Charting the Development of Oil-Based Enamel Paints Through the Correlation of Historical Paint Technology Manuals with Scientific Analysis

Maria Kokkori, Francesca Casadio, Ken Sutherland, and Marc Vermeulen

Abstract This paper presents an overview of developments in oil-based enamel paint technology in the first half of the twentieth century and discusses the selection of ingredients that had a significant impact on the properties of the paints: pigments, extenders, driers, oils and resins. A review of period literature published in French and English is complemented by analysis of historical oil-based Ripolin enamel paint samples produced in France in the years 1910–1950 and a small selection of artists' paint tubes of the same era from the Art Institute of Chicago's reference collection. A range of analytical techniques including x-ray fluorescence spectroscopy (XRF), Fourier transform infrared spectroscopy (FTIR), pyrolysis gas chromatography-mass spectrometry with thermally-assisted hydrolysis and methylation (THM-Py-GCMS), scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (SEM-EDX) and thermogravimetric analysis have been used for the characterisation of the paint samples.

Keywords Oil-based enamel paints • Paint technology • Ripolin

Introduction

Alongside traditional artists' oil tube paints, the twentieth century saw the rapid development of oil-based, ready-mixed house paints (Standeven 2011). These non-artists' paints are sometimes referred to as 'architectural', 'oleoresinous', 'industrial', 'protective', 'decorative', 'ready-to-use', 'enamel' or 'ripolin' (Sabin 1927). Ripolin is the trade name for a specific French brand of commercial paints manufactured for household and other uses; however, the term 'ripolin' was often used to refer to enamel paints in general (Labordere and Anstett 1913). From

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1897 until the end of the Second World War, Ripolin production took place on the premises of the famed fine artists' materials manufacturer Lefranc, in Issy-les-Moulineaux, a suburb of Paris. The close links between the production of oil-based tube paints and house paints is underscored by the fact that the administrators and President of the Ripolin factory were chosen from among the Lefranc family.

Artists including Pablo Picasso, Wassily Kandinsky, Francis Picabia, László Moholy-Nagy, René Magritte, Aleksandr Rodchenko, Nathan Altman and Le Corbusier, among others, are documented to have used commercially-available, non-artists' paints, such as Ripolin and other brands of house, architectural, car and boat paints, because of their desirable surface qualities and handling properties. Recent research at the Art Institute of Chicago for the first time fully explores the composition of French oil-based Ripolin enamel paints, providing a useful complement to ongoing research on the evolving formulations of artist's oil paint tubes of the first half of the twentieth century.

Oil-Based Enamel Paint Formulations

The term *oil enamel* was used to describe ready-to-use paints that contained linseed oil or a blend of oils with resins and pigments, and connoted a hard, glossy surface analogous to porcelain enamel. Enamel paints were formulated to have a number of desirable characteristics including gloss and colour retention, elasticity, opacity, consistency, spreading capacity, good levelling, and durability (Jennings 1919). Driers and thinners were used as required in order to achieve satisfactory application and performance characteristics.

Pigments, Extenders, and Driers

In the first half of the twentieth century the white pigments most commonly encountered in house paint recipes were lead white, zinc white, zinc sulfide, lithopone and titanium dioxide white. Different grades and modifications of each of these pigments affected the properties of the resulting paint. Zinc oxide and leaded zinc oxide, in addition to their use as primary pigments, were used as modifiers in conjunction with various other pigments in order to control such factors as dirt collection, chalking, fading and mildew (Nelson 1935a, 1940). Zinc-based pigments were very important in house paint formulations because of their high durability, achieved by the production of acicular particles and the elimination of colloidal fines (Eide and Depew 1936). Although French Ripolin paints were consistently produced exclusively with zinc oxide as the white pigment before 1950 (Gautier et al. 2009), other French manufacturers of enamel paints made use of other whites. This has been demonstrated by the analysis of three cans of white Valentine paint from the Parisian studio of Wassily Kandinsky (roughly dated to the 1940s) that were shown to contain titanium dioxide white (anatase) in combination with minor amounts of zinc white (McMillan et al. 2013), as well as analysis of oil-based enamel paints used by Pablo Picasso in Antibes in 1946, which were shown to contain zinc white in mixtures with barium sulfate, lithopone or titanium dioxide white (anatase) (Casadio and Gautier 2011; Casadio et al. 2013). Zinc pigments gained popularity in the paint industry over lead white because of health hazards associated with the latter (Truelove 1922; Nelson 1935b). For white house paint formulations, zinc white was often recommended as a fungicide and in some can linings as a sulfide scavenger (Trott 1928). SEM examination of Ripolin white enamel paint samples highlighted the predominant presence of particles of zinc oxide of small diameter (150–300 nm) with rare occurrences of acicular crystals. The latter, on the other hand, are more prevalent in samples of Lefranc zinc white artist's tube oil paints of the same period, which are also characterised in general by pigments of larger particle sizes (Figs. 1 and 2).

