

# Characterisation and accelerated ageing assessment of two twentieth century blue paints

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## 1. Introduction

Owing to the large variety of modern paints and more specifically their formulation, the characterisation of such materials is made difficult. It is nevertheless essential to achieve it, since both the safety and the conservation of modern art is becoming more and more problematic.

The poster focuses on two blue pigments whose binding media are most commonly found in twentieth century painting materials. This study was run in two simultaneous ways: characterisation of paint and understanding their behaviour with accelerated ageing test. A late XX<sup>th</sup> century painting is studied.

## 2. Background

The aim of the first part of the research was to create a corpus of works from the public collection of XX<sup>th</sup> century art within the Provence - Alpes - Côte d'Azur region such as:  
- FRAC (Fond Régional d'Art Contemporain) - Marseille - Musée Cantini - Musée d'Art Contemporain - Marseille  
- Musée des Beaux-Arts - Toulon - Musée d'Art Moderne et d'Art Contemporain - Nice  
This work has put forward what future conservation issues might be and therefore, identify and monitor the ageing properties of the materials used in paintings are of a prime concern.

## 3. Aim

First: - Characterisation of binders and pure and/or mixed pigments  
- Physico-chemical assessment of the ageing process of these binders and pigments  
- Determine the occurred physico-chemical phenomena  
Second: Compared analysis carried out on samples taken from contemporary works concerned by this study.

Pigments	Advantages / Drawbacks	Binding media		Finishing media	
Cobalt blue PB 28 CoO <sub>2</sub> AD30 Colour Index 77546	- Good light fastness as well as heat resistance and also to chemical acids and/or bases even when highly concentrated - Weak colouring and covering potential.	Alkyd Acrylic	Alkyd Senselizer	Lefranc Bourgeois (LB) Windsor & Newton (WN)	
Phthalocyanine blue PB 15 C32H8N8Cu Colour Index 74160	- Stable covalence - Do not react to acids or to alkalines - Most become green under the influence of TiO <sub>2</sub> - React to halogens and give rise to green colour compounds	Polyvinyl Polyvinyl - acrylic (PolyFlash)	Lefranc Bourgeois (LB) Lefranc Bourgeois (LB)	Lefranc Bourgeois (LB) Lefranc Bourgeois (LB)	

This study does not specifically concentrate on characterisation of numerous additives such as extenders and striaters.

## 5. Methodology

Tests were carried out on linen canvases measuring 12 cm<sup>2</sup> which were already treated with an universal primer (figure 1).

- Commercial paints were studied in two fashions:

- a mixture was made on a binder/pigment ratio equal to 9/1
- paints in tubes

- The mixtures made within the laboratory do not contain anti-ageing medium or added preservatives.

In both cases the mixtures, as well as the drying of the tests, were done at 20 °C < T < 23 °C and 50% < RH < 60 %.

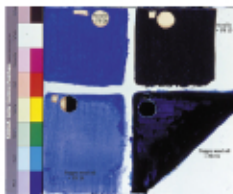


Figure 1 Test, example of poppy seed oil + PB 15/PB 28 and acrylic + PB 15/PB 28 (O acryp-PPV)

The region 3000-2840 cm<sup>-1</sup> allows differentiation to be made between the polymers studied (figure 3). Indeed, pigments and extenders do not interfere in this region.

## 6.1.2 XRD

Only extenders and PB28 are detectable by XRD. These are in fact well crystallized mineral compounds and in sufficient quantity (>5%). (See figure 2)  
However, the PB15 are not identified since they are present only in very weak concentrations in the paints.

## 6.2 Accelerated Ageing test

6.2.1 Colour measurement:  
The most significant colour changes took place during the first 200 hours of the ageing process, following which variations are less striking and of a fluctuating nature. The most important variations in chroma concern poppy seed oil. The other tests reach a comparable level of ΔE<sub>cmc</sub>. Alkyds paints have a greater colour difference than the others polymers, but are still inferior to poppy seed oil (figure 4).

