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A comprehensive study of early 20th-century oil-based enamel paints: Integrating industrial technical literature and analytical data

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ABSTRACT

This paper presents a comprehensive study of the developments in oil-based industrial paint technology in Europe and North America in the first half of the 20th century, focusing on the selection of pigments, extenders, driers, oils, and resins, and their contribution to the final properties of the paints. The study also discusses the industrial methods of paint preparation and emphasizes the changes that took place in paint technology in that period. A review of period literature is combined with scientific analysis of historical oil-based enamel paints produced in France in the years 1890 to 1950 from the Art Institute of Chicago's reference collection, with a special focus on Ripolin paints.

INTRODUCTION

Oil-based enamel paints, manufactured for household and other uses in the beginning of the 20th century, became popular among avant-garde European painters because of their surface qualities and handling properties: Pablo Picasso, Wassily Kandinsky, Francis Picabia, René Magritte, and others are reported to have used Ripolin house paints in their works. The Ripolin brand of paints originated in the Netherlands, where it was developed by the chemist Carl Julius Ferdinand Riep in the early 1890s (Pelgrim 1994). These paints were so renowned that the term "ripolin" was often used to refer to a broader class of enamel paints in general, and soon became synonymous with modernity, sophisticated technology, excellent quality, and high performance. Although extensive research has been conducted on paint tubes, there is surprisingly little information on the industrial paint chemistry and technology, including house, architectural, car, and boat paints produced in the beginning of the 20th century. Their characterization can be greatly informed and enhanced by close study of the technical literature.

METHODS OF STUDY

The methodology used in this study consists of a systematic investigation of primary and secondary sources related to the industrial paint technology of the first half of the 20th century. Specifically, this paper examines a European and North American sample of over 60 technical manuals, handbooks and treatises, and patent literature since 1900. The extensive technical information found in these sources is complemented with material found in trade magazines, which mainly included advertisements of suppliers, products surveys, and homemade paint recipes.

The study of archival sources from the period is combined with scientific analysis of oil-based historic industrial paints from the Art Institute of Chicago's reference collection (Ripolin paints in Figure 1). Comparison of analytical data with written accounts places these findings in context, while testing the reliability of the documentary sources.

OIL-BASED ENAMEL PAINTS

Prepared or ready-mixed industrial paints were unknown up to the end of the 19th century (Heckel 1928). When they first appeared on the market,

Figure 1
Ripolin and other early enamel paints from the Art Institute of Chicago's reference collection

commercial painters were reluctant to use them, preferring to mix their own product and following their own specifications. Accordingly, the manufacturers of prepared paints made only slight progress until about the first decade of the 20th century, when factories were established in great numbers and ready-to-use paints reached wider markets (Gardner 1917). Consequently, the study of paint was given great impetus and the properties of paint materials were systematically investigated, resulting in radical changes in their composition and manufacture (Job 1918). The formulation of paints became a challenging assignment in the early 20th century. The paint industry introduced many innovations in paint making for what is now called enamel, industrial, decorative, ready-to-use, or house paint, exploring different types of raw or heat-processed oils, as well as the selective addition of resins and organometallic curing agents (Standeven 2013).

The term *oil enamel* was used to describe a range of paints that contained blends of oils with finely ground pigments and resins and/or varnishes and connoted a hard, glossy surface analogous to porcelain enamel (Bearn 1923). The use of oil-based enamel paints extended well beyond the development of alkyd paints in the late 1920s and was pervasive until the late 1940s. Enamels were the most expensive and the best quality paints and were designed to have the following characteristics: gloss and color retention throughout their life; hiding power, film hardness, good levelling; resistance to chalking, cracking and flaking; good resistance to dirt collection, discoloration and mildew growth; and adequate protection to the surface for a long period of time (Parker 1943).

HISTORY, TECHNOLOGY, AND ANALYSIS

Binding media: Oils and resins

The binder commonly used in oil-based enamel paints was composed of raw or refined linseed oil of relatively low acid number and with relatively non-reactive pigments. Acid-refined linseed oil was recommended because of its good wetting and grinding characteristics. However, raw and refined oils were characterized by low viscosity, easy brushing, poor levelling, and relatively low gloss. A combination of refined linseed oil with heat-treated oil was also available where the heat-treated oil was added to improve durability, levelling, and gloss.