The size and form of the pigment particles were shown to have a great influence upon the life of enamel paints. Authors referred to a 'French' process for zinc oxide pigments, also called the 'seal' type, which produced a relatively uniform pigment particle size distribution resulting in a 'very fluffy product with exceptionally good suspended qualities, excellent packaging qualities, good leveling, holding-out qualities, high gloss and gloss retention, good colour, resistance to yellowing or change in tint, and washability, used in enamels of the highest grade.' (Nelson 1940) High-resolution, high sensitivity synchrotron radiation XRF nanoprobe analysis of the zinc oxide pigment particles employed for both the Ripolin enamels and Lefranc artists' tube paints have shown them to be of the highest purity, i.e. free of lead and cadmium impurities, and only containing trace amounts of iron, which have been demonstrated to correspond to the 'white seal' grade of the time and the purest white colour, typically reserved for pharmaceutical uses and gloss enamel paints of the highest quality (Casadio and Rose 2013).

Extenders were used to improve durability, eliminate running of paint and to reduce costs. Mica and magnesium silicate were preferred over other extenders such as barites, whiting, china clay, calcium sulfate, and ground silica. Magnesium silicate was widely recommended for use in trim paints to provide resistance to chalking, cracking and fading (Parker 1943). Interestingly, oil-based French Ripolin enamel paints before 1950 have been found to contain very few extenders, with small amounts of barium sulfate detected only in colour charts dating to the 1930s and 1940s (Gautier et al. 2009), while on the other hand artist's tube paints from Lefranc and a few other French manufacturers of the time have been often shown to contain extenders based on barium sulfate and calcium compounds (calcite and gypsum) and other whites such as lead white and titanium dioxide white (Casadio and Rose 2013). Importantly, the aluminium stearates and magnesium silicates that have been identified as problematic with regard to the condition of paintings made with modern oils have not been documented in Ripolin enamel paints (Noble and Boon 2007). The use of few or no extenders ensured very intense colours for the

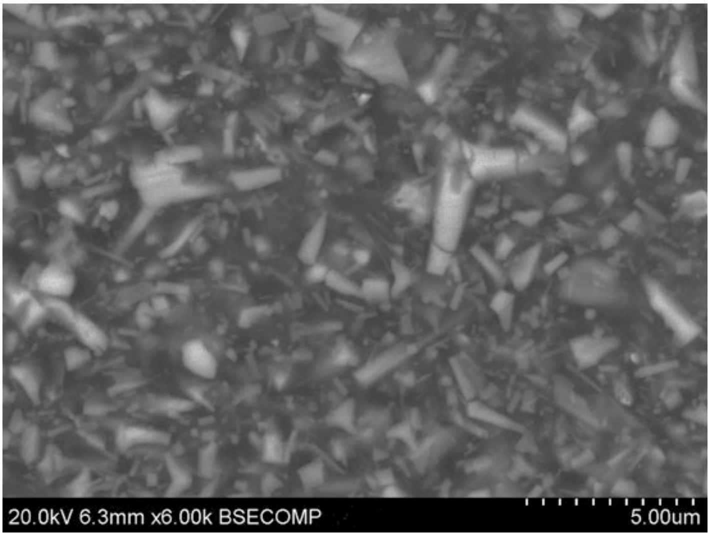

Fig. 1 Backscattered electron image of a Lefranc zinc white tube paint sample

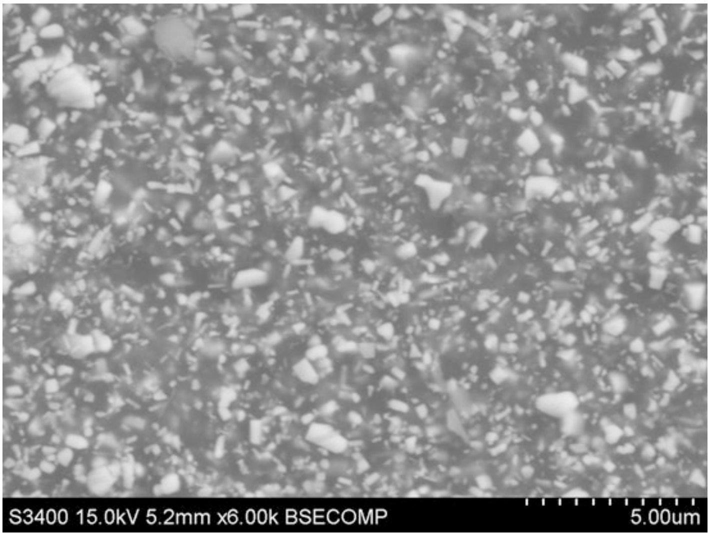

Fig. 2 Backscattered electron image of a Ripolin zinc white house paint sample

Ripolin paints, with superior hiding power (requiring a single coat of paint as opposed to the multiple applications necessary for other brands of enamels). This, together with a wide availability in a much broader range of ready-mixed colours than many of its competitors, likely contributed to the enormous commercial success of this brand of paint.

