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A typical postwar workshop: Insights into Simon Hantaï's oil paint palette

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A B S T R A C T

Simon Hantaï (1922–2008) was a highly influential postwar painter in Paris whose innovative serial practice, creative curiosity and theoretical convictions inspired a number of his contemporaries. His art media are typical of the period, consisting of commercial artists' products, sold in tubes and cans, which were available to artists in Europe and beyond. We have studied a series of samples from the brands Lefebvre-Foinet, Lefranc & Bourgeois and Valor using a combination of optical and electron microscopy, accelerator-mass spectrometry carbon-14 dating, infrared spectroscopy, structural analysis, chromatographic and mass spectrometry techniques. Of particular interest is the rare access to a coherent artist's studio collection and its dating in relation to the painter's works. We gained precise information on paint formulations, including main binders and pigments, as well as additives, such as free metal soaps, beeswax and pine resin. This suggests the value of further research into paint formulations and their identification in paintings from the second half of the 20th century. These materials were studied for their capacity as possible references for future analysis of the painter's artworks. The high degree of hydrolysis of the oil binder and alteration, notably by saponification, leads us to question the significance of these materials and the handling of the data generated towards comparative studies. These samples have a history; considering them as pristine references for comparative studies with the works of artists of the period cannot be done at the expense of their own materiality – and in particular their physico-chemical evolution over time in their specific environment

Keywords:

Artist palette

Simon Hantaï

Paint formulation

Contemporary painting

Paint alteration

1. Introduction

Starting from the 19th century, paint formulations have changed considerably, which tremendously impacted the appearance and stability of modern and contemporary paintings [1–5]. Considering advancements in manufacturing methods, paint makers were able to constantly modify their formulas in order to ob-

tain certain physical properties or visual aspects, while this information often remains undisclosed [6–9]. To fully understand the materiality of modern and contemporary paintings, address conservation issues and prevent degradation, we have a new set of tools to add to the chemical and physical characterization of a work of art: the scientific study and analysis of surviving materials from artists' workshops. Access to workshops of 20th century artists is very rare, and even with access, much information about these materials is often unknown [10,11]. Here, we focus on the chemical study of paint materials from the atelier of the abstract painter, Simon Hantaï, who worked in Paris in the postwar era. This col-

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lection included oil paints from the French brands Lefranc & Bourgeois, Lefebvre-Foinet, and Valor. These paints were used by other renowned contemporary artists in this period, including Nicolas de Staël, Joan Mitchell, Jean-Paul Riopelle [12], and Pierre Soulages [13]. French paint materials from this period remain largely under-documented despite several related works [4,14–16]. This study is intended as a first step towards the study of a selection of paintings from Hantaï's studio. It provides knowledge for 20th-century oil-based paint formulations in postwar Paris by identification of the original components, as well as the secondary compounds produced by reactions within the mixtures, while simultaneously providing insights into the creative practice of an artist in his studio.

2. Research aims

This study was carried out to collect detailed information on the chemical formulation of oil paints left by the painter Simon Hantaï, which include Lefebvre-Foinet, Lefranc & Bourgeois and Valor, companies that were majorly marketed in France. Beyond Hantaï's palette, this rare set of materials from the studio of a major 20th century artist can be useful to provide a reference point for art history and technical knowledge required in conservation. We describe and document the materials left behind, discuss the conservation of the materials analyzed, and explore the status of such studies of artists' workshops, both in terms of the chemical changes undergone by materials over time and in the context of an artist's practice.

3. Materials and methods

3.1. Sample set

Simon Hantaï (1922–2008) was a highly influential painter in the postwar era of Paris (Supplementary Text S2). The paint materials studied in this work come from the artist's workshop in Paris and Meun, France, where he stored many of his painting materials up to the end of his life (Fig. 1a). They are commercial oil paints from three French manufacturers, Lefebvre-Foinet, Lefranc & Bourgeois and Valor. In 2008 and 2015, A. Chevalier collected bulk pieces from twelve commercial paint tubes (Lefebvre-Foinet and Lefranc & Bourgeois, Fig. 1b–d) and two commercial paint cans (Valor, Fig. 1e) for the restoration of Hantaï's works and for archival purposes [17]. These paint pieces have since been stored in A. Chevalier's restoration workshop in Paris under the following conditions: (i) as a bulk material in glass jars (some sealed), or (ii) wrapped in plastic films, kept in low light conditions and in uncontrolled temperature and humidity conditions. The pieces in this study were sampled from this collection in 2020. In this work, the samples were designated according to the following convention [brand initials]–[nature of binder]–[paint designation initials], adding chemical names for Cd based samples to obtain unequivocal designation (Supplementary Table S3.2). This notation was given for the paint pieces and CS was added for samples prepared as cross sections (see acronyms in Supplementary Text S2).



Fig. 1. (a) Paint tubes and cans in Simon Hantaï's atelier in Paris, France, in 2015. (b–e) Typical material from Simon Hantaï's atelier in Meun, France studied in this work: Lefebvre-Foinet paint tube (corresponding to sample LF-O-PGD16, b), which had been stored in a cardboard box with handwritten inscriptions (c); a Lefranc & Bourgeois paint tube (sample LB-O-FW, d), and a Valor paint can (sample V-O-BC, e). Credits for all photographs: A. Chevalier.

3.2. Methods

Paints were dated by measurement of their ^{14}C content at the LMC14 laboratory [18]. Separative analyses of paint pieces including gas chromatography-mass spectrometry (GC-MS), pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), and liquid chromatography/flow injection analysis)-electrospray ionization quadrupole-time of flight tandem mass spectrometry (HPLCILARIATof / FIA-ESI-Q-ToF) were performed at University of Pisa. Sample preparation and analysis for Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM-EDX) was carried out at IPANEMA. High resolution synchrotron-based micro-X-ray diffraction (SR- μ -XRD) was performed at the ESRF (Grenoble, France). Additional information on the protocols used for each analysis is provided in Supplementary Text S4.

4. Results

The main results are indicated in Table 1, with additional detail provided in Supplementary Tables S9.1-S9.3.