Historically, the highest quality enamels were known to originate from Holland, where heat-treated oil was employed as binder. Heat-treated oils have higher viscosity and were used in oil enamel paints to improve application and performance characteristics (Chatfield 1947). In Holland, as well as in England and Germany, paint manufacturers also prepared a linseed oil of heavy consistency by boiling it without the addition of drying mediums, blowing air through it during the boiling process, and permitting the oil to age in tanks – the product was known as blown oil. The main characteristic of this oil was that no driers were added to the oil. Therefore, the blowing usually had to be continued for a longer period until there was a pronounced rise in the viscosity (*Drying oils and dryers* 1934). Enamels based on heat-treated oils had good gloss and color retention, and produced flexible, durable films. They also had greater body and were able to hold more pigment than other types of enamel paints, which meant that far fewer coats of paint application were required (Nylen 1965).

For optimum results and performance, several authors recommended the use of oils in admixture. For example, the use of tung oil in various combinations with linseed oil was recommended (Bohannon 1922, Jolly 1930), as well as the use of other drying oils such as perilla, oiticica, soya bean, fish, and dehydrated castor oil (Vannoy 1943, 278); however, it is challenging to distinguish these oils with mass spectrometric techniques.

Despite their good properties, heat-treated oil enamels were thick, viscous, and slow-drying; therefore, natural resins were used in the paint industry to improve the rheology of paints and to produce quick-drying, high-performance enamels (Cruickshank 1915). Several authors contended that genuine enamels comprised pure oil binders alone, and that any enamel containing resins or varnish should be described as “enamel-type paint,” whereas others stated that enamels could not be formulated without the addition of resins.

Early enamel paints, for interior and exterior work, were based on varnishes such as dammar (Horton Sabin 1904, Uebele 1913). The ratio of resin to oil in enamel paint played a major role in how it would behave as a finish, and hence what it would be best suited for. A “long-oil” mixture was one with a high ratio of oil to resin and, as a result, would produce a less hard and brittle finish, and retain its flexibility. A binder commonly used was composed of linseed oil and 8–12% heat-treated linseed oil; some paints were also produced with a binder composed of linseed oil fortified by the addition of 5–10% of resin; however, these proportions ranged considerably according to the paint industry and were adjusted for each color formulation.

In the first decades of the 20th century, high-gloss enamel paints comprised refined drying oils mixed with a semi-fossil resin, such as Congo copal, and/or a soft resin, such as colophony and good-quality opaque pigments. According to the technical literature, the resin was melted to “run” sufficiently and preheated linseed oil was added gradually. After its addition, the oil-resin mixture was reheated and the temperature was maintained until the oil had been incorporated satisfactorily and some “bodying” occurred. A small amount of rosin was often included to prevent the fossil resin from charring, and to aid its solubility in oil (Sanderson 1934). The mixture was thinned with spirit of turpentine. Authors emphasized the importance of heat control to avoid decomposition and cracking in order to obtain products of superior characteristics. The addition of glycerol was recommended to reduce acidity by esterification as well as the addition of basic pigment such as zinc oxide (Chatfield 1947). Other manuals described glossy vehicles containing an admixture of colophony; though this resin was regarded as a poor and unstable paint ingredient, it had been extensively used in enamel paint manufacture (Damitz et al. 1943, 228) in mixtures with drying oils and lime or zinc white or glycerol to control acidity (Scribe 1922). Technical manuals instructed commercial painters to make white and light-colored house paints using raw linseed oil and/or heat-treated linseed oil with very small quantities of resins, if any, whereas the addition of hard fossil resins in large quantities was strongly recommended for darker-colored enamel paints (Figure 2) (Damitz et al. 1943, 199–206).

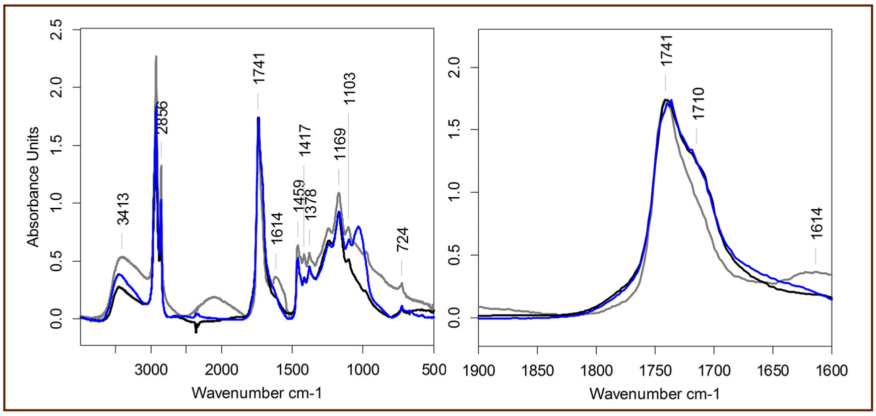

Figure 2

FTIR spectra of white, blue, and black Ripolin paints showing increased resin content for darker colors [HP009A Ripolin Blanc d'ivoire c. 1916; HP013C Ripolin Bleu outremer c. 1919; HP046D Ripolin Noir d'ivoire c. 1916]