Driers were mainly used in exterior house paints to set or harden the oil in the paint film so that it would not collect dust or dirt, and could withstand abrasion. Metallic soaps including stearates, palmitates, oleates and naphthenates of aluminium, calcium and zinc, were frequently used to accelerate the oxidation, polymerisation and gelation of the oil and produce desired flatting effects (Licata 1933). For example, lead and manganese linoleate or naphthenates were recommended for use to the extent of 0.6 % lead and 0.02 % manganese as metal, calculated relative to the non-volatile vehicle in the paint. Cobalt was not highly recommended as a drier for exterior paints since its presence was associated with chalking and fading. Linoleate driers were considered as satisfactory driers because they had good mixing and wetting properties. They also permitted a higher thinner content compared to other driers and yielded satisfactory brushing with good leveling and gloss. Analysis with micro-FTIR spectroscopy of Ripolin and artist's tube paints did not allow the detection of features specific to individual driers, most likely because in the percentages used they are below the detection limit of the technique. Ripolin enamel paints containing zinc white display broad FTIR bands centered at 1,580 and 1,440 cm^{-1} that are related to zinc carboxylates. These are most likely due to reaction of the oil-based binding medium with the zinc white pigment particles, and not original components of the paints. On the other hand for tube paints, while the broad zinc carboxylate bands remain, a sharp peak at 1,541 cm^{-1} that is characteristic of zinc stearate is clearly visible (Fig. 3). In addition to zinc driers, preliminary investigations with inductively-coupled plasma mass spectrometry highlighted the presence of driers based on lead, manganese and cobalt in both tube and Ripolin enamel paints (Muir et al. 2011).

In house paints the volume relationship of pigment to binder was considered more pertinent than the weight relationship because of its predominating influence

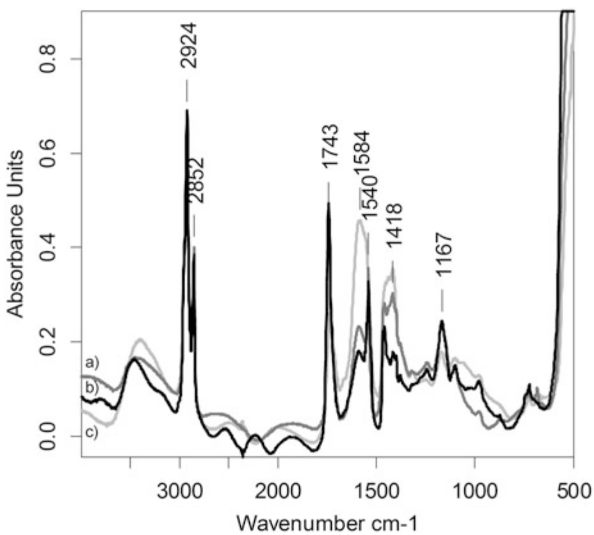

Fig. 3 FTIR spectra of (**a**) reference Lefranc tube paint sample of zinc white (#2007.48); (**b**) reference Lefranc tube paint sample of zinc white (#2007.70); (**c**) reference Ripolin house paint sample of zinc white (#HP002)

on the physical and optical properties of the paints (Pickett 1939). Qualitatively, even a simple visual assessment of the particle distribution and pigment/binder ratios in the SEM images of tube and Ripolin paints illustrated in Figs. 1 and 2 makes it immediately apparent that Ripolin paints have a higher proportion of binder to pigment, when compared to the tubes. This was confirmed with thermogravimetric analysis (Muir et al. 2011) that showed as much as a 30/70 % w/w ratio of pigment to binder in Ripolin ultramarine blue paints, as compared to almost the opposite ratio of 65/35 % pigment to binder in similarly pigmented tube paint.

The essential steps in the preparation of house paints as described in the technical literature included fine grinding of pigments, mixing, thinning and tinting. The primary purpose of the mixing was to distribute the ingredients into a uniform paste and to wet the pigments with the vehicle as thoroughly as possible. Grinding was associated with dispersing and reducing in size the individual pigment particles. The ground paste was mixed with additional quantities of oils, varnishes, driers, and thinners.

