

Hard Dry Paint, Softening Tacky Paint, and Exuding Drips on *Composition* (1952) by Jean-Paul Riopelle

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Abstract The painting *Composition* (1952) by Jean Paul Riopelle (1923–2002) is part of the Henie Onstad Art Centre’s collection in Norway. Examination of the painting revealed the presence of drips of soft medium exuding from the surface. The main aim of this paper is to report chemical characteristics of its hard, soft and dripping paints. Information was collected about Riopelle’s use of materials. Data were obtained from microsamples by analysis with Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) and Direct Temperature resolved Mass Spectrometry (DTMS). *Composition* (1952) is painted with 26 different colours or shades of paint. All these paints vary in their specific physical condition when tested on the painting. Paints were classified into three categories: hard, soft, softer and dripping. The most problematic of all paints contained cobalt blue pigment.

Dripping exudates show relative high DTMS features for polar compounds such as azelaic acid and midchain-oxygen-functionalised stearic acids. Lower relative amounts are present in softening paints. Hard paints are characterised by higher relative amounts of saturated fatty acids ranging from palmitic (C16) to lignoceric (C24) fatty acid. We infer that a physical separation mechanism is responsible for formation of polar micelles that form from oxidising semidrying oils in the paints used by Riopelle. Results from *Composition* (1952) are compared with another painting by Riopelle from 1956 and one by Pierre Soulages from 1954.

Keywords Jean-Paul Riopelle • Dripping paint • Soft paint • High impasto • Fatty acids • Pigments • Cobalt blue • Bone black • Pierre Soulages

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Introduction

Composition (1952) is painted with oil on canvas and measures 131.2 × 251 × 4.5 cm without the frame (see Fig. 1).¹ After stretching, the glue sized and pre-primed canvas was given a second ground. Riopelle then painted the motive using distinctly different colours or hues, mostly wet on wet with a palette knife. The last details he threw or dripped on.² In general the painting is multi-layered with high impasto details.

Examination in 2007 revealed the presence of drips of soft medium forming on and streaming over the paint surface of the painting (see Fig. 2).³ These drips are partly coloured and partly transparent brown. They may have developed slowly over a period of time, but because of the visually complex paint structure and the artist's technique of throwing the paint towards the canvas, it has been difficult in the past to see the difference of intended and solid drips and soft paint with non-intentional drips.

Much is known about Riopelle's use of materials from interviews, written sources and personal information. After Riopelle settled in Paris he and his wife

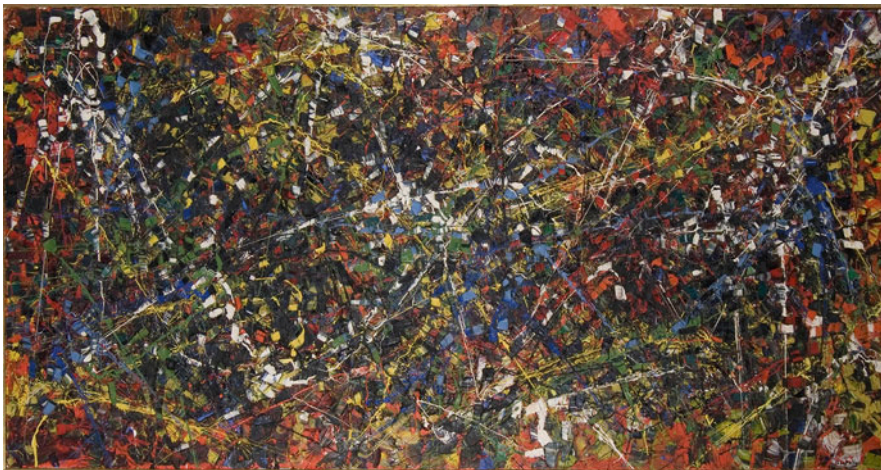


Fig. 1 *Composition* (1952) Jean-Paul Riopelle 131,2 × 251 × 4,5 cm (without frame). *Sans titre* 1952.018H.1952, Le Catalogue Raisonné de Jean-Paul Riopelle (Photo: Øystein Thorvaldsen)

¹As *Composition* is a title for many of Riopelle's paintings therefore the date of each painting is necessary to tell them apart.

²For more information on painting technique, see

Conservation challenges and physical changes in *Composition* (1952) by Jean-Paul Riopelle. A case study, by the same authors in *Public paintings by Edvard Munch and his contemporaries. Change and conservation challenges* post print Archetype (in press).

³The starting point for this project was the first author's MA Thesis (Bronken 2010).