4.1. Dating

Carbon-14 analysis dates the moment when the carbon in the sample ceases to be in equilibrium with the atmosphere. Dating of organic compounds of plant origin (in particular oils and resins) allows the determination of the moment when these plants were

cut. Linseed (or flaxseed) oil is made by the extraction of oil by mechanical pressing or, in modern cases, use of organic solvents [19]. Therefore, carbon-14 dating gives information on the plant from which the linseed oil was extracted, and the market date would fall later. Carbon-14 dating results were combined with information provided by the packages themselves, in particular the tube labels. In the case of the Lefebvre-Foinet tubes, each tube, except two, indicated the company's capital value ("S.A.R.L."). This value was either 1.700.000, 50.000 or 17.000 francs (Fr). In France, the new franc (Fr) was implemented on January 1st, 1960, worth the value of 100 old francs, thus dividing the capital value by 100. In addition, other information was retrieved from the photodocumentation of Hantaï's atelier, such as handwritten labeling, presumably by Hantaï, on boxes in which tubes were stored and labeled by paint designation and reference numbers (Fig. 1c). We can illustrate our interpretation with three cases. (i) For the sample LF-O-CdRV, ^{14}C dating led to two possible date ranges, 1963 and 1970–1972. The tube label (Fig. 1) showed a capital value of "1.700.000 Frs", thus the label would have been printed before January 1st, 1960 or early in the 1960s, as opposed to over 10 years after the change had been implemented. The date of 1963 was therefore retained. (ii) Two date ranges were also obtained for the sample LF-O-PGD16: 1963 and 1970–1972. The tube label showed a capital value of "17.000 Frs", in accordance with the new franc value, which led to the hypothesis that the date was in the 1970–1972 range. In addition, photodocumentation showed that a box in which the tube was stored had handwritten reference numbers, "11-72". The date of 1972 was therefore retained. (iii) For the

Table 1

Main results for all paint samples. Paint design.: paint designation by manufacturer (in English when written), Cbx: carboxylates, FMS: free metal soaps, MS: metal soaps, Ox: oxalates, PN: polymeric network.

Sample Paint design.	Estimated Date	Organic binder	Coloring materials and additives	Metal soaps and oxidized species
LF-O-CdR <i>Cadmium Red</i>	1969–1971	Linseed oil. Low oxidation, advanced curing, PN	$\text{CdS}_x\text{Se}_{1-x}$ ($x \approx 0.62$), Al oxides	MS formed with oil: unidentified Cbx (presumably Cd or Zn), Ox
LF-O-CdRO <i>Cadmium Red Orange</i>	1962–1963	Linseed oil. Curing is ongoing, PN	$\text{CdS}_x\text{Se}_{1-x}$ ($x \approx 0.74$), Al oxides	Cd-Cbx (formed with oil) and Zn-Cbx (possibly added to the paint formula), Ox
LF-O-CdRP <i>Cadmium Red Purple</i>	1958–1959	Linseed + safflower oil. Advanced oxidation, PN at lower degree of polymerization	$\text{CdS}_x\text{Se}_{1-x}$ ($x \approx 0.55$), Al oxides, beeswax	Cd-Cbx (formed with oil) and Zn-Cbx (possibly added to the paint formula), Ox
LF-O-CdRV <i>Cadmium Red Vermilion</i>	1963	Linseed oil. Low oxidation, curing is ongoing, PN	$\text{CdS}_x\text{Se}_{1-x}$ ($x \approx 0.66$), Al oxides	Cd-Cbx (formed with oil) and Zn-Cbx (possibly added to the paint formula), Ox
LF-O-CdYO <i>Cadmium Yellow Orange</i>	1963	Linseed oil. Low oxidation, curing is ongoing, PN	CdS, BaSO_4 , Al oxides	MS formed with oil: unidentified Cbx (presumably Cd or Zn)
LF-O-CdYM <i>Cadmium Yellow Medium</i>	1962–1963	Linseed oil. Low oxidation, relatively slow curing, PN	CdS, BaSO_4 , Al oxides	unidentified Cbx (presumably Cd or Zn); part of MS may be added to formula
LF-O-PGD4 <i>Permanent Green Deep</i>	1963–1965	Linseed oil. Low oxidation, curing is ongoing, PN	$\text{K}_2\text{Zn}_4\text{O}(\text{CrO}_4)_4 \cdot 3\text{H}_2\text{O}$, Cr_2O_3 , CrO_3	Zn-Cbx and other unidentified Cbx, possibly formed with the oil and added to the paint formula
LF-O-PGD16 <i>Permanent Green Deep</i>	1970–1972	Linseed + safflower oil. Advanced oxidation, PN	$\text{K}_2\text{Zn}_4\text{O}(\text{CrO}_4)_4 \cdot 3\text{H}_2\text{O}$, Cr_2O_3 , CrO_3	Unidentified Cbx
LF-O-CB <i>Cerulean Blue</i>	1966–1967	Linseed oil. High degree of hydrolysis, advanced oxidation, advanced curing	SnO_2 , Co_2SnO_4 , Co_3O_4 , $\text{Mg}_{1.6}\text{Co}_{0.4}\text{SnO}_4$	MS formed with oil: unidentified Cbx, Ox
LF-O-MB <i>Monacal Blue</i>	1979	Linseed oil. High degree of hydrolysis; low oxidation, PN	$\text{C}_{32}\text{H}_{16}\text{CuN}_8$, $\beta\text{-C}_{32}\text{H}_{16}\text{CuN}_8$; Contains Al, Si, P, S, Cl, K, Ca	Unidentified Cbx, possibly both formed with the oil and added to the paint formula
LF-O-UB <i>Ultramarine Blue</i>	1970–1972	Linseed oil. High degree of hydrolysis, low oxidation, advanced curing, lowest amount of reacted double bonds, PN	$\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4) \cdot \text{H}_2\text{O}$, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, Ca oxides, beeswax	Small amounts of MS, possibly both formed with the oil and added to the paint formula
LB-O-FW <i>Flake White</i>	1987–1990	Linseed oil. Low oxidation, curing is ongoing, PN	$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, PbCO_3 , CaCO_3 , Al oxides	High content MS formed with oil, Zn-Cbx, Pb-Cbx
V-O-BC <i>Bois Clair</i>	1958(?)	Linseed oil. Advanced oxidation, curing ongoing, no PN, polyunsaturated species still present	FeO_2 , Fe_2O_3 , CaCO_3 , BaSO_4 , <i>Pinaceae</i> resin	Small amounts of MS formed with the oil
V-O-IJ <i>Jaune de Jonquille</i>	1963 or 1966–1967	Linseed oil. High degree of hydrolysis, low oxidation, no PN, polyunsaturated species still present	Possibly Zn yellow; Contains Zn, Cr, K, CaCO_3 , BaSO_4 , <i>Pinaceae</i> resin	MS formed with oil, not added to formula; Zn-Cbx, Pb-Cbx

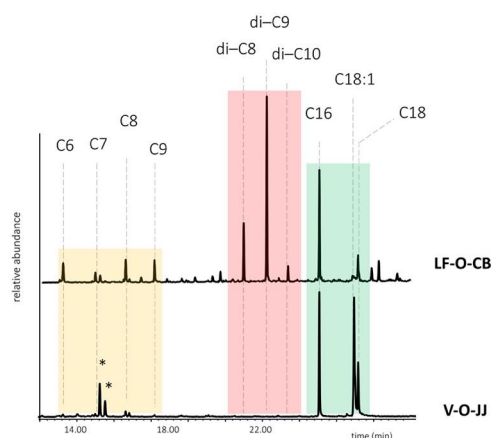


Fig. 2. Py-GC-MS extracted ion chromatograms of the fragment ion with m/z 117 of the samples LF-O-CB and V-O-JJ. C_n indicates the TMS ester of a linear aliphatic carboxylic acid with n carbon atoms. $C_n:i$ indicates the TMS ester of a linear aliphatic carboxylic acid with n carbon atoms and i unsaturations; di- C_n indicates the TMS ester of a linear aliphatic dicarboxylic acid with n carbon atoms. *glycerol di- and tri-TMS derivative.

sample V-O-BC, archival information from photodocumentation and on works by Raymond Gid, the graphic designer who modernized the Valor logo, provided clarity regarding the dating of the sample. These results are summarized in Supplementary Text S5.

