



# Spectroscopic methods for the identification and photostability study of red synthetic organic pigments in alkyd and acrylic paints



Marta Anghelone<sup>d,\*</sup>, Valentin Stoytschew<sup>b</sup>, Dubravka Jembrih-Simbürger<sup>a</sup>, Manfred Schreiner<sup>a,c</sup>

<sup>a</sup> Institute of Science and Technology in Art, Academy of Fine Arts Vienna, Vienna, Austria

<sup>b</sup> Laboratory for Ion Beam Interactions, Ruđer Bošković Institute, Zagreb, Croatia

<sup>c</sup> Institute of Chemical Technologies and Analytics, Vienna University of Technology, Vienna, Austria

<sup>d</sup> Institute of Conservation and Restoration, University of Applied Arts Vienna, Vienna, Austria

## ARTICLE INFO

### Article history:

Received 31 August 2017

Received in revised form 28 January 2018

Accepted 21 February 2018

Available online xxxx

### Keywords:

Synthetic organic pigments

Micro-Raman spectroscopy

Fourier transform infrared spectroscopy

UV–vis spectroscopy

Photodegradation

## ABSTRACT

The photostability of red synthetic organic pigments of three different chemical classes such as naphthol AS (PR112), diketopyrrolopyrrole (PR254 and 255), and quinacridone (PR122 and red shaded PV19) is investigated in the present work. In particular, the study focuses on pigments in powder form and in alkyd and acrylic paints which are widely used in art. The aim is to consider the influence of the pigments on the long-term stability of the paints when exposed to conditions of outdoor solar radiation. For this purpose, pigment powders as well as self-made and commercial paints were characterized by spectroscopic techniques before and after exposure to accelerated artificial solar radiation. Chemical and color changes were studied by micro-Raman, infrared, and UV–Vis spectroscopies. The pigment powders resulted to be stable to the ageing conditions applied. The photostability of the paints was evaluated by semi-quantitative interpretation of the infrared data, and it was found that the light ageing is indeed affecting the alkyd and acrylic binders, rather than the pigments. Additionally, in both, alkyd and acrylic aged paints a relative enrichment of pigments was registered on the surface, due to the photodegradation of the binders, which led to the formation of low-molecular-weight and volatile compounds. Finally, Hierarchical Cluster Analyses (HCA) of UV–Vis data proved that UV–Vis spectral features could be successfully used for the identification of the pigments in the paints, despite the light ageing.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

From the 19th century onwards synthetic organic pigments (SOPs) were manufactured and used in a variety of applications, especially in the print, coating, and paint industry [1]. The use in art posed questions about the durability and long-term stability of the new materials developed. In particular, the stability of a material towards photooxidation and damages induced by light is defined as photostability. Especially the light in the very energetic UV range, in combination with diffusion of oxygen into the material is causing photooxidative reactions and photodegradation. This can be considered a surface phenomenon, affecting *in primis* the uppermost layer of the paints (ca. 10 μm) [2]. For commercial paints produced for art it has to be kept in mind that the photostability of the material depends not only on the pigment itself but to a high extent also to the binder as well as a multitude of additives (e.g. fillers, light stabilizers, etc.), which are usually included but often not described and listed in the products' labels.

Therefore, the present work was carried out in order to investigate the photostability of selected SOPs in alkyd and acrylic paints typically found in modern and contemporary art works [3]. The focus was put on red azo pigments of three different chemical classes: naphthol AS, diketopyrrolopyrrole (DPP), and quinacridone [4]. Naphthol AS are monoazo pigments characterized by N=N linkage based on the coupling of diazotized substituted aniline with arylides of 2-hydroxy-3-naphthoic acid. In particular, Pigment Red 112 (PR112) was studied [1], which has three chlorine atoms. DPP and quinacridone are polycyclic pigments. DPP pigments are derivatives of 1,4-diketopyrrolo(3,4c) pyrrole. PR255 presents two phenyl groups in the structure, whereas PR254 has two chloro-phenyl groups [5]. Quinacridone pigments are dioxotetrahydroquinolinoacridine compounds, with a typical five-ring polycyclic system. The two quinacridone pigments selected, Pigment Violet 19 (PV19, having a crimson shade in its γ-polymorph) and PR122 (dimethylquinacridone) have both a linear-trans structure. The polycyclic compounds consist of a combination of cross-conjugated electron-donating (N–H) and electron-accepting (C=O) units. Common features of all these pigments are high stability (also towards photooxidation) and low solubility caused by the strong intermolecular interactions, i.e. hydrogen bonding and π–π stacking [5]. Also, the

