# Monoazo and Isoindoline Yellow reactivity in presence of Pb, Ti, Zn-based white substrates

Agnese De Carlo[1 2 3], Valerio Graziani[2 3], Paolo Branchini[2,3], Luca Tortora[1 2 3]

[1] *Department of Science, Roma Tre University, via della Vasca Navale 84 00146 Roma,*
*agnese.decarlo@uniroma3.it, luca.tortora@uniroma3.it*
[2] *National Institute for Nuclear Physics INFN — Roma Tre Division, via della Vasca Navale 84*
*00146 Roma, valerio.graziani@roma3.infn.it, paolo.branchini@roma3.infn.it*
[3]*Surface Analysis Laboratory Roma Tre LASR3, via della Vasca Navale 84 00146 Roma.*

*Abstract –* **This work explores the effects of accelerated aging conditions on two yellow synthetic organic pigments with good light fastness: PY 1 and PY 139 also known as Hansa Yellow G (or Monoazo yellow) and Isoindoline Yellow, respectively. The reactivity of PY 1 and PY 139 in presence of reactive inorganic whites such as basic lead carbonate, titanium oxide, and zinc oxide was investigated. The accelerated aging process was achieved through UV irradiation in a home-made climatic chamber for a set of bilayer paint mock-ups. Bilayered samples were realized to simulate the painting technique of superimposing multiple layers of thinly applied paint. Colorimetry, Fourier-Transform Infrared Spectroscopy, and Photoluminescence Spectroscopy were adopted to reveal physico-chemical changes occurred in such samples.**

## I. INTRODUCTION

A work of art is the artist's way to communicate emotion by means of the use of colors. Unfortunately, in a painting, due to the natural aging of materials or to the environmental conditions, photodegradation processes can occur [1], leading to color changes like fading, darkening, and blanching [2,3]. For this reason, the study of the aging and degradation processes of the materials used in paintings is essential [4,5]. There are several studies focusing their attention on the aging of pigments and their stability to light, called lightfastness [6].

Two classes of yellow synthetic organic pigments, sold as artists' materials, were selected and characterized before and after the UV aging process: monoazo and isoindoline pigments. These organic pigments are considered by ASTM International as stable, with very good lightfastness when mixed with oil. However, the lightfastness of pure pigments or oil paints interacting with inorganic whites in bilayer systems, is still not well known.

Monoazo pigments are among the oldest yellow pigments while isoindoline pigments can be counted among the newest synthetic yellows. The monoazo pigment here studied is the Pigment Yellow 1 (PY 1), also known as Hansa Yellow G, and the isoindoline yellow pigment is PY 139. Monoazo pigment was extensively used in a variety of applications, as in paints or in textile printings because of the good lightfastness and durability of the pigment in full shades [7]. As for the isoindoline pigment, it was used in plastics, paints, printing inks, in automotive and industrial paint [8] often in combination with inorganic white pigments as substrates.

Several studies are present in literature on photoaging processes of synthetic organic pigments, either in powder [9] or in combination with binders [10,11], but the large part of these is focused on pigments used as textile dyes [12]. Monoazo and isoindoline pigments were extensively studied and characterized by Raman spectroscopy, as pigments used in modern and contemporary paintings [13,14,15]. However, although photoaging was studied for pigments of the same molecular class [10,16], the degradation process of these specific pigments is still not yet fully understood.

In this work, the effect of highly reactive inorganic components such as basic lead carbonate, titanium oxide, and zinc oxide on the aging of paints is investigated by means of simplified models of bilayer paintings. These were realized through layer-by-layer deposition of inorganic white pigment and organic yellow pigment with linseed oil as binder. The challenge is to understand how materials age in artifacts where organic and inorganic materials are present [17,18], through different analytical techniques to reveal the mechanisms of degradation [19]. Physico-chemical changes in bilayer samples were explored combining colorimetry, Fourier-Transform Infrared spectroscopy in Attenuated Total Reflectance mode (ATR-FTIR) and Photoluminescence spectroscopy (PL).

## II. MATERIALS AND METHODS

### A. Materials

Monoazo Pigment Yellow 1 (Primary Yellow, C0001, PY 1), isoindoline Pigment Yellow 139 (Indian Yellow, C1998, PY 139), linseed oil (Cold pressed Linseed oil, Art.3310/), were purchased from Zecchi (Zecchi - Colori

Belle Arti, Firenze, Italy). Lead carbonate (lead(II) carbonate basic -325 mesh), Titanium dioxide (titanium(IV) oxide, mixture of rutile and anatase, nanopowder, <100nm particle size (BET), 99,5% trace metal basis) and Zinc oxide (zinc oxide, puriss. p.a., ACS reagent, ≥99.0% (KT)) were purchased from Sigma (Merk Life Science S.r.l. | Italy - Sigma-Aldrich). The purity of PY 1 and PY 139 was verified by ATR-FTIR and SEM-EDS microanalysis. Lead white is mainly constituted by a composition of cerussite and hydrocerussite, titanium white is a mixture of anatase and rutile, and zinc white is mainly composed of the wurtzite phase. The pigments and their chemical structure are represented in Fig. 1.

