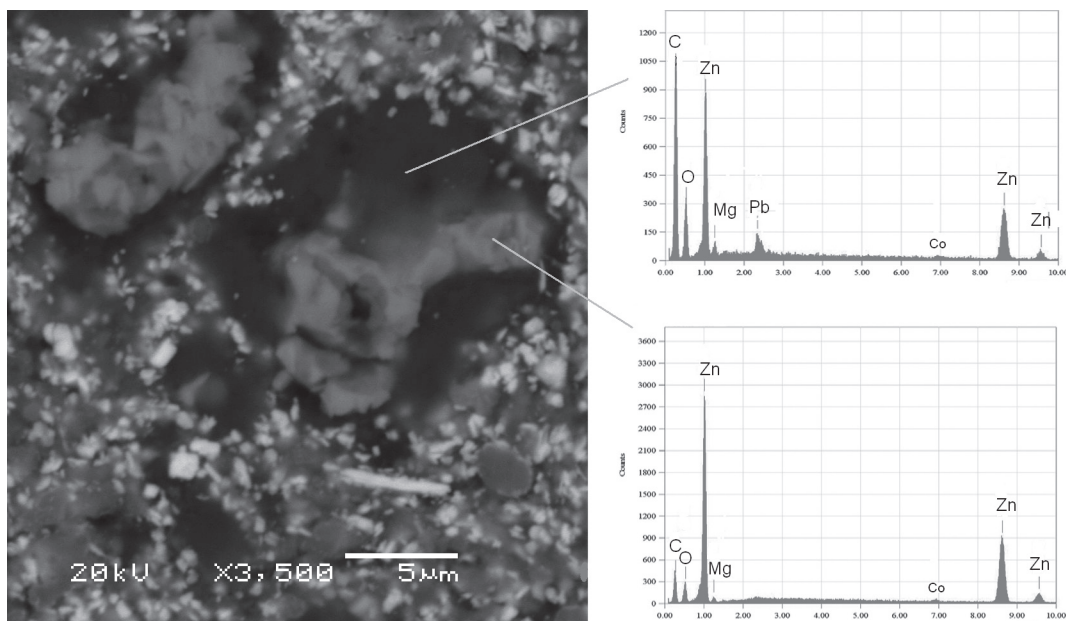


Figure 14. Rivers WS4 (detail). SEM-EDX spectra derived from points indicated in backscatter electron image show high zinc intensity associated with soap aggregation. Carbon intensity is significantly higher in the perimeter of the aggregate, consistent with organic (carboxylate) composition. Reduced carbon intensity towards the centre of the aggregate might indicate a degree of mineralisation.

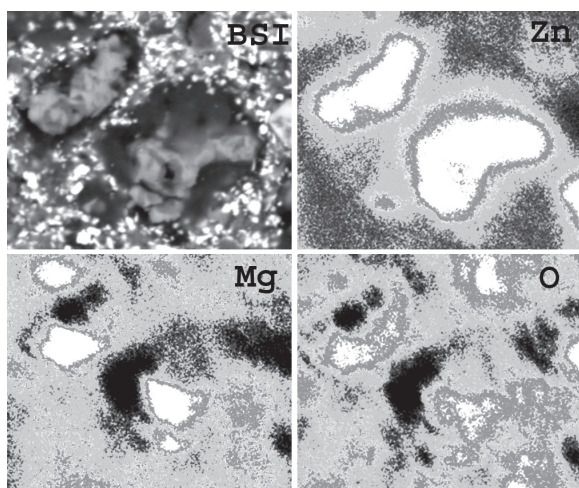


Figure 15. Rivers WS4 (detail). SEM-EDX backscatter electron image and maps for zinc, magnesium and oxygen suggest some correlation between magnesium and oxygen associated with aggregates.

mobility of zinc carboxylates themselves, observed in van Gogh's *Falling leaves*. Zinc carboxylates present in a sample from Lister, *Sydney Harbour...* (Table 1) were also clearly shown to be mobile when SEM imaging of a prepared cross-section revealed soaps emerging from the sample (Keune 2005).

