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

GWÉNAËLLE GAUTIER,* ANIKÓ BEZUR, KIMBERLEY MUIR, FRANCESCA CASADIO, and INGE FIEDLER

The Art Institute of Chicago, 111 South Michigan Avenue, Chicago, Illinois 60603-6404 (G.G., K.M., F.C., I.F.); and The Museum of Fine Arts, Houston, P.O. Box 6826, Houston, Texas 77265-6826 (A.B.)

This study reports the multi-analytical investigation of ready-mixed house paints used by artists such as Pablo Picasso (1881–1973) in the first half of the twentieth century. The pigment composition of paint swatches on four historic paint sample cards from the Art Institute of Chicago reference collection was characterized by thorough screening using Fourier transform infrared (FT-IR) and X-ray fluorescence (XRF) spectroscopies, followed by Raman spectroscopy when necessary. Spectroscopic investigations highlighted the dominance of zinc-based whites, the consistent choice of particular pigments or their mixtures, as well as the avoidance of others to achieve the various hues on the sample cards. Notable findings included the documentation of strong spectroscopic signatures of metal soaps. Given the similarities in composition of early twentieth century artists' and house paints, the results indicate that the identification of house paints in works by Pablo Picasso and others must be based on a combination of parameters rather than the detection of a single chemical marker. Results have been applied to the case study of Picasso's 1935 sculpture *Figure* (AIC 1988.428), which incorporates direct evidence of the use of house paint by the artist.

Index Headings: **Historic house paint technology; Pablo Picasso; Fourier transform infrared spectroscopy; FT-IR spectroscopy; Raman microspectroscopy; X-ray fluorescence; XRF; Art conservation.**

INTRODUCTION

Spectroscopic characterization of house paints is widely used in the context of forensic analysis.[1,2] Similarly, in the past twenty years, extensive databases of Fourier transform infrared (FT-IR) and Raman spectroscopic signatures of artists' pigments have been accumulated.[3–5] Here we illustrate the importance of a multi-analytical approach for the identification of artworks containing Ripolin® in the first half of the twentieth century and the necessity to establish extensive and detailed datasets of the composition of historic house paints to aid such identification.

Ripolin® is the trade name for an internationally renowned range of commercial non-artists' paints (in the following, we use the generic term "house paint" to refer to these ready-mixed, over-the-counter paints independent of their intended end use), which were manufactured in Europe beginning in the late nineteenth century for architectural, marine, and other uses. Several modern European painters, including Pablo Picasso (1881–1973) and Francis Picabia (1879–1953), are reported to have used Ripolin® in their works.[6–9] These paints offered the artist different visual and handling properties than artists' oil paints, including a unique range of surface gloss and colors, consistent hiding properties guaranteeing opacity over the entire color gamut available, greater fluidity, and relatively rapid drying times.

Scientifically confirming the presence of house paint in early twentieth century artworks through medium analysis is challenging because, until the end of World War II, the most widely used house paints were oil-based and, thus, chemically similar to artists' oil paints.[10] Previous published investigations into the question of Picasso's use of house paint remain inconclusive due, in part, to the lack of reference materials with which to compare the findings from analyses of artworks.[8,11] As a result, in the museum context, suppositions about the presence of house paint in specific works are usually based on a combination of visual characteristics, such as areas of bright, unmodulated color, minimal evidence of brush marks due to leveling of the paint, and/or relatively glossy surfaces. The research presented here aims to bridge this gap by correlating the analysis results from paint samples from works of art and those from contemporaneous Ripolin® paint samples.

Though many of the same components were used in early twentieth century artists' oil paints and oleoresinous house paints, formulations of the latter did differ due to production scale, economics, and because their desired performance characteristics, such as gloss level and drying rate, had to be achieved without the need for further modification by the user. The addition of a diluent, such as turpentine, is typically the main adjustment recommended by the makers of house paints (as reported directly on the brochures themselves). Artists, on the other hand, routinely modified their tube paints to a much greater extent through the mixing of colors, as well as the addition of mediums, thinners, driers, waxes, etc., to customize the handling and optical properties of their paints.[12] Research into the systematic patterns of use or avoidance of particular paint components in house paints is necessary to overcome the challenge of distinguishing them from tube oil paints.

To this end, a collection of Ripolin® paint sample cards ("brochures" in the following) and paint cans from the early twentieth century comprising several examples of available

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* Author to whom correspondence should be sent. E-mail: ggautier@artic.edu.