### B. Samples preparation

A scheme of the sample preparation is shown in Fig. 2. Samples with just powder pigments were realized following a procedure with isopropyl alcohol reported elsewhere [9], to create a momentary suspension and deposit the pigment on the glass slide. A sample with linseed oil as reference was prepared and left to dry for one month. Oil paint samples were realized by mixing the powder of the monoazo and isoindoline pigment with linseed oil, using a powder:binder mass ratio 1:2 and left to dry in room conditions for one month. Bilayer paint samples were prepared in combination with inorganic whites, for a total of 6 bilayer mock-ups. The procedure was as follows: a couple of oil paint samples for each inorganic white pigment were realized and left to dry for one month in room conditions, then they were used as a substrate for the two yellow pigments mixed with oil. All paint layers had an approximate thickness of 200-300 μm.

### C. Accelerated aging

Artificial UV aging was carried out in a home-made aging chamber equipped with four UVB Broadband lamps (TL 20W/12 RS SLV/25, Philips Lighting) [20], with a maximum of spectral power at 320 nm. The samples were exposed to a nominal irradiance value of 50.264 W/m$^2$ for 665 hours. The temperature was kept around 30°C and the relative humidity was in the range of 70-90% RH by using a saturated solution of NaCl in distilled water [21,22]. Both temperature and relative humidity were monitored with a sensor (Grove - Temperature and Humidity Sensor DHT1), throughout the whole aging process.

### D. Methods

Colorimetry was performed with Eoptis CLM-194, using standard D65 daylight illuminant and 10° observer. Data were measured in the CIE 1976 L*a*b* color space, using the CLM-19X software interface. The total color change ΔE was calculated for each sample after the aging process, according to the equation (1) [23,24]:

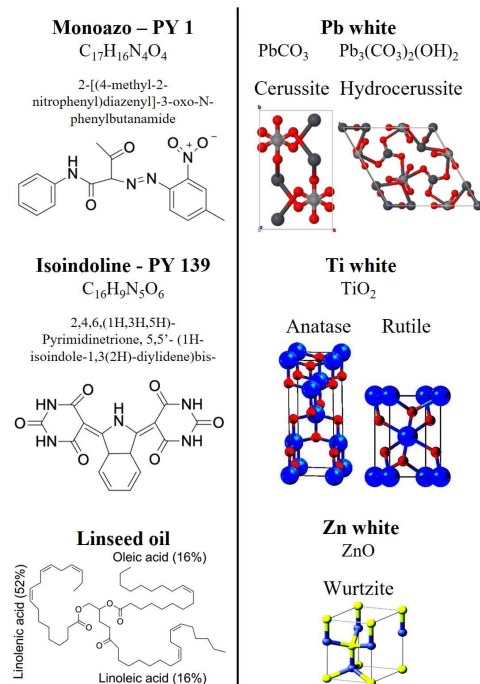$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}. \quad (1)$$



Fig. 1. Image of all the aged materials. Left for the organic components: monoazo and isoindoline pigments with their C.I. name, molecular formula, chemical name and molecular structure, and linseed oil with the main components of fatty acids. Right for the inorganic pigments: lead white, titanium white and zinc white with their molecular formula and main molecular structures.
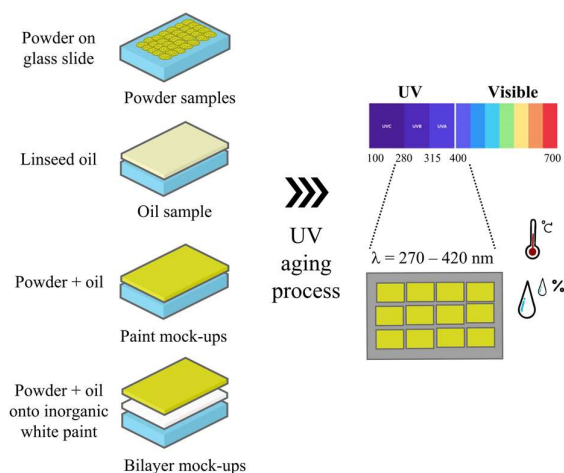


Fig. 2. Scheme of the samples realized for the UV aging. From top to bottom: powder deposited on glass slide, pure linseed oil, single layer of oil paint (powder + oil) and bilayer mock-ups realized whit a base layer of white inorganic + oil paint, for the two yellow pigments.

