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A multi-analytical study on the photochemical degradation of synthetic organic pigments

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ABSTRACT

This paper summarizes the results of a photochemical ageing study on selected synthetic organic pigments used in paint formulations both as artists' and industrial materials. Some of them are rated by the American Society for Testing and Materials (ASTM) as fugitive. We performed an accelerated ageing test for the first time on the neat pigment powders, without any binder, to determine the lightfastness of the pure pigments. Several techniques were used to compare the aged and un-aged pigments: colorimetric measurements, Fourier transform infrared spectroscopy (FTIR), and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Colorimetry highlighted a relevant change in colour ($\Delta E^* > 1$) after the ageing treatment, whereas Fourier transform infrared spectroscopy technique allowed us to identify specific differences in absorption. Pyrolysis-gas chromatography/mass spectrometry showed different pyrolysis products in the aged pigments, with respect to the un-aged ones.

1. Introduction

Today synthetic organic dyes and pigments dominate the colorant market and have almost completely replaced the traditional natural organic materials obtained from plants or animal sources. Synthetic pigments are classified in the Colour Index, which is a reference record for all the commercial dyes and pigments, created in 1924 by the Society of Dyers and Colourists. The pigments are recorded by a generic name and a number [1]. Today, the total number of synthetic organic pigments listed for different applications in the Colour Index International exceeds 500; if dyes are also considered, the number of synthetic organic colorants listed is a few thousands [1].

Paint manufactures commonly employ synthetic pigments in their formulations. Several synthetic pigments were produced for only a few years and then withdrawn from the market due to poor lightfastness or toxicity. Nonetheless, the ageing pathways of these types of pigments are not completely understood, and until now the literature focused mainly on the photochemical degradation of textile dyes [2–5], rather than on pigments employed in paint formulations.

Pigments characterized by poor lightfastness properties and employed in artists' paints - or in industrial paints employed by artists - can lead to serious conservation issues for the paintings, the most noticeable being the change in colour (fading, darkening). An example, in this respect, is the fading process undergone by Eosin, PR90, a synthetic pigment widely employed by many artists, including Vincent Van Gogh [6]. The understanding of ageing processes of pigments is of paramount importance in the field of conservation studies in order to disclose the original colour palette used by the artist, to estimate the period of production – in some lucky cases – of a work-of-art, and to devise appropriate conservation strategies. Ageing studies may also guide future developments of paint materials for industrial or commercial use.

Organic pigments are generally identified by Raman spectroscopy. Several applications of this technique to the characterization

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of artworks have been presented in recent years, and some publications contain databases of Raman spectra [7–12]. Yet, no relevant ageing study has been performed by this powerful technique.

FTIR is mainly used for inorganic pigments, but this technique gives excellent spectra also for organic pigments and could readily differentiate them in their dry, powder form [13].

Some authors have proposed pyrolysis coupled with GC/MS (Py-GC/MS) for the analysis of synthetic organic pigments [13–15], including our recent publication [16]. Synthetic pigments are usually analysed without any sample pre-treatment or derivatising reagent.

HPLC techniques, widely used for the characterisation of traditional natural organic dyes, food colorants, cosmetic dyes and soluble dyes in general, are not widely employed for the analysis of synthetic pigments, because they are often insoluble in the majority of the solvents. Up to now, both Py-GC/MS and HPLC were used by authors solely for the characterization of synthetic pigments, while a detailed study of their photochemical degradation was carried out in only a few cases [17].

In this paper, we aim at highlighting the colour changes undergone by widely used synthetic pigments upon accelerated ageing, and suggest some general, possible degradation pathways on the basis of Py-GC/MS and FTIR analyses.

2. Experimental

2.1. Reference materials

The synthetic organic pigments analysed were collected from the Getty Conservation Institute's reference materials collection. The pigments, and their manufacturers, are listed in Table 1 and their structures are provided in Table SM1. The selection includes some pigments known to have poor lightfastness properties, which have been withdrawn from the market, but also pigments less prone to fade and currently employed in paint formulations.

