**INTRODUCTION**

This paper describes a study for a possible method to treat soft and dripping paint on modern paintings. For this first part of the study, the aim was to learn whether it is possible to harden the binding medium or reduce the dripping of the oil paint layers in *Composition* (1952) by Jean-Paul Riopelle (1923–2002). Riopelle is probably one of the most important Canadian painters of the 1900s. In the 1950s and 1960s, he worked in Paris. Today his art is in collections in Canada, Great Britain, USA, Switzerland, France, Portugal, Norway, Sweden, Germany and Japan. The Henie Onstad Art Centre in Oslo, Norway has four Riopelle paintings in its collection. Two of these have condition problems in the form of soft paint, first highlighted by Bronken (2010). In several publications between 2004 and 2011, Corbeil and colleagues at the Canadian Conservation Institute (CCI) mention soft paint and a sticky medium in several oil paintings by Riopelle (Corbeil et al. 2011). Moffat and Miller in a paper from 1994 wrote about soft paint in paintings made by Paul-Émile Bourdas (1905–1960) while working in Paris between 1955 and 1960. Since then, more and more examples of softening paints have become known. Paintings by other artists working in Paris in the 1950s and 1960s are also known to display problems arising from soft paint (van den Berg et al. in press). The painters Pierre Soulages (b. 1919), Alfred Pellan (1906–1988) and Georges Mathieu (1921–2012) are all contemporary artists of Riopelle. Some of the common factors in the work of these artists are the application of more or less unmixed paint and occasionally pastose paint layers. It is clearly not a singular case. More recent cases are described in publications and relate to other contemporary paintings by artists such as van Hemert (pink paint), made between 1990 and 1995, with problems of dripping oil paint (Boon et al. 2007, and Boon in press). From the DTMS analysis of the Riopelle drips, Soulages drips and the van Hemert drips, we know that there are several similarities in the organic fingerprints in the drip material, for example high peaks for polar compounds at m/z 152, 155 and 280 (Boon in press).

Although our test for a possible treatment of soft paint is carried out on paint from one specific Riopelle painting, it is of relevance to other cases of soft and dripping paint. The main goal is to find a method that is practically applicable for the treatment of local soft paint. Furthermore, the method should be amenable for execution with relative ease by a trained conservator.
CONDITION

Eleven of the 26 different paint blends found in Composition (1952) show a range of condition problems connected to softness of the medium. Four of these have developed several liquid drips of binding-medium-derived substances on their surface. Eleven paints are soft and sticky, and the remaining 15 are solid. From the information obtained from condition tests with pressure, heat and solvents, the colours were categorised into three groups (Table 1) (Boon and Bronken in press). Category A contains the softest and dripping paints. Category B paints have signs of softness or condition problems connected to the softness of the medium. Category C paints and grounds have a solid to brittle condition. Examination of the painting has shown that each of the 26 paints is consistently either soft or solid throughout the painting, but that the degree of softness can vary (Figure 1).

DIRECT TEMPERATURE-RESOLVED MASS SPECTROMETRY AND ENERGY-DISPERSIVE X-RAY ANALYSIS

Micro-samples from stiff, soft and sticky paints and dripping material were collected from Composition (1952) to analyse their organic composition, pigment and filler content and stratigraphy. The direct temperature-resolved mass spectrometry (DTMS) analysis of these paints indicates that the binding-medium components of the stiff paints consist mainly of saturated fatty acids (palmitic and stearic), C9 diacids and network constituents. Moreover, the soft paint also contains a fraction in which mid-chain functionalised stearic acids (hydroxyl, keto and epoxy C18 fatty acids with marker m/z 155, 171 and 280) and diacids are more prominent (Boon and Bronken in press). Similar DTMS fingerprints were found in two other paintings in the Henie Onstad Collection, Composition (1956) by Riopelle and Peinture (1954) by Pierre Soulages.