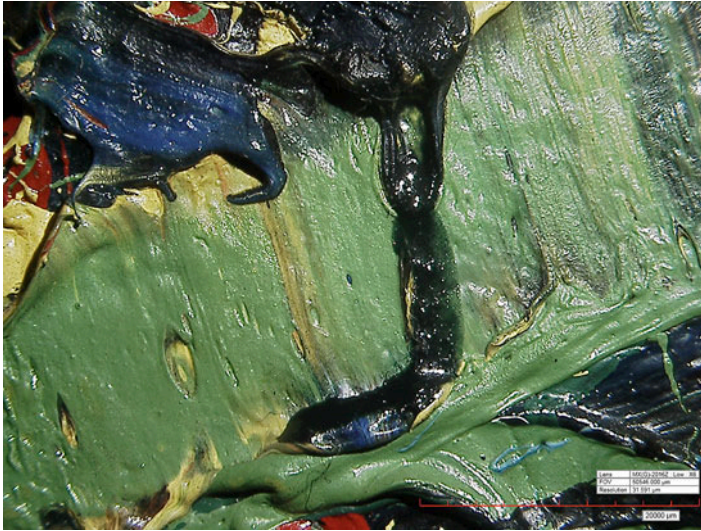


Fig. 2 Detail from *Composition* (1952), drip with partly coloured medium from cobalt blue paint (Blue 2). Photo made with Hirox 8700 (Emilien Leonhardt – Hirox Europe Inc.) mounted on MOPAS stand (Jaap Boon – JAAP Enterprise Inc.)

had to live of an annual allowance from his parents. As he hardly sold any paintings until his breakthrough in 1952, he did at times make his own paint because of his economic situation. Brunet-Weinmann says this was in the late 1940s and Jeffery Spalding refers to René Detroye claiming it was until 1952 (Bronken 2010; Spalding 2002). Viau claims that Riopelle painted directly from the paint tube in 1949, so it is possible he at times could afford to buy artist paint (Viau 2002). Riopelle referred to his use of eighteenth century paint recipes in an interview in his studio (Sainte-Marguerite du Lac Masson, October 2, 1985) with Brunet-Weinmann:

JPR: I was not knowledgeable. I found an old manual (in the stalls) along the Seine riverbank that dated from 1800. Because I did not have any money and the colour-men sold pigment powders, I bought oil, pine resin varnish and started to prepare paints myself.

I made my own paint during the night and painted everything during the day. What I found remarkable is that the products that I made myself never gave me any problems. I never had an accident.

I followed the manual literally as a recipe for cooking: the amount of siccative, the pigment powders, the kind of oil . . . I used it so often that I don't know anymore where I put it. I have lost it.

(Translation by Boon from French. Original text cited in Bronken 2010)

Riopelle mentions in this quote that he added siccatives to his self-made paints. However, he did not say what type of siccative or oil he used. In 1952 Riopelle sold all the paintings in his breakthrough exhibition. This changed his economic situation totally. It is still not known if *Composition* (1952) was made before or after this exhibition. We know from publications that Riopelle's choice of brands in the 1950s was the French paint manufacturers Lefebvre-Foinet (Corbeil 2004), and Lefranc Bourgeois (Leclerc 1992). Already in 1952 he bought paint in half

a litre and litre cans manufactured at Sennelier (Bronken 2010). According to Mr. Sennelier's daughter her father sold paint to Riopelle in the 1950s. She also informs that in some instances the firm used some grapeseed oil in their paints when linseed oil was difficult to purchase following the years after World War II (Bronken 2010). Grapeseed oil is a semi-drying oil. Ysuel Riopelle investigated her father's paintings in connection with the publication of his Catalogue Raisonné and she could not find the Lefebvre-Foinet stamp on the reverse of any painted canvas dated before 1955 (Bronken 2010).

Composition (1952) does not have a Lefebvre-Foinet stamp on the reverse of the canvas, but it does not exclude that Lefebvre-Foinet paint could have been used in the making of the painting. Canadian Conservation Institute researchers reported in 2011 that a Lefebvre-Foinet tube from Riopelle's estate contains safflower oil, which is a semi-drying oil (Corbeil et al. 2011). The fact that there were so many different suppliers makes it difficult to determine what he used in 1952. It remains possible that slow drying oils or non-drying oil may have been present in his paints.

In addition to the exuding dripping medium and changing surface gloss the painting also suffers from areas of unstable paint, deformations, numerous paint losses and surface dust. Prior to treatment of the painting the different coloured paints were tested for sensitivity to pressure, heat and solvents. The information gained was then further processed to create three categories for the analytical work. To be able to record the findings, all colours and hues were given a number (see Table 1).






























Investigation of the Painting and Sampling

All 26 different main colours and hues used in the painting were investigated and classified into three categories: A: soft and dripping, B: soft and weak, and C: stiff and brittle (see Table 1).

The obviously soft and dripping paints are placed in category A where the softest one is Blue 2. The paints that proved to be in better condition are placed in descending order. Blue 2, Black 2 and Red 2 are the only paints exhibiting dripping or oozing medium. Black 2 and Violet 1 reacted somewhat to water. Both saliva and water picked up colour from Violet 1 when swabbed, and if treated with White Spirit it could only be swabbed once. White Spirit did pick up a colour if swabbed a second time from several paints in category A. Ethanol dissolves paint in category A partly or completely if swabbed. In the cases where ethanol only partly dissolved the layer, the swab was yellowed as it leached medium from the paint layer.