2.2. Preparation of the samples

For the ageing study, each pigment, pure, was mixed with isopropyl alcohol (Sigma Aldrich) and then spread onto a glass slide and allowed to dry for 2 weeks. Even though the majority of the pigments tested was not soluble in alcohol, the suspensions were easily spreadable onto the glass slides, but it was not possible to achieve completely homogeneous surfaces. The glass slides were placed on a specimen holder. Half of each slide was covered by the holder, in order to have a colour reference of the un-aged pigment.

One extra sample (PV39) has already been prepared in methanol and naturally aged by exposure for five months to natural light, at the time the study started. Thus, it was tested without extra exposure in the weather-ometer.

It is important to highlight that the choice of glass slides as support, which is uncommon for colorimetric measurements, was the only viable choice due to the difficulties in properly casting the pigments and to avoid contamination in pyrolysis.

After completing the ageing protocol, for the FTIR-ATR and colorimetric measures the pigments were examined directly on the glass slides. Moreover, about 1 mg of the dried pigment was scraped off from the glass slide with a lancet and analysed with Py-GC/MS.

2.3. Apparatus

The artificial ageing was performed with a Ci4000 Xenon weather-ometer (Atlas, USA), equipped with a 6500 W water cooled Xenon lamp. To cut off the far-UV light, CIRA and Soda lime filters were employed. Specimen rack rotated at 1 revolution per minute around the Xenon lamp to provide uniform exposure. The ageing conditions were adopted from the ASTM D4303-10 protocol [18]: irradiance 0.35 W/m^2 at 340 nm and exposure of the specimens to 100% light to reach a total radiant exposure of 510 KJ/(m^2 nm); uninsulated black panel temperature at 63 °C; chamber air temperature at 43 °C; relative humidity 55%; total exposure time 410.5 h.

Pyrolysis – Gas Chromatography/Mass Spectrometry was carried out on a 7890A gas chromatograph, coupled with a 5975C triple axis mass spectrometer (Agilent Technologies, USA), coupled with a EGA/PY 3030D multi-shot pyrolyzer (Frontier Laboratories, Japan). The mass spectrometer was operated in the positive mode in electron impact (EI) ionization (70 eV). The pyrolysis was carried out at 550 °C for 12 s. The chromatographic separation was carried

Table 1
List of the synthetic pigments selected for the ageing study. The structures are provided in Table SM1. The/symbol indicates pigments that have not been tested by ASTM yet.

C.I. name	C.I. number	Manufacturer	Pigment class[a]	ASTM lightfastness[b](referred to a binder)
PB1	42595:2	EC pigments	Triarylcarbonium	V (gouache)
PO5	12075	Winsor & Newton	β naphthol	II (oil)
PO16	21160	Sun	Diarylide yellow	V (gouache)
PO46	15602	Sun	β naphthol, Ba	/
PR3	12120	Clariant	β naphthol	IV (oil)
PR48:1	15865:1	EC Pigments	BONA, Ba	/
PR49:2	15630:2	Sun	β naphthol, Ca	/
PR53:1	15585:1	Lansco	β naphthol, Ba	V (oil)
PR57:1	15850:1	EC Pigments	BONA, Ca	V (gouache)
PR83	58000	Winsor & Newton	Anthraquinone, Ca	III (oil)
PR112	12370	Golden	Naphthol AS	II (oil)
PR170	12475	Winsor & Newton	Naphthol AS	II (oil)
PV1	45170:2	Magruder	Triarylcarbonium	V (gouache)
PV27	42535:3	EC Pigments	Triarylcarbonium	/
PV39[a]	42555:2	Sigma Aldrich	Triarylcarbonium	IV (gouache)
PY3	11710	Golden	Monoazo Yellow	II (oil)
PY12	21090	Sun	Diarylide Yellow	/
PY100	19140:1	H. Kohnstamm & Co	Monoazopyrazolone, Al	V (watercolor)

Lightfastness III, ($\Delta E^* > 8, <16$) fair lightfastness; Lightfastness IV, ($\Delta E^* > 16, <24$) poor lightfastness; Lightfastness V, ($\Delta E^* > 24$) very poor lightfastness.
[a] According to W. Herbst and K. Hunger [19].
[b] ASTM lightfastness categories: I excellent; II good; III fair; IV poor; V very poor.