4.2. Chromatography and infrared analysis

Py-GC-MS

Analytical pyrolysis was carried out to investigate the formation of the polymeric network of the oil medium. Short chain saturated and unsaturated fatty acids – from six to nine carbon atoms – were detected in the pyrograms of cured drying oils, and derived from the thermal decomposition of the cross-linked network [20]. The pyrolytic profiles (Fig. 2) showed a well-established polymeric network for LF-O-CB, like the vast majority of the samples analyzed, whereas the pyrograms of V-O-BC and V-O-JJ did not show short chain saturated and unsaturated fatty acids. The latter sample came from paint cans (Valor), which were reported to contain stand oil, a pre-polymerized oil. The absence of signals ascribable to the pyrolysis of the polymeric network in the Valor paints could be due to the fact that the cross-linked fraction had deposited at the bottom of the can, and was thus not sampled for the analysis.

GC-MS

The qualitative and quantitative profiles of free fatty and dicarboxylic acids (FFA) were determined by derivatisation with HMDS (hexamethyldisilazane). The sum of the FFA and free metal soaps (FMS) was then determined on the same sample aliquot after drying the solution under nitrogen flow and derivatisation with BSTFA (N,O-Bis(trimethylsilyl)trifluoroacetamide) [21] (see details in Supplementary Text S4.2). These fractions are called FFA and FFA+FMS in the following. If the profile of saturated fatty acids in the FFA and FFA+FMS fractions are different, we may hypothesise the addition of free metal soaps or free fatty acids deriving from a different source than the hydrolysis of the oil or its reaction with the pigments and additives [22]. The presence of azealates in the FFA+FMS fraction is an indication that metal soaps are, at least in part, the results of the reaction between inorganic cations and the oil binder, as azelaic acid is a product of the oxidation of drying oils. This was observed by looking at the azelaic over palmitic acid ratio (A/P) and the sum of the relative content of dicarboxylic acids ($\Sigma D\%$) in the FFA+FMS fraction compared to the FFA fraction. A quantitative evaluation of the two profiles gave an indication of the degree of hydrolysis and saponification of the paint

[23]. The curing stage of the oil was estimated based on the detection of unsaturated fatty acids which are consumed by the curing reactions: oleic acid (and the oleic over stearic ratio O/S), and the more reactive linoleic and linolenic acids (Supplementary Fig. S6.1). As an example, Fig. 3 shows the result for two samples, the GC-MS chromatographic profiles of LB-O-FW presented an extremely high content of free metal soaps and very small amounts of free fatty acids: lead white is prone to the formation of metal soaps and any fatty and dicarboxylic acids released from the oil medium upon hydrolysis readily react with lead to form lead soaps. LF-O-CB contained a comparatively higher amount of free fatty acids and smaller amounts of metal soaps.

HPLC-ESI-Q-ToF

The HPLC-ESI-Q-ToF analysis performed on the paint samples allowed to obtain a complete picture of their lipid profiles by performing a molecular identification of the free fatty acids, mono-, di-, and triacylglycerols, together with their oxidation products. All the acylglycerol profiles obtained for the paint samples were characterized by the presence of high abundances of free fatty acids, monoglycerides, and diglycerides with respect to the triacylglyceride fraction, which is illustrated by the lipid profile for the paint tube LF-O-CdR (Fig. 4). This behavior can be linked to an oil with a high degree of hydrolysis. All the analyzed samples were characterized qualitatively by similar molecular features enabling us to identify the presence of linseed oil as paint binder. Only the two samples LF-O-CdRP and LF-O-PGD16 contained triacylglycerol with long chain acyl substituents, including ALL (m/z 833.8, $[M+Na]^+$), ALO (m/z 935.8, $[M+Na]^+$), ALS (m/z 937.8, $[M+Na]^+$), and BLO (m/z 963.8, $[M+Na]^+$), which can be associated to the presence of safflower oil. Finally, the lipid profiles of samples LF-O-CdRP and LF-O-UB were characterized by the presence of high molecular weight esters, which may be ascribed to beeswax and explained the presence of three different ion clusters by FIA-ESI-Q-ToF analysis (Fig. 5). The main results are reported in Supplementary Tables S6.1 and S9.1–9.3.

FT-IR

Infrared spectroscopy provided information about the presence of metal carboxylates and enabled speculation on their potential origin – whether they were generated spontaneously as a result of the reaction between the binder and the pigment, or introduced as an additive to the binding media. In this regard, samples could be categorized into three groups, based on the types of the characteristic $\nu(\text{COO}^-)$ bands observed in the carboxylate region ($1390\text{--}1610\text{ cm}^{-1}$). Due to the intense contributions of the oil binder, the identification of the different types of carboxylates was based on the bands within the range of $1500\text{--}1600\text{ cm}^{-1}$. (i) LB-O-FW, LF-O-CdRO, LF-O-CdRP, LF-O-CdRV, LF-O-PGD4, and V-O-JJ exhibited a broad band with evident peaks that allowed the attribution to specific carboxylates species (Fig. 6). Most contained a band centered between $1580\text{--}1595\text{ cm}^{-1}$, which may be ascribed to amorphous Zn carboxylates [24]. Additionally, in the region $1530\text{--}1535\text{ cm}^{-1}$, a relatively sharper peak may be attributed to crystalline Zn carboxylates [24]. (ii) LF-O-CdYO, LF-O-CdR, LF-O-CB and LF-O-MB are characterized by the presence of a broad band with weak shoulders whose unambiguous assignment was not possible. (iii) LF-O-PGD16, LF-O-UB, and V-O-BC showed no evidence of peaks nor shoulders in the bridge-like band region that would have been attributed to carboxylates. The diagnostic bands of barium sulfate BaSO_4 (1180 , 1120 , 1075 and 985 cm^{-1} [25]) were clearly detected in samples LF-O-CdYO, LF-O-CdYM and V-O-JJ (Supplementary Figures S6.2e,f and S6.4c). Meanwhile, in samples V-O-BC and V-O-JJ, strong signals related to the presence of calcium carbonate (2513 , 1796 , 1422 and 873 cm^{-1}) were identified [26,27] (Supplementary Figure S6.4b,c). Both barium sulfate and calcium carbonate are common extenders in oil paints.