The paints in category B are found to vary strongly in condition. A few paints are so soft that a light prod with a bamboo stick leaves a mark, but other paints did not react. In normal light it is not possible to see oozing medium on the paint surface in this category. One colour – Blue 3 – was thought to be solid, matt and cracking. It was suspected that it might have reached a critical pigment volume concentration (CPVC) and that this alone was the reason for its condition, but it also classified to be soft by DTMS analysis.

Table 1 Condition categories A, B and C of the 26 main colours on *Composition* (1952). Below data on pigments and fillers based on SEM-EDX and XRF on the 26 main colours and two grounds

Categories A-C					
A: Soft and dripping		B: Slightly soft or cracking		C: Stiff to brittle paint and grounds	
 Blue nr. 2	 Blue nr. 1	 Blue nr. 4	 Green nr. 5	 Red nr. 1	
 Black nr. 2	 Yellow nr. 3	 Blue nr. 5	 Green nr. 6	 Grey nr. 1	
 Violet nr. 1	 Yellow nr. 1	 Green nr. 1	 Yellow nr. 2	 White nr. 1	
 Yellow nr. 5	 Black ? nr. 1	 Green nr. 2	 Yellow nr. 4	 White Ground nr. 1	
 Red nr. 2	 Blue nr. 6	 Green nr. 3	 Orange nr. 1	 White Ground nr. 2	
	 Blue nr. 3	 Green nr. 4	 Orange nr. 2		

Category A: Soft and dripping	Category B: Slightly soft or cracking	Category C: Stiff to brittle paint and grounds		
Blue nr. 2	Blue nr. 1	Blue nr. 4	Green nr. 5	Red nr. 1
Cobalt blue,	Bone black	Ultramarin	Viridian	Zinc oxide
Calcium carbonate,	Ultramarin	Titanium oxide	Potassium zinc chromate	Titanium oxide
Silicon dioxide	Cobalt blue	Zinc oxide	Zinnoxide	Barium sulphate
Black nr. 2	Yellow nr. 3	Calcium sulphate	Calcium sulphate	Grey nr. 1
Bone black	Potassium zincchromate	Blue nr. 5	Green nr. 6 (XRF only)	Barium sulphate
Calcium carbonate	Calcium sulphate	Cobalt blue	Emerald green	Calcium carbonate
Mars black	Silicon dioxide	Lead white	Calcium carbonate	Zinc oxide
Violet nr. 1	Yellow nr. 1	Zinc oxide	Chrome green	White nr. 1
Silicon dioxide	Lead white,	Green nr. 1	Yellow nr. 2	Zinc oxide
Calcium carbonate	Zinc white	Zinc oxide	Zinc oxide	Titanium oxide
Yellow nr. 5	Calcium sulphate	Calcium sulphate	Calcium sulphate	White Ground nr. 1
Calcium sulphate	Black ? nr. 1	Green nr. 2	Yellow nr. 4	Zinc oxide
Silicon dioxide	Calcium sulphate	Zinc oxide	Potassium zincchromate	Calcium carbonate
Zinc oxide	Ultramarin	Calcium sulphate	Calcium carbonate	Potassium zincchromate
Red nr. 2	Blue nr. 6	Green nr. 3	Orange nr. 1	Silicon dioxide
Calcium carbonate	Zinc oxide	Zinc oxide	Calcium sulphate	White Ground nr. 2
	Titanium Oxide	Titanium oxide	Zinc oxide	Zinc oxide
	Cobalt blue	Green nr. 4 (XRF only)	Orange nr. 2	Titanium oxide (more than in White 1)
	Blue nr. 3	Emerald green	Calcium sulphate	
		Calcium carbonate	Zinc oxide	
			Barium sulphate	

The colours within category C proved to be more resilient oil paint judging from their response to pressure and heat. The paint has cracked in some cases, but with a more conchoidal fracture pointing to glass-like brittle behaviour. These paints could withstand heat up to or over 50 °C. White 1 has a film of medium on its surface that is clearly visible with the naked eye, but the paint was solid in all cases observed.

The main observational result from all the tests, and the results from DTMS analysis (see below), is a confirmation of a consistent difference between the three categories whether the paint layers were thin or thick.