Hand-held XRF gave a first indication of the heavier elements in the paints. How these relate to the composition in individual paint layers was investigated by SEM/EDX analysis of very small samples of paint mounted without further preparation (Table 1). This part of the study points to a common factor: the softest colours are more or less pure without lead or zinc white pigment and many of them contain organic dyes. The pigments used for the soft colours also correlate with the findings of Mecklenburg et al. concerning poor film formation (Mecklenburg et. al 2013, Boon and Bronken in press).

HYPOTHESES

The dripping, cracks and deformations are mostly found in one type of cobalt-blue paint. This paint is affected everywhere in Composition (1952); in both thick and relatively thin layers (Figure 2). The softening and fluidisation of oil paint is a complex phenomenon that strongly points to phase separation of more oxidised and non-chemically-bound fractions in oil paints. The polar fractions that form over time appear to fuse into larger ‘pools’ of the same substances at the surface until a critical concentration is reached, leading to drips. The authors’ current hypothesis is that these polar fractions fail to find anchor points on the mineral surfaces inside the paint (Boon in press, Boon and Bronken in press).
Table 1
Condition categories A, B and C of the 26 main colours in *Composition* (1952), with identified pigment and fillers. Table: Ida Bronken

<table>
<thead>
<tr>
<th>Category</th>
<th>A: Soft and dripping</th>
<th>B: Slightly soft or cracking</th>
<th>C: Stiff to brittle paint and grounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue no. 2</td>
<td>Blue no. 1</td>
<td>Blue no. 4</td>
<td>Green no. 5</td>
</tr>
<tr>
<td>Cobalt blue</td>
<td>Bone black</td>
<td>Ultramarin</td>
<td>Viridian</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>Ultramarin</td>
<td>Titanium oxide</td>
<td>Potassium zinc chromate</td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>Zinc oxide</td>
<td>Zinc oxide</td>
<td>Zinc oxide</td>
</tr>
<tr>
<td>Black no. 2</td>
<td>Yellow no. 3</td>
<td>Blue no. 5</td>
<td>Green no. 6</td>
</tr>
<tr>
<td>Bone black</td>
<td>Potassium zincchromate</td>
<td>Cobalt blue</td>
<td>Lead white</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>Calcium sulphate</td>
<td>Zinc oxide</td>
<td>Zinc oxide</td>
</tr>
<tr>
<td>Mars black</td>
<td>Silicon dioxide</td>
<td>Calcium sulphate</td>
<td>Calcium sulphate</td>
</tr>
<tr>
<td>Violet no. 1</td>
<td>Yellow no. 1</td>
<td>Green no. 1</td>
<td>Yellow no. 2</td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>Lead white</td>
<td>Zinc oxide</td>
<td>Calcium sulphate</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>Zinc white</td>
<td>Calcium sulphate</td>
<td>Calcium sulphate</td>
</tr>
<tr>
<td>Yellow no. 5</td>
<td>Black? no. 1</td>
<td>Green no. 2</td>
<td>Yellow no. 4</td>
</tr>
<tr>
<td>Calcium sulphate</td>
<td>Calcium sulphate</td>
<td>Zinc oxide</td>
<td>Potassium zinc chromate</td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>Lead white</td>
<td>Zinc oxide</td>
<td>Zinc oxide</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>Calcium sulphate</td>
<td>Calcium sulphate</td>
<td>Calcium sulphate</td>
</tr>
<tr>
<td>Red no. 2</td>
<td>Blue no. 6</td>
<td>Green no. 3</td>
<td>Orange no. 1</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>Zinc oxide</td>
<td>Zinc oxide</td>
<td>Calcium sulphate</td>
</tr>
<tr>
<td></td>
<td>Titanium Oxide</td>
<td>Titanium oxide</td>
<td>Zinc oxide</td>
</tr>
<tr>
<td></td>
<td>Cobalt blue</td>
<td>Ultramarin</td>
<td>Calcium sulphate</td>
</tr>
</tbody>
</table>

Note: (XRF only) indicates that the analysis was conducted by means of X-ray fluorescence spectroscopy.
**DISCUSSION**