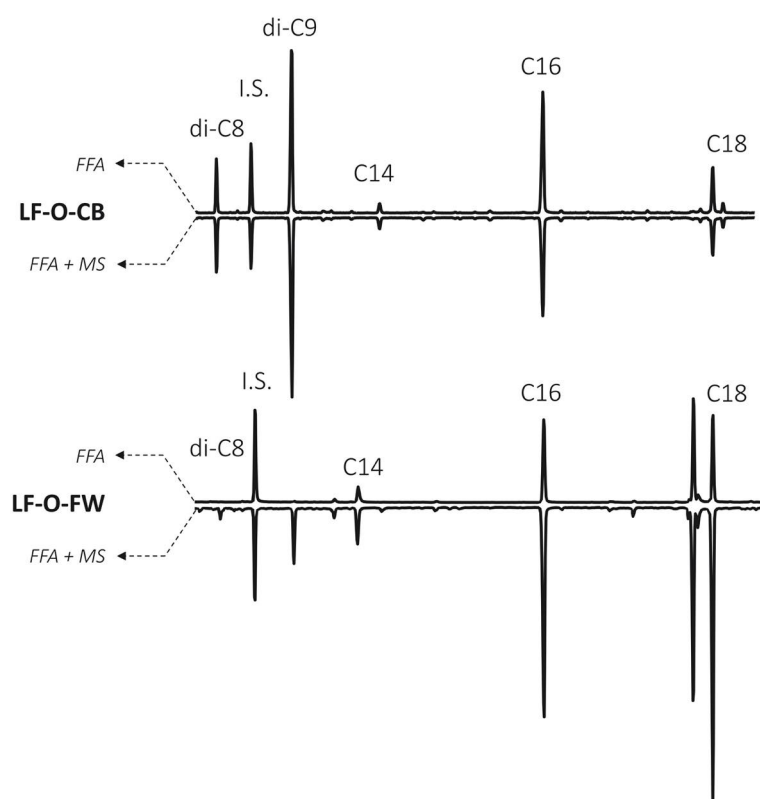


Fig. 3. GC-MS extracted ion chromatograms of the fragment ion with m/z 117 relative to samples LF-O-CB (top) and LF-O-FW (bottom). FFA (chromatographic curve pointing up): chromatograms relative to free fatty and dicarboxylic acids; FFA+MS (chromatographic curve pointing down): chromatograms relative to free fatty and dicarboxylic acids and free metal soaps of fatty and dicarboxylic acids; IS: internal standard; C_n indicates the TMS ester of a linear aliphatic carboxylic acid with n carbon atoms and i unsaturations. $di-C_n$ indicates the TMS ester of a linear aliphatic dicarboxylic acid with n carbon atoms. The chromatograms were normalized FOR or BY? the intensity of the peak of the internal standard.

4.3. Structural and elemental analysis

SEM-EDX

We observed that the cross-section of paint samples showed a stratigraphy near the borders of the sample, consisting of two, or occasionally three, main layers, ascribed to the drying of these samples. The thickness of these layers varied between samples. This is observed most notably, but not limited to, paints which had been stored in glass jars covered, but not sealed, from air. The SEM-EDX mapping of LF-O-CdR-CS was used as an example to reveal a more complex structure than observed by optical microscopy. Optical microscopy showed two distinguishable layers: (1) a bright red layer, $\sim 300 \mu\text{m}$ thick, attributed to the dried part of the sample that had been exposed to air, and (2) dark red paint, relating to the bulk material that had not been exposed to air, nor entirely dried. The cross-section under AsB electron detection showed three layers, as opposed to two, in which the dried layer 1 was comprised of two sublayers (Fig. 7): (1a) a thin layer, $\sim 75 \mu\text{m}$ thick along the edge of the cross-section, attributed to the dried part of the sample that had been exposed to air, concentrated in elements associated with the pigment (Cd, S, Se), and (1b) an intermediate layer, $\sim 200 \mu\text{m}$ thick, mostly concentrated in organics (C, O). The bulk material (2) was concentrated in elements relating to the pigment (Cd, S, Se) at a higher concentration than in layer 1a. A zone of small particles containing Al and O was detected between layers 1b and 2, as well as a Si oxide particle in layer 1b. Al and Si are mostly concentrated in zones where elements related to the pigment (Cd, S, Se) were localized. Minor trace elements included Zn, P, and Ba, and were also localized where there was a

high concentration of pigment material. Identification of inorganic ions was sought by SEM-EDX for metal soaps that could not be unambiguously identified by FT-IR. For the case of Lefebvre-Foinet Cd based paints and Cr based paints (LF-O-PGD4, LF-O-PGD16), traces of Zn were present, supporting the possible presence of Zn metal soaps. No Zn soap agglomerate could be observed by SEM imaging. For the Valor paint cans (V-O-BC, V-O-JJ), lead, which is prone to Pb soap formation even in small concentrations, was identified in both mixtures in low amounts.

Synchrotron μ -XRD

Analysis of paint pieces identified crystal phases related to the pigment for all paints. The high-resolution synchrotron diagrams allowed for the identification of several additives, including the previously mentioned BaSO_4 (LF-O-CdYO, LF-O-CdYM, V-O-JJ), CaCO_3 (LB-O-FW, V-O-JJ) and $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (LF-O-UB). The Cd pigments from Lefebvre-Foinet were all wurtzite structured (hexagonal crystal system, space group: P63mc), with the characteristic diffraction peaks slightly shifted. Detailed information can be found in the Supplementary Tables S9.1–9.3, with SEM-EDX analysis in Supplementary Text S7 and XRD diffractograms in Supplementary Figures S8.1–S8.3.

5. Discussion and perspectives

5.1. Composition of the paint materials

5.1.1. Organic binder and specific formulations

All paints are based on linseed oil (HPLC), which has been by far the most commonly used drying oil in artistic and house

