THE COURTAULD
Institute of Art

STEDELIJK MUSEUM AMSTERDAM

The Getty Conservation Institute

Cultural Heritage Agency
Ministry of Education, Culture and Science

Cultural Heritage Agency
Ministry of Education, Culture and Science

28 AND 29 MARCH 2013

Issues in Contemporary Oil Paint

Book of Abstracts

Issues in Contemporary Oil Paint

ICOP

Cultural Heritage Agency
Ministry of Education, Culture and Science

Symposium
28/29 March 2013
Amersfoort
The Netherlands

Colophon

Symposium *Issues in Contemporary Oil Paint* (ICOP)

Amersfoort, 28/29 March 2013

Book of Abstracts

Editors:
Klaas Jan van den Berg
Matthijs de Keijzer, Tom Learner, Gunnar Heydenreich, Jay Krueger, Aviva Burnstock and Alberto de Tagle

Design: Agnes Brokerhof, Bart Ankersmit, Klaas Jan van den Berg

Printing: Print X-press, Amersfoort

Photo credits (outside abstracts, for which authors are responsible):
Klaas Jan van den Berg, except for Laura Mills (cover); Louise Wijnberg (p.3a, 31b), Aviva Burnstock (p.3b), Muriel Geldof (p.13a,c) Emilie Froment (p.113a,e), Henk van Keulen (p.113b) Tiarna Doherty (p.129c)

Table of Contents

Sensitivity of modern oil paints to solvents: effects on synthetic organic pigments

Diana Blumenroth,[a] **Stefan Zumbühl,**[b] **Nadim C. Scherrer**[b] and **Wolfgang Müller**[c]

[a] Cologne Institute of Conservation Sciences, University of Applied Sciences, Germany
[b] Bern University of Arts, Bern University of Applied Sciences, Switzerland
[c] H.Schmincke & Co. GmbH & Co. KG, Erkrath, Germany

Introduction

Modern oil paints show a new complexity of performance and sensitivity in comparison to "classic" oil paints. An important part of this new characteristic is the wide use of synthetic organic pigments. These can be present in works of art since the early 20th century and are now the most important group of pigments in the bright hues of modern artist's paints. Some synthetic organic pigments found in "classic modernism" paintings of the early 20th century, proved to be well soluble. As a consequence, the specific particle properties as well as the sensitivity to solvents pose a particular challenge in conservation treatments of modern oil paint.[1] The solvent sensitivity of these pigments is not evident in their chemical structure as the properties are altered by selective modifications of the structure and encapsulation. It is thus likely that early pigments may behave different to contemporary ones. Properties of dissolution are thus influenced by the chemical nature, crystal structure, particle size, as well as surface modifications of the pigment products.

Analysis/Experiments

The sensitivity to solvents of artist's paints containing organic pigments arises not only from the solubility of the pigment itself, but also from the characteristics of the surrounding binder matrix and the swelling behaviour of the system as a whole. The solvent resistance of 23 organic pigments in oil paint was tested with 6 solvents (n-hexane, toluene, chloroform, diethyl ether, acetone and ethanol). The solubility of the pigments was determined quantitatively by immersion of the pure pigments in solvents, and by immersion of artificial aged oil paint films. The time-resolved extraction was determined by UV-VIS spectroscopy. Following solvent treatment by immersion of paint films, the influence of pigment extraction along the surface was examined applying infrared spectroscopy FTIR-ATR. Raman spectroscopy was used to study morphological effects of extraction on polished crosssections of embedded oil paint films. Structural damage was examined under practical conditions with clean cotton swabs using the 6 solvents.