Binders and Resins

Traditionally household paints contained linseed oil alone, but as oils from an increasing array of plant and animal sources became available to paint manufacturers throughout the twentieth century, the use of oils in admixture became common to obtain optimal results. Authors recommended the use of tung oil in various combinations with linseed oil (Jolly 1930; Bohannon 1922) as well as other drying oils such as perilla, oiticica, soya bean, fish and dehydrated castor oil (Damitz et al. 1943). With respect to linseed oil, the refined oil was recommended because of its good wetting and grinding characteristics, however, it was characterised by low viscosity, easy brushing, poor levelling and relatively low gloss. A combination of refined with boiled linseed oil was also available where the heat-treated (boiled) oil was added to improve durability, levelling and gloss. Heat-treated oils have higher viscosities and were used in oil enamel paints to improve application and performance characteristics. Enamels based on heat-treated oils had good gloss and colour retention, and produced flexible, durable films. They were also able to hold more pigment than the resin-based enamels, which meant that fewer coats were required (Nylen 1965).

Historically, the highest quality enamels were known to originate from Holland, where oxidised linseed oil was employed as the vehicle (Chatfield 1947). In the Netherlands, as well as in England and Germany, manufacturers also prepared a linseed oil of heavy consistency known as blown oil by boiling at moderate temperatures, without the addition of drying mediums, and blowing air through the oil during the boiling process (Andés 1901).

Mass-spectrometric analysis (electrospray and direct-temperature-resolved mass spectrometry) of Ripolin paints suggested a high degree of cross-linking and chemical modification of the oil medium resulting from pre-polymerisation, and

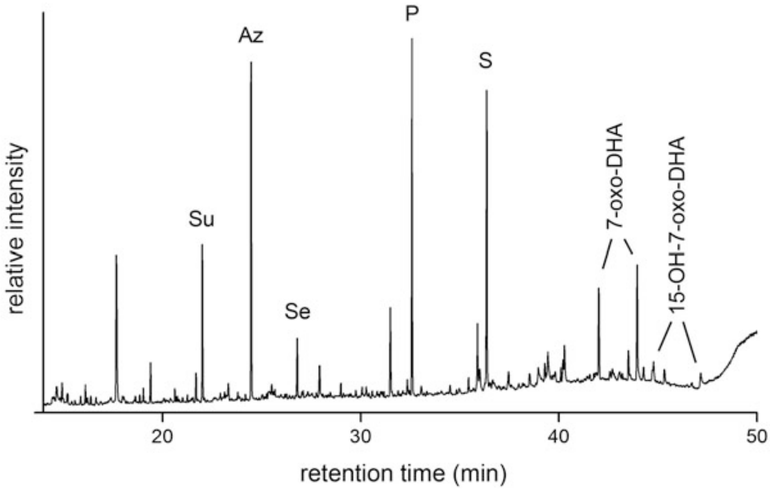

Fig. 4 THM-Py-GCMS total ion chromatogram of a reference Ripolin house paint sample of black paint (#HP064). *Su* suberic acid, *Az* azelaic acid, *Se* sebacic acid, *P* palmitic acid, *S* stearic acid, *7-oxo-DHA & 15-OH-7-oxo-DHA* oxidised forms of dehydroabietic acid; all compounds detected as methyl derivatives

THM-Py-GCMS analysis confirmed the presence of drying oil, in most cases combined with diterpene (Pinaceae) resin (Fig. 4) (Kokkori et al. 2013) a practice also described in the literature (Horton Sabin 1904; Uebele 1913; Cruickshank 1915). Castor oil was identified only in two samples of red Ripolin paint pigmented with alizarin; the identification of other types of drying oil such as soybean, perilla or fish oil recommended in the technical literature was not possible because of the lack of specific chemical markers for these materials. Aside from some variations in the proportions of oil and resin in the binders relating to the requirements of specific colours, the composition of Ripolin paints appears to have remained fairly consistent in the first half of the twentieth century. On the other hand, preliminary analyses of binding media in artists' tube paints carried out for this study suggested a higher degree of variability in formulations with respect to oil types and additives. The organic components of the Ripolin and tube paints will be discussed in more detail in separate papers (Kokkori et al. 2013 (*in preparation*), 2014).

Conclusions

The work presented here considers the composition of Ripolin paints, a very important brand of early twentieth century French oil-based enamel, as compared to artists' tube paints of the same period. Scientific data are interpreted in the larger context of industrial technical literature of the time. While much useful information has been uncovered in the process, a more in-depth study of the composition of modern oil paints needs to take place in order to fully understand works of art that contain them, and to inform their preservation. Open questions remain, in particular, the investigation of zinc carboxylates, their structure in relation to the particle size and shape of zinc oxide pigment, their mobility and their tendency to form aggregates. Additionally, a focus on the development of new strategies for the identification of different oils and resins in modern paints, especially those that may have undergone chemical modification as a consequence of the industrial processes of paint preparation, will be of great value.

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