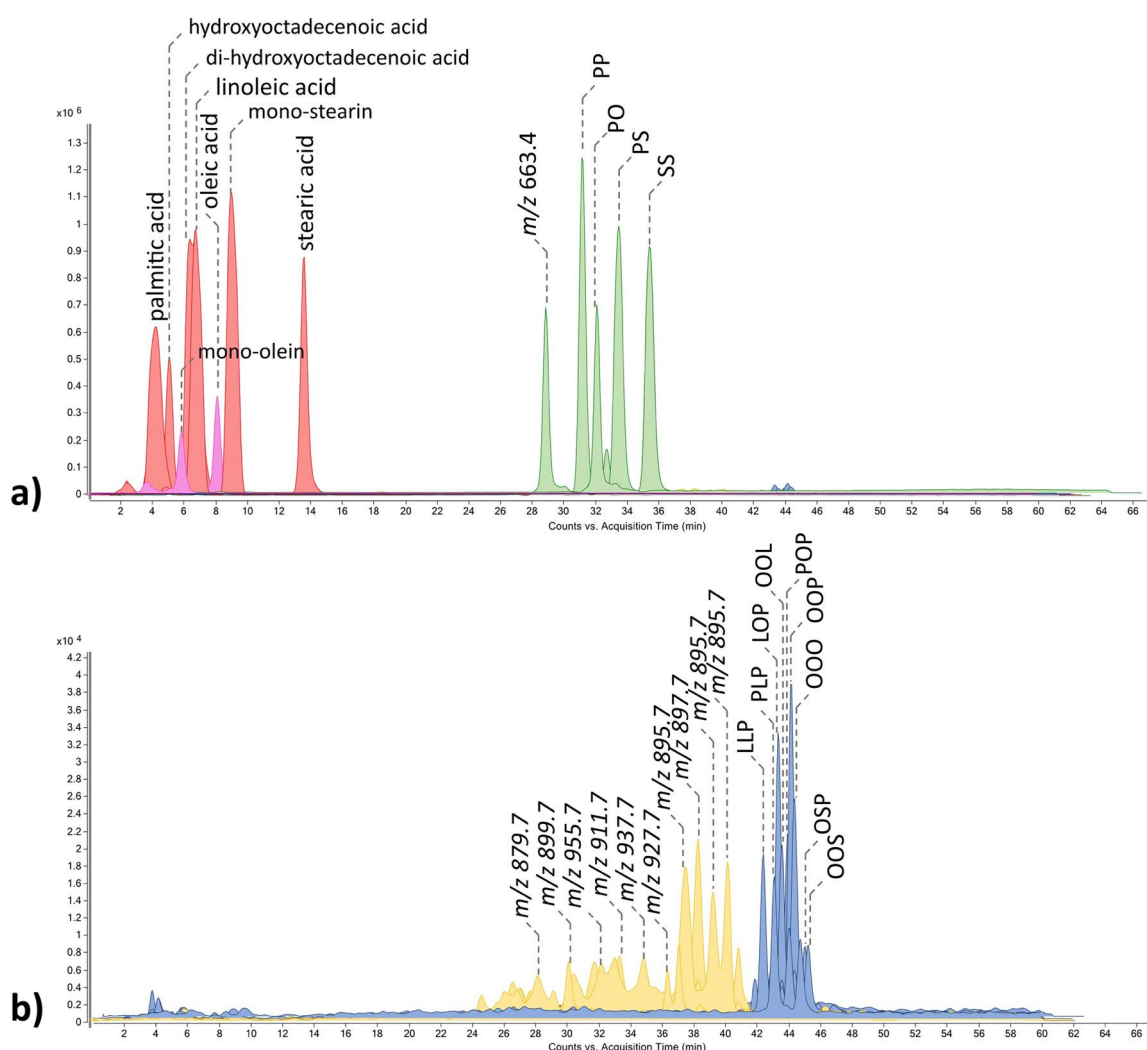


Fig. 4. HPLC-ESI-Q-ToF extracted ion chromatograms (EICs) obtained for sample LF-O-CdR. (a) EICs of all the acylglycerols. (b) EICs of TAGs and oxidized TAGs.

paints for a very long time [28]. Paint curing has begun for all sample. This could be concluded from: (i) the detection of mono and di-hydroxyoctadecanoic and hydroxyoctadecenoic acids, which are intermediate products of oxidation of (poly)-unsaturated oleic, linoleic and linolenic acids in the HPLC-MS chromatograms; (ii) the detection of dicarboxylic acids, stable products of oxidation of a drying oil, among which azelaic acid is the most abundant in the GC-MS and Py-GC-MS chromatograms; (iii) the presence of relatively small amounts of unsaturated fatty acids in HPLC-MS, GC-MS and Py-GC-MS chromatograms: oleic acid (as indicated by the O/S ratio) was detected in all samples, linoleic acid was present in some samples, and linolenic acid, the most reactive, was detected in a very few of them; (iv) the detection of oxalates in some samples (FT-IR); (v) the formation of short chain saturated and unsaturated fatty acids upon pyrolysis which are observed in the Py-GC-MS chromatograms, and derive from the thermal decomposition of the oil polymeric network, with the only exception of samples from the Valor paint cans, which will be discussed later on; (vi) the evident tailing and broadening of the carbonyl stretching band at about 1740 cm^{-1} (the shoulder at 1720 cm^{-1} indicated the formation of ketone compounds) detected particularly in samples LF-O-CB, LF-O-MB, LF-O-UB, V-O-BC, and V-O-JJ.

All samples showed a very high degree of hydrolysis. This was evident from the broadening of the carbonyl band in the infrared spectra: the shoulder at 1710 cm^{-1} is ascribable to carboxylic acid moieties, which are produced upon oxidation and hydrolysis [29,30]. It is worth mentioning that the samples LF-O-CB and LF-O-MB featured a split carbonyl absorption band, appearing as a doublet at $\sim 1740/1710 \text{ cm}^{-1}$, which may indicate a higher degree of hydrolysis of the sample [31]. The GC-MS and HPLC data confirmed this observation as free fatty and dicarboxylic acids were detected with a high relative abundance. The degree of hydrolysis observed in all samples was unexpectedly very high [20,23,32,33], irrespective of the manufacturers, fabrication dates, forms of packaging, and types of pigments. We thus hypothesized that hydrolysis must be related to the environmental conditions in which the paints were stored, post-sampling from the tube, together with some of the pigments being quite hygroscopic, as seen with Cd based paints and often with blue pigments or water absorbing inorganic additives present such as zinc oxide, MgCO_3 or hydrated alumina [31].

The presence of metal soaps was evidenced in all samples, although in variable amounts (FT-IR, GC-MS). Metal soaps are common paint additives: the addition of Al stearate as an extender began around 1920 to minimize the quantity of pigment required,

