Zinc white: a review of zinc oxide pigment properties and implications for stability in oil-based paintings

Gillian Osmond

University of Queensland Queensland Art Gallery / Gallery of Modern Art gillian.osmond@qagoma.qld.gov.au

Abstract

Zinc oxide became a frequent component of 20th-century paints following its first commercial availability in the previous century. Aspects of zinc oxide pigment production and paint formulation which influence the reactive tendencies of zinc oxide in oil-based paints are reviewed. Particular attention is given to the formation and aggregation of zinc soaps which have been linked to deterioration in paintings. Pigment particle properties, fatty acid profiles, paint additives and environmental conditions are all significant factors.

Keywords: zinc oxide, zinc white, oil paint, paintings conservation, zinc soap, zinc stearate

Introduction

The advent of zinc oxide as a white pigment for oil painting introduced an alternative to the traditional toxic lead white in artist and industrial paint markets. The beneficial properties of zinc oxide led to its frequent incorporation in both white and coloured paints from its commercial origins in the 19th century and for much of the 20th century. However, the reactivity of zinc oxide in oil-based media posed industrial challenges for managing shelf life and durability of house paints. Zinc soaps readily form in oil-based paints in the presence of zinc oxide. Zinc soaps have also recently been associated with deterioration of various paintings from the 19th and 20th centuries. The prevalence of zinc oxide in paintings from throughout this period creates a clear imperative to improve understanding of the degradation phenomena. This paper reviews aspects of zinc oxide production and paint formulation with significance for stability in oil-based paintings.

Industry development Pigment production

The early history of zinc oxide pigment development is well covered in the literature and is not repeated in detail here (Gardner 1917, Brown 1957, Kühn 1986, Carlyle 2001). Although zinc oxide has been known since ancient times, its popularity as a white pigment was not possible until commencement of industrial-scale zinc oxide production during the 19th century.

The majority of zinc oxide pigment is produced via

one of two pyrolytic processes: the direct (American) process which involves smelting ore in a furnace, and the indirect (French) process, which produces the oxide via burning zinc metal in air. In France there was early concern surrounding the toxicity of lead-based pigments, so attempts to introduce zinc white as a pigment for paint there date from 1780 (Kühn 1986). Development of the metallurgical indirect process and commercialisation of production in the 1840s then facilitated a rapid and wider adoption of zinc oxide to protect the health of French pigment manufacturers and painters (Heckel 1934, Bomford et al. 1990).

Direct-process zinc oxide was developed in 1852 to take advantage of large Franklinite (lead-free ore) deposits in the United States and as a more economical form of production than indirect process (Gardner 1917, Brown 1957). Abundant sources of ore ensured that direct process pigment dominated American industrial paint production consistently from the late 19th century until the second half of the 20th century (Jolly 1993). Direct process pigment, however, was of inferior purity and contained heavy metal contaminants deriving from the ores, especially those predating development of flotation methods of separation (Cocks and Walters 1968). Zinc oxide containing from between 5% and 35% basic lead sulfate (up to 50% prior to 1910), obtained from mixed lead and zinc ores and known as 'leaded zinc' was also intentionally produced for the housepaint market (Gardner 1917, Heckel 1934).

In Australia, large ore deposits at Broken Hill

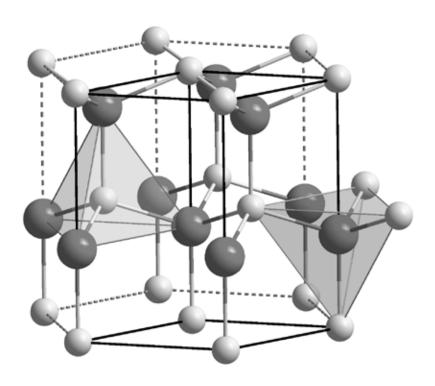


Figure 1. Crystal structure of zinc oxide (wurtzite) with coordination tetrahedra. Zinc atoms are represented by the smaller white balls and oxygen atoms by grey. Image: Wikimedia Commons, http://en.wikipedia.org/wiki/File:Wurtzite_polyhedra.png, accessed 11 August 2011.

ensured an active local zinc oxide industry from the first decades of the 20th century which, in addition to domestic production, supplied zinc concentrates for European markets (Cocks and Walters 1968). Mascot Smelting Company, Botany, began producing direct process zinc oxide in 1917, rapidly increasing domestic consumption (The decorator and painter for Australia and New Zealand 1925). The Australian product claimed to be heavier and denser, with superior covering power to any imported zinc oxide due to an innovative 'concentrating plant' (ibid.), and contemporary sources state that 'practically all the zinc oxide used in the Australian paint industry is prepared in Australia' (Farquharson Boan 1924, p. 96). Production of French Process zinc oxide commenced in Sydney in 1947 following Durham Chemicals acquisition of Mascot Smelting (The Argus Melbourne, 23 July 1947, 'Durham Chemicals for Australia'), introducing technology from the English parent company.

Uptake by the paint industry

There is reference to 'extensive' use of zinc oxide in artists' paints in France as early as 1784 (Gardner 1917). In Britain, zinc white watercolour paints appeared in 1834 following an improvement in pigment density by Winsor and Newton via

mechanical compression while 'red hot' (Carlyle 2001). The first appearance of zinc white in oil tubes was significantly later, listed in a British catalogue (Reeves) in 1860, although mixtures containing zinc oxide with lead white or barium sulfate appear to have been available a decade or so earlier (Carlyle 2001). There is documentary evidence that zinc oxide was progressively being incorporated in prepared paints and pigment supplies, often not declared but in addition to or substituted for more traditional materials (Townsend et al. 1995, Carlyle 2001). An 1899 German text mentions use of zinc oxide for brightening lake pigments in preference to barium sulfate (Josef Bersch,

Lexikon der Farben-Technik 1899, cited in Pilz 2005) and investigations of paintings suggest its presence as a component in coloured paints possibly more than in whites (Kühn 1986).