The results of Py-THM-GC/MS analysis of Ripolin paints indicated the presence of drying oil, in most cases combined with diterpene *(Pinaceae)* resin (Figure 3). Two isolated cases of a red (Rouge de Chine) paint formulated with the addition of castor oil were also identified. Compounds characteristic for copal resins have not been identified in the examined samples. However, in copal/oil mixtures, the aging process changes dramatically the relative amount of compounds characteristic for copals, especially when the resins have been subjected to severe heat treatments in combination with drying oil. This especially holds for diterpenoid, low-molecular-weight compounds that are traditionally used as markers for GC/MS analysis (van den Berg et al. 1999, 2002, 2003).

Mass spectrometric analysis of Ripolin paints highlighted a high degree of prior cross-linking and chemical modification of the paint medium (prepolymerization). The relative amount of free radicals would have been

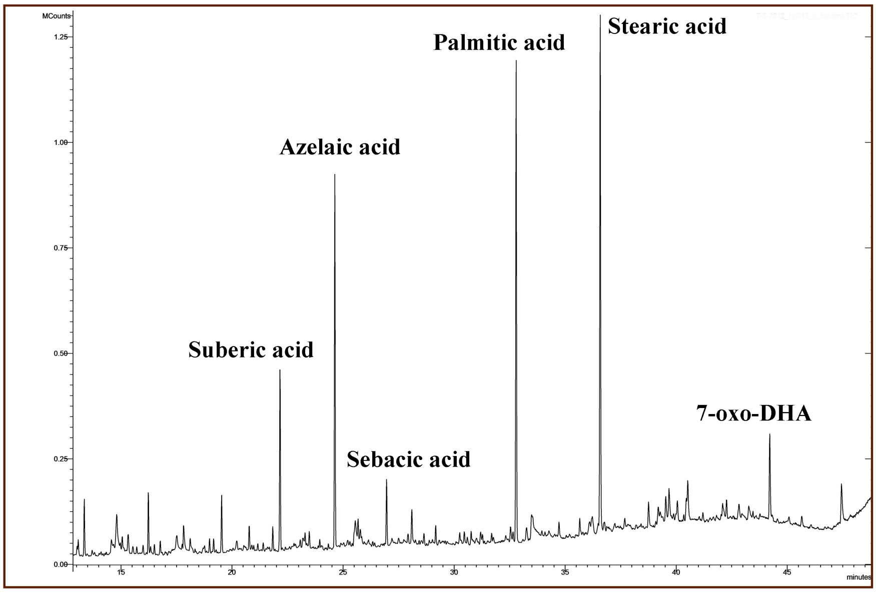

Figure 3

Py-THM-GC/MS spectrum of a reference Ripolin sample of blue paint [HP013C Ripolin Bleu outremer] high in the end product, and one way to quench those was by mixing the paint with diluents rich in unsaturated hydrocarbons. Knowledge of this process chemistry was reflected in the Ripolin labels, instructing to use only turpentine as diluent. Thinners were used to bring the paint to a good working consistency. The thinner content was important; high thinner content contributed to low costs, high spreading rates, and thin films.

Pigments, driers, and extenders

The white pigments most commonly encountered in the technical literature for house paints produced in the beginning of the 20th century included zinc oxide, zinc sulfide, lead white, lithopone, and titanium white (Nelson 1935). According to Gardner (1911), paint made from any mixture of more than one white opaque pigment, either when used alone or in combination with very small percentages of inert pigments, was considered superior to any one single pigment paint.

For white enamel paint formulations, zinc white was recommended because of hygienic reasons and as a fungicide, and in some can linings as a sulfide scavenger (Trott 1928). A careful selection of colors was considered necessary to assure that house paints would have good tint retention. For colored paints, earth pigments were considered satisfactory as well as chrome-pigments, alizarin, red lake, ultramarine, Prussian blue, phthalo-pigments, and carbon black. There were many grades and modifications of each of these pigments which obviously affected the properties of the resulting house paint.