LF-O-UB FIA-MS Mass Spectrum

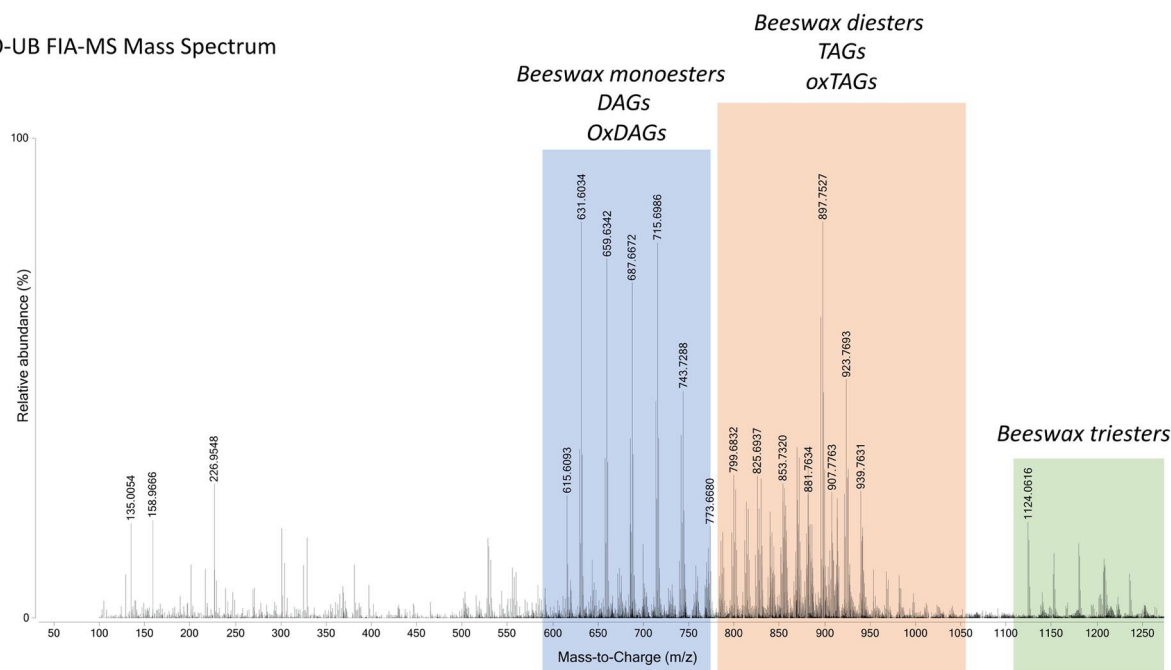


Fig. 5. Results of the FIA-ESI-Q-ToF analysis showing the presence of monoesters, diesters, and triesters relating to beeswax in the LF-O-UB paint sample.

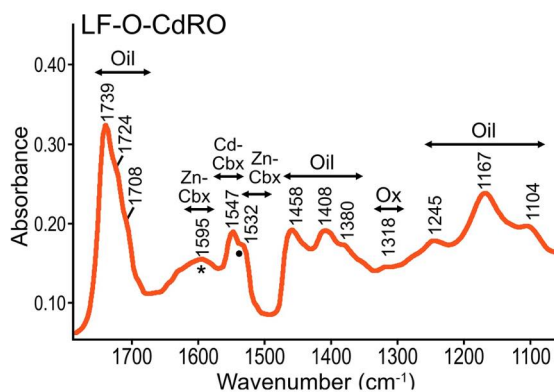


Fig. 6. FT-IR spectra of LF-O-CdRO highlighting the band in relation to the oil binder, the presence of amorphous (*) and crystal (•) forms of Zn carboxylates (Zn-Cbx), Cd carboxylates (Cd-Cbx) and oxalates (Ox).

as it increases the body of the paint and, prevents separation of the pigment from the binder, as an extender [34]. Metal soaps can also form in oil paints by reaction of certain pigments or additives with fatty acids and glycerides [35]. Given the very similar profiles of saturated free fatty acids and free metal soaps of fatty acids as analyzed by GC-MS (P/S and M/S values), we could not conclude that metal soaps were added to the paint formulation in any of the samples analyzed. Moreover, the presence of soaps of azelaic and other dicarboxylic acids strongly suggested that metal soaps were due, at least in part, to the local reaction between the binder and the inorganic component present in the paint formula, either as pigment or additives. Two types of carboxylate compounds were distinguished (FT-IR): crystal metal soaps presented sharp peaks at lower wavenumber with respect to the amorphous carboxylates which showed broader bands shifted towards high wavenumber in the same region [36]. The detection of Pb and Zn by SEM-EDX accompanied by the characteristic FT-IR peaks at 1545 cm^{-1} [37] and 1530 cm^{-1} [24] suggested the presence of Pb and Zn car-

boxylates in sample V-O-JJ (Supplementary Fig. S6.4c1). The position and the shape of the FT-IR band of Zn carboxylates may suggest a crystal form. LB-O-FW exhibited a broad band centered at around 1595 cm^{-1} (Supplementary Fig. S6.4a1), which could be attributed to amorphous Zn carboxylates [24]. Despite the presence of Pb in this sample, it was difficult to distinguish an evident peak attributed to Pb carboxylates among several inconspicuous peaks that formed a bridge-like broadband in the 1500–1600 cm^{-1} region. Since Pb, the main source of pigment, is sensitive to soap formation, we suggest that Pb soaps in the matrix contribute this broadband, though the expected band is not clearly distinctive.

Beeswax was positively identified in two Lefebvre-Foinet samples, LF-O-CdRP and LF-O-UB (FIA-ESI-Q-ToF). The presence of beeswax was mentioned in the formulation of several 20th century artists' paints [4,38,39]. Waxes, also castor wax, were common additives used as paint stabilizers [4], which may also help to increase the body of the paint and give it a matte finish. The detection of 7-oxo-dehydroabiatic acid and dehydroabiatic acid indicated the use of a resin extracted from a conifer tree of the *Pinaceae* (pine) family in the samples from the Valor cans (GC-MS). Plant resins, including fossil resins, were common additives of oil-based enamel paints, used to improve drying rates and rheological properties [40]. The advanced state of oxidation of V-O-BC showed by GC-MS, and absence of a polymeric network observed by Py-GC-MS in both samples, could indicate that phase separation had occurred; the polymeric component – possibly including the highly polymerized fossil resin – had deposited at the bottom of the can, and was thus not sampled in our study for analysis.

We observed phase separation between different drying states of paints (SEM-EDX). LF-O-CdR was studied closely for the ongoing mechanisms during paint drying, because a separation in three layers was observed. The cross-section exhibited the presence of a slightly higher concentration of elements related to the pigment at the surface of the drying paint. The Cd based oil paints presented, in general, a low degree of oxidation (A/P ratio of 0.1 for both FFA and FMS components; GC-MS). The low oxidation in combination with the saponification of the medium may have caused this phase

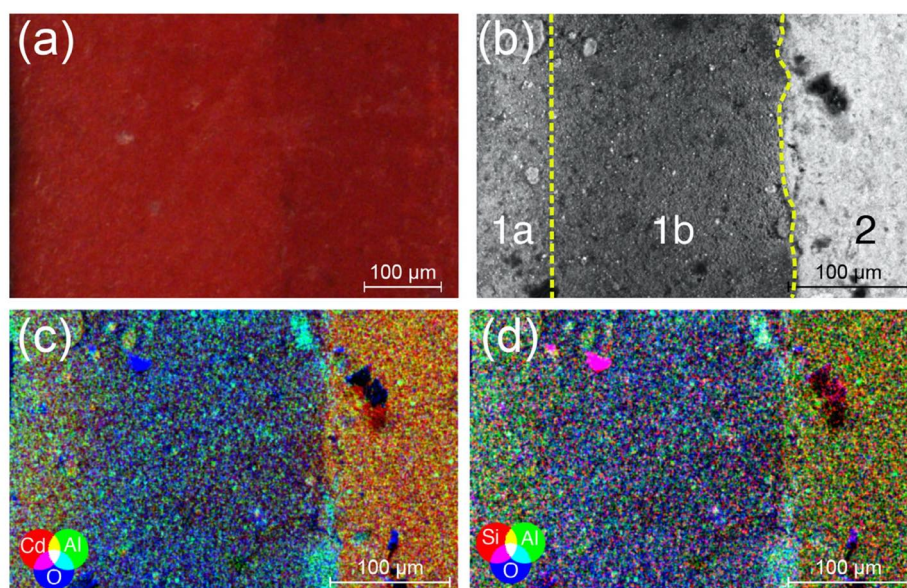


Fig. 7. For LF-O-CdR: (a) optical microscopy image, (b) SEM image in AsB detection. Contrasting intensities throughout the paint shows three zones of phase separation between heavy (bright) and light elements (dark), relating to the pigment and oil: medium intensity at edge of the cross-section at the surface of the paint (1a), low intensity in the intermediate layer between the surface and the bulk (1b), and high intensity within the bulk of the paint layer (2). RGB composite images of (c) Cd, Al and O, showing a zone of small particles containing Al and O present between layers 1a and 1b, and (d) Si, Al and O showing presence of Si oxides, and Al and Si as a trace element with localization corresponding to the pigment.

separation between the low polarity of the slow polymerizing oil in the paint layer and the presence of polar metal soaps.