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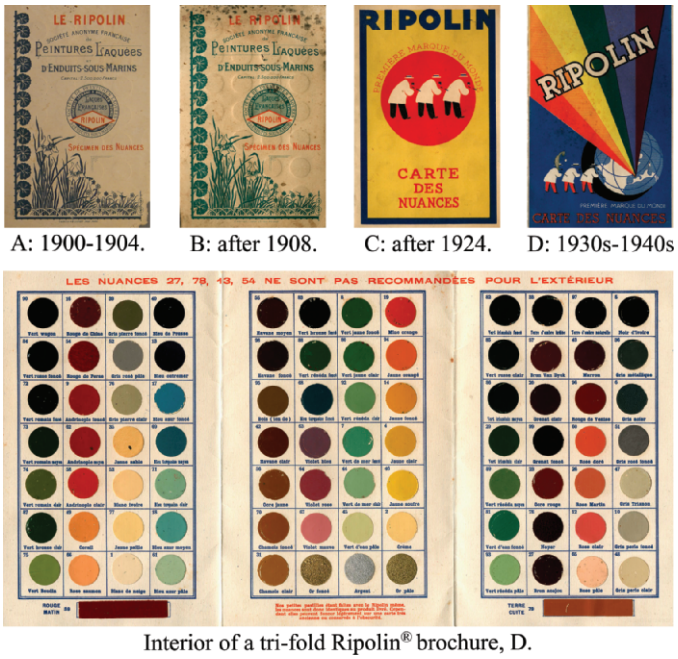

FIG. 1. Exterior (front page) and interior of Ripolin® brochures with estimated dates.

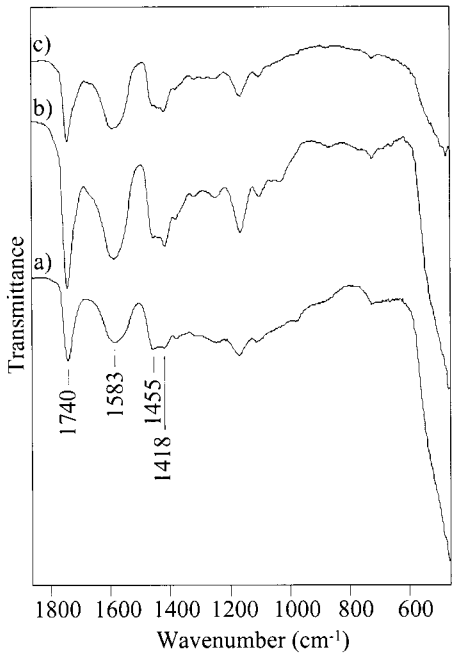

FIG. 2. FT-IR spectra of (***a***) a sample from a small can of Ripolin® *53 blanc d'ivoire*; (***b***) a sample from swatch *53 blanc d'ivoire* (brochure D); and (***c***) a sample from *Figure* (AIC 1988.428) by Pablo Picasso (1935).

product lines has been assembled (with trade names Ripolin Mat®, Ripolin Express®, Ripolin Carrosserie®, Glacis Ripolin®, Ripolac®, and Ripolin Fletto®) and the contents analyzed in order to identify their components (including pigments, binding media, and driers). Though none of the brochures are dated, their relative order and approximate age may be estimated based on the listing of prizes awarded in specific years, the net worth of the company (capital) printed on the front page, and the terminal dates for pigments identified in the paint swatches. The core of the collection consists of brochures produced before 1945. The two earliest brochures, A and B, share the same design (Fig. 1): brochure A boasts of awards received in 1895 and 1900 while brochure B includes additional references to prizes earned in 1904, 1905, 1906, and 1908. Thus, brochure A is likely from 1900–1904 and brochure B postdates 1908, but predates C and D, which contain Hansa yellow (p-chloro-o-nitroaniline coupled with chloroacetoacetanilide, PY3, Color Index (CI) # 11710) in the formulation of *46 jaune soufre* and thus must have been produced after 1911, the year in which Hansa yellow was discovered.[†,13] While paint samples in brochures A through C contain zinc oxide white pigment (ZnO, PW4, CI# 77947), brochure D distinguishes itself by the use of barium sulfate ($BaSO_4$, PW21, 22, CI# 77120) and anatase (TiO_2, PW6, CI# 77891), mixed with zinc oxide. Laver[20] reports that the barium sulfate-extended form of anatase (the composite titanium dioxide) was accessible in 1919, while 1923 is the date cited for the availability of "pure" anatase in France.[21] Archival research into the annual reports of the company[22,23] and contemporary publications including examples of actual brochures[24] have allowed us to infer that brochure C may be dated after 1924 and before 1946 and that brochure D postdates brochure C given the evolution of the formulation of its whites.