\* Corresponding author.

E-mail address: [marta.anghelone@uni-ak.ac.at](mailto:marta.anghelone@uni-ak.ac.at) (M. Anghelone).

color properties, light absorption, and scattering of such pigments are lattice dependent [6].

So far no systematic study was carried out to investigate the photostability of the SOPs mentioned above towards accelerated conditions of outdoor solar radiation in modern paints. Some works are dealing just with the photostability of SOPs in powder form, e. g. naphthol AS analyzed by Pyrolysis-Gas Chromatography/Mass Spectrometry [7]. Other studies were performed concerning the photostability of SOPs e.g. quinacridone applied as inks in tattooing [8]. Several works focused on the optical properties of DPP since they are largely used as semiconductors [5,9–11]. The photostability of PR112 and PR122 in acrylic paints was investigated after exposure to UV lamp (ca. 254 nm) by Fourier Transform Infrared Spectroscopy [12].

On the other hand, the identification of SOPs in powder form and in original artworks by different analytical methods is a more treated topic [13–22]. As yet, systematic studies about identification and stability of SOPs towards accelerated solar radiation conditions were carried out only on paints containing phthalocyanine pigments [23,24].

Based on these investigations and combining these results with the requirements for the material analysis of art works, which have to be carried out in a non-destructive way, it was decided to study the effect of accelerated solar exposure on the selected materials by using non-invasive, surface sensitive methods, which might be applied also in situ: Micro-Raman spectroscopy, Fourier Transform Infrared Spectroscopy in Attenuated Total Reflection mode (FTIR-ATR), and finally UV-Vis spectroscopy were employed. Numerous studies already confirmed the potentials of Raman and FTIR-ATR spectroscopy for the identification of synthetic organic pigments, dyes, and binding media [21,25]. Both methods are surface sensitive (intended as uppermost  $\mu\text{m}$ ), and in particular FTIR-ATR has been widely used for degradation studies of modern materials [24,26–28]. Finally, UV-Vis spectroscopy can give not only qualitative information about the paint systems in a completely non-invasive approach [29] but can also be used for quantifying the color changes caused by light ageing [7]. Moreover, in the present work the combination of UV-Vis spectroscopy with multivariate analysis of the data obtained by Hierarchical Cluster Analyses (HCA) yielded a clear interpretation of the results.

## 2. Experimental

### 2.1. Sample preparation

Two-components self-made paints were prepared by mixing the red synthetic organic pigment powders (Kremer Pigmente, Germany) of the chemical classes (listed in Table 1) with the binders Alkyd Medium 4 (Lukas, Germany) and with Plextol D498 (Kremer Pigmente, Germany), a poly(butyl methacrylate-co-methyl methacrylate) - p(nBA/MMA). The paints were prepared with varying ratios of pigment/binding medium (P/BM) depending on the consistence of the paint achieved. The paints were cast on microscope glass slides with a thickness of 150  $\mu\text{m}$ , and left drying at room conditions for two weeks. Commercial paint tubes (Winsor & Newton, U.K.) containing the same pigments as the self-made paints, as listed in Table 1, were selected and applied according to the same procedure. Both, self-made and commercial paints were exposed to accelerated light ageing for two (called