5.1.2. Coloring materials

XRD analysis of paint pieces, combined with the EDX results, allowed for identification of the major crystal phases associated to the mineral pigments and additives for all paint samples.

Crystal identification in the Lefebvre-Foinet Cd based paints showed an interesting result. CdS is a yellow pigment, which shifts towards orange and red to dark red with an increasing substitution of Se to S in its crystal structure [41]. Increased Se in $\text{CdS}_x\text{Se}_{1-x}$ leads to a greater d_{100} distance along the (100) direction, which allowed estimating the Se elemental content from the high angular resolution synchrotron XRD data (Supplementary Text S8.2). The yellow and orange paints, LF-O-CdYM and LF-O-CdYO crystal phases were both detected as CdS. Se was normally expected in the crystal structure for LF-O-CdYO as Cd orange pigments have been sighted of having Cd/Se ratios of 100/12 or 100/15 for red orange [41]. Se not being detected in neither XRD, nor SEM-EDX, provided insights into the preparation of the paint: preparation of the LF-O-CdYO could have been similar to the preparation of LF-O-CdYM, but rather than adding Se to the formula, the acidity of the paint mixture would have been lowered by increasing the amount of ammonium sulfide, which would have shifted the pigment color towards orange [42]. The lightest red, LF-O-CdRO, showed an elemental ratio of Cd/Se at approximately 100/26 corresponding to bright red [41]. LF-O-CdRV and LF-O-CdR were slightly darker red paint samples and showed higher ratios of Cd/Se at approximately 100/34 and 100/38, respectively and corresponded to maroon red and dark red [41]. The darkest red LF-O-CdRP showed the highest amount of Se and two sets of peaks, attributed to a mixture of two phases with slightly different Cd/Se ratios, 100/45 and 100/40, in agreement with dark maroon red [41].

5.2. Simon Hantai's artistic practice

The carbon dating results showed that the materials studied were manufactured over a broad period (1958–1990), covering a

large part of Hantai's artistic career. The dates of Hantai's painting productions have been documented by a variety of sources [43–47]. We compared the measured dates of the paint pieces with the dates published in the recent catalogue raisonné [43] to compare the paint color with the evolution artist's color palette throughout his career (Fig. 8). The paint materials appear to be more concentrated in four distinct phases: 1958–1967, 1969–1972, 1979 and 1987–1990. The Lefebvre-Foinet yellows and reds were dated in the late 1950s – early 1960s. This period corresponds to pivotal time in Hantai's creation: referred to as *Ordinary painting* (1958–1959) by Warnock, where his works consisted of small scrapings of black paint to reveal colors, such as red and yellow, seen in two paintings from this period. This period constitutes “a vast field of experimentation” of very physical gestures, related to Jackson Pollock's *action painting*, while he used traditional oil-based techniques, even noted as “archaic” by Warnock [48]. He produced *Écriture rose* (1958–1959) for one year, and then, moved away from explicit religious evocations and began creating his *pliage* series. This development highly influenced his entire career, starting with his series *Mariales*, a number of which are in yellow–red tones, e.g., *Mariale m.a.4* in 1960 (red), *Mariale m.a.2* in 1960 (yellow), and *Mariale m.d.4* in 1962 (orange). Later, the appearance of greens and blues in our sample set is in close agreement with the evolution of Hantai's color range of the following periods where he explored a variety of shades of blue, brown and green in his *Catamurons* (1963–1965) and *Panses Saucisses* (1964–1965). The *Meuns* (1966–1968) and *Études* (1968–1971) series, consisted of mostly monochromatic paintings using large flat colors, and Hantai gradually opened his work to a wider and more contrasted color palettes, with reference to Matisse. The series *Meuns* (1966–1968) specifically referenced two paint colors, “Cadmium yellow in one work. Phthalo blue in another” and was described as “seemed to be made with paint squeezed directly from the tube and thinned with turpentine or another medium” [49], though no analysis has been done to confirm these materials. No tubes were dated between 1974 and 1979, which is in agreement with Hantai's production from this period, which consists mainly of acrylics [44]. The *Monacal Blue* tube dated 1979. This predates the *Tabulas* (1980–1982), his last publicly

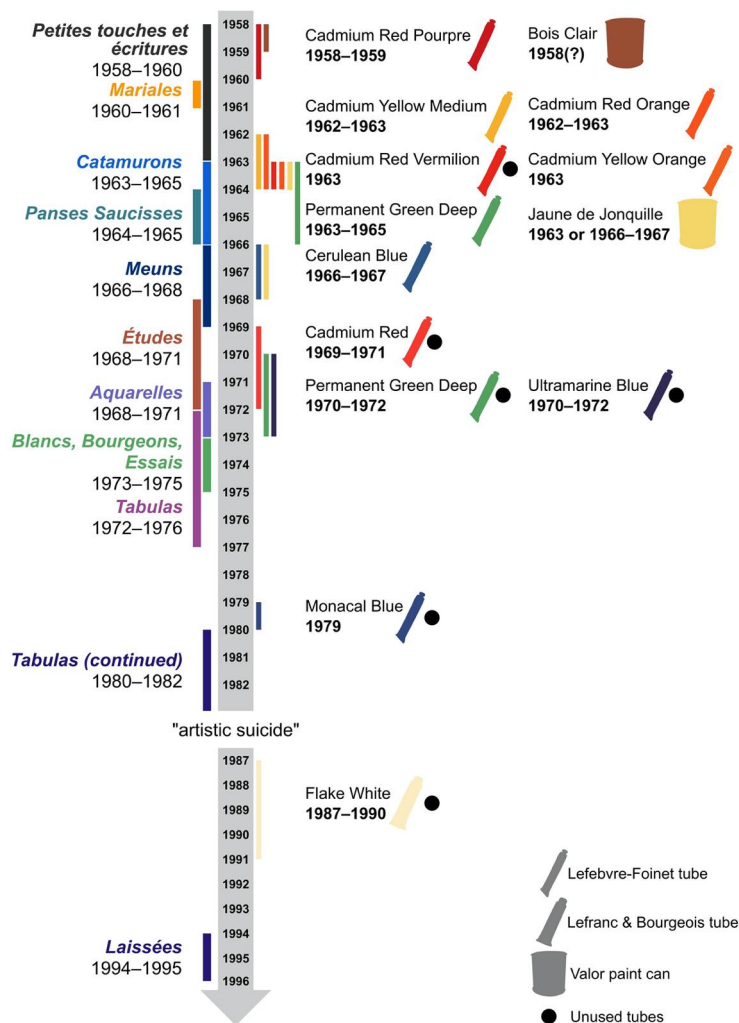


Fig. 8. Joint timeline of Hantaï's artistic periods, listing his main periods from the catalogue raisonné of Baldassari [43] (left), and date of production of the material studied in this work (right).

exhibited series of 9m x 15m format paintings, [44]. The Lefranc & Bourgeois paint, dated from 1987–1991 corresponds to a period referred to as “artistic suicide” [50], where Hantaï removed himself from displaying his works publicly, though he continued working [51]. He made a series entitled the *Laissées* (1994–1995), but these paintings were made up of fragments cut from the *Tabulas* (1980–1982). Although the exact use of the paint sample dated to the late 1980s is unclear, the wide range of dates demonstrates that his artistic activity was a lifelong endeavor.

