



Photostability and influence of phthalocyanine pigments on the photodegradation of acrylic paints under accelerated solar radiation



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ABSTRACT

Self-made and commercial acrylic paints containing phthalo blues (C. I. Name PB15:1, PB15:3, PB15:6, and PB16), and phthalo greens (PG7 and PG36) were exposed to artificial ageing in a Xenon Arc simulator (910 W/m²). The ageing conditions are reproducing the typical outdoor solar radiation, which artworks conceived for outdoor spaces might be exposed to. Complementary analytical techniques were employed in order to study the photodegradation process occurring on the paints. By means of micro-Raman spectroscopy the pigment component in the paints was investigated, while Py-GC/MS in double shot mode was employed for the characterization of photodegradation products of both binder and pigments. Furthermore, FTIR-ATR analyses allowed semi-quantitative considerations about the influence of each selected pigment on the degradation of the acrylic binder. Finally, UV-Vis spectroscopy allowed the discrimination of the pigments in the paints and the study of the colour changes.

Raman spectra acquired on both, unaged and aged specimens did not show any difference concerning the pigment bands, whereas Py-GC/MS in double shot mode, revealed a decrease in the thermal stability of the pigments as well as of the acrylic binders identified (nBA/MMA, EA/MMA, nBA/Sty/2-EHA, and 2-EHA/MMA). Typical photooxidation products of acrylic binders, such as increased monomers and oligomers, related to side-chain scission as well as main-chain scission reactions, were characterized by means of Py-GC/MS and FTIR-ATR. Commercial paints revealed also whitening and chalking phenomena, mainly due to the presence of white fillers and additives in the paints formulations. These phenomena could be registered also by UV-Vis spectroscopy.

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1. Introduction

In modern and contemporary art many artworks are conceived for the outdoor environment, and it is of great importance therefore to study the chemical behaviour of the materials used for their production, when exposed to outdoor influences. The final goal for addressing such studies is to foresee possible degradation processes, to develop appropriate conservation and preventive conservation strategies, and to contribute to the improvement of the formulation of artists' materials [1]. In the outdoor environment one of the most severe causes of degradation is the solar radiation, which includes wavelengths falling within the chemical bond dissociation energy of many synthetic organic materials used in

works of art. The solar radiation together with the presence of oxygen promotes photooxidative reactions on synthetic organic materials, mostly based on chain scission and cross-linking reactions of polymers used as binders in artists' paints, such as acrylics [2]. Photodegradation reactions cause changes in the physical and mechanical properties of the materials such as yellowing phenomena, cracking, embrittlement, and stiffening of the paint films as well as changes in solubility. As described in the literature [3], the general photodegradation processes on polymers are initiated by the absorption of photons by the molecules. The hence excited molecule loses the absorbed energy by e. g. breaking of chemical bonds, and forming polymer alkyl radicals (initiation reactions). Radical chain reactions follow (propagation), till new non-radical products are formed by the combination of radicals (termination). The recombination of macroradicals leads to cross-linking, causing an increase in brittleness and hardness of the

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film [3]. In case of acrylates, two processes, chain scission and cross-linking, are possible and are competing, depending on the length of the side groups [4]. The carbonyl groups present in the acrylic structure are also sensitive to secondary photodegradation reactions, such as Norrish reactions [5]. The photooxidation takes generally place at first in the uppermost layer of the paints and proceeds towards the bulk, depending on the radiation, oxygen diffusion, time of exposure, and on the characteristics of the materials exposed to the radiation. The additives present in the paints formulations might interfere with the photooxidative reactions. In particular, pigments can act by catalysing and promoting or preventing photodegradation reactions, depending on their chemical properties and colour [6].

Several studies focused on the photostability of acrylic paints [4,7–9] and on the influence of inorganic pigments on the photodegradation of acrylic paints [10–12], but no systematic investigation emphasizing the influence of synthetic organic pigments (SOPs) [13] on the degradation of such materials has been carried out so far. Moreover, as SOPs present organic structures, they can be susceptible of photooxidation themselves.

Among the techniques used for the identification and characterization of SOPs [14–16], Raman spectroscopy is widely used due to its high sensitivity. The method is employed also for monitoring acrylic film formation and for characterizing acrylic materials [17,18], but when they are mixed with good scatterers, such as SOPs [19], only the latter are detected in the Raman spectra. Therefore, Infrared Spectroscopy is often applied as complementary method, which in the Attenuated Total Reflection (ATR) mode is also non-invasive. FTIR-ATR is of particular use for characterizing binding media, additives, and SOPs, as well as their degradation products [7–9,20]. Additionally, both micro-Raman spectroscopy and FTIR-ATR are surface sensitive methods [21], thus suitable for investigating phenomena such as photooxidation, which is affecting *in primis* the uppermost layer of the material (ca. 10 μm [6]). Finally, Pyrolysis–Gas Chromatography/Mass Spectrometry (Py-GC/MS) is widely employed for analysing acrylic paints and SOPs [22–24], as well as for photodegradation studies of artists' paints [10,25]. The possibility of using this method in double shot mode allows the same sample to be analysed in two steps: thermal desorption and flash pyrolysis. In this way most volatile compounds can be identified in the thermal desorption step, and considerations about the thermal stability of the sample can be drawn [10].