Increased mobility of components in paint has also been discussed in relation to temperature and relative humidity (Ordonez and Twilley 1997; Rimer et al 1999). The Queensland Art Gallery is located in subtropical Brisbane. The Gallery's collection has only been housed in purpose-built facilities since 1982. Paintings from the earliest years have experienced many hot, humid summers. A study of metal soap formation in comparable paintings located in cooler

climates offers potential to explore this theory.

There is some speculation regarding likely sources of zinc in the affected paintings. The paint in sample RWS3 is dark and unlikely to contain significant quantities of white. White paint present in RWS5 appears to be lead-based. Paint layers in RWS4 and RWS5 are mixtures with white; both zinc and lead are present but almost completely contained in separate 'phases'. It is not known to what degree mobility of components in the paint might have contributed to this separation. The absence of zinc (and soap aggregates) from some layers and entire samples from the same paintings suggests zinc is most likely present as a component in selected commercially prepared paints. Kuhn (1986) reports detection of zinc white in coloured paints more than whites, suggesting its addition to various pigments by manufacturers as a lightening agent. Carlyle (2001) refers to various 19th century sources describing the addition of zinc compounds to manipulate the drying or handling properties of oil paints. In addition to zinc oxide, possible zinc-containing compounds include lithopone, (a mixture of barium sulphate and zinc sulphide) or white vitriol (zinc sulphate and zinc stearate). Lithopone is unlikely to be the zinc source in this painting as barium was not detected with EDX in two of the three paint samples (barium chromate was detected in RWS4). No sulphur was detected in the EDX spectra of affected layers either, so it is unlikely that white vitriol was used. Zinc stearate could have been added to the paint, but the ratios of palmitate to stearate detected in affected layers of RWS5 are normal and do not give any indications for additional stearic acid. However, in the 19th century, zinc stearate was not a pure compound,



but more likely a mixture of stearic and palmitic acids (Mayer 1951). So zinc soaps as an addition to the paint cannot be excluded. In any event, information on the origin of the zinc is lost due to the chemical reactivity of the various paint components.

An interesting feature of the soaps documented here is the presence of magnesium. Trace amounts of cobalt are also detected more commonly than not. The form and source of these constituents has not been established; however, magnesium carbonate was a commonly used extender in nineteenth century paint preparations [7]. Magnesium correlates strongly with zinc where soaps contain defined centres. In RWS3, where no centres are discernible, magnesium is present in the soap-affected layer but does not coincide with the highest zinc concentrations. The presence of magnesium and cobalt together with zinc, carbon, and oxygen is a trend also observed in preliminary SEM-EDX analysis of inclusions in the majority of paintings listed in Table 1. Further research is required to determine the composition of these regions and what, if any, significance the minor components play in soap aggregation. A systematic study of comparable paintings from Australian collections would greatly assist ongoing work to determine the causes and mechanisms of soap formation. Comparison with zinc containing paintings where soap aggregation is not evident may also give insight into the phenomenon.

## Conclusion

Paintings from the Queensland Art Gallery collection identified with zinc soap aggregation tell a consistent story and one which corresponds well with research undertaken by others into lead soap formation. This has been demonstrated by a detailed study of paint samples from a representative painting by R. Godfrey Rivers. Zinc, carbon, and oxygen were reliably detected in affected regions and the presence of zinc carboxylates confirmed. Minor amounts of magnesium and cobalt also regularly occur. Aggregates have formed in layers with high carbon concentration, indicative of paint with high oil content. This supports the theory that soap aggregation occurs in paints with a high mobile component. Slow-drying paints, pigments requiring a high ratio of oil, and paintings which have experienced hot, humid conditions, are all possible influences. The documentation of paintings with metal soap formation is crucial to further understanding the phenomenon and to managing its long-term implications.

## Notes

1. Petria Noble and Jaap Boon, Mauritshuis/AMOLF collaboration.

2. Philips LaB6 XL30 high vacuum scanning electron microscopy (SEM), equipped with EDAX brand, super ultra thin window (SUTW), 138 eV nominal resolution, SiLi crystal, Energy Dispersive X-ray Spectrometer (EDX). EDAX Phoenix (V3.10) software used to collect and analyse data.
3. JEOL JSM-6460 LA low vacuum analytical scanning electron microscopy (SEM) equipped with an integrated JEOL hyper mini-cup, 133eV resolution, ultra thin window (UTW), SiLi crystal, energy dispersive X-ray spectrometer (EDX). Integrated JEOL Analysis Station (V3.2) software used to collect and analyse data.
4. Bio-Rad Stingray (Bio-Rad, Cambridge, MA, USA), combining the Bio-Rad FTS-6000 spectrometer equipped with a Bio-Rad UMA 500 infrared microscope with a  $64 \times 64$  mercury-cadmium telluride (MCT) focal plane array camera was used to record the FTIR images. Analysis of the embedded cross-section was carried out in reflection mode recorded with a  $16 \text{ cm}^{-1}$  spatial resolution, a step scan frequency of 1 Hz, and an UDR of 4. The reflection measurements were corrected by the Kramers-Krönig transformation.
5. The static SIMS experiments were performed on a Physical Electronics (Eden Prairie, MN, USA) TRIFT-II time-of-flight SIMS (TOF-SIMS). The surface of the sample was scanned with a 15 keV primary ion beam from an  $^{115}\text{In}^+$  liquid metal ion gun. The pulsed beam was non-bunched with a pulse width of 20 ns, a current of 600 pA and the spot size of  $\sim 120 \text{ nm}$ . The surface of the sample was charge compensated with electrons pulsed in between the primary ion beam pulses. To prevent large variations in the extraction field over the large insulation surface area of the paint cross-section a non-magnetic stainless steel plate with slits (1 mm) was placed in top of the sample. The paint cross-section was rinsed with hexane to reduce contamination of polydimethyl siloxanes.
6. FTIR-imaging analysis of a sample from the painting not included in this paper, RWS1 (FOM-AMOLF). A peak at  $1530 \text{ cm}^{-1}$  was assigned to the presence of metal carboxylates. SEM/EDX analysis confirmed the presence of zinc. The combined results point to the presence of zinc soaps.
7. Winsor and Newton archive, Leslie Carlyle personal communication.

## Acknowledgements

Special thanks to Ron Rasch, University of Queensland Centre for Microscopy and Microanalysis, for his generous assistance and considered advice.

Heleen Zuurendonk (AMOLF 2003–2004) undertook FTIR analysis of RWS5.

Leslie Carlyle (ICN) made the connection between images of paint samples in Brisbane and relevant MOLART research.

Deborah Lau (CSIRO) has made helpful comments at various stages of the manuscript.

Thanks also to Conservation colleagues at the Queensland Art Gallery, particularly Nicola Hall and Alyssa Aleksanian for shared sessions on the scanning electron microscope, and also Anne Carter and John Hook, for advice, encouragement and support.

## References

- Boon, J. van der Weerd, J. Keune, K. Noble, P. and Wadum, J. 2002, 'Mechanical and chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17<sup>th</sup> century paintings', *Preprints of the ICOM Committee for Conservation 13<sup>th</sup> Triennial Meeting*, Rio de Janeiro, ed. R Vontobel, James and James, London, pp. 401–06.
- Carlyle, L. 2001, *The artist's assistant: oil painting instruction manuals and handbooks in Britain 1800-1900 with reference to selected eighteenth century sources*, Archetype Publications, London.
- Higgitt, C. Spring, M. and Saunders, D. 2003, 'Pigment-medium interactions in oil paint films containing red lead or lead-tin yellow', *National Gallery Technical Bulletin* vol 24, pp. 75–95.
- Keune, K. 2005, *Binding medium, pigments and metal soaps characterised and localised in paint cross-sections*, MOLART 11, FOM-AMOLF, PhD Thesis, University of Amsterdam, Amsterdam (<http://www.amolf.nl/publications/theses/>).
- Keune, K. Ferreira, E. and Boon, J.J. 2005, 'Characterisation and localisation of the oil binding medium in paint cross-sections using secondary ion mass spectrometry', *Preprints of the ICOM Committee for Conservation 14<sup>th</sup> Triennial Meeting*, The Hague, James and James, London, pp. 796-802
- Koller, J. and Burmester, A. 1990, 'Blanching of unvarnished modern paintings: a case study on a painting by Serge Poliakoff', *Cleaning, retouching and coatings, IIC Preprints of the contributions to the Brussels Congress, 3-7 September 1990*, pp. 138-143.
- Kühn, H. 1986, 'Zinc white', *Artists' pigments* vol. 1, ed. R.L. Feller, Cambridge University Press, Cambridge, pp. 169–186.
- Mayer, R. 1951, *The artist's handbook of materials & techniques*, first edition, Faber and Faber Limited, London.
- Mills, J.S. and White, R. 1994, *The organic chemistry of museum objects*, Butterworth Heinemann Limited, London.
- Noble, P, Wadum, J, Groen, K, Heeren, R, and van den Berg, K.J. 2000, 'Aspects of 17<sup>th</sup> century binding medium: inclusions in Rembrandt's 'Anatomy lesson of Nicolaes Tulp'', *Art et chimie, La couleur, Paris, Actes du Congrès (1998)*, pp. 126–129.
- Ordonez, E. and Twilley, J. 1997, 'Clarifying the haze: efflorescence of works of art', *WAAC Newsletter* 20 (1) 1998 pp. 11 (reproduced from *Analytical Chemistry* vol. 69, 1997 pp. 416A–422A).
- Rimer, B. Fiedler, I. Miller, M. Cunningham, M. and van den Berg, J. 1999, 'Investigation of fatty acid migration in alizarin crimson oil paint in two works by Frank Stella',