Keune and Boon (2007) have proposed that lead soaps are important for the stability of aging paint. The authors describe that lead acetate when used as a drier will react with fatty acids to form soaps. Schultz (2008) suggested that it might be possible to bind some of the acidic oxidation products in dripping paint by introducing metal ions. As the drip material is identified to contain an abundance of fatty acids, lead II acetate could be a good candidate for creating soaps. The lead salt has to be in a solution as it is the Pb^{2+} ions that are the reactive component. Experimental evidence is presented as to whether the fatty acids become chemically bound, and whether there are changes in surface texture, gloss or colour due to an introduction of lead acetate. A positive outcome will be to stimulate development of an adjusted, conservation-friendly setup later on.

To develop this pilot study towards a possible treatment method, it is imperative that the treatment is local. Furthermore, shrinkage of the soft paint and damage by solvents must be avoided. It was decided that the mixture should be applied to the surface in this first part of the study. Introduction by injection or gels will be an aspect for the second phase of the study because the samples used for this part of the experiment are so small. It was decided that the study should be executed in a way that would be comparable to a solution being brushed locally onto the surface of a paint layer.

Introducing lead ions onto the paint is not reversible. Altering original materials chemically is not a desired outcome under normal circumstances, but if a painting shows a rapidly deteriorating condition caused by softness or dripping, the increasing amount of exuding fatty acids will change the paint both visually and structurally. If the appearance of a painting has changed so much that it no longer fulfils its original artistic intent, it is worthless and might be subject to experimental treatment. Several art works by artists other than Riopelle are known about that have been destroyed, repainted or donated to research as a result of their condition. In addition, it is hoped that this study will be of relevance to the paint industry, particularly for artists’ paint manufacturers that often use slow drying oils.

**EXPERIMENTAL**

The experiment is based on the idea that lead (II) acetate in solution is a good candidate for testing if parts of the binding medium will link up again. The soft paint is very solvent sensitive, but lead (II) acetate crystals can be fully dissolved in water and partly in ethanol. All the soft paints in category A and B can be treated safely with water. It would be beneficial for the chemical reaction if the surface is slightly swollen and thereby further softened. Hence, a solution with ethanol was chosen to see if there was a different result or increased effect between dissolving the lead salt in ethanol compared to water. This part of the study is carried out on some of the samples already taken from *Composition* (1952) for pigment identification.

**Set up**

Nine specimens from eight colours and one drip from *Composition* (1952) were divided into 20 samples. Stereo microphotographs of all samples were
taken in visual and UV light before and after treatment. This was done to see whether the surface of the samples would change in appearance over time, firstly during the three-month duration of this study and later on after circa one year. Five samples were covered in ethanol and lead (II) acetate mixture, six were covered in water with lead (II) acetate and nine were kept as controls. Enough solution was applied to the samples until they were covered and there was some excess solution on the edges. These were stored in an uncontrolled dust-free climate for three-and-a-half weeks before the first analysis (Table 2).

Two cross sections of slightly soft paint that had been treated two months earlier and an untreated control were embedded. The cross sectioning was done to see how deep the penetration of the lead would be and to compare the fluorescence under UV. One important question was whether the lead penetrated deeper when dissolved in ethanol compared to when dissolved in water.

One drip sample was divided into two and dissolved in ethanol. The solution was fluorescent. A few lead-acetate crystals were dissolved in a few drips of ethanol-and-water-combined mixture. This lead solution was then mixed into one of the drip solutions.

Fourier transform infrared spectroscopy and scanning electron microscopy with energy-dispersive x-ray

The instrument used was a PerkinElmer FT-IR microscope, Spectrum One. All analyses were done in transmission mode. The resolution was set at 4 cm⁻¹. The cross sections were analysed with a JEOL, JSM 840 scanning
electron microscope. The analyses were done in high vacuum. The samples were sputter covered with a thin layer of carbon for conduction.

**Results**

Examination of the samples under the stereo microscope after treatment revealed no signs of changes in colour, but both the glass plate and edges of the samples exhibited newly formed crystals. These crystals were not water soluble. There was more crystal formation after application of the water solution. No crystals were observed on the surface of the paint specimens and drips in visual light. The fact that the crystals were no longer water soluble is proof that a reaction had taken place with the paint medium.