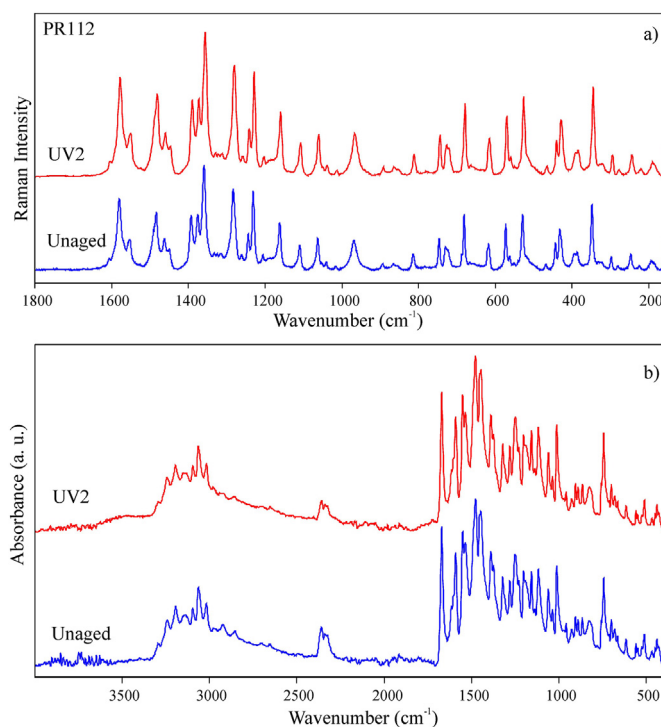


Fig. 1. Micro-Raman (a) and FTIR-ATR (b) spectra of unaged and UV2 (aged for four months) PR112 pigment powder. Spectra are baseline corrected and vector-normalized.

UV1) and four (called UV2) months. Therefore, the samples were placed in a Xenon Arc Simulator SOL2/500 (Dr. Hönle UV Technology, Germany) equipped with a H2 filter, with emission between 295 and ca. 3000 nm, full nominal irradiance 910  $\text{W}/\text{m}^2$ . This value corresponds to ca. seven times of the natural irradiance typical for central Europe [24,30]. Temperature and relative humidity (RH) were not customizable and values were measured ( $T = 40^\circ\text{C}$  and  $\text{RH} = 10\%$ ) by means of sensors AQL S500 (Aeroqual Limited, New Zealand). Additionally, the pigment powders used for the preparation of the paints were dispersed in isopropanol (Neuber, Austria) and applied on glass slides [7]. After complete evaporation of the solvent the pigment powders on the glass slides were exposed for four months (UV2) to the same ageing conditions as the paints.

### 2.2. FTIR-ATR spectroscopy

For the FTIR-ATR investigations an Alpha-FTIR instrument with a platinum ATR module (Bruker Optics, Germany), equipped with a deuterated triglycine sulphate detector (DTGS) and a diamond crystal could be used. Spectra were acquired in the range between 4000 and 370  $\text{cm}^{-1}$  performing 128 scans with a resolution of 4  $\text{cm}^{-1}$ . Three spots per sample were measured directly on the paints. For the identification of the paint materials measured spectra were compared with FTIR databases, e. g. IRUG (Version 2000) [31] and Tate Organic Pigment Archive (Millbank, London SW1P4RG).

Table 1

List of self-made and commercial paints containing red SOPs. Ratio pigment/binding medium (P/BM) used for the preparation of the self-made paints is given.

Pigment class	C.I. Name	Alkyd paints			Acrylic paints		
		Alkyd medium 4	P/BM	Griffin (W&N)	Plextol D498	P/BM	Artist's acrylic (W&N)
Naphthol AS	PR112	✓	1:10	–	✓	1:16	✓
Diketopyrrolopyrrole	PR254	✓	1:10	–	✓	1:10	✓
	PR255	✓	1:10	–	✓	1:10	✓
Quinacridone	PR122	✓	1:10	–	✓	1:20	✓
	PV19	✓	1:10	✓	✓	1:70	✓

Download English Version:

<https://daneshyari.com/en/article/7640729>

Download Persian Version:

<https://daneshyari.com/article/7640729>

[Daneshyari.com](https://daneshyari.com)