Unlike current paint sample cards,[‡] the historic brochures studied contain oil-based paint that was confirmed to be identical to the actual product sold in cans. This is supported by statements on two of the brochures that postdate 1924, which assert in French: "Since our small swatches are prepared using the Ripolin® itself, their hues are identical to the product delivered. However, these hues may darken slightly on a very old card or if they have been kept in the dark". Further corroboration is provided by the FT-IR spectra of an off-white paint from a small can of Ripolin® *53 blanc d'ivoire*, which showed a good match with those of *53 blanc d'ivoire* from the brochures (Fig. 2), containing zinc oxide, zinc-, cobalt- and lead-containing metal soaps (either intentionally used as driers or due to the interaction of zinc white with organic fatty acids from the oil medium), small amounts of lead chromate ($PbCrO_4$, PY34, CI# 77600), and an oleoresinous binder.

A multi-analytical approach was applied, starting with preliminary screening of the Ripolin® paint samples using FT-IR and X-ray fluorescence (XRF) spectroscopy. When necessary, complementary analyses were also carried out, primarily with Raman spectroscopy, and in some cases using polarized light microscopy (PLM) and scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX).

This paper focuses on the spectroscopic characterization of the inorganic and organic pigments found in the Ripolin® paint

[†] Uncertainties still exist on the actual date of commercial availability of this pigment: Schunck and Hunger[14] cite 1928, while Lomax[15] cites 1912. Additionally, catalogues of artist's pigments from the manufacturers Bourgeois Ainé[16–18] and Lefranc[19] dated from 1908 to 1927 did not mention Hansa yellow (PY3) as an available pigment in the range they offered, so it is possible that Hansa yellows started to be used extensively only after the 1930s.

[‡] Nowadays, due to a mass market production that creates the need for printing thousands of brochures at one time, printed inks are used to represent colors, or the same pigments used in the actual paints are employed but with a different binder that guarantees ultra-fast drying.

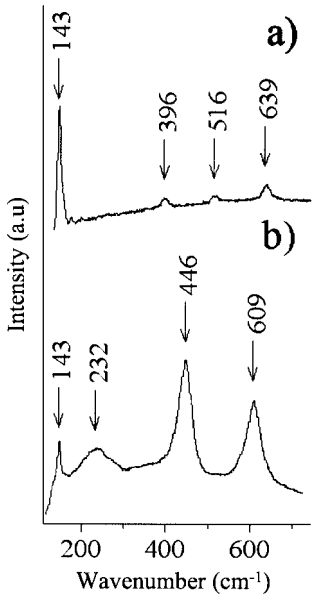

FIG. 3. Raman spectra of TiO_2 pigments in Ripolin® paint formulations: (***a***) white grains from *61 bleu azur pâle* in brochure D, likely dated 1930/40 ($\lambda_0 =$ 785 nm, 70 seconds acquisition, 2 accumulations; pigment identified as anatase); (***b***) white paint from a can of Ripolin Fletto®, representing paint formulations in use after World War II ($\lambda_0 = 785$ nm, 20 seconds acquisition, 3 accumulations; pigment identified as rutile).

samples to establish a dataset of the characteristic components of this important early brand of house paints. Detailed results on the characterization of brochure D are reported along with an important piece of direct evidence of Picasso's use of this brand of paint: his 1935 sculpture *Figure* (AIC 1988.428) from the collection of the Art Institute of Chicago. Significant differences in paint composition in other brochures are discussed in comparison with brochure D.

EXPERIMENTAL

Historic Paint Reference Materials. A total of 20 brochures currently form part of the AIC reference collection together with 13 paint can samples. Four brochures (A, B, C, and D) are discussed in detail in this publication. All of the brochures show a consistent format. They were constructed by adhering small, painted paper disks (approximately 13 mm in diameter) to the interior of a tri-folded card stock sheet (see Fig. 1). Paint layers on the paper disks measure between 30 and 50 μm in thickness. Each paint swatch is associated with a number, in the range of 1 through 99, and the name of the color. With one exception,[§] numbers and color names remain consistent in the brochures studied. The earlier brochures (dating before 1904) contain 84 color swatches. Between 1904 and 1908, two unnumbered rectangular paint swatches, *rouge matin* and *terre cuite* (approximately 7 mm by 40 mm) were added along the bottom edge of the brochure interior, increasing the total number of color samples to 86. These swatches were later assigned numbers 59 and 79, respectively. Thus, in addition to a white (*1 blanc de neige*) and a black (*5 noir d'ivoire*) paint, Ripolin®, in its brochures, offered first 82, then 84 hues, that can be categorized as yellow, blue, red, orange, pink, green, gray, brown, violet, and metallic. Several hues were available in different levels of brightness or lightness such as *pâle* (pale), *clair* (light), *moyen* (medium), and *foncé* (deep).