The different 26 paints in all areas of the painting appear to be the same colour blends. Some of the greens are very similar in colour, but still can be divided in six distinct different blends when examined closely. So it seems that the paint was prepared either by one manufacturer or by the artist himself. This view is supported by one of Riopelle's own statements:

...I never begin a painting without having ready to hand, all the colours I need. (Érouart 1995)

Because the colours show such distinct differences in condition, it became a priority to understand the composition of the materials used to make the different paints. All colours were analysed by handheld X-Ray Fluorescence (XRF) (Table 1). All readings of the paint with XRF show a high intensity peak for zinc possibly from deeper layers or the ground since several paints did not contain any zinc when analysed by SEM-EDX. Hence, we conclude that XRF is not precise enough for our study. Small crumbs were then sampled from several of the paints, two cross sections were made and a canvas sample was taken from the tacking edge with ground. All of these samples were analysed by light microscopy and SEM-EDX (Table 1). The main aim of these analyses was to look for factors that would support the distinction between category A, B and C. To get information about the organic composition at the same time samples of drips, soft paint and solid paint were taken. Samples from drips came from category A. Samples of soft paint came from category A and B. The solid samples considered as healthy paint came from category C.

Analysis by SEM EDX

All stubs and cross sections were analysed by SEM EDX to identify pigments and fillers. The results from the identification of heavy elements are shown in Table 1. No attempt was made to identify the organic dye colours since this requires other methodologies. At this stage of the study, we believe that there is enough information even though organic dyes have not been identified.

Category A paints appear to consist of relatively pure colours. Only Yellow 5 contains some zinc white. Most paints in this category probably contain organic dyes. The worst condition is associated with cobalt blue.

Although cobalt blue is a good initial drier, it is also a poor film former (on Melinex) when used alone in drying oil (Mecklenburg 2012;

Mecklenburg et al. 2013). So far our list of problematic colours in *Composition* (1952) contains pigments that are being described as poor film formers such as cobalt blue, bone black and ultramarine (Mecklenburg et al. 2013). No traces of manganese or lead and just a small amount of zinc white were found in category A samples. So the paint layers on the painting are relatively pure except Yellow 5 that has some traces of white pigment. No signs of added driers but EDX is usually not sufficiently sensitive to observe these. SEM EDX only gave an identification of the fillers in several paints and from this we conclude that organic dyes were probably used.

Tests have shown that especially barium sulphate can result in poor quality paint films (Tumosa and Mecklenburg 2013). We identified four different fillers in *Composition* (1952). Barium sulphate has been used only in the stable category C paints, which contradicts Tumosa and Mecklenburg. Calcium carbonate, silicon dioxide and calcium sulphate were found in category A paints. So the information from literature on fillers does so far not give any clues that could explain the softness in the paint.

One general difference between category A and C is that all the colours in C have some zinc containing compounds like zinc white or potassium zinc chromate, and in some cases lead white. In category A only Yellow 5 contains some zinc, but then comparatively very little. Note that this paint is the only colour in category A that does not drip or bleed. In category B there is not such a distinct difference. So from an inorganic composition point of view we conclude that the paints that display the worst condition have very few or no heavy elements present that are normally associated with good film formation and drying. This implies that polar organic fractions that develop over time may not be stabilised sufficiently by metal organic chemical bonds (Boon 2006; Boon et al. 1997).

Medium Analysis of the Composition 1952 Paints

Visually, the tackiness and dripping of medium from paints suggests issues caused by the present chemical or physical condition of the oil medium inside the paints. We have to assume that the paints in *Composition* (1952) dried and hardened fully after completion. We think that Riopelle would have noticed if the paints did not dry properly. In the course of time some of the paints might have hydrolysed prematurely thus destabilising the viscous cross-linked material that we call dry oil paint. If he was using semi-drying oils, it is indeed possible that some of the triglycerides of these oils could not become part of this cross-linked oil network. These fractions may have segregated after oxidation of their double bonds accumulating into polar micelles and eventually leading to exudation. This process is more prominent if fatty acid moieties can not be stabilised on the surfaces of the pigment or filler particles (Osman and Suter 2002). In order to study the medium in its present state after about 60 years, mass spectrometry was used (Boon et al. 2007). Direct Temperature resolved Mass Spectrometry (DTMS) was used, which

is a micro-analytical technique that produces mass spectral fingerprints as a function of temperature. Micro samples homogenised in ethanol is placed by pipetting to a thin platinum-rhodium wire that is resistively heated when the analytical probe is inside the ion source of the mass spectrometer (Boon 1992). During this process loosely bound fractions evaporate first, followed by stronger bound compounds and finally compounds appearing from cross-linked fractions that decompose into smaller molecules. The desorption profile tells more about the condition of the paint sample. The mass spectra indicate what kinds of compounds are evolved (van den Berg 2002).

Five samples from drips, four samples of soft paint and four samples of solid paint were taken from *Composition* (1952) and analysed by DTMS.

Figure 3 shows the total ion current trace and summary spectra excluding Mass spectrometry data from cross-linked fractions of a sample of category C healthy stiff named colour Blue 4, and category A dripping medium from paint named colour Blue 2. The stiff paint shows a different TIC (Fig. 3a) than the material taken from the drip (Fig. 3b). The drip material shows a higher concentration of material which is stronger chemically bound or more polar than the dried healthy stiff paint. This is especially obvious in the 50–60 scan range of the TICs. The corresponding mass spectra in Fig. 3c, d point to a difference in organic composition.

