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INTERDISCIPLINARY INVESTIGATION OF EARLY HOUSE PAINTS: PICASSO, PICABIA AND THEIR "RIPOLIN" PAINTINGS – REVISION1

Keywords: early 20th century house paints, Ripolin paints, Pablo Picasso (1881-1973), Francis Picabia (1879-1953), paint reconstructions

ABSTRACT

This paper reports the results of an interdisciplinary research project focused on the scientific investigation of early oleoresinous Ripolin house paints, combined with a comprehensive survey of the visual characteristics of "Ripolin paintings" and a practical exploration of manipulations to artists' tube paints that can confer a "Ripolin look". A large reference collection of early 20th-century paint swatches and paint cans from Ripolin and other manufacturers, as well as contemporary artists' oil paints, were studied and a multistep analytical protocol was established to identify the distinguishing characteristics of Ripolin paints. The scientific methodology, which has been applied to samples from contemporary artworks, including Francis Picabia's *Untitled (Match-Woman I)* of 1920, offers criteria for the identification of Ripolin paints in early 20th-century artworks.

RÉSUMÉ

Cet article rapporte les résultats d'un projet de recherche interdisciplinaire portant sur l'étude scientifique des anciennes peintures pour bâtiments oléorésineuses Ripolin combinée à une étude complète des caractéristiques visuelles des « peintures Ripolin » et à une exploration concrète des manipulations des peintures d'artiste en tube susceptible de produire un « aspect Ripolin ». Une vaste collection de référence d'échantillons de peintures et de pots de peinture du début du xx^e siècle de chez Ripolin et d'autres fabricants, ainsi que des peintures d'artistes à l'huile contemporaines ont été étudiés et un protocole d'analyse en plusieurs étapes a été établi afin d'identifier les caractéristiques distinctives des peintures Ripolin. La métho-

INTRODUCTION

Ripolin, a brand of commercial ready-mixed paints formulated for architectural, marine and other applications, originated in the Netherlands where it was developed by the chemist Carl Julius Ferdinand Riep in the early 1890s (Pelgrim 1994). In 1897, the Briegleb paint company, as it was then known, formed a partnership with the French firm Lefranc, the well-known manufacturer of artists' materials. The merged company was named Ripolin, in honor of Riep, and a Ripolin factory was established in France. Ripolin paints were so renowned that the word "ripolin" became synonymous with enamel paints in general and entered the French dictionary as early as 1907.

Several modern European painters, including Pablo Picasso (1881–1973) and Francis Picabia (1879–1953) are reported to have used Ripolin (Leiris et al. 1984, 167–69; Picabia 2002, Cowling 2006, 110–11). The conclusive identification of Ripolin in their artworks, however, has posed a dilemma for conservators and conservation scientists because of the compositional similarities between early 20th century Ripolin and contemporary artists' oil tube paints (Picasso et al. 1981, Koussiaki 2002): the principal binder for both classes of paints prior to the widespread use of alkyd resins in the late 1940s was drying oil (Standeven 2006). Consequently, suppositions about the materials used in particular artworks have been based on visual appearance or anecdotal information. The interpretive nature of visual assessments and the possibility that artists manipulated traditional tube paints to achieve a house paint look, combined with the possibility that documentary sources may have used "ripolin" in a generic sense to describe the medium of particular paintings, all highlight the need for an interdisciplinary approach to the study of potential Ripolin paintings involving technical examination, scientific analysis and archival research.

THE RIPOLIN LOOK: VISUAL OBSERVATION AND SURVEY RESULTS

Although visual assessment is a valuable first step in the examination of so-called "Ripolin" paintings, particularly for highlighting promising cases for further scientific analysis, it cannot be considered a conclusive diagnostic tool for the identification of house paints. With the aim of compiling a database of potential "Ripolin" paintings and understanding the key visual indicators of the "Ripolin look", a survey was distributed to approximately 20

dologie scientifique, qui a été appliquée à des échantillons provenant d'œuvres d'art dont *Untitled (Match-Woman I)* (1920) de Francis Picabia, fournit les critères permettant d'identifier la présence de peintures Ripolin dans les œuvres d'art du début du XXe siècle.