In the house paint industry, zinc oxide is said to have transformed the early production of ready mixed paints due to its good suspension properties in oil-based media (Brown 1957). It was a component in the first patented 'prepared' paint in America in 1867 (Heckel 1934). By the early 20th century, Gardner (1917, pp 27-8) states that 'the use of zinc oxide is universal with the paint manufacturers of the United States and it is rapidly becoming standard practice with the painting craft to use zinc oxide in nearly all interior and exterior paints'. Australia's 1925 range of Mascot Zinc in Oil and Ready Mixed Zinc Paints included 30 different tints and shades and three different whites (The decorator and painter for Australia and New Zealand 1925). Generally used in combination with lead-based pigment and, later, titanium dioxide, zinc oxide improved strength and mould resistance of exterior house paints (Nicholson and Mastin 1942, Salvin 1944). It afforded paints protection from ultraviolet radiation, found to be optimal at 30% pigment concentration in mixtures of basic lead carbonate or rutile titanium dioxide (Elm 1957), at which percentage it was routinely used in exterior paints for much of the early-mid 20th century (Brown 1957). For interior applications, zinc oxide was valued for minimising yellowing of paints (Elm 1957, Kühn 1986).

Zinc oxide remained popular until the mid-20th century, by which time titanium white had come to

dominate. However, titanium-based paints often incorporated zinc oxide to improve film strength (Kühn 1986). Today, zinc oxide is no longer routinely used in general purpose alkyd paints because of its reactivity (Dixon 2009). Zinc oxide does, however, remain a common component in artists' paints (Mecklenburg et al. 2005, O'Hanlon 2007) and special purpose industrial paint formulations (Dixon 2009).

Artist uptake

Although typically of inferior hiding and drying power and substantially higher cost than lead white, zinc white paints had little tendency to yellow and did not blacken in the polluted, sulfurous air common to many 19th century cities (Harley 1970; Kühn 1986; Bomford et al. 1990). Before widespread incorporation in artists' paint formulations, zinc white was consciously sought and used by some artists including Camille Pissaro (Bomford et al. 1990), and some of the Pre-Raphaelites working in mid-19th century Britain who included zinc white in special primings or in localised ground applications as a reflective base for the bright transparent palette they favoured (Hackney et al. 2002, 2004). An 1870 painting by American Thomas Eakins shows alternating layers of lead- and zincbased paint (Currie and Smith 1994), and Australian artist JP Russell, based in France, is known to have replaced lead white with zinc oxide for uppermost paint layers in at least one painting, likely with the aim of avoiding future deleterious darkening (Dredge 1996). Paintings by other artists working in France, including van Gogh (Kühn 1986, Roy 1987) and Australian E. Phillips Fox, are also found to commonly include zinc white (Osmond 2010). Joan Miró writes of his preference for incorporating zinc oxide into plaster grounds to attenuate its absorbency, a technique reportedly based on the practice of Henri Matisse (O'Donoghue et al. 2006).

Paintings by artists who were early adopters of house paints are also likely to contain significant amounts of zinc oxide. Pre- and post-WWII Ripolin paints much favoured by artists including Picasso and Sidney Nolan have been found to widely include zinc oxide (Gautier et al. 2009, Dredge et al. 2012).

Pigment properties

Pure zinc oxide crystals have complex surface chemistry. This is due in part to electrostatic instability arising from the two opposing polar surfaces Zn-ZnO and O-ZnO. Recent experimental and theoretical research on the topic has been comprehensively reviewed (Wöll 2007). The properties of zinc oxide and its behaviour in oil-based paints will vary according to the individual properties of the pigment particle.

Particle size

Direct process zinc oxide particles typically have larger particle size and are more acicular (needle-shaped) than the finer, nodular indirect pigment (Oil and Colour Chemists' Association 1966). Acicular boule-shaped crystals can be formed with slow burning of zinc vapour (Kühn 1986), while increased airflow accelerates oxidation and cooling and favours fine particle formation (Oil and Colour Chemists' Association 1966). Reheating crystals enables particle size to be increased (Brown 1957). Larger particle size typically reduces surface area for a given measure of pigment and is associated with reduced oil absorption (Kühn 1986). Studies on particle size effects, however, describe zinc oxide pigment as forming stable aggregates in the dry state. These aggregates essentially function as a kinetic unit, translating primary particle sizes of 0.25-1µm to effective particle sizes of 1-5 µm, and typically of more spherical shape (Princen and Devena-Peplinski 1964). The presence of coarse aggregates in a pigment mix is given as possible explanation for a lack of correlation between paint properties and notional particle size in some studies (Barnett 1949).

Crystal structure

Zinc oxide belongs to the hexagonal crystal system. Zinc and oxygen centred tetrahedra join at a common zinc atom forming a nucleus for additional tetrahedra, developing crystal lattice of the wurtzite type (Brown 1957) (Figure 1). Alternate layers of zinc and oxygen atoms in the c (longitudinal) axis of the crystal promote the formation of needle-shaped crystals. Zn-O distance along the c axis is shorter than the other two axes; this departure from tetrahedral symmetry is considered to be due to a covalent bond along the c axis (Brown 1957).

Many metal atoms can enter a zinc oxide crystal at elevated temperatures (such as in the course of production) and introduce marked change in properties (Brown 1957). Direct process pigment is associated with stoichiometric proportions of zinc and oxygen. French process pigment is more likely to contain interstitial zinc (Morley-Smith 1958). One consequence is the effect on ultraviolet (UV) fluorescence properties. Stoichiometric zinc oxide is associated with bright green fluorescence in contrast to lower purple-blue fluorescence associated with interstitial zinc (Morley-Smith 1958).