Figure 3c from the stiff paint shows mass peaks of saturated fatty acids like palmitic acid (m/z 256; C16:0), stearic acid (m/z 284; C18:0), arachidic acid (m/z 312; C20:0), behenic acid (m/z 340; C22:0) and lignoceric acid (m/z 368; C24:0 – present but outside the mass range shown). There are also indications for oleic acid (m/z 264; C18:1) and even linoleic acid (m/z 262; C18:2) or their structural isomers. Peaks indicative for azelaic acid (C9 diacid) at m/z 98 and 152 are also observable.

The summary spectrum in Fig. 3d from the dripped exudate is quite different. Here high intensity peaks are observed for m/z 98, 152, 155, 171 while the features of saturated fatty acids are relatively low. The mass peaks m/z 155 and 171 are interpreted as indicative of mid chain functionalised stearic acids with an epoxy, keto or hydroxy function (MS atlas of fatty acids (Van den Berg 2002; Izzo 2011)). The mass peak m/z 280 is strongly related to these two peaks and is interpreted as a [M-H₂O] of hydroxyl stearic acid compounds. The high m/z 152 and 98 are indicators for azelaic acid. Polar fatty acids and diacids are clearly more prominent, while the most remarkable feature when comparing the two samples is the abundance of saturated fatty acids in the exudate. The ratio of the mass peak indicators m/z 152, 155, 256, 264, 280 and 284 over m/z 129 was calculated to compare DTMS data from a larger number of paint samples.

Figure 4 shows that all drip exudates show relatively high amount of the polar fractions (m/z 152, 155 and 280) while the soft paint have intermediate values compared to the stiff dried paint. Considering that polar fractions appear at the surface and even exude from some of the paints, we postulate that such fractions can not be accommodated sufficiently in the paint mass and are separated according to a physical mechanism possibly after forming polar micelles i.e. acid groups at the surface and apolar aliphatic chain inside.

Composition (1952) is not the only painting by Riopelle with issues of soft, cracking and/or lifting paint. Several publications from Corbeil, Helwig and Poulin