RESUMEN

Este artículo presenta los resultados de un proyecto interdisciplinario enfocado en la investigación científica de pinturas con oleorresinas de la marca Ripolin, combinado con una investigación integral de las características visuales de las "pinturas Ripolin" y una exploración práctica de la manipulación de las pinturas en tubo para artistas que pueden dar un "aspecto Ripolin". Se estudió una gran colección de referencia de muestras de pintura y latas de pintura de principios del siglo XX de Ripolin y de otros fabricantes, así como de pinturas al óleo de artistas contemporáneos, y se estableció un protocolo analítico con varios pasos que permite identificar las características distintivas de las pinturas Ripolin. La metodología científica, que se ha aplicado a muestras de obras de arte contemporáneas, incluyendo la obra *Sin título (Mujer con cerillas I)* de Francis Picabia de 1920, ofrece criterios para identificar las pinturas Ripolin en obras de arte de principios del siglo XX.

museums in the US and Europe.[1] The survey asked conservators to identify works in their collection thought to contain house paint and to provide observations about the visual characteristics of the suspected house paint (e.g. surface texture, gloss, fluidity) and its application (e.g. straight from the can, in mixtures, layering). The questionnaire also sought documentation mentioning Picasso's use of materials for particular paintings. Information about treatment history, examination and analysis techniques applied to the artwork and conservation issues was also solicited. From the survey responses, certain common indicators of the "Ripolin look" emerged, such as bright colors, smooth, glossy surfaces and evidence of paint flow in the form of drips. The fluid quality of Ripolin allowed brush marks to level out before drying, providing a smoother, typically glossier surface than what could be achieved with artists' paints from the tube. The presence of distinctive wrinkling patterns and tiny pinholes was frequently observed in association with suspected Ripolin paint. Although such characteristics are not specific to house paints and may be more a function of application or substrate, the intrinsic qualities of Ripolin, including the need to stir the paint to incorporate medium separated out in the can, as well as unconventional uses, such as thick applications or layering, may account for the frequent occurrence of pinholes and wrinkling.

The survey results highlighted certain limitations of assessments based on visual characteristics alone. Obviously, oleoresinous enamel formulations by makers other than Ripolin could achieve similar surface effects and textures. Conservation treatments, such as varnishing, could affect the look of the paint in misleading ways. Furthermore, the artist could mix Ripolin, or another commercial house paint, with artists' paints to achieve effects intermediate between the two paint types, or manipulate tube paints with additional medium to alter their handling and visual properties in ways that could achieve surface qualities similar to Ripolin. In fact, receipts from the early 1920s indicate that Picasso purchased Ripolin at this time, as well as *Siccatif de Harlem* (McCully 2007), likely an oleoresinous medium which, when added to tube paints, could impart a more fluid consistency and glossy surface.[2] Knowledge of Picasso's use of this material prompted empirical investigations into the effects of adding oil-copal mediums to artists' tube paints.

EXPERIMENTAL DETAILS

Paint reconstructions

Because much has been surmised about artists' use of Ripolin on the basis of visual assessment, it was deemed important to empirically explore whether the Ripolin look could be achieved using artists' materials alone. Weighted amounts of modern copal-based mediums thought to be similar to *Siccatif de Harlem* were added incrementally to a modern artists' tube oil paint and applied by brush and palette knife to primed canvas board (see Materials list). Observations were made about the handling of the paint and the paint-outs were photographed over the course of drying.

Reference collection of early 20th century house paints and artists' tube paints

An extensive reference collection has been formed and studied, comprising over 25 house paint cans and 28 Ripolin paint sample cards ("brochures", each containing 20 to 86 swatches of actual paint), which represents the entire color range produced by the company in France and roughly covers the period 1897–1950 (Gautier et al. 2009). Additionally, a selection of early 20th century artists' tube paints has also been gathered.