Photostability

Zinc oxide absorbs UV radiation. In paints this may help the pigment protect an organic binder from destructive radiation, but may also 'be the source of troublesome photochemical reactions' (Barnett 1949). Zinc oxide with interstitial zinc or other lattice irregularities is considered more likely to dissipate energy capable of initiating photochemical reactions in adjacent materials (Winter and Whittem 1950; Morley-Smith 1958). Degradation of binding media and fading of organic pigments (Kühn 1986), and weakening of supports including paper (Kemp et al. 2004) and textiles (Kühn 1986) have been associated with zinc oxide.

Consistent with typical stoichiometry, paint films containing direct process pigment were found to be more resistant to surface degradation than French process (Hoffmann and Saracz 1969). Stability issues also arose in Australia following introduction of French process pigment into local housepaint formulations (Morley-Smith 1950). Zinc oxide paints previously produced with direct process pigment had claimed superior durability to lead-based paints even in Queensland, where the semi-tropical environment is severe upon light painted surfaces' (The decorator and painter for Australia and New Zealand 1925). Conditions in Australia evidently initiated degradation in paints formulated with the French Process oxide which had not been significant in milder British and European climates. Research led to pigment modifications, effectively increasing particle size, which improved the performance of paints (Morley-Smith 1950). However, it appears direct process zinc oxide was quickly resumed for use in exterior paint applications (Morley-Smith 1958).

Subsequent studies of zinc oxide in a variety of synthetic resin binders found that radiation in the range 385–415nm was the most significant in film decomposition, compared to shorter wavelengths for titanium dioxide–pigmented films (Hoffmann and Saracz 1971). Decomposition was also accelerated by increasing relative humidity (RH), without affecting wavelength sensitivity, however, the weathering of direct process–pigmented films was more dependent on RH, and lead content in the direct grade was considered a possible factor in addition to particle size (Hoffmann and Saracz 1969).

Today, high-purity French process zinc oxide dominates international production (Shelton 2010), however, direct process pigment still has a market in the paint industry, where its lower reactivity is advantageous (International Zinc Association 2009). Features distinguishing direct and indirect grades are likely to be less certain in modern zinc oxide samples given the greater production control now possible over crystal and particle properties.

Reactivity of zinc oxide in oil

The prevalence of zinc oxide in paintings becomes significant when its reactivity in oil-based media is considered. Zinc oxide is amphoteric and is capable of neutralising both acids and alkalis (Oil and Colour Chemists' Association 1966). In oil-based paints this manifests in reaction with fatty acid components of the paint medium to form zinc soaps. Zinc carboxylate—based lumps may form in paint either during storage or in the film (Bell 1970). The housepaint industry directed considerable research over many decades towards managing the interaction in order to retain the beneficial properties of the pigment. In addition to generic stability issues associated with pigment grade, the fatty acid composition of paint and environmental conditions are significant for reactivity in oil.

Temperature

Temperature influences the solubility of zinc soaps in the oil medium in accordance with concentration, with separation occurring when the temperature drops below that corresponding to the solubility limit at the prevailing concentration (Hansen and Klauss 1971). Elm (1957) found that during paint production, crystalline seeds' of zinc stearate and palmitate may form on cooling following paint grinding, with rapid cooling producing small soap crystals and slower cooling favouring larger soap crystals which are more likely to affect texture. Aggregation of soaps has been shown to occur under extreme fluctuations, especially in warmer climates based on cycling tests to 60°C which yielded seeded paints at approximately half the time of those cycled to 47°C (Hansen and Klauss 1971). This tendency led to the concept of temperature cycling to determine seeding propensity of different paint formulations (55-60° C for 48 hours, cooled over 48 hours, repeated (Elm 1957); 60°C for 5 days, followed by slow cooling and standing at room temperature for two days (Hansen and Klauss 1971). Variations are still used by paint manufacturers today with one local producer reporting that paints are expected to remain stable in the wet state during a month of daily temperature cycling between 20°C-50° C (Dixon 2009).

Fatty acid composition and formulation

Control of acid level is important for minimising zinc oxide reactivity (Elm 1957, Bell 1970). Different oils comprise triglyceride structures based on different types and relative proportions of saturated and unsaturated fatty acids. Oil processing methods also influence triglyceride composition and inherent reactivity (van den Berg et al. 2004). Experiments have shown that all straight-chain saturated fatty acids yield zinc salts capable of forming seeds (Elm 1957). Zinc soaps produced from a standard grade of zinc oxide pigment in combination with different fatty acids showed that as chain length increased, rates of reaction decreased (Morley-Smith 1958). A rapid increase

in soap formation was observed with zinc oxide in linseed oil of acid no. 12 in comparison with linseed oil of lower acid group concentration (acid no. 4) (Jacobsen and Gardner 1941); acid number indicates the milligrams of potassium hydroxide required to neutralise the free fatty acids in one gram of oil. Alkyds containing oils with high proportions of saturated or mono-unsaturated fatty acids such as soya or tall oils have been found to be more prone to film disruption caused by zinc soap protruberances, however, distillation or segregation of the oil to reduce the proportion of saturated fatty acids was found to reduce susceptibility (Elm 1957, Bell 1970).