## 6.2.2 FTIR / XRD

When the spectra are compared, some differences are revealed concerning the stretching frequency at 3350-3300 or 1660-1610 cm<sup>-1</sup> which correspond to hydroxy compound (figure 5 & 6). On the whole, the binders which are most likely to contain free OH are :

- Poppy seed oil
- PolyFlash 2001
- Alkyd
- Acrylic Senselizer

In the case of PB 28 XRD analysis did not provide results showing any modifications after ageing process.

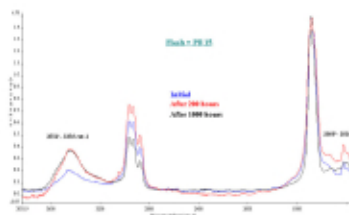


Figure 5 Flash + PB 15

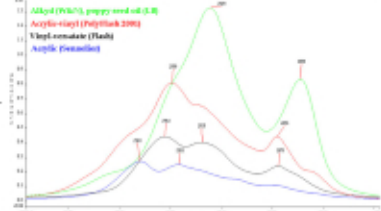


Figure 3 IR spectra of binding media, region 3000-2840 cm<sup>-1</sup>

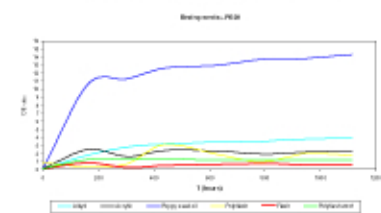


Figure 4 ΔE<sub>cmc</sub>(ΔT), Binding media + PB 28

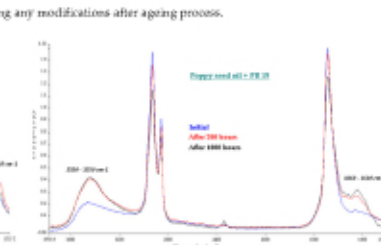


Figure 6 Poppy seed oil + PB 15

## 6.3 Discussion

- A discreet link can be drawn between colour and chemical changes. Improved knowledge of the compounds (stretches) as well as longer ageing time might have made it possible to explain this link.
- Commercial paints are highly resistant to ageing: excepting paints which contain alkyd binder.
- The commercial paints which show most yellowing are paints which belong to the polyester family such as poppy seed oil and alkyd binder. The least significant yellowing concerns the following paints: Acrylic, Flash, PolyFlash.
- The pigments chosen in this study are very resistant. What is brought to the fore, are binder alterations.
- The mixtures we have studied showing significant chemical changes are poppy seed oil, Senselizer acrylic, PolyFlash 2001 and Alkyd binder. However, the PolyFlash used in the mixture along with pure pigments does not change, at least not dramatically.

## 7. Conclusion

- The study of ageing process by spectrophotometry has brought to attention the yellowing phenomena of materials, especially for polyester type components.
- The presence of hydroxy in the tests after the ageing period is most significant. In fact, this type of grouping can be linked to the presence of hydrolytic degradation compounds.
- There is no significant increase of hydroxy after ageing of commercial paints. However, laboratory tests carried out on polyester binders, as well as on specific acrylic polymers display important differences.
- On the whole it would appear that polyvinyl - acrylic binder (PolyFlash) show more satisfactory results on both the colorimetric and the chemical front.
- Various hypotheses are put forward and have to be checked out by prolonging the ageing period and/or coupling the FTIR to other techniques of analysis.

## 8. Case Study

A Klementiewicz Piotr painting *Une guerre en une histoire sans parole* in 1983 (FRAC PACA) has been studied (figure 7).