Analytical strategy

X-ray fluorescence (XRF) spectrometry and micro-Fourier-transform infrared (micro-FTIR) spectroscopy were used as preliminary survey tools, complemented by Raman microscopy where needed (for experimental details see Gautier et al. 2009). Thermogravimetric analysis (TG), inductively coupled plasma/mass spectrometry (ICP/MS) after HF digestion in a high pressure closed vessel (Parr bomb), and digital image analysis (ImageJ) after scanning electron microscopy (SEM-EDX) of cross-sections were also used to fully explore the molecular and chemical composition of house paints and characterize the particle size distribution and morphology of the paint constituents at high resolution.

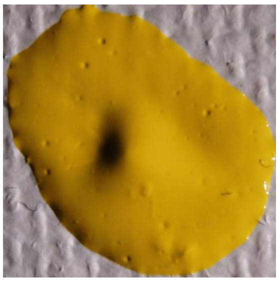
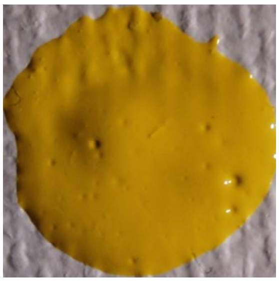
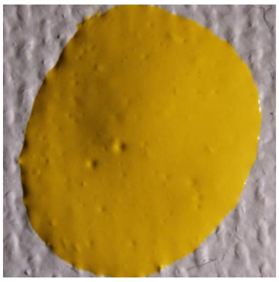
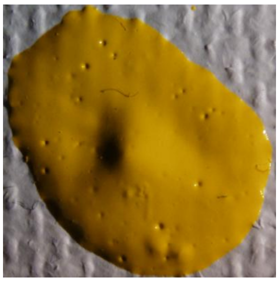
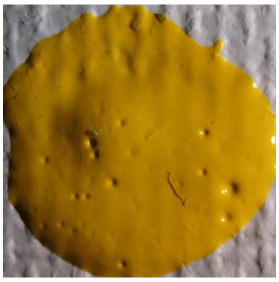
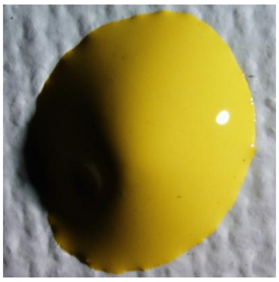
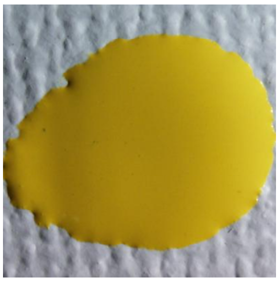
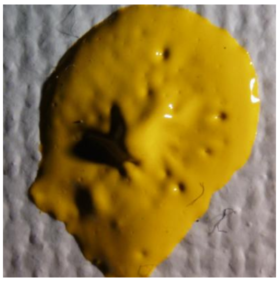
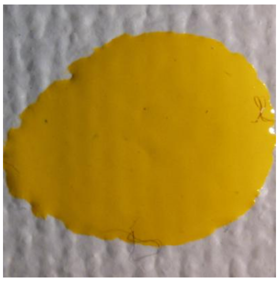
RESULTS AND DISCUSSION