Fatty acids may also derive from other sources in the paint. Aluminium stearate is one common additive likely to be a potential source of stearic acid (Elm 1957, Ordonez and Twilley 1997, Tumosa 2001, Burnstock et al. 2007, Hoogland et al. 2007). Propionic acid has been used to form zinc propionate at the surface of zinc oxide pigment to modify oil/pigment interaction and properties in the wet state (Barnett 1949). Metal salts of organic acids are the form of many driers developed for the paint industry, including those prompted by the poor drying properties of zinc oxide in oil (Kastens and Hansen 1949, Taylor and Marks 1969). Additives such as calcium napthenate and cobalt driers, as well as resin acids from another early additive, rosin, were found to increase the solubility, dispersion and concentration of zinc soaps in oil, so paint in the tin would become progressively thicker but without skinning or separation (Ware and Christman 1916, Finnie et al. 1936, Hansen and Klauss 1971). In the applied film, high fatty acid concentration appeared to restrict oxygen absorption and drying; large zinc soap masses formed and enveloped portions of the cobalt drier, preventing the intended increase in oxygen uptake (Nicholson 1940). The opposite effect was observed when acidity was increased in films pigmented with titanium dioxide or zinc sulfide, shortening the induction period. An earlier study determined that zinc oxide has a reducing effect on cobalt driers, while titanium dioxide oxidises, influencing oxygen absorption (Finnie et al. 1936).

Water and relative humidity

Moisture has long been recognised as a factor in reducing the shelf life of mixed paints (Ware and Christman 1916). As little as 0.25% water was found to favour zinc-based seeding, with water facilitating liberation of fatty acids in oil-based paints via hydrolysis (Hansen and Klauss 1971). Addition of water caused zinc oxide–pigmented alkyd paints to thicken in storage and to have reduced opacity, but was also found to improve the gloss retention of paint films, the postulate being that soaps formed in milling improved dispersion in the paint (Bell 1970). Water was similarly found

to catalyse saponification in reconstructed recipes for lead soaps (Cotte et al. 2006), and high relative humidity levels had a similar effect (Keune et al. 2009). This sensitivity is significant given that oil-based paints pigmented with zinc oxide have been found to be strongly moisture-absorbing with accompanying volumetric swelling (Browne 1955) and to have high permeability to water vapour relative to paints pigmented with titanium dioxide or a variety of iron oxide pigments (Suryanarayana 1970).

Co-pigmentation

Zinc oxide has most commonly been used as a co-pigment in oil-based paints to confer various desirable properties both in artist and industrial paint formulations. Other metal ions with potential to influence paint film chemistry may also be present deriving from components other than pigments, for example, lead present in zinc paints as an impurity or via addition as a drier in traditional formulations.

Studies of zinc-related deterioration of paintings show that incidences commonly occur in the presence of lead white (Osmond et al. 2005; Shimadzu and van den Berg 2006; Maor and Murray 2008; Shimadzu et al. 2008). Zinc carboxylate aggregation in van Gogh's painting Les Alyscamps occurred in a zinc oxide-containing lead chromate layer (Van der Weerd et al. 2003). Additionally, zinc oxide present in a Naples yellow (lead antimonite) linseed oil paint reconstruction resulted in rapid zinc carboxylate formation under conditions of high humidity and light intensity (Keune et al. 2009). Research into settling of pigments in linseed oil housepaints revealed that addition of zinc oxide (at almost any ratio) to lead-based oil paint produced a thinner paint more prone to settling, with both pigments settling in proportion consistent with original composition (Beakes 1928).

Zinc and titanium oxides also interact strongly due to oppositely charged colloidal particles and mutual flocculation tendencies. These vary with particle size and relative proportions of the two pigments and can strongly influence the viscosity of water-based paint formulations and the stability of the resulting film (Princen and Devena-Peplinski 1964, Diebold et al. 2003). In oil-based alkyds addition of zinc oxide to rutile titanium paints also has an effect, with one study finding that lowering zinc oxide content with aim to reduce zinc soap protuberances may actually result in fewer larger aggregates disrupting the paint film (Bell 1970).

Paint films based on lead or titanium whites which independently demonstrate quite distinct physical/mechanical responses behave more like zinc oxide pigmented films in stress/strain tests when mixed with even small percentages of zinc oxide (Mecklenburg

2008). Similarly, addition of zinc oxide to oil films pigmented with basic lead carbonate or titanium dioxide was found to increase their water absorbency and swelling closer to that recorded for films pigmented with zinc oxide alone (Browne 1956).

Consequences for paintings conservation

Reactivity of zinc oxide in premixed paints on the shelf' and following exposure to relatively extreme environments such as paints used in exterior applications has not had immediate apparent consequences for easel paintings containing zinc oxide, although some early sources do remark on the brittleness of zinc oxide-based paints, (Arthur Herbert Church: The Chemistry of Paints and Painting, London 1890, cited in Carlyle 2001), supported by a body of anecdotal evidence and more recently articulated concerns (O'Hanlon 2007). A recent study links widespread structural instability in a group of mid 20th century abstract expressionist paintings to the presence of preparatory layers of zinc oxide based house paint (Rogala et al. 2010). A similar phenomenon is identified in a 1938 painting by Joan Miró where additions of the relatively slow-drying poppy oil are suggested as a contributing factor (O'Donoghue et al. 2006). And flaking of zinc containing oil paints from acrylic ground layers has been attributed to accumulation of zinc soaps at the interface (Maor and Murray 2008).

It is only in the past decade that deterioration of some paintings has been linked to the aggregation of zinc soaps. One example includes a work by Vincent van Gogh where lumps have erupted through the surface of the painting (Van der Weerd et al. 2003). Other studies have also identified zinc carboxylate aggregates within paintings, apparently similar to the phenomenon of lead carboxylate protrusions responsible for deterioration of earlier paintings (Boitelle and van den Berg 2005, Osmond et al. 2005, O'Donoghue et al. 2006, Shimadzu and van den Berg 2006, Zümbuhl and Fuesers 2006). Impacts of zinc oxide saponification on surface appearance have also been considered (Shimadzu et al. 2008); increased transparency of paints affected by lead soap formation is now recognised to be responsible for devastating changes in appearance of some paintings (Zucker 1999, Noble et al. 2005, Noble and Boon 2007, Townsend et al. 2007, Zucker and Boon 2007). Remineralisation within zinc soap aggregates has also been observed, typically zinc carbonate (Keune 2005) but also zinc sulfate precipitation in two 1950s paintings from Hanoi, Vietnam, which implies a link between environment and manifestation given the relatively humid, polluted environment to which these paintings have been exposed (MacMillan 2007; Ebert 2008). Formation of zinc carbonate was also found by

German researchers in association with hardening and cracking of early 20th century zinc-based housepaints (HW 1925).