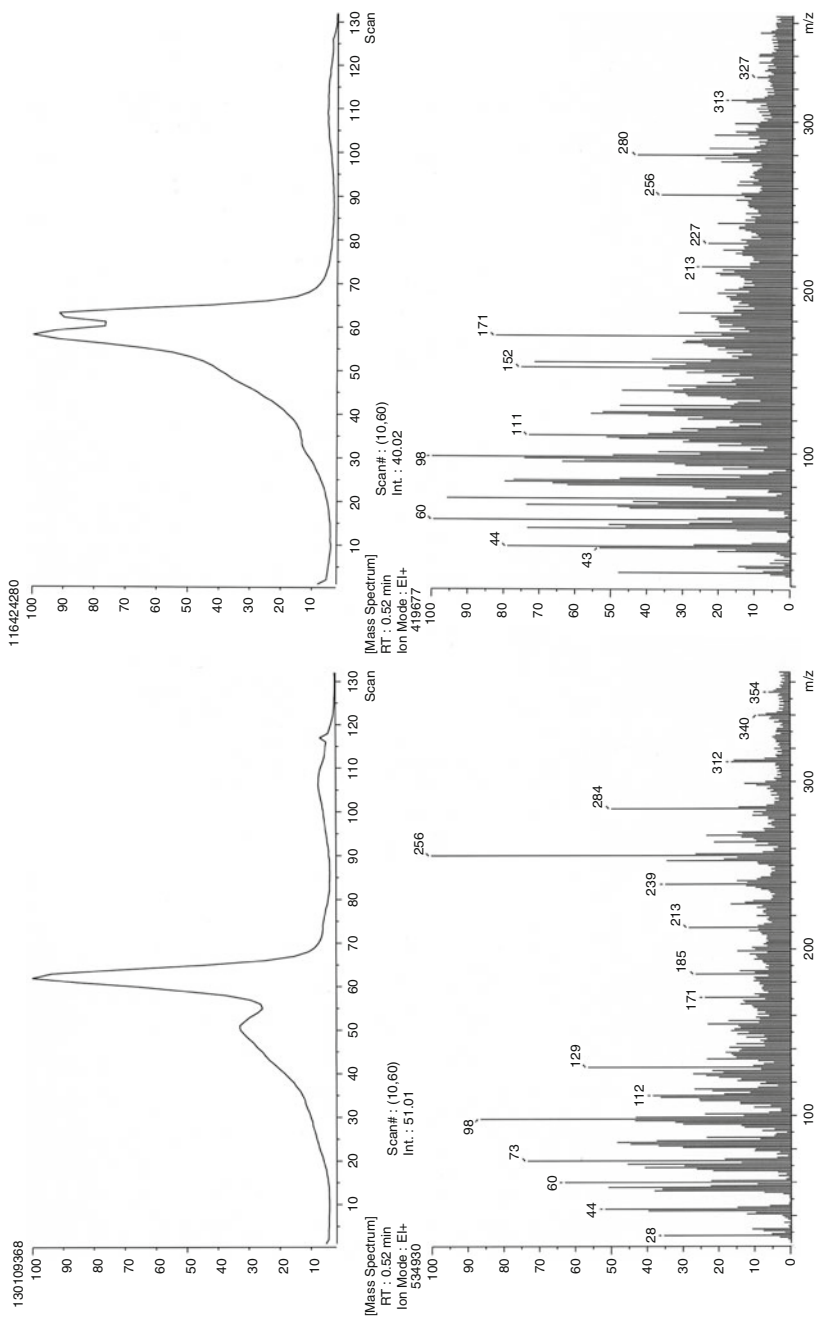


Fig. 3 Total ion current trace and partial low voltage DTMS summary spectra (scan 10–60 summed) from a sample of solid gray 4 (A – TIC and C – MS), and a drip from blue 2 (B – TIC and D – MS)

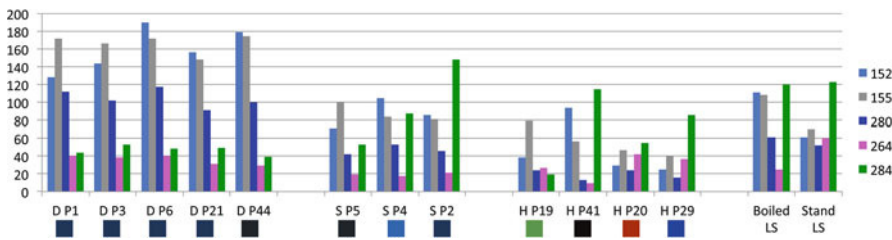


Fig. 4 Discriminating DTMS features of drips (*D*), soft paints (*S*), hard paint (*H*) and 5 years natural light aged linseed boiled and stand oil (Talens). The m/z 152, 155, 280, 264, 284 calculated as a ratio over m/z 129 are plotted (see text). The sample numbers correspond to the colours in Tabel 1: P1, P3, P6 and P21 [Blue 2], P44 and P5 [Black 2], P4 [Blue 3], P2 [Blue 2], P19 [Green 5], P41 [Black 1], P20 [Red 1 background], P29 [Blue 4]

in Canada at the CCI point to problems in the same direction. Between 2002 and 2011 thirty-three paintings in oil from 1944 to 1977 were sampled and analysed (Corbeil et al. 2004; Corbeil 2006; Corbeil et al. 2011). There is no report about dripping in the publications, but several of the condition problems like solvent sensitivity, weak and cracking paint and tacky medium on the surface are comparable to what we are observing in *Composition* (1952). The researchers from CCI conclude that the softness is related to an elevated azelaic/palmitic (A/P) ratio and must be a result of an excessive chain scission during drying of the paint or aging of the paint (Corbeil et al. 2011). They found elevated A/P ratios especially in black and blue colours. It is not clarified why more azelaic acid would be formed in some of the paints. However it correlates well with our observation that polar fractions are more prominent in softer paints. We want to stress also that analysis shows that the paints have initially chemically dried as original features of drying oils are no more present. There is no evidence for extensive hydrolysis of ester bonds. Further hydrolysis of such bonds could however weaken the condition of the paints dramatically and might move paints from category B to A.

Comparing Riopelle's Composition (1956) and Peinture (1954) by Soulages to Composition (1952)

Two other paintings *Composition* (1956) by Riopelle and one sample from *Peinture* (1954) by Pierre Soulages in the Henie Onstad Art Centre collection were also available for study. Both paintings show signs of soft paint.

Riopelle did not make his own paint anymore in 1956 according to written sources. Also the canvas in *Composition* (1956) has a weak outline with the same oval as the manufacture stamp from Lefebvre-Foinet. *Peinture* (1954) by Soulages also had traces of a similar oval stamp on the back of the canvas.

Examination of the paintings shows that the paint has some of the same softness, even if they visually do not look so similar. *Composition* (1956) has stronger impasto

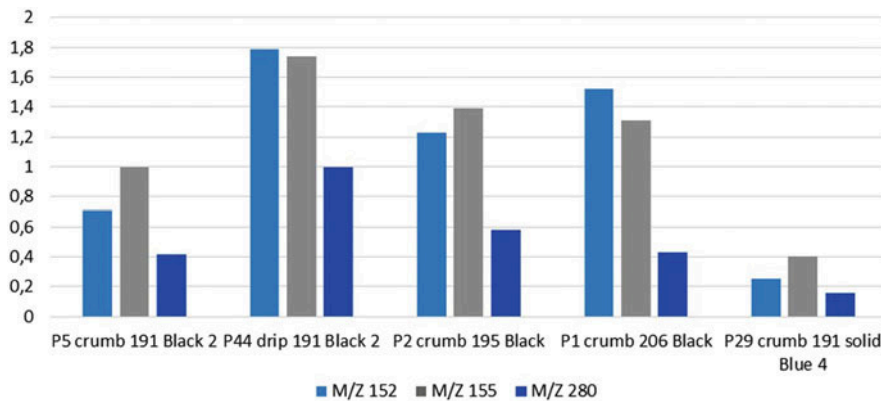


Fig. 5 Discriminating DTMS features of Black paints and a drip from Black paint sampled from *Composition* (1952) and *Composition* (1956) by Riopelle and *Peinture* (1954) by Pierre Soulages. Solid paint Blue 4 from *Composition* (1952) is plotted for comparison

