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Azo-pigments effect on UV degradation of contemporary art pictorial film: A FTIR-NMR combination study

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ABSTRACT

In this study, The behavior of Acrylem AC 33—a waterborne paint binder, chemically a ethyl acrylate-methyl methacrylate copolymer-after an UVB-artificial ageing was evaluated. In particular, it has been investigated its behavior in presence of three different azo-pigments – Pigment Red 9, Pigment Yellow 3 and Pigment Yellow 74-, in order to evaluate the effects of these pigments on photodegradation processes of the medium. For this aim, Fourier Transformed InfraRed, both in Attenuated Reflectance and transmission mode, and Nuclear Magnetic Resonance Spectroscopies were used. Thanks to this multi-analytical approach, the chemical variations, both on the surface and on the bulk of the pictorial film, have been assessed and the degradation products of surfactant present in the binder were identified. Furthermore, specific effects of these synthetic organic pigments on the photodegradation of the matrix and its additives were observed. The information obtained from this study can be employed in the characterization of differential ageing phenomena in artworks, especially in case of outdoor exposition as it occurs in street-art conditions.

1. Introduction

Acrylic polymers are extremely important materials for art and restoration of the XX century, in fact they are widely used as consolidation products, protectives, adhesives and painting media [1]. In particular, waterborne acrylic emulsions constitute common binders for contemporary pictorial arts, because they are easy to use, not soluble in water, health safe and cheap. Their characteristics in terms of adhesive and esthetic properties are responsible of their huge diffusion as paint binders [2,3]. Finally, their compatibility with several pigments and additives has made possible the availability of acrylic paint tubes in different shades and chromatic combinations [4].

Regarding their chemical properties, acrylic polymers are generally stable. In particular, several studies have tested their photostability with different radiation sources [5–15] describing the principal degradation mechanisms and reactions which they can be subjected to. Generally, acrylic polymers undergo to de-esterification of side-chain, while oxidation processes can occur through formation of ketones, hydroperoxides and carboxylic acids [6,7]. Two important factors in photodegradation mechanisms should be considered: the presence of a methacrylic group in the polymer and the length of side-chain ester. Methacrylic polymers are typically more stable than acrylic ones since the presence of methyl groups slow hydrogen abstraction processes and as such the main degradation process is chain-scission. For what concerns the long-chain ester groups, cross-linking reactions are remarkable and they can cause the formation of polymer networks, which influence mechanical properties of film [6–8].

Nevertheless, together with the acrylic polymer, other components are present in a pictorial film [4] and their co-presence can influence the degradation of the medium, as it happens for ancient art binders [16–18]. For example, all the acrylic emulsion contain surfactants, necessary to maintain the stability of dispersion. These components can be subjected to degradation as the main polymer, influencing the conservation characteristics of the pictorial film [5].

Several studies showed that some inorganic pigments can promote photodegradation of the binder [19], while others affirm that pigments can induce a stabilization effects on the polymer matrix [20,21].

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While inorganic pigments and their effects on medium stability are well known, very poor information are available on the influence of synthetic organic pigments –typically employed in contemporary art-on degradation of acrylic binders. One of these studies [22] shows how the dioxazine pigment (PV 37) stabilizes the photodegradation of a styrene-acrylic copolymer, while the phthalocyanine PB 15:1 promotes the formation of insaturations in the same binder. These opposite behavior can be explained considering that synthetic organic pigments belong to different classes of compounds –azo-pigments, quinacridones, anthraquinones, phthalocyanines, etc.- and, for this reason, taking into account their proper chemical properties, they influence the photodegradation of binder in different ways. Potentially, in a general polymeric matrix, they can act both as light absorbers, stabilizing the medium, and as starters of photochemical reactions [23–25].

The aim of this study is the evaluation of the behavior of acrylic binder mixed with some synthetic organic pigments under photoageing conditions. The attention is focused on the effects of the pigmentation on the polymer matrix in order to observe either stabilization or promotion on photodegradation. These information can be interesting in the conservation of art-objects when different pigments are combined with the acrylic binder: different pigment-binder interactions could cause a differential ageing on the pictorial film, with consequences on the preservation of the whole artwork.

In particular, it has been investigated the effect of three azo-pigments commonly used in contemporary art - Pigment Red 9, Pigment Yellow 3 and Pigment Yellow 74- on Acrylem AC 33, a waterborne dispersion constituted by an ethyl acrylate-methyl methacrylate copolymer, under UVB (280–320 nm) photo-exposure. This light-source was chosen because most acrylic polymers are transparent to visible light and their main absorption line is in the UV range. This means that Ultraviolet light can influence the photodegradation of the binder. Moreover, UVB radiation is the most energetic radiation that arrives on Earth surface; even if it is filtered by window glass and it is not present in indoor conditions, it can play an important role in photodegradation of street-art and art-objects exposed in an outdoor environment [26].