Paint reconstructions

With all of the copal mediums tested, higher proportions of added medium result in increased fluidity and leveling of the paint. The proportion of medium required to emulate the "Ripolin look" depends on the concentration of resin in the medium, as some formulations are more diluted with volatile solvents than others. At lower percentages, the medium imparts increased body to the paint with an accompanying slight increase in surface sheen. As shown in Table 1, with an approximately 25 percent w/w addition of different copal mediums, the surface becomes smoother and the paint maintains only soft peaks. With greater percentages of added medium, the paint becomes increasingly fluid, capable of forming flat, smooth and glossy surfaces. The incorporation of air into the paint during mixing often resulted in pinholes at the surface of the dried film. Pronounced wrinkling, similar to that encountered in "Ripolin" paintings, was observed in some paint mixtures. This occurs when the surface sets up while the bulk of the paint film continues to dry. As seen in the aged samples of the Studio Products copal medium, the degree of wrinkling is related more to the thickness of the paint application than to the percentage of added medium. These experiments demonstrate that artists' paints can be manipulated to achieve visual and handling properties similar to Ripolin paints, thus underscoring the caution that must be used in presuming the presence of house paint based on visual assessment alone.

Table 1

Mixtures of artists’ oil paint and copal mediums. Average size of paint daubs is 0.5-1.0 cm.

Artists’ tube paint (without addition)	Unaged			
Percentage addition of copal medium (w/w)		41	53	71
James Groves Copal Oil Varnish	Unaged			
	Aged (2 months)			
Percentage addition of copal medium (w/w)		26	45	73
Studio Products Congo Copal	Unaged			
	Aged (2 months)			

Compositional analysis of reference Ripolin paints

Ripolin paint samples have been systematically analyzed and extensive results on pigment composition are discussed elsewhere (Gautier et al. 2009). However, it is worthwhile summarizing important observations about the paint formulations, corroborated by ongoing analysis of additional historical reference materials.

French Ripolin paints are high quality house paints, containing very few or no fillers. No calcium sulfate, calcium carbonate, or silicates, which are common in other brands of house paint, were detected. The only pure white Ripolin hue – *blanc de neige* – is consistently obtained with zinc oxide in all samples examined. ZnO is also the predominant white pigment used to produce the lighter hues before *c.*1950: only one brochure out of 28, estimated to date after 1950, shows the white component to be a mixture of zinc oxide, titanium dioxide and barium sulfate. Barium sulfate is detected at trace levels with XRF in a handful of additional cases (at the limit of detection of FTIR), with the only exceptions being *rouge matin* and *rouge de Perse*, which contain organic pigments.

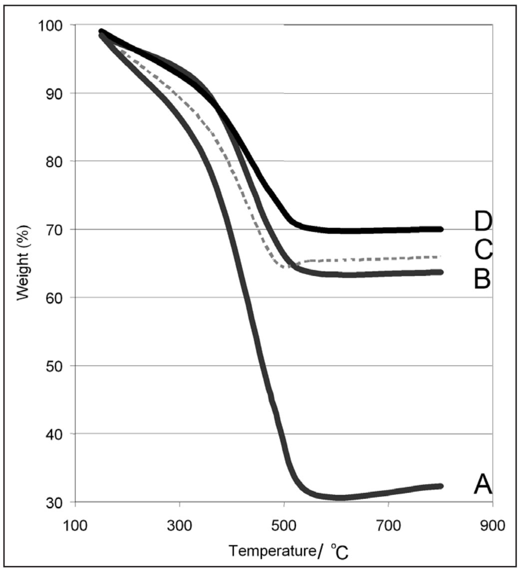
Although subtle changes in pigment usage and proportions are documented over time, hues are generally achieved with a consistent range of pigments. When new pigments became commercially available, e.g. Hansa yellow (PY3), toluidine red (PR3) and titanium dioxide (anatase first, then rutile), they were subsequently adopted (Gautier et al. 2009).

This detailed study of pigments and extenders defined important preliminary criteria that help to differentiate Ripolin from artists' tube paints of the period. The first condition to be met is to identify zinc oxide as the primary white pigment without significant amounts of extenders. France was an early adopter of zinc white for house paints because of toxicity concerns with lead white. As early as 1909, archival documentation shows that legislation prohibited the use of lead white in certain applications (Anon. 1909). Thus, the vast majority of Ripolin colors do not contain basic lead carbonate, a pigment commonly found in paintings executed with artists' tube paints. Lead white was identified only in a few of the over 1700 swatches examined, where it is consistently associated with yellow hues as a byproduct of chrome yellow preparation. In the house paint formulations secondary and tertiary colors are always combinations of primary colors. Many common artists' pigments are not present in Ripolin, for example, cadmium pigments, emerald green, and cobalt violets. Vermilion was identified only in three swatches of red of the Ripolin carrosserie line (car and boat enamels).