Instrumental Analysis Methods. ***X-ray Fluorescence Spectroscopy.*** Paint swatches in brochures were analyzed *in situ* using a portable Bruker Tracer III-V energy dispersive X-ray fluorescence spectrometer with an X-ray tube equipped with a rhodium (Rh) transmission target. The detector is a thermoelectrically cooled Ag-free SiPIN device with a 13 μm Be window and resolution of approximately 175 eV for the full width at half-maximum of the Mn Kα line. Two sets of acquisition parameters were used: (1) 20 kV potential, 15 μA current, air removed from beam path within instrument using a vacuum pump (~2 Torr), and acquisition times (live time) of 300 s; and (2) 45 kV, 1.5 μA, 120 s acquisition time (live time) using a Ti/Al filter in the beam path.

Fourier Transform Infrared Spectroscopy. Samples from the paint swatches were removed with a scalpel blade, after scraping off the superficial layer of the swatches, to avoid contamination or possible clear coating layers applied on the paint in the brochures. The samples were flattened between the windows of a diamond micro-compression cell and analyzed individually using a transmitted infrared beam with a Bruker Tensor 27 spectrometer, with mid-infrared glowbar source, coupled to a Hyperion 2000 Automated FT-IR microscope with nitrogen-cooled mid-band and broad-band MCT detectors (covering the range 7000–600 cm^{-1} and 10000–450 cm^{-1}, respectively). The spectra collected are the sum of 128 scans at a resolution of 4 cm^{-1}.

Raman Spectroscopy. A Jobin Yvon Horiba Labram 300 confocal Raman microscope, equipped with an Andor multi-channel Peltier cooled open electrode charge-coupled device (Andor DV420-OE322) detector (1024 × 256), BXFM open microscope frame (Olympus), holographic notch filter, and a dispersive grating with 1800 grooves/mm was used. The excitation line of a solid state diode laser ($\lambda_0 = 785.7$ nm) was focused through a 100× objective on to the samples and Raman scattering was back-collected through the same microscope objective. Power at the samples was kept very low (never exceeding a few mW) by a series of neutral density filters in order to avoid any thermal damage. Raman spectra were abscissa calibrated with the 520.7 nm line of a silicon wafer.

RESULTS AND DISCUSSION

Ripolin® Paint Swatches. The pigment composition of paint swatches from brochure D is summarized in Table S-I and described in comparison with the results from other brochures. Based on this work, a number of important observations can be made regarding the characteristic features of the pigments and driers used in Ripolin® paint formulations in the first few decades of the twentieth century.

Blacks. Despite the name *5 noir d'ivoire*, the colorant in the black swatch on the brochures was identified by Raman spectroscopy and confirmed by PLM as carbon black (PBl08, CI# 77268), rather than ivory or bone black (PBl09, CI# 77262). Only Ripolin Mat® formulations actually contain ivory or bone black as the black pigment in *noir d'ivoire* swatches.

Whites. The only swatch of pure white present on the brochures is *1 blanc de neige*, which is consistently obtained

[§] The number 47 swatch, *Gris*, appears as *Gris Trianon* in two brochures postdating 1924. The re-naming of the hue may have been related to a significant historic event at the end of World War I: the signing of a peace treaty on the 4th of June, 1920, at the Grand Trianon Palace in Versailles (France) between the Allies of World War I and Hungary.

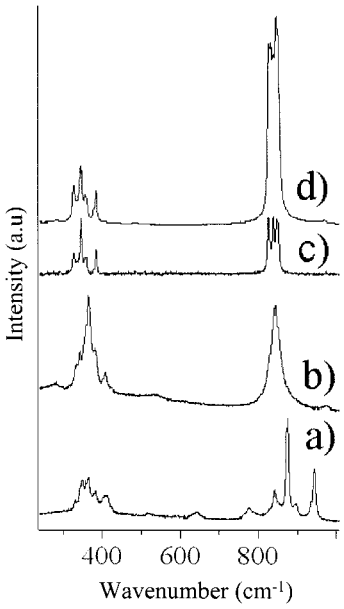

FIG. 4. Raman spectra of the Ripolin® swatches from brochure D: (***a***) *75 vert Beudin* ($\lambda_0 = 785$ nm, 90 seconds acquisition, 2 accumulations): pigments identified as lead chromate with zinc potassium chromate ($4ZnO{\cdot}K_2O{\cdot}4CrO_3{\cdot}3H_2O$: 343m, 772m, 872vs, 892m, and 941m cm^{-1}); (***b***) *80 vert jaune clair* ($\lambda_0 = 785$ nm, 120 seconds acquisition, 1 accumulation): pigment identified as lead sulfochromate ($PbCrO_4{\cdot}xPbSO_4$: 339w, 358–361s, 378m, 400m, 840vs, and 975 cm^{-1}); (***c***) *77 jaune paille* ($\lambda_0 = 785$ nm, 110 seconds acquisition, 2 accumulations): pigment identified as phoenicochroite ($Pb_2O(CrO_4)$): 322m, 341s, 353m, 380m, 825s, 837s, and 847s cm^{-1}); and (***d***) a sample of an artists' pigment labeled "Golden Chrome, 1904" from the Forbes pigment collection, also containing bright orange particles with the characteristic spectrum of phoenicochroite.