Related research and insights

Substantial research has been undertaken in relation to deterioration of paintings associated with lead soap aggregation, and indications are that similar mechanisms are involved when the more reactive zinc oxide is present. Both lead- and zinc-based aggregates have been shown to comprise soaps of the saturated C16 and C18 monocarboxylic fatty acids, palmitic and stearic acid, rather than of the more reactive and prevalent unsaturated C_{18:1-3} carboxylic acids originally present in the oil (Higgitt et al. 2003; Keune and Boon 2007). Problematic crystalline lumps forming in paint stock have been characterised as zinc salts of the same fatty acids (Elm 1957; Hansen and Klauss 1971). In paintings, azelaic acid, a common product of oxidative degradation of unsaturated C18 fatty acids predominant in drying oils, is frequently found around the perimeter of aggregates (Boon et al. 2005). A phase separation appears to occur, possibly explained by differences in polarity or unfavourable chain packing configurations (Plater et al. 2003). The presence of two phases within an aggregate has been taken to suggest that the compounds were present and mobile at the same time, implying soap formation occurred during the drying of the oil (Keune and Boon 2007). In other paintings monocarboxylic fatty acids appear to have separated from the mature crosslinked network and reacted with lead-containing pigment, causing localised volume expansion and deformation of surrounding paint (Keune and Boon 2007). Monocarboxylic lead soaps have also been implicated in the formation of white crusts on 17th century paintings; moisture gradients and capillary forces are discussed as possible drivers of migration to the surface (van Loon 2008). This is in contrast to findings in relation to efflorescence on modern paintings, where colours containing pigments capable of forming soaps tend not to be affected, and the formation of fatty acid soaps is thought to immobilise and prevent migration of stearic and palmitic acids to the surface (Ordonez and Twilley 1997).

Oleic acid levels may be a significant indicator of the predisposition for paints based on zinc oxide to be brittle and subject to flaking. Recent research has identified high levels of oleic acid in mid-20th century paintings exhibiting structural weakness (Rogala et al. 2010). These levels are unusual for paintings of this age as oleic acid (C_{18:1}) would normally oxidise to azelaic acid in the course of paint cure. The particular crystal lattice orientation of zinc carboxylate molecules within paint layers is postulated to lock oleic and

other unsaturated fatty acids acid in place, restricting oxidation and cross-linking reactions (Rogala et al. 2010). The result is a hard, brittle film. Mechanical testing of paints containing zinc oxide confirms a high modulus with extremely low-breaking strain (Suryanarayana 1970, Mecklenburg 2008).

Conclusion

Zinc oxide is a prevalent pigment in oil-based paintings from the late 19th century through until the present day. Developments and variety in pigment production and paint formulation, and artists' use of paints intended for both artist and industrial applications mean that a range of properties can be expected in these paints. The reactivity of zinc oxide in oil-based media has implications for the stability of paintings containing the pigment. Knowledge of specific pigment properties, fatty acid composition, and the influence of additives and environmental conditions on component interactions is critical to our interpretation of the appearance, condition and chemical analysis of these works. Greater understanding of the circumstances likely to favour development of associated degradation phenomena will improve our capacity to identify the most vulnerable paintings and to implement appropriate conservation strategies.

Acknowledgements

Thanks go to all those who made work available in unpublished or manuscript form, including Marion Mecklenburg, Dawn Rogala, Bettina Ebert and Leslie Carlyle; to Paula Dredge for sharing valuable findings made in the course of her own research; to John Dixon for willingly sharing his recollections of time in the paint industry; and to my supervisors, Profs John Drennan and Michael Monteiro, for their support. The ARC and industry partners are acknowledged for their contributions to Linkage Project, *The Twentieth Century in paint*.

Author biography

Gillian Osmond has a B. Applied Science in the conservation of cultural materials (paintings) from the University of Canberra (CCAE), 1988. During 1991–92 she was a research intern at Tate in London 1991–92 using microscopy of paint cross-sections to compare artists' oil paints exposed to different ageing environments. She has been conservator, paintings, at the Queensland Art Gallery/Gallery of Modern Art since 1988 and is currently a PhD candidate at the University of Queensland investigating the role of zinc oxide in deterioration of oil-based paints under the auspices of ARC linkage grant, *The Twentieth Century in Paint*.

References

- Barnett, CE 1949, 'Physics and Chemistry of Pigments',

 Industrial & Engineering Chemistry vol. 41, no. 2, pp. 272–9.