FTIR analysis highlighted the presence of oil binders mixed with variable quantities of resinous matter (currently under investigation with various mass spectrometric methods), used in higher proportions for the darker hues. This is in agreement with general literature reviewing the history of oleoresinous paints (Standeven 2006) and specific historical literature where Ripolin is often described as a lacquer containing linseed oil, resinous gums, some essence and zinc white (Labordere 1913) or as a "peinture vernissée" containing hard-gums (Rives 1900). Light colors often show prominent spectral signatures of metal carboxylates, likely representing products of interaction between ZnO and the oil medium, as well as cobalt, manganese, and lead, detected by XRF and SEM-EDX, probably from driers. Preliminary ICP/MS investigation documented widespread use of such driers and quantified them at levels of a few tens of ppm w/w (Table 2).

Table 2
Quantification of metallic ions in house and artists' paints with ICP/MS. While Co and Mn are purely used as driers, in some of the paints Pb is also a pigment component

Units:	mg/kg		
Element:	Pb	Co	Mn
Ripolin, Blanc de neige 2 (La Porcelaine Liquide can, HP007H)	1168	48	29
Ripolin, Blanc d'ivoire 53 (French can, HP008E)	2211	21	12
Lefranc blanc de zinc (tube paint ; 2009.32)	565	105	< 2
Lefranc blanc de zinc (tube paint pour decoration artistique; 2009.70B)	2790	< 0.6	< 3



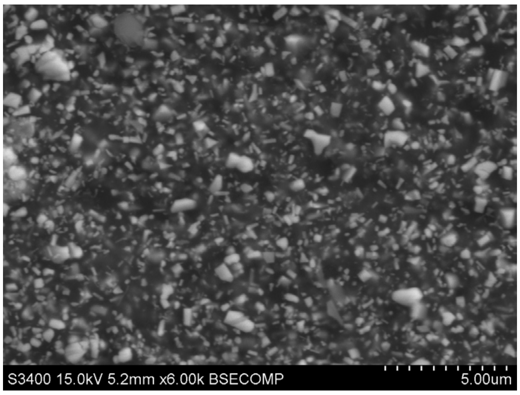


Figure 1
Percentage weight loss with increasing temperature in N_2 atmosphere of: a) Ripolin can *Bleu Outremer 13* (HP013); b) Ripolin can *Blanc de neige 1* (HP002); c) Lefranc tube *Outremer n2., clair* (2007.15); d) Lefranc tube *Blanc de zinc* (2007.48)

Figure 2
Backscattered Electrons SEM image of a detail of a cross-section of paint from a historical can of Ripolin *Blanc de neige 1* (HP002) documenting the extremely fine and regular particle size of this industrially produced, high quality oleoresinous enamel paint.

The in-depth study of white and ultramarine blue samples of Ripolin and artists' tube paints illuminates the technological advancements that were likely responsible for Ripolin's handling characteristics and astounding international renown.

In addition to a significant proportion of resin additives, gloss and leveling of Ripolin may be related to a higher binder/pigment ratio than artists' paints, systematically detected at levels that depend on the particular hue. Specifically, thermogravimetric analysis of Ripolin paints gave values of 63.5 wt% pigment and 36.5% binder (comprising oil and resin) for white paint (*Blanc de neige*) and 31% pigment and 69% binder for blue paint (*Bleu Outremer*) respectively, compared with 70% pigment and 30% binder for white and 65% pigment and 35% binder for blues, for artists' tube paints of similar pigment composition (Figure 1).

Scanning electron micrographs of reference paints revealed notable differences between Ripolin whites and artists' zinc white tube paints, suggesting that different grades of zinc oxide may have been specific to the different end uses (Kühn 1986). The artists' paint samples appear to contain larger particles and consist of more elongated and acicular particles, whereas Ripolin zinc white samples consistently exhibit smaller and more nodular-shaped particles (Figure 2). Digital image analysis after segmentation of the BSE SEM images to isolate the ZnO pigment particles allows a precise quantification of this visual perception. Two critical ranges are identified: particles with surface area between 0.01 and 0.03 μm^2 – more densely represented in Ripolin –, and larger particles (0.1-0.5 μm^2) of which tube paint is slightly richer (Figure 3). Advanced methods of sample preparation and imaging are currently under study to improve image segmentation and reduce errors.

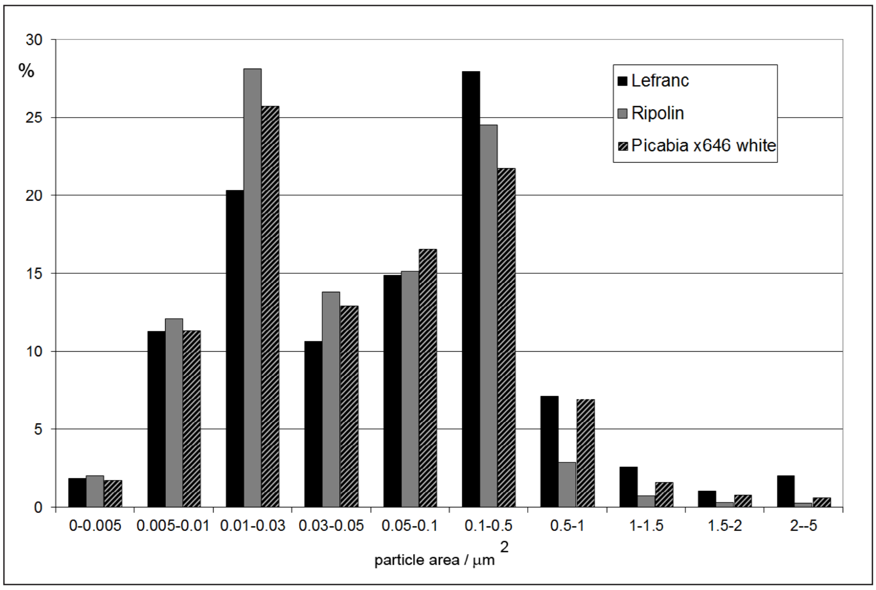


Figure 3
Particle size distribution curves for the Ripolin paint illustrated in Figure2, compared to the white paint in a cross section (x646) from *Untitled (Match-Woman I)* and an example of artist's zinc white paint, Lefranc, *Blanc de zinc* (2007.48) (bars represent normalized averages over several areas captured at 6000x magnification)

Figure 4
Francis Picabia, *Untitled (Match-Woman I)*, 1920 (92.1 x 73.3 cm). The Art Institute of Chicago. Linda and Edwin Bergman Collection (AIC 1999.945). © 2010 Artists Rights Society (ARS), New York / ADAGP, Paris.

Figure 5
Detail of Figure 4, from intersection of turquoise, blue, and white paints at top of woman's head.

Case study: Francis Picabia's *Untitled (Match-Woman I)* (1920)

The materials based knowledge of Ripolin paints described above was applied to the investigation of a painting by Francis Picabia in the collection of the Art Institute of Chicago, which, by visual examination, showed areas with the characteristic appearance of house paint.