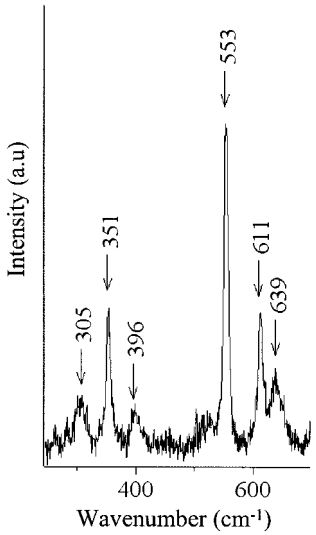

FIG. 5. Raman spectra of the Ripolin® swatch *18 bleu azur moyen* from brochure D ($\lambda_0 = 785$ nm, 360 seconds acquisition, 1 accumulation); pigment identified as anhydrous chromium (III) oxide (Cr_2O_3: 305w, 351w, 553vs, and 611w cm^{-1}). The bands at 396w and 639m cm^{-1} can be attributed to anatase.

with zinc white in all the specimens examined. However, notable differences over time can be documented in white pigments that are used in combination with colored pigments to produce lighter tints, i.e., to adjust the brightness or value of the color. In the earlier brochures (A, B, and C), zinc white is used in combination with colored pigments. In brochure D, on the other hand, the white component of the paint is a mixture of zinc oxide, barium sulfate, and titanium white. The latter is present in the anatase form, as confirmed by the observation of Raman bands at 143vs, 396w, 516w, and 639m cm^{-1} (Fig. 3a) in a sample of *61 bleu azur pâle*. Analyses of later paint formulations revealed the use of the rutile form of titanium dioxide (with Raman bands at 143w, 232m (br), 446s, and 609s cm^{-1}), which became available in Europe after World War II, as observed in a white paint sample from a can of Ripolin Fletto®, extended with barium sulfate (Fig. 3b). When the white component of the colored paint swatches is discussed, the term "white" refers to zinc oxide in the context of brochures A, B, and C, and to the mixture of zinc oxide, titanium dioxide (anatase), and barium sulfate in the context of brochure D.

Colored Swatches. Off-white colors (*53 blanc ivoire* and *2 crème*) are obtained by mixing lead chromate and zinc white. In brochure D only, *2 crème* contains titanium dioxide (anatase) and barium sulfate in addition to lead chromate. Sub-micrometer particles of iron oxide were also identified by PLM and confirmed by XRF.

Yellows are frequently obtained using lead chromate, alone or in combination with zinc potassium chromate ($4ZnO{\cdot}K_2O{\cdot}4CrO_3{\cdot}3H_2O$, PY36, CI# 77955). These two are also the pigments of choice to obtain green hues by admixture with blue as shown in Fig. 4a for *75 vert Beudin*. Of the five yellow shades offered, *35 jaune sable* lacks lead chromate but includes some iron oxide yellow (as identified by PLM), and in brochure C and D the color *46 jaune soufre* contains the organic pigment Hansa yellow (PY3) as a replacement for zinc potassium chromate, which was used in brochures A and B for the same swatch. The chromate pigments offered a wide range of different hues from light yellows to orange reds, depending on temperature, pH, concentration of precursors, and reaction time, production parameters that affect the crystal morphology, composition, and particle size of the pigments. This has been documented both for contemporary[25] and early modern[26] chromate pigments. Mixed crystals of lead chromate and lead sulfate, called lead sulfochromate ($PbCrO_4{\cdot}xPbSO_4$, PY34, CI# 77603), are characterized by lighter, greenish hues, which are used to obtain yellow-green hues in the Ripolin® brochures (such as *80 vert jaune clair*, Fig. 4b). Yellow-orange swatches such as *66 rose saumon*, *77 jaune paille,* and *19 mine orange* contain small orange particles whose Raman spectrum is shown in Fig. 4c. The observed bands at 322m, 341s, 353m, 380m, 825s, 837s, and 847s cm^{-1} can be attributed to phoenicochroite ($Pb_2O(CrO_4)$),[27] a phase that has also been documented as a component of certain chromate-based artists' pigments[26] and has been found also in a sample of artists' pigment labeled "Golden Chrome, 1904" in the E.W. Forbes reference collection.[‖]