and less layers, and is in general in better condition. *Peinture* (1954) by Soulages is thinly painted and suffers from the ‘characteristic’ lifting of paint layers (Helou-de La Grandier et al. 2008).

Samples of black paint from these three paintings were analysed with DTMS and compared with sample P29 from healthy paint Blue 4 from *Composition* (1952) (see Fig. 5). The values for azelaic acid (m/z 152) and the oxidised stearic acids (m/z 155) shown in blue in the graphs are higher in the samples of soft paint, and even higher in the drip from a bone black paint layer. These paintings have very challenging condition problems and we believe that these problems are related to the softness of the paint. It is interesting to find that the black paint in *Peinture* (1954) is soft even if it was painted relatively thinly compared with some of the Riopelle paintings. A heavily dripping painting in *Black on Red* from 1960 painted by Soulages and presently in the Art Institute of Chicago, is under study but show the same type of polar fractions exuding from bone black paint (Boon and Lister 2014). Some comparative data are available from 5 year-old dried linseed stand oil and boiled oils (Talens, NL) spread on glass slides and exposed to daylight. Both prepolymerised oils show the m/z 280 feature and higher relative intensities of m/155 and 152 in their DTMS spectra (see Fig. 4). These numbers suggest that such prepolymerised oils may have been added to modify the rheology of paints used by Soulages and Riopelle.

Discussion

One of the first questions of a conservator facing softer paint in an artwork asks is: what type of oil could have been used? A paint layer without good film formation could point to slow- or non-drying oils. Researchers still identify the type of oil used

from the palmitic acid: stearic acid (P/S) ratio (Mills and White 1994). However further research into the migration and aging of oil has shown that palmitic acid does evaporate four times faster than stearic acid (Schilling et al. 1999). It has been suggested to use the ratio between azelaic acid and stearic acid (A/S) instead, as the difference in evaporation is at half rate compared to P/S (Ferreira et al. 2005). For unvarnished paintings made with modern oil paint that might contain additives like metal stearates or are made with several different oils mixed together, this means a P/S ratio for identification of oil type is unrealistic or at least should be considered with extreme caution. In our case study with so many signs of migration and evaporation of medium the P/S ratio was considered unreliable. On the other hand when Riopelle was making his paint, he used a late eighteenth century manual so it is likely that he tried to obtain linseed oil. Sennelier used grapeseed oil as a substitute to linseed oil, which tells us that the brand usually used linseed oil. So it is probable that the paint he used in 1952 contained linseed oil.

Indications for very long chain fatty acids found in some of the samples might give a hint to semi-drying oils. Izzo (2011) reports C20-C24 fatty acids in Lefranc Bourgeois paint, which she ascribes to additions of sunflower oil. Such fatty acids are also prominent in rapeseed oil produced in large quantity after the Second World War (Shahidi 1990). It is well known that semi-drying oils never dry and form tacky surfaces. So we can't rule out that Riopelle's paints do contain some semidrying oils or have been enriched with such oils by the artist. Monique Sennelier describes that her father did have difficulty getting enough linseed oil in the years following World War II. Could it be that some suppliers sold low quality "linseed" oil blends?

Whatever the type of oil that has been used it seems very likely that the softness of some colours are a result of a combination of factors, resulting in a variety of symptoms. Returning to matt Blue 3 one of the colours in category B, which was sampled from an area showing weakness, cracking, matt-ness and is relatively thinly applied. At first it was suspected that the binding medium was not the problem in this case. However, after DTMS analysis the levels of organic moieties show the same composition profile as samples of soft paint category B. There is nothing in the application of this paint that would indicate oxygen deprivation during the drying. But both suspected pigments, cobalt blue and ultramarine, are mentioned as poor film formers (Mecklenburg 2012). It is identified mainly cobalt and aluminium content in the sample from preliminary analysis, but this needs to be further investigated.

Another sample believed to be solid and matt was a layer in Black 2 paint. The sample was taken because the area was believed to be an example of paint in good condition, as it did not respond to being prodded by a bamboo stick with light pressure. This sample however shows the same m/z ratios as other soft paints in the DTMS analysis (see Fig. 5). Black 2 contains a lot of bone black pigment. Ferreira et al. (2005) posed the question if their bone black pigmented paint had some kind of antioxidant properties as it was still showing some unsaturation in the film after 350 years. It is uncertain if it is relevant in our case study. Many of the paints however, show some preservation of oleic acid or an isomer (m/z 264 from C18:1).