To study these processes several spectroscopic techniques were employed. Fourier Transform Infrared (FTIR) spectroscopy in Attenuated Total Reflectance IR (ATR) mode can provide information on surface degradation of pictorial film induced by UV radiation [19,27], highlighting the main processes that happen on the exposed side of pictorial film. FTIR spectroscopy in transmission mode results are complementary to ATR [27,28]: it evidences the degradation processes that involve the whole layer of pictorial film, providing information on "bulk" reactions through changes of functional groups of the polymer Finally, Hydrogen Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy, both in 1- and 2-D modes, was employed in order to confirm information about degradation processes involving both the polymeric species and the additives –pigments and surfactants-present in the film [29]. The FTIR-NMR combined approach we employed allowed us to obtain a more comprehensive description of the effects of UVB exposition on complex pictorial-like structures.

2. Experimental

Acrylem AC 33 is a commercial acrylic binder distributed by Chroma Srl, while Pigment Red 9, Pigment Yellow 3 and Pigment Yellow 74 are produced by Kremer Pigmente.

Pure acrylic binder was casted on glass-slides to obtain about 100 μm thickness film. Pictorial film mock-ups were obtained mixing the binder with each pigment (Pigment mass rate in total mixture ≈ 10%) and casting the mix on glass slides. All the films were left to dry for a month.

UVB exposure was performed in a UV Accelerated Weathering Tester produced by Q-Lab (QUV-spray model); temperature of the chamber was set at 45 °C and irradiance was set at 0.75 W/m^2/nm at 310 nm (maximum emission wavelength of the lamp). The chamber does not allow to set the Relative Humidity, that was only monitored and it was about 10%.

ATR and NMR spectroscopy analysis were performed at Day 0 (before UVB exposure) and at different ageing steps (10, 20, 40, 60 and 80 Days from the beginning of UV exposure), while transmission FTIR measurements were performed at Day 0, 40 and 80.

2.1. FTIR measurements

FTIR measurements were performed using a JASCO FTIR410 spectrometer working in ATR as well as transmission modalities. In the ATR-FTIR mode the infrared beam produced from a source experiences multiple internal reflections between the plane sides of a non-absorbing ZnSe crystal. In any single reflection, the quantum-mechanical nature of the radiation produces an evanescent field at the interface between the crystal and outer medium; this radiation can be used to probe the absorption spectrum of the sample rising from chemical bonds, primarily stretching and bending motions. The solid samples prepared as described above were deposited by adhering the UV exposed sample surface on the temperature controlled ZnSe crystal holder set at 25 °C.

In transmission FTIR mode, the whole Acrylem layer films were formed onto CaF_2 substrates from $CHCl_3$ solvent evaporation.

The recording conditions for each FTIR spectrum were: 256 scans, a triangular apodization function and a resolution of 2 cm^{-1}.

The spectra were acquired and corrected from water vapour, CO_2 and ATR artifacts by the Spectra Analysis software platform JASCO, and then elaborated through IGOR PRO software. Specifically, spectra normalization was operated using as reference the peak a 1380 cm^{-1} in ATR (1382 cm^{-1} in transmission spectra). Spectra difference was used to highlight variations in intensity of signals due to UVB exposure. Finally, to compare chemical changes when the binder is pure and when it is mixed with pigments, intensity variation percentage of some bands was calculated as it follows:

$$Intensity\ Variation\ \% = \frac{(I_X - I_0)}{I_0} \cdot 100$$

Where I_x is the intensity of the band at Day X, while I_0 is the intensity of the same band before ageing (Day 0).

^{1}H-NMR spectra were acquired on a Bruker Avance III 400 spectrometer (Bruker Spectrospin, Karlsruhe, Germany) operating at 9.4 T. Samples for NMR analysis were prepared solubilizing 5 mg of pictorial film in 600 μl of $CDCl_3$ (Sigma Aldrich). The samples were soluble in $CDCl_3$. There was a solid residue left only for the samples of pure acrylic binder after 60 and 80 days of ageing, but the amount was very small and it was not soluble in more polar solvents, so the comparison of the spectra in $CDCl_3$ was preferred. Monodimensional spectra were collected adding 128 scans, the data matrix was of 64k data points, the spectral width of 15 ppm corresponding to an acquisition time of 5.45s. In order to achieve complete relaxation between successive scans, a recycle delay of 9.5s was applied. Bidimensional ^{1}H-^{1}H TOCSY experiments were carried out employing a data matrix of 8k x 256 data points collecting 80 scans for point of the indirect dimension. The spectral width is of 15 ppm for each dimension, interscan delay was of 2 s and mixing time was of 80 ms.

To put in evidence degradation phenomena, the integrals of some signals were measured and the following ratios were calculated: