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DEVELOPMENT OF STANDARD PAINT FILMS BASED ON ARTISTS' MATERIALS

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Abstract

The degradation of art objects is caused by the combination of all indoor environmental factors. To investigate the deterioration processes in paintings and at the same time to design a risk assessment system, chemical sensors based on artist's materials are developed. Therefore standard paint films of egg yolk tempera with lead white $2PbCO_3{\cdot}Pb(OH)_2$, azurite $2CuCO_3{\cdot}Cu(OH)_2$ or smalt were investigated. With accelerated ageing experiments the simulation of natural degradation processes is aimed. First markers for chemical changes were found in the FTIR and TG/DSC measurements.

Keywords: azurite, egg tempera, IR spectroscopy, lead white, smalt

Introduction

Knowledge of indoor environment al conditions has became very important for considering the storage and exhibition conditions of art objects [1]. Measurements of individual environmental factors such as temperature, relative humidity, light or pollutant gases have already been carried out. But the degradation of art objects which is caused by the combination of all these factors and their fluctuation, in particular the relative humidity and the interaction with pollutants, needs to be evaluated.

To investigate the deterioration processes in paintings and at the same time to design a risk assessment system we are developing chemical sensors based on artist's materials. Therefore we prepared standard paint strips using egg yolk tempera with different pigments. With accelerated ageing experiments we aim on one hand to simulate the natural degradation [2, 3] and on the other hand to sensitise the coating. We expect the sensitised monitors to react faster to the environment when exposed in the museum.

For a complete characterisation of the standard samples we investigated chemical, physical and morphological properties. In this paper we are going to focus on the thermochemical and spectroscopic aspects. Further investigations using complementary methods are going to be published.

Experimental

Egg yolk tempera is a dispersion of pigment in egg yolk and was first mentioned by Theophilius at the beginning of the 10th century [4]. The technique is particu-

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larly associated with Italian artists of the 14th and the 15th centuries. We prepared our tempera according to the historical recipe described in Cennini's Il Libro dell' Arte [5]. To improve the quality of the paint film, a modified binder containing resin mastic was investigated [6].

To detect chemical changes occurring during the ageing of standards and to correlate them with extremely small samples from original paintings a Perkin Elmer FTIR2000 equipped with a beam condenser and a diamond cell was used.

The thermoanalytical measurements were carried out on a Perkin Elmer. For morphological investigations a Philips SEM 515 was used.

Accelerated aging experiments were carried out in an ageing chamber of the Tate Gallery. The light ageing conditions were 200000 lux at 28°C and 40% relative humidity (RH). Thermal ageing was carried out at 55% RH and 60 or 70°C.

Results and discussion

Unpigmented binder

The characterisation of the unpigmented organic binders is important in order to separate from pigment induced degradation mechanisms. Pure egg yolk is a complex mixture of different lipids, proteins and carbohydrates [7]. The infrared spectrum is dominated by the bands listed in Table 1. Out of these, suitable markers are chosen to follow chemical changes in pigmented tempera and aged samples.

First ageing experiments using the unpigmented egg yolk tempera show observable changes in the infrared spectra (Fig. 1). After light and heat ageing the loss of cis unsaturation (3012 $\mathrm{cm^{-1}}$) is visible. The carbonyl band at ~1745 $\mathrm{cm^{-1}}$ increases and an additional shoulder is visible. The amide I band has a shoulder at 1632 $\mathrm{cm^{-1}}$ clearly separated from the 1651 $\mathrm{cm^{-1}}$ feature. Comparing this spectrum with a spectrum of egg yolk aged naturally for 50 years, recently published in Stud-

Table 1 Assignments for infrared features in egg yolk (*marker)