Finally, UV-Vis spectroscopic measurements accomplished the systematic studies, identifying the different phthalocyanine pigments and detecting the colour changes of the investigated aged samples.

In the present work the influence of different types of SOPs [26,27], such as phthalo blue and phthalo green on the photostability of acrylic binders [11] is studied. Investigations were carried out on unaged and artificially aged self-made and commercially available acrylic paints. Thus, paints were exposed to artificial accelerated ageing using a Xenon Arc simulator, with spectral range comparable to outdoor solar radiation.

Phthalo blue and green are the trade names for phthalocyanine pigments which are widely found in original modern and contemporary artworks [28,29]. In the present work copper containing phthalocyanines (CuPc), having Colour Index (C. I.) name Pigment Blue 15 (PB15), and metal-free phthalocyanine (H₂Pc), PB16, are considered. The PB15 can present polymorphism (PB15:x), and each crystalline form is characterized by different chemical and colour properties [30], thus different CuPc blue pigments were selected. The phthalo greens are copper phthalocyanines which are completely chlorinated (Pigment Green 7), or chlorinated and brominated (PG36).

2. Experimental

2.1. Sample preparation and accelerated ageing

“Two-components” self-made paints were prepared by mixing the pigment powder with acrylic binder in order to get pasty consistence of the paints without addition of any additives. In this way, the influence of further additives that might be included by the manufacturers in the commercial paints formulations on the photodegradation process could be limited, and the study was selectively focused on the influence of the SOPs on the ageing processes. Synthetic organic pigments and acrylic binder Plextol D498, which consist of poly butyl acrylate/methyl methacrylate (nBA/MMA) copolymer, and according to [10] additionally contains a polyethoxylated surfactant, were provided by Kremer Pigmente, Germany (Table 1). The pigments used were metal free phthalocyanine PB16, copper phthalocyanine blue PB15:1, PB15:3, and PB15:6, chlorinated copper phthalocyanine green PG7, and chlorinated brominated copper phthalocyanine green PG36.

Furthermore, mock-ups were prepared using commercially available acrylic paints of different manufactures as listed in Table 1, such as: Artists's acrylic (Winsor & Newton, UK) containing PB15:1 (product number 2320514), PG7 (2320522), and PG36 (2320521), Acryl Pastos (Lukas, Germany) containing PB15:6 (4144), and PB16 (4123), and finally Akademie Acrylcolor (Schminke, Germany) containing PB15:3 (23548).

All paints were cast on glass slides with an approximate thickness of 150 μm , and dried at room conditions for 15 days. Three sets of each paint were prepared, one set was kept as reference (unaged), one set was aged for two months (UV1), and one was aged for four months (UV2). The ageing procedure consisted in exposing the paints to artificial solar radiation in the Xenon Arc Simulator UVACUBE SOL 2/400F (Dr. Hönle, Germany) with an incorporated H₂ filter, cutting off wavelengths below 295 nm. Continuous illumination with radiation between 295 and 3000 nm and nominal irradiance 910 W/m² was provided. Temperature and relative humidity (RH) were not customizable, and they were measured to be around 40 °C and 10 RH (%) by means of sensors AQL S500 (Aeroqual Limited, New Zealand).

2.2. Micro-Raman spectroscopy

Analyses were done with the confocal micro-Raman system LabRAM ARAMIS (Horiba Jobin Yvon, Germany), equipped with CCD detector (1024 × 256, Peltier cooled –70 °C) in backscattered configuration. Wavenumber calibration was performed using silicon ν_1 line at 520.7 cm⁻¹. Excitation at 532 nm (Nd:YAG) was selected depending on the resonance effects, the absence of fluorescence, and the good signal-to-noise ratio achieved. For the measurements a 50× long working distance objective, ca. 1 mW power at the sample, and 600 gr/mm grating were used. The acquisition time per spectrum was varied depending on the paint analysed (20–40 s). All paints were analysed directly at the surface, without sampling, and selecting three random spots for measurement.

2.3. Fourier transform Infrared Spectroscopy - Attenuated Total Reflection (FTIR-ATR)

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 in the Internal Reflection Element (IRE) was available. Spectra were acquired in the range between 4000 and 370 cm⁻¹ performing 128 scans with a resolution of 4 cm⁻¹. In order to

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