Results and discussion

Almost all pigments produced suspensions due to the very small particle size and low density. After filtration with a 0.2µm syringe filter, the soluble pigments became apparent. These were the yellow and orange azo pigments PY3, PY97, PY153, PO5, the orange pyrazolochinazolon PO67, the red anthraquinone PR83:1, phthalocyanine blue PB15:6, and the dioxazine PV23, and to a lesser extent the red azo pigments PR188, PR177, as well as the anthraquinone perylene PR179. The solubility is similar to the sensitivities known from the literature and industry. The time-resolved quantitative extractions were determined on the 8 pigments above in artificial aged oil paint films. The azo PY3, PY97 and PO5 exhibited particularly high extractability. This is, of course, partly due to the solubility of the pigments, but it is also influenced by the swelling behaviour of the surrounding binder matrix. Accordingly, based on the strong dispersive force interaction, chloroform often showed the highest extraction capacity. Good solubility usually is encountered along the polarity scale from the polarisable toluene up to the dipolar acetone. Towards the non-polar end of the polarity scale, the solubility decreases in general. The non-polar n-hexane is a poor solvent with synthetic organic pigments. The blue phthalocyanine PB15:6 also exhibits high solvent sensitivity, with the highest extraction rate observed in toluene.

The structural changes within the paint film were investigated using an artificial aged oil paint film containing the yellow azo pigment PY3 and exposed to chloroform. Applying infrared spectroscopy FTIR-ATR to the surface of the leached films, the surface pigment response was tested following solvent exposure of 1, 2, 5, 10 and 15 minutes. After an immersion time of 1 minute almost no pigment could be detected on the surface. With Raman spectroscopy, the pigment concentration was examined along profiles across the embedded paint films on polished cross-sections. The pigment gradually leached from the exposed surfaces. Immediate leaching of the pigment occurs within the swollen parts of the film (Figure 1). This suggests tremendously fast solubilisation of the pigment, as the solubility of the pigment is greater than the rate of diffusion of the solvent in the paint film. Upon drying of the paint film, a porous film is left due to pigment elimination.

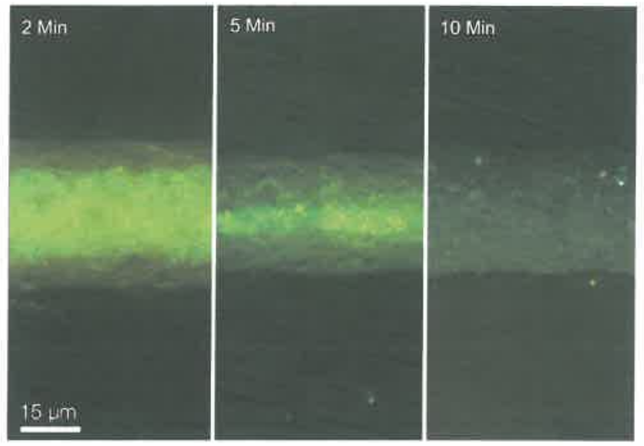

Fig. 1: Cross sections of samples immersed in chloroform. Pigment loss is visible: after 10 minutes no pigment is left in the paint film.

To test the sensitivity to solvents of paint layers containing synthetic organic pigments under realistic conditions, cotton swab wipe tests with minimal pressure application were performed. This allows the solvent to act in combination with minor mechanical action on the surface. The wipe samples showed that all verified pigments reacted very sensitively, some exhibited pigment extraction already on first contact with the cotton. This was independent whether the pigments were soluble or insoluble in the above examinations. In general, abrasion/extraction was lowest on cotton swabs soaked with non-polar solvents [Figure 2]. Solvents producing strong swelling of the oil binder caused an enhancement of this effect. However, in contrast to the general solubility, polar solvents were very harmful. This may be explained by photochemical degradation and the change of the

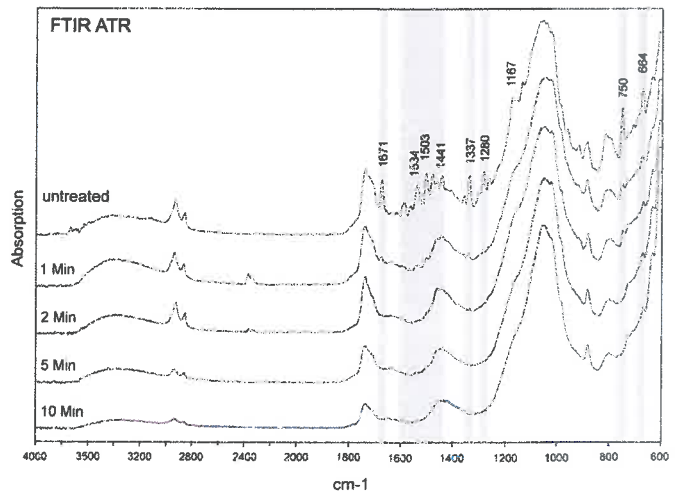

Fig. 2: FTIR-ATR spectra show almost complete leaching of the pigment from the surface after 1 minute immersion. After 2 minutes no more pigment can be detected.