The two deep blue hues are achieved using Prussian blue ($Fe_4[Fe(CN)_6]_3$, PB27, CI# 77510, detected in *40 bleu de Prusse*) or ultramarine blue ($3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2Na_2S$, PB29, CI# 77007, detected in *13 bleu outremer*). Prussian blue is often detected in combination with small amounts of barium sulfate and is also the predominant blue pigment used

[‖] The Forbes reference collection was acquired in the beginning of the twentieth century by Edward Waldo Forbes (former director of the Fogg Art Museum at Harvard University, Cambridge, MA). It contains specimens of artists' materials in excess of 1600 and is widely used as a source of reference materials for museum research.[28]

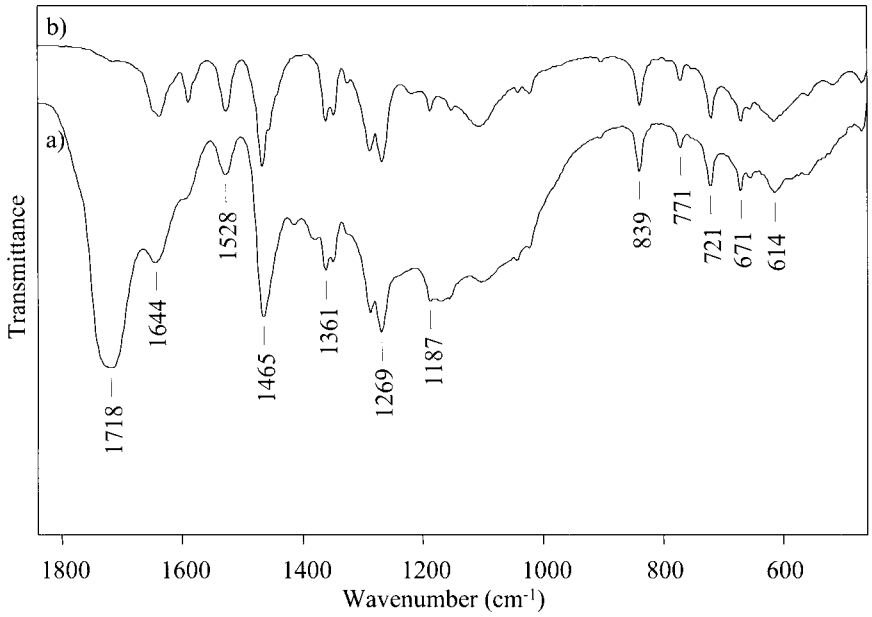

FIG. 6. FT-IR spectra of (***a***) Ripolin® swatch *16 rouge de Chine* (brochure D); (***b***) a sample of an artists' pigment labeled "alizarin crimson, Ansbacher" from the Forbes pigment collection.

in mixtures to achieve light blue or green hues, while ultramarine blue is mostly used in mixtures to create violet hues. Lighter blue colors (the *bleu azur* series) and turquoise blues (the *bleu turquoise* series) also contain small amounts of lead chromate and chromium (III) oxide in its two forms: Cr_2O_3 (PG17 CI# 77288) illustrated in Fig. 5 by the Raman spectrum of *18 bleu azur moyen*,[4] and $Cr_2O(OH)_4$ (PG18 CI# 77289).

The Ripolin® green colors were all found to comprise a combination of yellow (lead chromate or sulfochromate, zinc potassium chromate) and blue (Prussian blue, ultramarine blue) pigments in different proportions to obtain the desired hue and brightness marketed under the names *clair*, *pâle*, *moyen*, and *foncé*. White was also added to certain hues. As mentioned above, only swatches from the series *bleu turquoise* and *bleu azur* contain small amounts of an actual green pigment (anhydrous chromium (III) oxide).

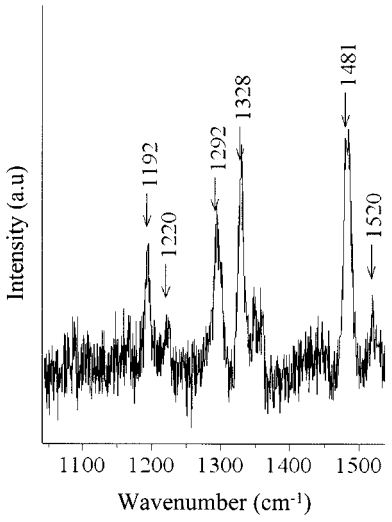

FIG. 7. Raman spectrum of a pink particle in the Ripolin® swatch *63 violet blue* from brochure D ($\lambda_0 = 785$ nm, 160 seconds acquisition, 2 accumulations): pigment identified as alizarin (1190m, 1292m, 1328m, 1481s, and 1520m cm^{-1}).