 Beakes, HL 1928, 'Settling of Pigments in House Paints',

 Industrial & Engineering Chemistry vol. 21, no. 7, pp. 732–4.
- Bell, SH 1970, 'Zinc oxide hazing', Paint and Varnish Production April 1970 pp. 55–60.
- Boitelle, R and van den Berg, KJ 2005, 'A technical examination of Odilon Redon's paintings from the Bonger Collection, Van Gogh Museum', *ArtMatters: Netherlands technical studies in art* vol. 3 pp. 66-81.
- Bomford, D, Kirby, J, Leighton, J and Roy, A 1990, Art in the making: Impressionism, London, National Gallery Publications Limited.
- Boon, J, Keune, K and Zucker, J 2005, 'Imaging analytical studies of lead soaps aggregating in preprimed canvas used by the Hudson River School painter FE Church', *Microscopy and Microanalysis* vol. 11(Supplement 2), pp. 444–5.
- Brown, HE 1957, Zinc oxide rediscovered, New York, New Jersey Zinc Company.
- Browne, FL 1955, 'Swelling of paint films in water III: Absorption and volumetric swelling of bound and free films from air of different relative humidities', *Forest Products Journal* vol. 5 pp. 92–6.
- Browne, FL 1956, 'Swelling of paint films in water VIII: Swelling of linseed oil paints in water and organic liquids', Forest Products Journal vol. 6, pp. 312–8.
- Burnstock, A, van den Berg, KJ, de Groot, S and Wijnberg, L 2007, 'An investigation of water sensitive oil paints in 20th century paintings,' in Learner, TJS, Smithen, P, Krueger, JW, and Schilling MR (eds), Modern Paints Uncovered: Proceedings from the modern paints uncovered symposium, Tate Modern, London, May 16–19, 2006, The Getty Conservation Institute pp.177–88.
- Carlyle, L 2001, The artist's assistant: oil painting instruction manuals and handbooks in Britain 1800-1900 with reference to selected eighteenth-century sources, London, Archetype Publications.
- Cocks, EJ and Walters, B 1968, A history of the zinc smelting industry in Britain, London, George G Harrap & Co. Ltd.
- Cotte, M, Checroun, E, Susini, J, Dumas, P, Tchoreloff, P, Besnard, M and Walter, P 2006, 'Kinetics of oil saponification by lead salts in ancient preparations of pharmaceutical lead plasters and painting lead mediums,' *Talanta* vol. 70, pp. 1136–42.
- Currie, C and Smith, J 1994, 'The Biglin brothers turning the stake boat', by Thomas Eakins: a technical study reveals surprising techniques', AIC Paintings Specialty Group Postprints: papers presented at the 22nd annual meeting of the AIC, Nashville Tennessee, 10 June 1994, AIC pp. 18–23.
- Diebold, MP, Bettler, CR and Mukoda, DM 2003, 'Mechanism of TiO2/ZnO instability in latex paints', Journal of Coatings Technology vol. 75, no. 942 pp. 29–36. Dixon, J 2009, Personal communication with Technical

- Services Manager, Wattyl Australia P/L, email 12 September 2009.
- Dredge, P 1996, 'John Russell: a study of his Impressionist technique' in S-A Wallace, J Macnaughtan and J Parvey (eds), The articulate surface: dialogues on paintings between conservators, curators and art historians, Canberra, The humanities research centre, Australian National University/National Gallery of Australia pp. 265–77.
- Dredge, P, Schilling, MR, Gautier, G, Mazurek, J and Learner, T 2012, 'Lifting the lids off Ripolin. A collection of paint from Sidney Nolan's studio', Proceedings: From Can to Canvas. Early uses of housepaint by Picasso and his contemporaries in the first half of the 20th century, Marseille, May 25–26 and Antibes, May 27 2011, Journal of the American Institute for Conservation, special issue in press.
- Ebert, B 2008, Volume II: A scientific investigation into the degradation processes of zinc-based paints together with art historical research, MA thesis (Conservation of Fine Art), Northumbria University, Newcastle.
- Elm, AC 1957, 'Reevaluation of the function of pigments in paints', Official Digest (April) pp. 351–85.
- Farquharson Boan, R 1924, 'The manufacture of mixed paints', The Australasian Decorator and Painter, Melbourne, J.E. Bishop, January 1 pp. 94–9.
- Finnie, W, Grant, R and McColm, K 1936, 'The adsorption of metallic driers by pigments', *American Paint Journal* vol. 21 no. 8 pp. 7–10.
- Gardner, HA 1917, Paint researches and their practical application, Press of Judd and Detweiler, Inc., Washington D.C.
- Gautier, G, Bezur, A, Muir, K, Casadio, F and Fiedler, I 2009, 'Chemical Fingerprinting of Ready-Mixed House Paints of Relevance to Artistic Production in the First Half of the Twentieth Century. Part I: Inorganic and Organic Pigments,' Applied Spectroscopy vol. 63, no. 6, pp. 597–603.
- H.W. 1925, 'Notes on the durability and manipulation of zinc paints', The decorator and painter for Australia and New Zealand, Sydney, Bishop Bros., 1 October pp. 7–8.
- Hackney, S, Ridge, J and Townsend, JH 2002, 'Pre-Raphaelite technique and its consequences', *Preprints of the ICOM-CC 13th Triennial Meeting, Rio de Janeiro*, James and James pp. 426–31.
- Hackney, S, Townsend, JH and Ridge, J 2004, 'Pre-Raphaelite methods and materials' in JH Townsend, J Ridge and S
 Hackney (eds) Pre-Raphaelite painting techniques 1848–1856, London, Tate Publishing pp. 51–75.
- Hansen, CM and Klauss, HC 1971, 'Mechanism of paint seeding,' Industrial and Engineering Chemistry Product Research and Development vol 10 no. 2. pp 189–92.
- Harley, RD 1970, *Artists' pigments c.*1600-1835, London, Butterworths and IIC.
- Heckel, GB 1934, 'A century of progress in the paint industry', Journal of Chemical Education, vol. 11 no. 9 pp. 487–93. 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.
- Hoffmann, E and Saracz, A 1969, 'Weathering of Paint Films I. Chalking Caused by Zinc Oxide in Latex Paints', Journal of the Oil & Colour Chemists Association vol. 52 no. 2 pp.113–32.
- Hoffmann, E and Saracz, A 1971, 'Weathering of paint films III. Influence of wavelength of radiation and temperature on the chalking of latex paints', *Journal of the Oil & Colour Chemists Association* vol. 54 pp. 450–70.
- Hoogland, FG, van der Horst, J and Boon, JJ 2007, 'Liquefying oil paint in some late twentieth-century paintings' in Learner, TJS, Smithen, P, Krueger, JW and Schilling MR (eds), Modern Paints Uncovered: Proceedings from the modern paints uncovered symposium, Tate Modern, London, May 16–19, 2006, The Getty Conservation Institute: 282-283.
- International Zinc Association 2009, Commercial grades of zinc oxide, Viewed 7 June 2010, http://www.znoxide.org/commercial_grades.html>.
- Jacobsen, AE and Gardner, WH 1941, 'Zinc soaps in paints: zinc oleates', *Industrial and Engineering Chemistry* vol. 33 no. 10 pp. 1254–6.
- Jolly, JH 1993, 'Materials flow of zinc in the United States 1850–1990', Resources, Conservation and Recycling vol. 9 nos. 1–2 pp. 1–30.
- Kastens, ML & Hansen, FR 1949, 'Drier soap manufacture', Industrial & Engineering Chemistry vol. 41 no. 10, pp. 2080–90.
- Kemp, F, Wise, A and Hamilton, B 2004, 'Re-inventing Diddy: The examination and treatment of a pastel drawing on paper by Grace Cossington Smith', Collaboration and Connections: Postprints of the AICCM Paper, Books and Photographic Materials Special Interest Group Symposium, Sydney 1-3 April 2004, AICCM pp. 115–24.
- Keune, K 2005, Binding medium, pigments and metal soaps characterised and localised in paint cross-sections, PhD thesis, University of Amsterdam, Amsterdam.
- Keune, K and Boon, JJ 2007, 'Analytical imaging studies of cross-sections of paintings affected by lead soap aggregate formation', Studies in Conservation vol. 52 no. 3 pp. 161–76.
- Keune, K, Hoogland, F, Boon, JJ, Peggie, D and Higgitt, C 2009, 'Evaluation of the "added value" of SIMS: A mass spectrometric and spectroscopic study of an unusual Naples yellow oil paint reconstruction,' *International Journal of Mass Spectrometry* vol. 284 nos. 1-3, pp. 22–34.
- Kühn, H 1986, 'Zinc white', in Feller, RL (ed) *Artists' pigments*, Cambridge University Press, vol. 1, pp. 169–86.
- MacMillan, S 2007 A report on the art historical investigation, condition, technical examination and initial investigations into the conservation treatment of two paintings on canvas by Vietnamese artist Nguyen Trong Kiem (1933–1991) dated 1963; in conjunction with scientific investigation of various tube paints used by Vietnamese artists during the mid C20th, and