The variety of pigment colors in the samples in this study demonstrate Hantaï's quest for “phenomenal color”, which he defined as the “color that is not literally present on the canvas but nonetheless appears under certain viewing conditions” [52]. In his most renowned works, the *pliages*, he created a “push and pull” between bright pigments and the minimal background, either unpainted or painted white [53]. He also considered white as a color, and searched for a perfect white, whose reflection would be bright enough to blend into the wall, and thus the colors would appear to come out of the wall, as opposed to originate from a canvas [54]. This was to show a perfect visual representation of color by use of a negative grid [49] in which the white background brought out the colored foreground.

5.3. Alteration

The results showed the evolved state of alteration of the original paint composition in the paint tubes and cans, which, even for the least altered ones, is significant; oxidation, polymerization, hydrolysis, saponification, and phase separation took place. These observations lead to multiple questions about our scientific process: how was the sampling carried out? What biases were introduced at this stage of the scientific process? The way paint pieces were collected, then exposed to air, and the way they were archived had a significant impact on their measurable composition. Although it was not the subject of this study, it would be interesting to see whether these results correlate with the alteration of certain areas in the artist's works, if such changes were observed. Of particular interest, then, is that the historicity of these objects *after only a few decades* cannot be overlooked. These paint pieces have had a unique history that has exposed them to a microenvironment in which chemical evolution must be characterized in order to obtain insights into the original composition. The very notion of *initial composition* may be questioned: even using a vast array of analytical techniques, the definition of the original composition of the paints at times was not straightforward. For example, the



Fig. 9. A test of the “pliage” method using paper provided by Jean Fournier, produced by Simon Hantaï and given by the artist to AC.

hydrolysis and the saponification of the oil binder, which occurred over time, prevented us to make a precise conclusion on the addition of free fatty acids and metal soaps to the original paint formulation. While it is widely accepted that metal carboxylates can form in the presence of oil and reactive metal ions [55–57] (whether in a tube or work of art), there are many parameters that contribute to their formation, from the initiation of the involved reactions to their eventual crystallization [58–60]. Care thus must be taken when using the chemical composition of such historical reference materials as a basis for understanding the corresponding historical paintings, as their degree of alteration cannot be neglected. We therefore raise this point for consideration if such products are envisaged as reference materials in future collaborative studies.

5.4. Studying the artist's workshop

The paints analyzed in this study are not representative of all the materials found in Hantaï's studio as we know he used other media, as illustrated by photographs of his atelier (Fig. 1). Also, Hantaï created many artworks over several decades, during the time period when alternative media, such as acrylic emulsion paints, were introduced into the market [7]. His studio environment was described as being covered with paintings overlapping one another “like a sort of skin that has formed on the wall of the studio” [50], an accumulation of layers of *pliages* still-folded, completed paintings, fragment pieces, and canvases hanging from the walls and in piles on the floor, a display which would vary throughout they day as lighting changed [53], as also described by Georges Didi-Huberman in 1998 (Supplementary Text S2). From around the early 1970s, Hantaï began making his works using watercolors, acrylic- and vinyl-based media [44], yet oil paints manufactured around these periods were still observed in his studio.

The simple observation of oil paints in his studio at a time when the artist appears to no longer use them questions his personal practices in a very concrete way. What are these tubes *representative* of? Were they tubes that the artist had bought in the past and did not want to discard? Were they tubes and cans kept for occasional use, either for retouching old works or for making works that were not part of his major corpus from that time? Some of the tubes did not appear to have been opened by Hantaï. For those that were, it is important to recall that Hantaï's work consisted mainly of very large paintings, many several meters in size. Tubes must not have been very useful for these large formats. We therefore hypothesize that they were used by Hantaï to pursue his research on color, the guiding theme of his work. We have

indeed observed that the purchase of several of them predates or coincides with his most active artistic periods. They could, for example, testify to his practice of creating small models of his works of art that he tested on different papers from his art dealer, Jean Fournier, in search of new colors and a new materiality (Fig. 9).

This work led us to question the most everyday behaviors of the practice of the artist in his workshop – sorting, tidying, conserving, storing, discarding, etc. in a space that was integral to Hantaï's artistic process. By having direct access to the materials in his studio, we can assume to have privileged access to materials associated with the artist's production. In any case, much more so than purchasing reference materials during the investigation process. Nevertheless, the complexity of taking into account the very materiality of these *historic* samples, as well as the socio-historical context in which they were industrially produced, used and later discarded by the artist himself in order to reach us today, is evident here.

Authors' contribution

L.Ber. and A.C. designed the original project, and coordinated the research. L.D., I.B., J.L.N., M.L.H., C.M., L.Bec., I.C. and E.D-K. conducted the experiments. L.D., L.Ber, A.C., I.B., J.L.N., L.Bec. and E.A. interpreted the results. All authors contributed to the discussion of the data. L.D. and L.Ber. coordinated the writing of the manuscript, with contributions from all authors. All authors read and approved the final manuscript.

CRedit authorship contribution statement

Lauren Dalecky: Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Ilaria Bonaduce:** Investigation, Writing – review & editing. **Étienne Anheim:** Investigation, Writing – review & editing. **Jacopo La Nasa:** Investigation, Writing – review & editing. **Maëva L'Hérondelle:** Investigation, Writing – review & editing. **Clément Morel:** Investigation, Writing – review & editing. **Emilio Catelli:** Investigation, Writing – review & editing. **Silvia Prati:** Investigation, Writing – review & editing. **Zelan Li:** Investigation, Writing – review & editing. **Lucile Beck:** Investigation, Writing – review & editing. **Ingrid Caffy:** Investigation, Writing – review & editing. **Emmanuelle Delqué-Količ:** Investigation, Writing – review & editing. **Aurélia Chevalier:** Conceptualization, Supervision, Investigation, Writing – review & editing. **Loïc Bertrand:** Conceptualization, Supervision, Formal analysis, Investigation, Writing – original draft, Writing – review & editing.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at

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