One factor that comes forward strongly is that paints that drip have less of the kind of pigments that could react to compensate the acidity of the aging oil by creating metal-ionic bridges with the organic moieties in the film to help stabilise the paint when compared to the pigments in the solid paint category C. Lead, zinc, copper and even calcium can help to stabilise the aging film (Keune and Boon 2007; Keune et al. 2008). Lack of this anchoring stabilisation leads to accumulation of polar fractions and results in softening and eventually dripping of the paint. It is remarkable in this respect that soft and dripping paints from different paintings show the same kind of mass spectrometric features.

Maybe the total thickness of the structure could be of importance? According to the CCI-team Riopelle normally did not use either a second ground or a background colour (Corbeil et al. 2011). *Composition* (1952) has two grounds as well as a red background colour. This background colour can be seen on the edges but also in several of the areas of loss further into the motive. Could a combination of the materials in the colours together with the total thickness of the structures have affected both the initial drying process? We are considering that superposition of paints with different PVCs might have adverse effects on drying leaving some of the in between layers that Riopelle applied with paints supersaturated with oil. This is an underestimated aspect of superposition of multiple fresh paint layers.

The findings from our SEM-EDX analysis so far correspond to results published in 2012 and 2013 on how pigments effect the development of film formation in drying oils (Mecklenburg 2012; Mecklenburg et al. 2013). The paints that display the softest paint and dripping in *Composition* (1952) are mainly organic pigments and pigments, like cobalt blue or bone black. They are more or less without the presence of white pigments. It is therefore probable that these pigments are playing a big part in determining the variations between the different colours and their difference in condition.

We can not be certain about what oil has been used as we do not have any analytical technique at present that could provide a certain identification in twentieth century paintings. Analysis with DTMS shows that the soft paints have a higher content of diacids and polar fatty acids compared to hard paint. The drips have an even higher content of polar material. This could be related to the presence of semi drying oils as their triglycerides are too saturated to be accommodated in the rapidly cross-linking material from drying oils. These fractions could in the course of time lead to unbound polar fraction inside the paint mass. Our hypothesis is that the polar oxidation products can not be accommodated in the paint mass and appear at the surface as the paint becomes more apolar with time and possible polar micelles grow. In other paintings (Boon and Hoogland 2014) thickness plays a role but mainly as reservoir while on thinner paints tackiness is more apparent. In some paintings, large amounts of medium also appear at the reverse where it accumulates in the canvas. Such relationships are hard to quantify. However, the exuding materials are highly fluorescent and this is a means for the conservator to monitor accumulation of non-bound medium fraction in paintings. It is also important that this fluorescence can be misinterpreted as a local varnish. UV fluorescence of the exuding medium is rapidly apparent when dissolved medium

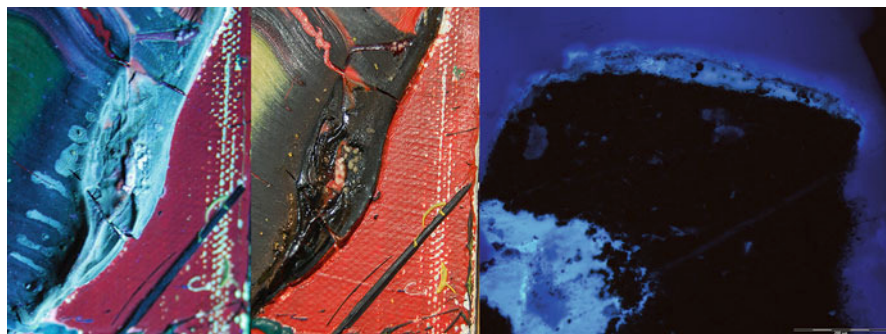


Fig. 6 Partially delaminating black paint with oozing exudate at the surface from Riopelle's *Composition* (1952) seen in UV-light on the *left*, the same area in visual light in the *middle*. To the *right* a detail from a cross section from a crack in the same area in UV-light. The oozing material has a *greenish grey* fluorescence when examined on the painting

is examined under UV light. Figure 6 makes this clear on the painting where an area with black paint is wet with exudate. Under UV light that same area shows a greenish grey fluorescence.

Experimental Details

A Hirox 8700 on a MOPAS 1 stand system was used for digital microscopy. XRF was performed with a Thermo Scientific handheld XRF model Niton XL3t. A Philips-FYE XL-30 FSEM coupled to an EDAX energy dispersive analyser was used for SEM-EDX. Paint crumbs were mounted on carbon sticky tape and covered with a few nm of gold in vacuo using a sputter coating system. A JEOL SX102-102A mass spectrometer was used for DTMS equipped with a Pt/Rh (9/1) filament (diam. 100 μm) for in-source MS. Spectra were obtained at 16 eV electron ionisation over a mass range of 1,000 Da at a cycle time of 1 s and acceleration voltage of 8 kV.

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