Figure 7 painting (148 x 150 cm) (O acryp-PPV)

The binding medium is a vinyl paint (Flash) characterised by the PVA co-polymer stretching frequency 2923 - 2872 + shoulder at 2900 cm<sup>-1</sup> and the carbonyl absorption at 1735 cm<sup>-1</sup>. A peak in small proportions is also present at 875 cm<sup>-1</sup> from chalk extender. The pigment is not identified (figure 8).  
The most characteristic zone of the spectrum is the broad hydroxy stretching frequency between 3600 cm<sup>-1</sup> and 3200 cm<sup>-1</sup> with a maximum at 3345 cm<sup>-1</sup>. Some hydrolysis degradation is suspected. Further analysis should be carried out on some other part of the painting to confirm this hypothesis.

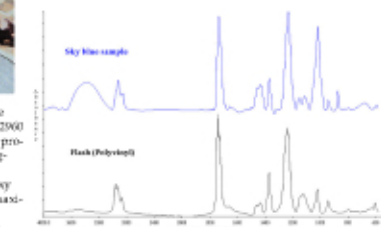


Figure 8 FTIR spectra of a sky blue sample/Flash

Ageing and characterization techniques used		Physico-chemical analysis	
Accelerated ageing chamber Votach VC4054	Spectrophotometer HUNTER- LAB Miniscan XE	FTIR Spectrum 2000 Perkin-Elmer	XRD Philips X'Pert Pro Diffractometer
Dermo-hygrometric ageing process with presence of oxygen, respecting the following cycle (°): 3 hours at 40°C and 85 % RH 1 hour at 40°C and 20% RH	- Diffuse mode with DS5/10° - Viewing area of 4 mm diameter - CIE XYZ values - ΔE <sub>cmc</sub> tolerance	- Spectrum range 4000-400 cm <sup>-1</sup> - Resolution 4 cm <sup>-1</sup> - Samples prepared in a KBr pellet (concentration range 0.5 mg /100 mg KBr)	- Monochromatic CuKα radiation combined with Bragg-Brentano optics - Diffraction patterns scanned with an angular step of 0.01° with a counting time of 0.35 sec./step, over the range 15°- 70° - Spinning sample holder

(\* This temperature was focused as it is inferior to the vitreous transition temperature of relevant polymers. It is maintained at a constant level in order to avoid contractions and decontractions of the frame which would modify it mechanically rather than chemically. It also represents an extremum found in museums.

## 6. Results

### 6.1 Characterisation

#### 6.1.1 FTIR

Two important groups arise:  
- Saturated and alkyds (both are polyester)  
- Synthetic polymers

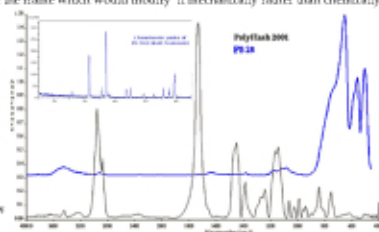


Figure 2 Example of PolyFlash + PB28 FTIR spectrum and PB 28 XRD

Main stretching vibrations region (4000 - 400 cm <sup>-1</sup> )	Pigments					Binding media				
	PB 15 (Senselizer)	PB 28 (Senselizer)	Poppy seed oil (LB)	Alkyd (WB&N)	Acrylic (Senselizer)	Flash (LB)	PolyFlash (LB)	PolyFlash 2001 (LB)		
Hydroxy compound 3540 - 3000 cm <sup>-1</sup>			x	x	x	x	x	x		
Alkyd group 3035 - 2855 cm <sup>-1</sup> 2990 - 2835 cm <sup>-1</sup>	x		x	x	x	x	x	x		
Carbonyl compound - ester or possibly ketone 1745 - 1710 cm <sup>-1</sup>			x	x	x	x	x	x		
Aromatic compound - possibly hydroxy 1530 - 1430 cm <sup>-1</sup>	x									
Aromatic organosulfur compound 1510 - 1480 cm <sup>-1</sup>	x									
Inorganic compound - metal oxide 800 - 705 cm <sup>-1</sup>		x								