Infrared spectrophotometry in μ-ATR mode was performed with a ThermoFisher ®Nicolet iS50 FTIR Spectrometer coupled with ®Nicolet Continuum Infrared Microscope. A germanium crystal was used, attached to the 15x objective on the microscope. The spectra were acquired in the range to 4000 a 650 cm$^{-1}$, as a sum of 120 scans with a spectral resolution of 8 cm$^{-1}$. IR spectra were collected and processed with Omnic 6.0 software.

Photoluminescence measurements were carried out by Edinburgh Instruments FLS1000-SS with Steady State Spectrometer. Excitation and emission spectra were obtained using a 450 W Xe2 Xenon Arc Lamp as a light source, at room temperature and in front-face geometry. All data were acquired with Fluoracle 1.9.1 Software.

## III. RESULTS AND DISCUSSION

### A. Powder samples

The total color changes ΔE are represented in Fig. 3. After the UV aging, in general the powder samples showed an increase in the a* and a decrease in the L* and b* parameters. These variations pointed out a decrease of the red and yellow components and a slight darkening of the color. In particular, the yellow pigment PY 1 showed the largest total color change after the aging (ΔE close to 30). It was mainly due to a strong decrease in the yellow component, as shown by the high variation Δb*, also appearing visibly darker to an observer. Regarding the pigment PY 139, it exhibited a great stability to light as the total color change ΔE is just over 1.

Fig. 4a shows the comparison between the ATR-FTIR spectra, before and after UV aging, for PY 1 sample. Comparing the relative intensities of the most intense peaks, it is evident an increase in signal intensity at 3530 and 3402 cm$^{-1}$ related to the O-H stretching, a notable decrease to 1507 cm$^{-1}$ of the aromatic stretching -C=C, an increase to 1115 cm$^{-1}$ of the stretching C-N and N=N, and an increase of the signal at 670 cm$^{-1}$ attributable to the out-of-plane O-H bending. The increase of O-H stretch signal is in agreement with the loss of yellow component in the powder pigment previously detected by colorimetry. In conjugated systems, substituent heteroatom with electronegativity higher than that of carbon and with free lone pairs can exert a strong positive mesomeric effect [25]. In the ATR-FTIR spectra of PY 139 powder sample, the characteristic bands of the fingerprint region appear overlapped (1800-650 cm$^{-1}$), proving the high lightfastness of this molecule (data not shown).

The powder samples were also studied by PL spectroscopy. Fig. 5 shows the emission scans for PY 1 sample before and after UV aging, and Fig. 6 the excitation-emission scans for PY 139. After the aging, the photoluminescence scans for PY 1 powder sample showed a little shift in the maximum of emission scans from 544 nm to 548 nm at $\lambda_{ex}$ = 450 nm (solid and dashed red line in Fig. 5). This evidence is in accordance with the positive
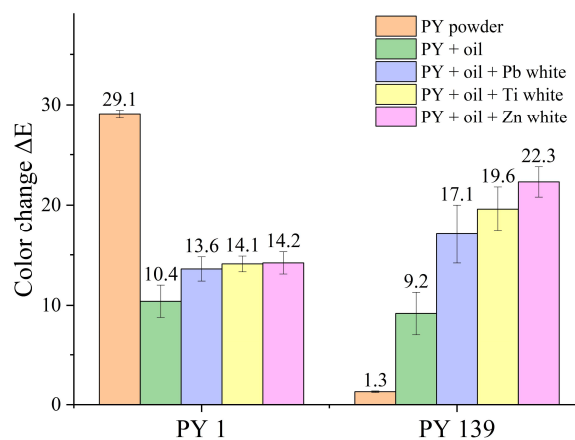