- AIC Paintings Specialty Group Postprints 1999*, pp. 1–14.
- Robinet, L. and Corbeil, M.C. 2003, 'The characterisation of metal soaps', *Studies in Conservation*, 48, pp. 23-40.
- Strumpf, J. 1996, *Looking beyond biography: interpretations of two works by Richard Godfrey Rivers*. BA (Honors) thesis, University of Queensland.
- van den Berg, J.D.J. van den Berg, K.J. and Boon, J.J. 2001, 'Determination of the degree of hydrolysis of oil paint samples using a two-step derivatisation method and on-column GC/MS', *Progress in Organic Coatings*, vol. 41, pp. 143-155.
- van den Berg, J.D.J. 2002, *Analytical chemical studies on traditional linseed oil paints*, MOLART 6, FOM-AMOLF, PhD Thesis, University of Amsterdam, Amsterdam.
- van der Weerd, J. 2002, *Microspectroscopic analysis of traditional oil paint*, MOLART 7, FOM-AMOLF, PhD Thesis, University of Amsterdam, Amsterdam.
- Van der Weerd, J. Gelddof, M. van der Loeff, L.S. Heeren, R. and Boon, J. 2003, 'Zinc soap aggregate formation in 'Falling leaves (Les Alyscamps)' by Vincent van Gogh', *Zeitschrift für Kunsttechnologie und Konservierung* vol. 17, no. 2, pp. 407–416.
- Williams, R. Scott 1988, 'Blooms, blushes, transferred images and mouldy surfaces: what are these distracting accretions on art works?' *Proceedings of the 14<sup>th</sup> annual IIC-Canadian Group conference, Toronto, Canada, May 27-30, 1988* pp. 65–84.

---

Gillian Osmond graduated from the University of Canberra (CAE) with a Bachelor of Applied Science, Conservation of Cultural Materials (Paintings Conservation) in 1988. In 1991-92 she was a research intern at the Tate Gallery, London. She is currently Conservator, Paintings at the Queensland Art Gallery, where she has worked since 1988.

Katrien Keune graduated in chemistry from the University of Amsterdam (2000). She subsequently joined the De Mayerne project team in the Molecular Paintings Research group of Prof. J. J. Boon. She completed her PhD thesis, titled 'Binding medium, pigments and metal soaps characterised and localised in paint cross-sections' at the University of Amsterdam in 2005.

Jaap J. Boon was trained in geology and chemistry and was awarded a PhD from Delft Technical University in 1978. He became research associate at the FOM Institute for Atomic and Molecular Physics in 1983 and coordinated the NWO Priority project MOLART (Molecular aspects of ageing in Art) granted in 1995. Boon is Professor of Analytical Mass Spectrometry at the University of Amsterdam and Head of the Molecular Paintings Research group at AMOLF performing research on the molecular chemistry and chemical microscopy of pigments and binding media and their interactions in paintings.

Please address correspondence to Gillian Osmond at <[gillian.osmond@qag.qld.gov.au](mailto:gillian.osmond@qag.qld.gov.au)>.