- the materials, degradation mechanisms and conservation issues regarding the two paintings, MA thesis (Conservation of Fine Art), Northumbria University, Newcastle.
- Maor, Y and Murray, A 2008, 'Delamination of Oil Paints on Acrylic Grounds', Materials issues in art and archaeology VIII, Materials Research Society, Symposia Proceedings, vol.1047, pp. 127–36.
- Mecklenburg, MF 2008, Meccanismi di cedimento nei dipinti su tela: approcci per lo sviluppo di protocolli di consolidamento Failure Mechanisms in Canvas Supported Paintings: Approaches for Developing Consolidation Protocols, I Talenti. Metodologie, tecniche e formazione nel mondo del restauro, Il Prato, Padova
- Mecklenburg, MF, Tumosa, CS and Erhardt, D 2005, 'The changing mechanical properties of aging oil paints', *Materials Issues in Art and Archaeology VII*, Materials Research Society Symposium Proceedings vol. 85, pp 23–4.
- Morley-Smith, CT 1950, 'The development of anti-chalking French Process zinc oxides', *Journal of the Oil & Colour Chemists' Association* vol 33, pp 484–501.
- Morley-Smith, CT 1958, 'Zinc oxide—a reactive pigment', Journal of the Oil & Colour Chemists' Association vol. 41(January), pp. 85–97.
- Nicholson, DG 1940, 'Drying of Linseed Oil Paint Effect of Acidity upon Rate of Oxygen Absorption', *Industrial & Engineering Chemistry* vol. 32 no. 9, pp. 1259–61.
- Noble, P and Boon, JJ 2007, 'Metal soap degradation of oil paintings: aggregates, increased transparency and efflorescence,' AIC Paintings Specialty Group Postprints: papers presented at the 34th Annual Meeting of the AIC, Providence, Rhode Island, June 16–19 2006, AIC pp. 1–15.
- Noble, P, van Loon, A and Boon, JJ 2005, 'Chemical changes in old master paintings II: darkening due to increased transparency as a result of metal soap formation', *Preprints of the ICOM Committee for Conservation 14th Triennial meeting, The Hague 12–16 September 2005*, James and James pp. 496–503.
- O'Donoghue, E, Johnson, AM, Mazurek, J, Preusser, FD, Schilling, MR and Walton, MS 2006, 'Dictated by media: conservation and technical analysis of a 1938 Joan Miro canvas painting', The object in context: Crossing Conservation Boundaries: Contributions to the Munich Congress 28 August–1 September 2006, IIC pp. 62–8.
- O'Hanlon, G, 2007, 'Zinc white: problems in oil paint', viewed 24 October 2007, <www.naturalpigments.com/education/article.asp?ArticleID=127>.
- Oil and Colour Chemists' Association 1966, 'Pigments, dyestuffs and lakes', Paint technology manuals, London, Chapman and Hall for the Oil and Colour Chemists' Association.
- Ordonez, E and Twilley, J 1997, 'Clarifying the haze: efflorescence on works of art' in WAAC Newsletter vol. 20 no. 1, reproduced from *Analytical Chemistry* 69(13): A416-A422, viewed 14 October 2009, < http://cool.conservation-us.org/waac/wn/wn20/wn20-1/wn20-108.html>.