---

[1] D. Blumenroth, Die Lösemittelempfindlichkeit synthetisch-organischer Pigmente in Ölfarben, MA-Thesis, Bern university of applied sciences, conservation and restoration HKB, Bern (2010).

Abstracts Friday

polarity of the binder in the paint layer's surface. It also shows that the low wipe resistance is likely due to the small particle dimension of the pigments.

The overall results demonstrate the delicate behaviour of such oil paint layers containing synthetic organic pigments when they come into contact with solvents (Figure 3). This should be regarded as a serious problem of practical conservation and restoration treatments applied to modern paints with a considerable potential to harmful consequences.

Pigment				Paint samples						Cleaning samples					
C.I.	Pigment class	Sensitivity		Pigment solubility						Solvent sensitivity					
		Literature	Pigment pure	Hexane	Diethyl ether	Toluene	Chloroform	Acetone	Ethanol	Hexane	Diethyl ether	Toluen	Chloroform	Acetone	Ethanol
PY3	Monoazo	***	***	o	*	**	***	***	*	*	**	**	***	***	***
PY97	Monoazo		***	o	o	*	***	**	o	*	**	**	***	***	***
PO5	b-Naphthol	***	***	o	*	*	**	*	o	*	*	*	***	***	**
PR188	Naphthol AS		*	o	o	o	o	o	o	*	**	***	***	***	***
PY151	Benzimidazolone	o	o	o	o	o	o	o	o	o	*	*	**	***	***
PY155	Bisacetoacetarylide	o	o	o	o	o	o	o	o	o	*	**	***	***	***
PR242	Disazo condensation	*	o	o	o	o	o	o	o	*	**	**	***	***	***
PY153	Metal complex	*	*	*	*	*	*	*	o	o	*	*	***	***	**
PY139	Isoindolinone	o	o	o	o	o	o	o	o	o	*	**	***	***	***
PB15:6	Phthalocyanine	***	***	*	*	***	**	**	*	o	*	*	**	**	**
PG7	Phthalocyanine	o	o	o	o	o	o	o	o	o	*	*	**	**	*
PG36	Phthalocyanine	o	o	o	o	o	o	o	o	o	o	**	***	***	**
PV19	Quinacridone	o	o	o	o	o	o	o	o	o	**	**	***	***	***
PR122	Quinacridone	o	o	o	o	o	o	o	o	*	**	**	***	***	***
PR209	Quinacridone	o	o	o	o	o	o	o	o	*	**	***	***	***	***
PR179	Perylene	o	*	o	o	o	o	o	o	*	**	**	***	***	***
PO43	Perinone	o	o	o	o	o	o	o	o	*	**	***	***	***	***
PR177	Antraquinone	o	*	o	o	o	o	o	o	o	**	***	***	***	***
PR83:1	Antraquinone CA	***	**	*	*	*	*	*	*	o	*	*	**	***	**
PB60	Indanthrene	o	o	o	o	o	o	o	o	*	**	**	***	***	***
PV23	Dioxazine	*	*	o	*	*	*	*	o	o	*	*	***	***	**
PR264	Diketopyrrolo-pyrrole		o	o	o	o	o	o	o	o	*	***	***	***	***
PO67	Pyrazoloquinazolone	***	***	o	o	*	***	*	o	o	*	**	***	**	*
PW4	Zinc white		o	o	o	o	o	o	o	o	o	*	*	*	*

Solvent sensitivity: o insoluble, * low, ** high, *** very high

Fig. 3: Summary

Delegates

Acknowledgements;
Project members
Partners