Wavenumber/$\mathrm{cm^{-1}}$	Assignment	Group	Protein/Lipid	Comment
3299	ν(N–H)	amide	protein	amide
3008	ν(N–H)	amide	protein	amide II overtone
3012	ν(=C–H)	methylene	lipid	cis unsaturated
2959*	ν_{as}(C–H)	methyl	mainly lipid	long chain fatty acids
2928*	ν_{as}(C–H)	methylene	mainly lipid	long chain fatty acids
2857*	ν_{s}(C–H)	methylene	mainly lipid	long chain fatty acids
1744*	ν(C=O)	carbonyl	lipid	ester
1655*	ν(C=O)	amide	protein	amide I
1543*	δ(N–H)	amide	protein	amide II
1239	ν(C–O)	ester	lipid	ester linkage
1164	ν(C–O)	ester	lipid	ester linkage
1090	ν(C–O)	ester	lipid	ester linkage

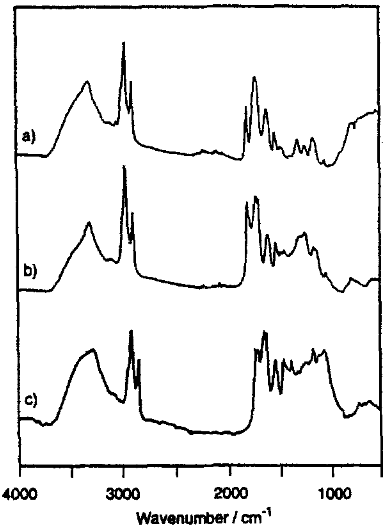

Fig. 1 FTIR spectra of unpigmented egg yolk films: a) unaged, b) light aged 431 h and heat aged 504 h at 70°C, c) naturally aged for 50 years

ies and Conservation [8], a trend to similar features can be seen. The presence of new carbonyl features suggest oxidation of the triglycerides in aged egg. The amide II band remains unaltered but the triplet bands associated to ester linkages have changed significantly. The explanation is the autoxidation of the lipid part of the egg what has been confirmed by mass spectroscopic experiments. Comparable features are known from the polymerisation in linseed oil [9].

The infrared spectrum of the modified binder is highly dominated by the features of the egg yolk. In the microscope, these paint films show a net of hair fissures with air-bubbles trapped along them. These are spots of potential changes during the ageing process.

Heat ageing of this complex binder film at 60°C produces a slight darkening of the colour and a crumbling of the film along the hair fissures. This may infect the physical properties but no changes can be seen in the infrared spectra. It might be that the presence of mastics in the mixture inhibits changes at these conditions.

Lead white tempera

Lead white, $2PbCO_3 \cdot Pb(OH)_2$, is one of the oldest artifically produced pigments, described for the first time in the 4th century B.C. [10].

In the FTIR spectra of unaged standard samples one can distinguish between binder and lead white (Table 2). Three of the markers chosen for the binder are visible. The C–H stretch and the carbonyl band representing the lipid part of the egg yolk show no changes. The amide II band is hidden by the wide pigment band. But a significant difference is observed in the amide I band. Its relative intensity decreased drastically compared with the unpigmented binder. We found that this decrease is dependent on the amount of lead white admixed. The FTIR spectra of the two extreme 40 and

Table 2 Assignments for infrared features in lead white tempera

Wavenumber/ cm^{-1}	Assignment	Group	Pigment/ medium	Comment
3541	ν(O–H)	$Pb(OH)_2$	pigment	sharp feature
3294	ν(N–H)	amide	medium	amide
2957	ν_{as}(C–H)	methyl	medium	long chain fatty acids
2926	ν_{as}(C–H)	methylene	medium	long chain fatty acids
2857	ν_s(C–H)	methylene	medium	long chain fatty acids
1742	ν(C=O)	carbonyl	medium	ester
1656	ν(C=O)	amide	medium	amide I
1545	δ(N–H)	amide	medium	amide II
1490–1350	$\nu(CO_3)$	$PbCO_3$	pigment	broad band, antisymm. stretch
1046	$\nu(CO_3)$	$PbCO_3$	pigment	sharp band, symm. stretch
682	$\delta(CO_3)$	$PbCO_3$	pigment	sharp band, rocking deform.

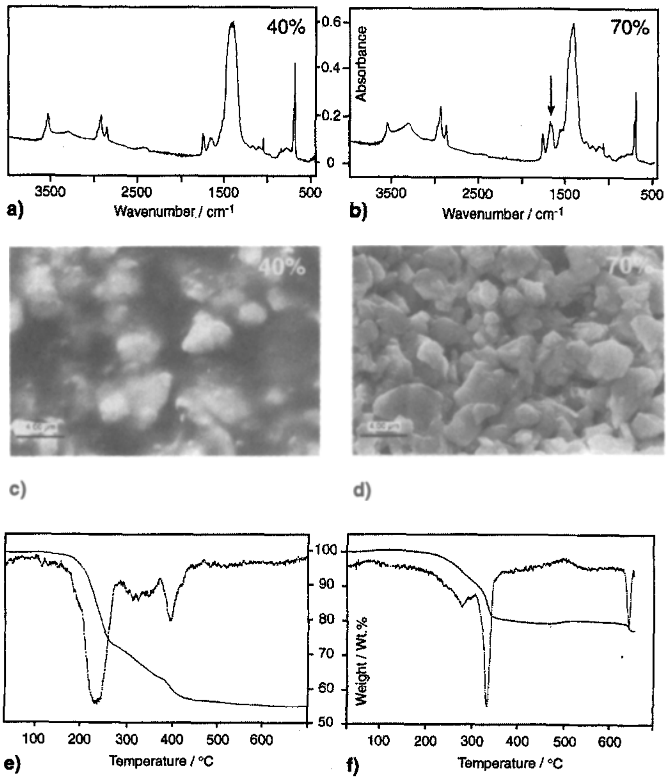

Fig. 2 Comparison of unaged lead white tempera with different ratios of pigment in egg yolk: FTIR spectra: a) 40 wt% and b) 70 wt%, SEM micrographs: c) 40 and 70 wt%; TG/DTG curves e) medium rich and f) medium poor samples

70 wt% of a series are shown in Figs 2a–b. The observable changes are an indication for an interaction of the protein and the pigment simply by mixing them together. A complexation of the lead by the amide group of the protein is probable [11] and has to be investigated by further methods such as EXAFS measurements.

Looking at the SEM pictures of the two paint films, the pigment particles are clearly visible and exposed to the atmosphere when few medium is present (Fig. 2d). With a high medium content the particles are embedded and well conserved by the medium (Fig. 2c). An interesting difference of the thermochemical behaviour can be seen when heating them in oxygen up to 700°C. The TG of the medium pure sample (Fig. 2f) is dominated by the decomposition behaviour of the lead white. $2PbCO_3 \cdot Pb(OH)_2$ decomposes under CO_2 release to form lead monoxide. When heated to higher temperatures PbO is oxidised and becomes red lead Pb_3O_4. The reduction of Pb_3O_4 to PbO at 650°C leaves a strong marker in the DTG curve. The same experiment carried out with a medium rich samples shows no oxygen uptake by PbO. The marker has disappeared (Fig. 2e). The oxidation must be inhibited by the extensive cover of medium preventing enough oxygen contact.

Azurite tempera

An important blue pigment used for egg tempera is the mineral Azurite $2CuCO_3 \cdot Cu(OH)_2$. For these standard samples chemical changes introduced by accelerated ageing experiments are measurable by DSC (Fig. 3a). Two exothermic peaks caused by the decomposition of the basic copper carbonate, overlapping with that of the organic binder, are distinguishable. Aged samples show changes in the ratio of the two peaks and the shape of the low temperature shoulder. First indication for the chemical changes during the degradation is given by infrared spectra (Fig. 3b), such as light induced alteration in the amide II region and additional carbonyl features for heat aged samples. At this stage DSC and FTIR provide significant markers for ageing processes. The investigation of the chemical nature of these processes by mass spectrometry is still in progress.

Smalt tempera

Smalt is a cobalt containing silica-glass first used in the 15th century. Looking for changes in the IR spectra caused by accelerated ageing the markers chosen for the organic binder are again of interest.

In Fig. 4 a series of heat aged samples are shown (60°C for 7, 14 and 21 days in the dark). With increasing ageing time in the carbonyl region a new peak (1599 cm^{-1}) grows. If one compare the same sequence of the spectra with the unpigmented tempera film, no changes can be observed between aged and unaged binder. Therefore smalt, probably the cobalt ion, may have a catalytic effect on the oxidation of the lipids in the egg tempera.

Conclusion

To find a handle for the interpretation of original samples it is unavoidable to investigate model systems. With ageing experiments one tries to simulate the deterio-

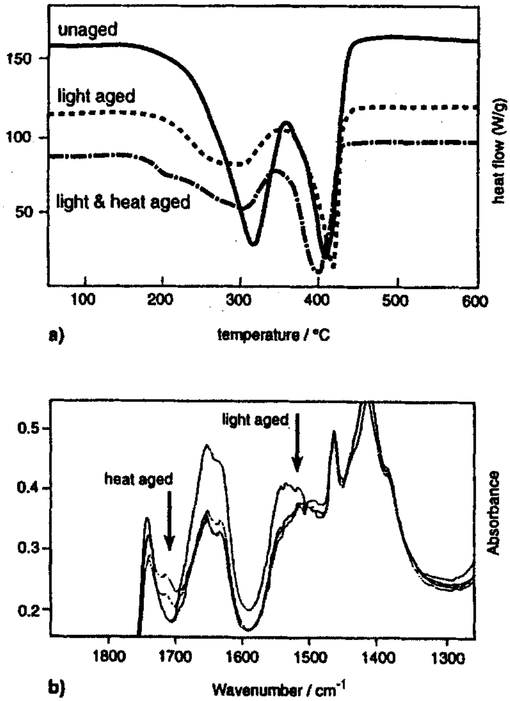

Fig. 3 Tempera of azurite in pure egg yolk binder. Comparison of unaged, light aged 413 h and light aged 413 h + heat aged 504 h at 70°C samples. a) DSC spectra, b) FTIR spectra

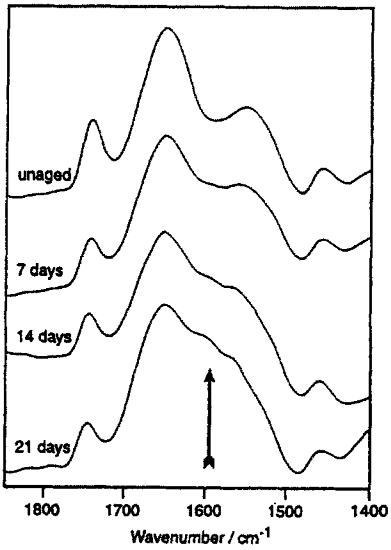

Fig. 4 FTIR spectra of a series of heat aged smalt tempera (60°C for 7, 14 and 21 days in the dark). Sequence of the carbonyl regions

ration process and aims at a calibration of changes. The investigation methods have to yield significant markers to identify chemical processes fast and reproducibly. By additional investigation methods we aim to explain the markers and the processes going on during the degradation. Finally, a data base of standards and original samples has to be built up to realise a qualified judgement of unknown samples. From these standards, environmental monitors are designed and are going to be exposed to standard environment as well as the real museum conditions.

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References

1 Gary Thomson, 'The Museum Environment', 2nd ed., Butterworth Heinemann, London 1995.
2 C. V. Horie, 'Materials for conservation. Organic consolidants, adhesives and coating, Butterworth Heinemann, London 1987.
3 R. Howells et al., Adhesives and Consolidants, Preprints of IIC Congress, Paris 1984.
4 P. Theophilius, 'On Divers Arts', Trans. J. G. Hawthrone, Dover Publications Inc., New York 1979.
5 C. Cennini, The craftsman's handbook 'Il libro dell'arte', trans. D. V. Thompson, Dover Publications Inc., New York 1960.
6 S. Bellucci, private communication.
7 R. W. Burley and D. V. Vadehra, 'The Avian Egg: Chemistry and Biology.', John Wiley & Sons, London 1989.
8 R. J. Meilunas, J. G. Bentsen and A. Steinberg, Studies in conservation, 35 (1990) 33.
9 K. Moor, private communication.
10 'Theophrastus's History of Stones', Trans. Sir J. Hill, London 1774.
11 G. Battistuzzi, M. Borsari, L. Menabue, M. Saladini and M. Sola, Inorg. Chem., 35 (1996) 4239.