- Osmond, G, Keune, K and Boon, J 2005, 'A study of zinc soap aggregates in a late 19th century painting by RG Rivers at the Queensland Art Gallery', AICCM Bulletin vol. 29 pp. 37–46
- Osmond, G 2010, Unpublished results of SEM-EDX analysis of samples from 6 paintings by E Phillips Fox, reports dated 30.07.10, 06.08.10, 25.08.10, 02.09.10, 23.09.10.
- Pilz, K 2005, 'Zinc white', Student report (Department of Restoration and Conservation Studies), University of Applied Sciences, Cologne.
- Plater, MJ, De Silva, B, Gelbrich, T, Hursthouse, MB, Higgitt, CL and Saunders, DR 2003, 'The characterisation of lead fatty acid soaps in 'protrusions' in aged traditional oil paint', *Polyhedron* vol. 22 no. 24, pp. 3171–9.
- Princen, LH and Devena-Peplinski, M 1964, 'Effect of particle size on the mutual flocculation between zinc oxide and titanium dioxide', *Journal of Colloid Science* vol. 19 no. 9, pp. 786–97.
- Rogala, D, Lake, S, Maines, C and Mecklenburg, M 2010, 'Condition problems related to zinc oxide underlayers: examination of selected Abstract Expressionist paintings from the collection of the Hirschhorn Museum and Sculpture Garden, Smithsonian Institution', Journal of the American Institute for Conservation vol. 49 no. 2, pp. 96–113.
- Roy, A 1987 'The materials of van Gogh's 'cornfield, with cypresses', *National Gallery Technical Bulletin*, vol. 11, pp. 50–9.
- Salvin, SB 1944, 'Influence of zinc oxide on paint molds', Industrial and Engineering Chemistry vol. 36, pp. 336–40.
- Shelton, R 2010, Personal communication between Umicore Australia Ltd. via John Dixon (Wattyl Paints), email 28 June 2010.
- Shimadzu, Y, Keune, K and van den Berg, KJ 2008, 'The effects of lead and zinc white saponification on surface appearance of paint', Preprints of the ICOM Committee for Conservation: Preprints of the 15th Triennial Meeting, New Delhi, 22–26 September 2008, New Delhi, Allied Publishers Pvt Ltd, vol. II, pp. 626–2.
- Shimadzu, Y and van den Berg, KJ 2006, 'On metal soap related colour and transparency changes in a 19th century painting by Millais', Reporting Highlights of the de Mayerne Programme, JJ Boon and ESB Ferreira, The Hague, Netherlands Organisation for Scientific Research (NWO) pp. 43–52.
- Suryanarayana, NP 1970, 'Critical pigment volume concentration of some oxide pigments', *Journal of the Colour Society* vol. 9, no.2, pp. 2–6.
- Taylor, CJA and Marks, S, (eds.) 1969, Solvents, oils, resins and driers, Paint technology manuals, London, Chapman and Hall on behalf of the Oil and Colour Chemists' Association.
- The decorator and painter for Australia and New Zealand 1925, 'The Mascot Smelting Works', Sydney, Bishop Bros. April 1 pp. 187–8.
- Townsend, J, Carlyle, L, Khandekar, N and Woodcock, S 1995

- 'Later nineteenth century pigments: evidence for additions and substitutions' *The Conservator* vol. 19, pp. 65–78.
- Townsend, JH, Jones, R and Stoner, K 2007, 'Lead soap aggregates in sixteenth- and seventeenth-century British paintings', AIC Paintings specialty group postprints: papers presented at the 34th Annual Meeting of the AIC, Providence, Rhode Island, June 16-19 2006, AIC pp. 24–32.
- Tumosa, CS 2001, 'A brief history of aluminium stearate as a component of paint', WAAC Newsletter vol. 23, no. 3, viewed 14 October 2009, http://cool.conservation-us.org/waac/wn/wn23/wn23-3/wn23-304.html.
- van den Berg, JDJ, Vermist, ND, Carlyle, L and Holčapek, M 2004, 'Effects of traditional processing methods of linseed oil on the composition of its triacylglycerols', *Journal of Separation Science* vol. 27, pp. 181–99.
- Van der Weerd, J, Gelddof, M, van der Loeff, LS, 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. 407–16.
- van Loon, A 2008, Color changes in chemical reactivity in seventeenth century oil paintings, PhD thesis, University of

- Amsterdam, Amsterdam.
- Ware, EE and Christman, RE 1916, 'A study of the effect of storage on mixed paints', *The Journal of Industrial and Engineering Chemistry* October 1916, pp. 879–83.
- Winter, G and Whittem, RN 1950, 'Fluorescence and photochemical activity of zinc oxides', *Journal of the Oil & Colour Chemists' Association* vol. 33 (November), pp. 477–83.
- Wöll, C 2007, 'The chemistry and physics of zinc oxide surfaces', *Progress in Surface Science* vol. 82, pp. 55–120.
- Zucker, J 1999, 'From the ground up: the ground in 19th-century American pictures' *Journal of the American Institute for Conservation* vol 38, pp. 3–20.
- Zucker, J and Boon, J 2007, 'Opaque to transparent: paint film defects in the work of Frederick Church and the Hudson River School', AIC Paintings Specialty Group Postprints: papers presented at the 34th Annual Meeting of the AIC, Providence, Rhode Island, June 16–19 2006, AIC pp. 33–41.
- Zümbuhl, S and Fuesers, O 2006, 'The formation of protrusions in the later works of Alexej von Jawlensky', The object in context: crossing conservation boundaries: contributions to the Munich Congress 28 August–1 September 2006, Munich, IIC, pp. 309.