Fig. 3. Total color changes ΔE for all the samples. On the left the samples with monoazo PY 1 and on the right the samples with isoindoline PY 139. In the legend, PY means the yellow pigment indicated in the x-axis.
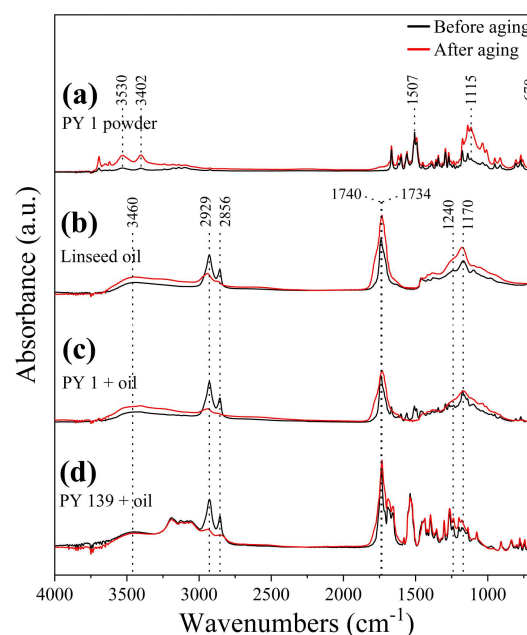


Fig. 4. Comparison of ATR-FTIR spectra before (black) and after (red) the UV aging in the range 4000-650 cm$^{-1}$. ATR-FTIR spectra of monoazo PY 1 powder (a), linseed oil (b), paint PY 1 + oil (c) and paint PY 139 + oil (d).

mesomeric effect induced by the presence of OH-substituents. However, the signal is very noisy due to the poor emission intensity of the sample. Unlike the monoazo powder PY 1, the unaged isoindoline PY 139 exhibited an intense fluorescence signal with maximum emission around 572 nm at $\lambda_{ex}$ = 530 nm [26]. After 665h of UV aging, no significant differences were observed (solid and dashed red line in Fig. 6).

## B. Oil paint samples

Unlike pigment powders, the PY 1 and PY 139 + oil samples exhibited a similar behavior, as shown by the color changes ΔE in Fig. 3 (ΔE = 9.2–10.4). A large variation of the b* coordinate indicating a loss of yellow component, together with an increase of the red component resulted in a general darkening of the oil paint. These results led us to conclude that for the mixture PY 1 + oil the loss of the yellow component decreased whereas the darkening effect of the sample increased. In opposition, PY 139 + oil acquired a blue component due to aging, whereas its powder alone showed a great stability to light.

The ATR-FTIR spectra for the oil paint samples were compared with the pure linseed oil sample in Fig. 4. In particular, ATR-FTIR spectrum of the aged PY 1 + oil sample seems to be quite similar to that one of the pure linseed oil, whilst the ATR-FTIR spectrum of the aged PY 139 + oil maintained some spectral features of the pigment. In both cases, all the variations were compatible with an oxidative polymerization mechanism of the oil binder [27,28] like the increase of the band at 3460 cm$^{-1}$ related to the O-H stretching, decrease at 2929 and 2856 cm$^{-1}$ of the symmetric and asymmetric C-H stretching vibrations, broadening and increase at 1740-1734 cm$^{-1}$ of the C=O carbonyl stretching and increase of the C-O stretching vibrations at 1240-1170 cm$^{-1}$ from glycerides linkages. In such paint mock-ups, the photo-oxidation process could be mainly attributable to the degradation of the linseed oil rather than to the pigments [16,29].

The oil paint mock-ups were also studied with PL spectroscopy and showed a clear emission due to the addition of oil to the samples. The emission scans performed before and after aging for the PY 1 oil paint sample are shown in Fig. 5 (solid and dashed purple line). A shift of the emission band was observed. At the same excitation wavelength, the maximum emission presents a shift from 537 nm to 545 nm, of about 8 nm. As for PY 139 oil paint sample, the comparison of excitation-emission scans, before and after aging, is shown in Fig. 6 (solid and dashed purple line). The excitation band showed a bathochromic shift from $\lambda_{ex}$ = 530 nm of about 7 nm, and the emission presented a broadening of the band towards longer wavelengths.

## C. Bilayer samples

Colorimetric variations for the bilayer samples are shown in Fig. 3. In general, after the UV aging, the mock-ups of both yellow oil paints with different inorganic whites as substrate revealed color changes with ΔE ranging from 13 to 22. For what regards PY 1 + oil + inorganic white samples, the presence of underlying layers constituted by different metal oxides does not seem to affect the colorimetric variations reported in Fig. 3. On the contrary, the inorganic whites seem to play a role when PY 139 oil paint is superimposed as additional layer. The samples realized with the Zn white showed a larger change
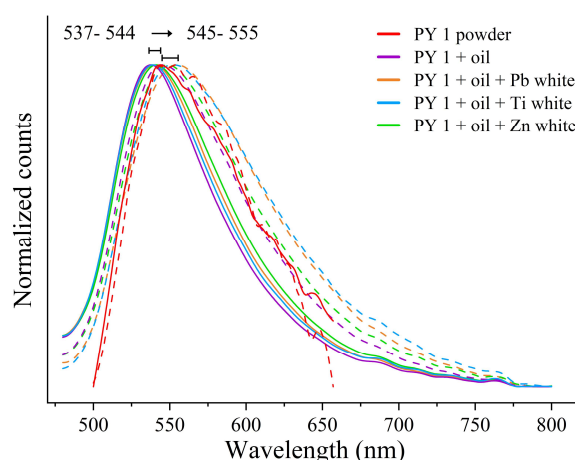