There is more efflorescence in some of the samples when examined under UV light. The fluorescence of the paint specimens is associated with an excess of lead containing crystals on the surface of the glass (Figure 3). The surface fluorescence on the ethanol/lead-treated drip material changes from a blue to a more yellow-pink fluorescence in areas on the surface and on edges of the sample (Figure 4, bottom). The water-treated drip material showed a visible edge under UV light (Figure 4, centre).

FTIR was used to investigate whether there is a chemical change due to treatment with lead ions (Table 2). When pressing the small yellow paint crumbs during preparation for analysis, a distinct difference was noticeable between the treated and untreated samples. The various drip samples, whether treated or not, do not show differences in their FTIR spectrum. Apparently, the visual changes at the surface were insufficient to change the chemistry inside. The strongest FTIR change is observed in the yellow shown in Figure 5. The FTIR of the untreated paint shows strong peaks for CH vibrations at 2924 and 2854 cm\(^{-1}\) and a peak for the carbonyl C=O vibration of free acids at 1737 cm\(^{-1}\), with a shoulder at 1716 assigned to ester and free acid respectively, like an azelaic-acid glycerol ester, for example. Treatment results in a diminishing of the carbonyl absorption
and a strong increase in the 1538 cm⁻¹ peak indicative of lead soaps (Keune and Boon 2007). In the case of the treated yellow paint, the goal to convert acids to metal soap has been achieved. In the case of the red paint, there is not much of a difference between treated paint and the untreated control. The difference between both treated paints is the use of an ethanolic solution for the yellow paint and an aqueous solution for the red paint. It is inferred that ethanol opens, i.e. swells, the paint in contrast to water. The treated red paint did show a higher peak for carbonates at 1460 cm⁻¹, which points to a possible reaction of the lead acetate with CO₂ from the atmosphere during the exposure period.

It is also of interest to investigate how far the water/lead and ethanol/lead solutions have penetrated into the paint. Two treated samples were prepared for cross-section study and analysed using SEM/EDX. Both cross sections have a thin layer of lead on the outer edge of the samples, but an unbroken and evenly thick layer after contact with the ethanol solution. When compared to an untreated sample under the stereo microscope, it appears that the solution has created a new layer on the surface of the paint. Both SEM/EDX and UV analysis on the water-treated sample indicate a reaction on the edges of the sample (Figure 6). The drip solution that was mixed with a lead acetate/ethanol/water solution reacted immediately. The solution cleared up and a soft medium precipitated. These soft lumps are still fluorescent, but no longer dissolve in ethanol (Figure 7, top right). The drip solution without lead dried in an even pattern (Figure 7, bottom right). This shows that the drip material does react when in solution, but not when treated at the surface.

**CONCLUSION**

Treatment with water/lead solution compared to treatment with ethanol/lead mixture gives a different result. The ethanol/lead mixture creates a more even and harder crust around the paint. FTIR points to a reaction with acid groups and the formation of lead soaps. SEM demonstrated that lead is indeed introduced into the paint. A possible problem with the ethanolic solution is that ethanol dissolves several of the soft paints, as was demonstrated before. The approach is promising as the phase-separated polarity in the paint is balanced and the free-acid group are fixed as lead soaps. Further studies will be done using gel-based methods to introduce coordinating metals or organic cat-ions.

**ACKNOWLEDGEMENTS**

All analysis with FTIR was done by Hartmut Kutzke at the Museum of Cultural History at the University of Oslo.

**REFERENCES**

SOFTENING PAINT AND DRIP FORMATION IN PAINTINGS BY JEAN-PAUL RIOPELLE (1923–2002): IMPROVING THEIR CONDITION WITH METAL COORDINATING IONS


MATERIALS LIST

Lead II acetate
Ethanol added methyl isobutyl ketone and methyl ethyl ketone, kemetyl
Technovit 2000 LC Kulzer: for embedding cross sections

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