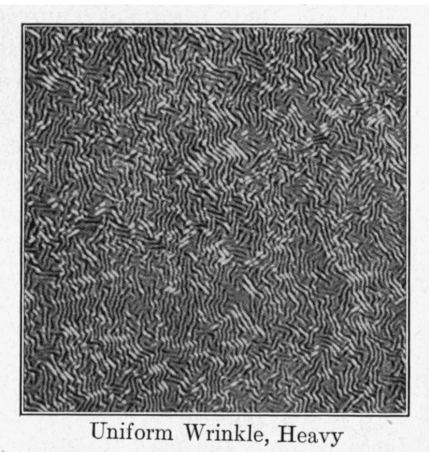

Figure 4
a) wrinkling pattern of a reference Ripolin alkyd sample [HP065A];
b) wrinkling pattern as documented in technical literature

Selected extenders were recommended for use to obtain improved durability as well as to reduce costs, such as magnesium silicate, barites, silica, alumina, whiting, china clay, and calcium sulfate (Parker 1943). Oil-based French Ripolin paints before 1950 have been found to contain very few extenders, with small amounts of barium sulfate detected only in color charts dating to the 1930s and 40s (Casadio and Rose 2013). The use of few or no extenders ensured very intense colors for the Ripolin paints, with superior hiding power.

Driers commonly used included cobalt, lead, and manganese linoleate. Metal stearates have been used in the paint industry to help suspend pigments in oil to prevent separation, to reduce the amount of oil needed to wet the pigment, and/or to increase the body of the paint by forming a gel with the oil, thereby requiring less pigment (Gardner 1927). Also, metallic soaps including stearates, palmitates, oleates, and naphthenates of aluminum, calcium, and zinc were frequently used to accelerate the oxidation, polymerization, and gelation of the oil and produce desired flatting effects (Licata 1933).

Experiments with different ratios between resin and oil and the addition of selected driers in the 1920s led to the development of a group of novel products known as “wrinkled finishes” or “textured enamels.” These paint materials were designed to form an uneven surface of regular pattern upon drying (Figure 4). The early experiments concentrated on methods to control the wrinkling properties of tung oil when mixed with heat-treated linseed oil, copal and rosin resins, and selected driers such as cobalt and manganese (Root 1928).

In oil-based enamel paints the volume relationship of pigment to binder was also pertinent because of its predominating influence on the physical and optical properties of the paints (Pickett 1939). Generally, pigment volumes of about 25% to 50% were considered most acceptable because high pigment volumes had the tendency toward excessive chalking, whereas very low pigment volumes had a greater dirt affinity and a tendency to cracking. The darker tints, as well as the solid-color trim paints, had no standard recommendations for pigment concentration since pigments differ widely in hiding, paint-thickening power, and particle sizes.

In accordance, multi-analytical investigation of Ripolin paints highlighted the dominance of zinc-based whites as well as pigment percentage (w/w) with respect to binder of 63% for white and 31% for blue-colored paints (Muir et al. 2011). Analysis of oil-based enamel paints or other unknown brands used by Pablo Picasso in Antibes in 1946, were shown to contain zinc white in mixtures with barium sulfate, lithopone or titanium white (anatase) (Casadio and Gautier 2011, Casadio et al. 2013). Also, a mixture of zinc white, barium sulfate, and titanium white was identified in a Ripolin paint color chart from the late 1950s (Gautier et al. 2009).

All pigments described in the literature have been identified in reference Ripolin samples produced before 1950, with the exception of phthalo-pigments: the absence of cadmium pigments, emerald green, cobalt blues and violets, and vermilion was also confirmed. Correspondence with the Ripolin company documents the availability of phthalo-blue and monastral green pigments, but these have not been detected in the pre-1950 reference paints analyzed (Cloquet 1982).

The grinding and mixing operations were crucial steps for the production of oil-based enamel paints (Holley 1935). The reduction of size of both pigments and extenders was carried out using a burrstone mills or roller mills, and the mixing procedures aimed to distribute the ingredients into a uniform paste.

CONCLUSION

The study of early 20th-century oil-based enamel paints in artworks benefits from an interdisciplinary approach, addressing topics ranging from studies of contemporary paint technology to visual observations and investigation of molecular and elemental aspects of historic paint samples.

The study of industrial paint technology literature reveals how oil paint formulations changed over time, what materials were introduced and experimented with, which procedures were followed, and how processes were revised to improve quality. This information from bibliographic sources is pivotal in interpreting and contextualizing analytical results, especially for what concerns media analysis. Integrated with analysis of reference Ripolin paints, this study contributes to elucidating the technology of manufacture of industrial paints from the first half of the 20th century, an important factor for the knowledge and future preservation of artworks painted with such innovative media.

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