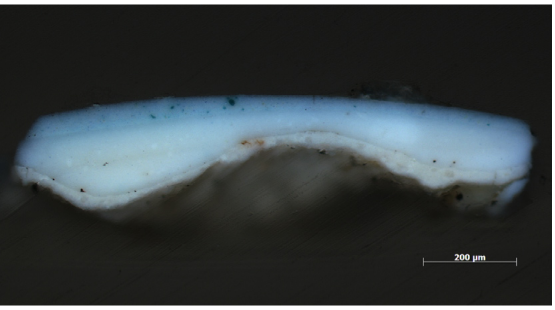
Picabia's *Untitled (Match-Woman I)* (Figure 4) is a painting on canvas with applied elements, including wooden matchsticks, hairpins, coins, leather hair rollers and string. The artist reworked the painting at a later date when he added the darker blue paint on the right side of the undulating diagonal. The reworking was probably necessitated by paint losses incurred near the top edge. The turquoise and blue tones used in the original painting visually match colors available in the Ripolin range. Where more thickly applied, the paint has leveled out and there is almost no evidence of brush marks. This contrasts with the repainted area, which exhibits crisp brushstrokes and appears more consistent with traditional artists' tube paint (Figure 5).

FTIR analysis of the darker blue artist's overpaint detected lead white and some viridian, as well as oil and metal soaps, confirming the use of traditional artists' tube paint. The detection of phtalocyanine blue pigment with Raman spectroscopy dates the application of this layer to after 1935 (Lomax 2005).

Analysis of the turquoise paints, on the other hand, indicates that the primary components are a drying oil and zinc white: the small amounts of viridian responsible for the turquoise hues escape FTIR investigation, but are detected with SEM-EDX.

When paint samples are viewed in cross-section, the pigment particles appear to be very finely dispersed, like Ripolin reference samples, and exhibit similar zinc white fluorescence under ultraviolet light (Figure 6, 7). Particle size analysis of the white paint provided a distribution consistent with Ripolin paints (Figure 3), further strengthening the scientific identification of these paints as Ripolin.

Overall, samples taken from areas displaying a "Ripolin look" could be matched to the elemental and molecular fingerprint of corresponding Ripolin reference colors. Specifically, the white paint of the figure's hair, which extends across the right side of the painting underneath the blue layers, matches Ripolin *blanc de neige*. The light blue paint below the neck of the woman, right of center, matches *bleu azur foncé*, and the turquoise blue from the left side of the painting corresponds to either *bleu turquoise clair*, *bleu azur moyen*, or *bleu azur pale* (Figure 8). Formulations of the latter colors are distinguished only by slight variations in the proportions of viridian and/or Prussian blue and change over time, so that a perfect match remains elusive.



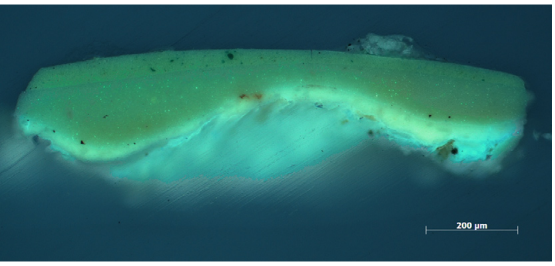


Figure 6
Cross-section (x646) from *Untitled (Match-Woman I)*, from original paint layers at bottom edge in area of blue paint, lower right of woman's neck. Three layers are present (from bottom up): white ground, white paint, and light blue paint.

Figure 7
X646 under ultraviolet light.

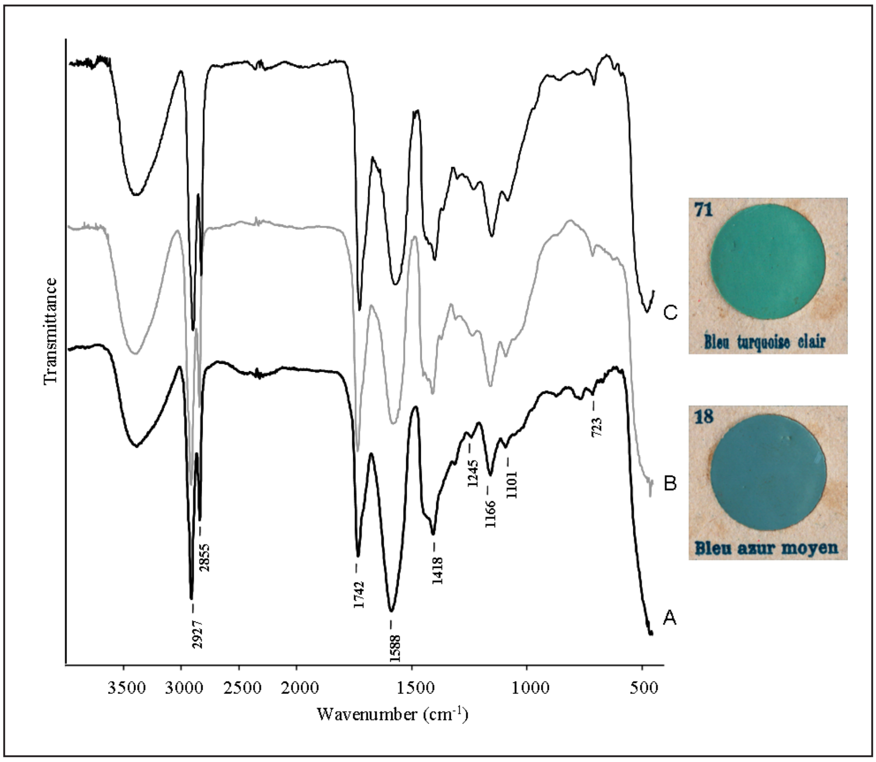


Figure 8
FTIR spectra of (A) sample of original turquoise paint layer from *Untitled (Match-Woman I)*; (B) swatch *18 Bleu azur moyen* (brochure B13, c.1920s); and (C) swatch *71 Bleu turquoise clair* (brochure B13).

CONCLUSIONS

Due to similarities in composition of early 20th century oleoresinous Ripolin paints and artists' tube paints, the identification of Ripolin in works of art depends on a combination of factors rather than the detection of a single chemical marker. Through a multifaceted approach, several diagnostic differences between the two formulations have been established and criteria for positive identification of Ripolin have been defined. Many of these key features have been confirmed in samples from Picabia's *Untitled*

(Match-Woman I), a painting that shows juxtapositions of traditional artists' oil and Ripolin paints. Analysis reveals a perfect match between the Picabia paints and available paints in the Ripolin range, which the artist appears to have used straight from the can.

This project has generated a solid foundation of knowledge on the composition of reference samples of French Ripolin house paints from between 1910 and 1950. The results expand our knowledge of the formulations of early 20th century artists' and non-artists' paints and the relationship between their composition and their working and visual properties.

Future work will continue to explore ways of differentiating Ripolin paints from artists' paints (especially in the challenging case of ZnO based artists' tube oils) as well as identifying differences between Ripolin and other house paint brands. Studies on the aging of oleoresinous Ripolin paints and the conservation implications of various cleaning approaches will also be explored.

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NOTES

[1] In most cases, the survey was completed by the conservator of the respective institution. In some cases, the survey was completed by Muir in consultation with the conservator of the host institution.

[2] Differences in proprietary formulas of *Siccatif de Harlem* and the lack of reference samples make it difficult to determine precisely what Picasso was using. Historical sources suggest that, in the 19th century, *Siccatif de Harlem* was an oleoresinous medium based on copal resin (Carlyle 2001).

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MATERIALS LIST

Old-Holland Classic Oil Colours, Cadmium yellow light (D11), cadmium zinc sulfide
www.oldholland.com

James Groves Copal Oil Varnish (50% Agathis hard copal from Indonesia in walnut oil with slight dilution in turpentine)
www.jamescgroves.com/mediums.htm

Studio Products Congo Copal Concentrate #16228 (24% Congo copal concentrate, cooked in linseed oil)

www.studioproducts.com

Blick canvas board (100% cotton canvas primed with white acrylic gesso); item # 07008-0816
www.dickblick.com