Reds are based on the organic pigment alizarin crimson (1,2-dihydroxyanthraquinone lake, PR83, CI# 58000) (Figs. 6 and 7) with some calcite ($CaCO_3$, PW18, CI# 77220) and iron oxide red (Fe_2O_3, PR101, CI# 77491). Only the swatch *59 rouge matin* contains some lead chromate in addition to the above pigments. An evolution in the formulation of *16 rouge de Chine* was noted: in brochure A, the color results from a mixture of alizarin crimson and red lead (Pb_3O_4, PR105, CI# 77578); in brochure B, it contains a mixture of alizarin crimson and lead chromate; and in brochures C and D, it contains alizarin crimson and a very small amount of iron oxide red.

Orange paints contain basic lead chromate ($xPbCrO_4 \cdot yPbO$, PO21, CI# 77601). The *andrinople* series also contains some organic reds: alizarin crimson in brochures A and B, and toluidine red (1-((4-methyl-2-nitrophenyl)azo)-2-naphthalenol, PR3, CI# 12120) with some calcite in brochures C and D.

Pink colors contain mixtures of lead chromate, alizarin crimson, and white.

Violet colors are obtained by the combination of ultramarine blue and alizarin crimson with white pigments, in different proportions according to the hue.

Browns are mainly obtained using iron oxide or a natural earth pigment (identified based on the co-occurrence of iron oxide and kaolinite clay) in combination with some lead chromate and/or white pigment. Occasionally, ultramarine blue is mixed in with synthetic iron oxide pigments (Mars reds), as in the case of the Ripolin® swatch *99 grenat foncé*.

Gray swatches contain mixtures of primarily white and carbon black (identified by PLM) along with minor quantities of blue (either ultramarine or Prussian blue), yellow (lead chromate), and red (iron oxide or an organic red, very likely alizarin crimson) pigments.

Each brochure also contains three metallic paint swatches: one silver- and two gold-colored. Silver swatches are made

using tiny flakes of aluminum and iron. Gold swatches contain iron and brass flakes, the latter composed of varying copper-to-zinc ratios depending on the values *pâle* or *foncé* (the former having a higher zinc content than the latter). SEM-EDX analyses indicated the presence of sulfur due to atmospheric corrosion.

Metal Soaps. Fourier transform infrared analysis indicated the presence of metal salts of organic acids in the Ripolin® paint samples:[29] these include products of interaction of the oil medium with the zinc white paints, as well as actual driers likely based on cobalt and lead, as suggested by elemental analyses (XRF and SEM-EDX) as well as contemporary treatises.[30–33] For example, the FT-IR spectrum of *53 blanc ivoire*—containing mostly zinc white pigment, a little lead chromate, and the medium—displays bands at 1583br, 1455, and 1418 cm^{-1} that can be attributed to metal soaps (Figs. 2a and 2b). This, along with the detection of cobalt with XRF, suggests the presence of cobalt salts of fatty acids and zinc soaps.[34] As a point of reference, cobalt naphthenate—a modern cobalt-based drier introduced after World War II—has strong bands centered approximately at 1593 cm^{-1} and between 1456 and 1418 cm^{-1} as published in the literature.[35] Further work is in progress to characterize the spectra of cobalt, lead, and zinc salts of fatty acids from natural sources so as to correctly assign the observed bands for the species whose spectra are absent from the literature.

The in-depth analyses summarized above highlight the consistency with which pigment combinations were used to achieve the various hues in all the Ripolin® brochures. Changes in formulation only occurred when new pigments became available commercially, as in the cases of Hansa yellow (PY3), toluidine red (PR3), and titanium dioxide (anatase). The identification of basic lead carbonate ($2PbCO_3 \cdot Pb(OH)_2$, PW1, CI# 77596) in only four out of over 340 swatches examined, and the detection of trace levels of mercury and bromine (detected using XRF and possibly representing use of biocides), represent minimal departures from the pigment-use trends discussed. Lead white was found in the following swatches: *58 andrinople clair* (brochure A), *62 andrinople moyen* (brochure A), *80 vert jaune clair* (brochure B), and *29 vert irlandais clair* (brochure C). Mercury was detected in three swatches—*80 vert jaune clair*, *74 vert romain clair*, and *88 vert réséda foncé*—in brochure A, while bromine is present in *58 andrinople clair* and *62 andrinople moyen* in brochure A.