*Fig. 5. Emission scans before (solid line) and after (dashed line) the UV aging for all the monoazo PY 1 samples, in the emission range 480-800 nm.*
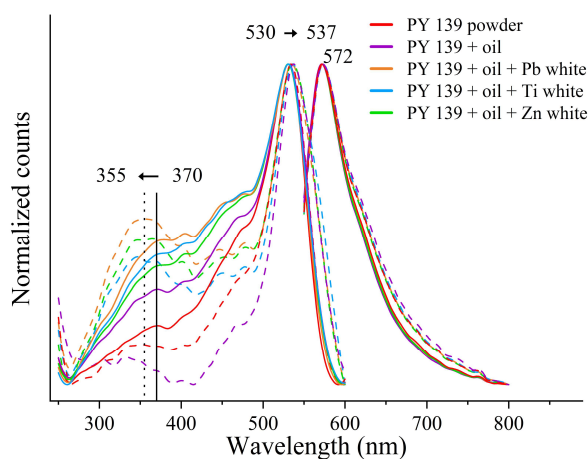


*Fig. 6. Excitation-emission scans before (solid line) and after (dashed line) the UV aging for all the isoindoline PY 139 samples, in the excitation range 250-600 nm and in the emission range 550-800 nm.*

in yellowness/blueness Δb* compared to sample with Ti white and Pb white. The variation of b* component corresponds to the darkening of the paint layer.

ATR-FTIR spectra performed on the samples after the UV aging process did not provide any useful information when compared to the aged samples with just the oil paint. Expected reactions like the saponification with the formation of metal soaps were not observed [30,31].

The emission spectra for PY 1 bilayers (see Fig. 5) conversely showed remarkable shift of about 10-15 nm of the emission peak towards longer wavelengths. Such

spectral shifts are larger respect to the those observed in the single layer of PY 1 + oil paint sample. This effect may be due to a more accelerated aging process of the oil in presence of metal oxides. For PY 139 bilayer samples, all the emission peaks are centered at 572 nm showing the same broadening towards longer wavelengths as a consequence of the aging, with no substantial differences with the bilayer samples (see Fig. 6). On the other hand, it is interesting to note clear changes in the related excitation spectra. Comparing the excitation scans before and after the aging, an increase of intensity at 370 nm and a shift towards shorter wavelengths at 355 nm were observed. The excitation component at 370 nm is mainly due to the contribution of the aged oil present in the samples [32]. In addition, a 7 nm shift of the main peak at 530 nm was observed. The shift towards longer wavelengths of the main peak and the increase of intensity in the high energy region could be interpreted as a bathochromic and hyperchromic effect [33], respectively, and could be attributable to a stronger aging effect operated by the UV radiation on the linseed oil in presence of PY 139 and inorganic white substrates.

## IV.    CONCLUSIONS

The artificial aging carried out on the two powder samples resulted in a clear interaction between PY 1 and OH- substituents inducing a positive mesomeric effect on the colored molecules. Accordingly, the fluorescence presented a bathochromic shift. PY 139 resulted to be stable under the same conditions, confirming the high stability of the isoindoline molecule.

For the oil paint samples (powder + oil) no significant difference was observed between the two yellows. For this reason, it is not possible to affirm experimentally that there was a different interaction between the monoazo and isoindoline powder with the oil. Nevertheless, FTIR evidenced that all the variations are compatible with the oxidative polymerization of the linseed oil.

In the bilayer mock-ups, the results allow us to conclude that the yellow paints were found to be more sensitive to oil changes than the single layer ones. In particular, the color change ΔE showed that this effect is more pronounced for the bilayer samples prepared with isoindoline pigment, rather than the samples realized with monoazo pigment. The mechanism of interaction among the yellow pigments, the oil binder and the underlying layers was not completely deciphered through FTIR and PL spectroscopy and it needs therefore more investigations to be proved. However, PL spectroscopy and colorimetry suggested that the inorganic white substrates can induce a larger drying activity on the oil binder, even if far from the surface layer.

## V.    ACKNOWLEDGMENTS

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