In addition to giving insight into the technology of historic house paints, this analytical campaign has allowed the deduction of criteria that differentiate Ripolin® paints from artists' tube paints produced in the first few decades of the twentieth century:

(1) The vast majority of colors do not contain basic lead carbonate, a pigment that is commonly found in paintings executed in artists' tube paints.
(2) Many common pigments used in artists' tube paints are not present in the Ripolin® paints, e.g., vermilion (HgS, PR106, CI# 77766), cadmium red (CdS·xCdSe, PR108, CI# 77202), cadmium yellow (CdS, PY37, CI # 77199), emerald green ($Cu(OOCCH_3)_3 \cdot 3CuO(AsO_2)_2$, PG21, CI# 77410), and cobalt violets (such as $Co_3(PO_4)_2 \cdot 8H_2O$, PV14, CI# 77360).
(3) In house paint formulations secondary and tertiary colors are always combinations of primary colors, an observation that is supported by historic manuals and house paint technology literature.[30,36]

FIG. 8. (***a***) Pablo Picasso, *Figure*, 1935, The Art Institute of Chicago (Mary L. and Leigh B. Block, Alyce and Edwin DeCosta, Walter E. Heller Foundation Endowments), accession number 1988.428; (***b***) detail of the Ripolin® paint can lid from *Figure* (recto); (***c***) an example of Ripolin® can *1 blanc de neige*.

Case Study: Pablo Picasso, *Figure*, 1935 (AIC 1988.428). Pablo Picasso's use of Ripolin® brand paint is documented in the artist's personal correspondence and suppliers' receipts, as well as in contemporary accounts and photographs.[8,37–42] Direct evidence of Picasso's access to, and likely use of, Ripolin® comes in the form of his 1935 sculpture *Figure* (AIC 1988.428). This work incorporates the lid of a Ripolin® paint can used to create the head of the *Figure* (see Fig. 8). The top of the lid has a light blue factory-applied paint coating on it, which indicated the color of paint inside the can. Interestingly, this sculpture also includes a wooden box that once held tubes of Lefranc oil paint and is thus emblematic of Picasso's use of both artists' and house paints throughout his career.

The color of the light blue paint remnants on the underside of the Ripolin® paint can lid visually resembles that of three paint swatches in the brochures: *71 bleu turquoise clair*, *18 bleu azur moyen*, and *61 bleu azur pâle*. FT-IR analysis of the light blue paint provided infrared spectra that matched very closely with that of the light greenish-blue swatch, *71 bleu turquoise clair*, from brochure C. The infrared spectrum, reported in Fig. 2c, indicates that the primary components of the paint are a drying oil, a natural resin, and zinc white. Strong bands at 1583, 1456, and 1418 cm^{-1} are characteristic of metal soaps as discussed above. Some chromium was detected using XRF in the three greenish-blue swatches and also in the paint sample from *Figure*. This likely relates to the use of chromium (III) oxide in small amounts (confirmed by PLM), well below the detection limit of FT-IR. This finding, coupled with the results of FT-IR spectroscopy, confirms that the light greenish-blue paint residue represents the original contents of the paint can, which was likely one of the light blue shades mentioned above.

CONCLUSION

The multi-analytical study of paint samples presented here is the first to report the detailed composition of inorganic and

organic pigments of historic house paints manufactured by the French Ripolin®. This particular brand is relevant to artistic works of important twentieth century artists such as Picasso, Picabia, and Kandinsky. The findings indicate that, in order to identify the presence of house paints in artists' paintings, researchers must rely on a combination of factors rather than on the detection of a single chemical marker. These factors include: (1) the strong spectroscopic signatures of characteristic metal soaps; (2) the dominance of zinc-based whites; (3) the presence and/or absence of certain pigments; and (4) the use of mixtures of primary colors to achieve secondary and tertiary colors. Future work will focus on the in-depth study of the binding medium in order to trace changes in formulation, to identify the type of natural resin present, and to detect the possible presence of other organic materials or additives specific to these paints.

The detailed results on the characterization of paint swatches from Ripolin® sample cards were successfully correlated with an important piece of direct evidence of Picasso's use of this brand of paint: his 1935 sculpture *Figure* (AIC 1988.428) from the collection of the Art Institute of Chicago. The newfound information on house paint composition will be used to inform and direct further analyses of Picasso's works in museum collections so as to conclusively confirm the artist's use of Ripolin® paints. Ultimately, this study will provide a scientific basis for media descriptions in exhibition catalogues and museum labels for works of important artists who made pioneering use of this product.

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SUPPLEMENTAL MATERIAL

The Supplemental Material mentioned in the text, Table S-I, is available on-line in the electronic version of the journal (http://www.s-a-s.org).