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Photochemical Degradation Processes of Painting Materials from Cultural Heritage

Rodica-Mariana Ion, Alexandrina Nuta,
Ana-Alexandra Sorescu and Lorena Iancu

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Abstract

This chapter describes some recent studies and applications of photochemistry in the physical–chemical characterization of two acrylic paint materials based on phthalocyanines and the study of the photodegradation (photobleaching) processes which could occur, caused by exposure to artificial irradiation, similar as in the museum. The studies in this paper has been conducted on phthalocyanines, these compounds being known as organic colorants in painting. Their color depends not only on the chemical nature of the colorant, which play an important role in the kinetics and degree of aging, but also on the compounds added to the paints (TiO₂, micas, arylamide yellow). The techniques used in such studies involve UV–Vis spectroscopy, gloss, and colorimetric measurements, comparing our results with similar ones from the literature.

Keywords: phthalocyanine, absorption, photobleaching, artifacts

1. Introduction

Photochemistry is the science that deals with the study of physical and chemical processes that arise from the interaction between radiation used for irradiation and absorbing molecules [1].

The light radiation together in the presence of oxygen induces 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. The general photodegradation processes on polymers are initiated by the absorption

| Pigment CI name | Pigment chemical name | Paint marketing name | Structure |
|-----------------|--|--|-----------|
| PB15:1 | <i>Alpha copper phthalocyanine</i> (1935) | Winsor Blue RS Phthalo Blue RS Phthalo Blue Red Phthalo Blue Berlin Blue | |
| PB15:3 | <i>Beta copper phthalocyanine</i> (1933, 1935) | Phthalocyanine Blue Phthalo Blue Blockx Blue Winsor Blue GS Phthalo Blue Green Phthalo Blue GS Primary Blue Primary Blue-Cyan Manganese Blue Hue | |
| PB15:6 | <i>Epsilon copper phthalocyanine</i> (1935) | Phthalo Blue (red shade) Helio Blue RS | |
| PB16 | <i>Metal-free phthalocyanine</i> (1936) | Turquoise Green Phthalo Turquoise Marine Blue Caribbean Blue | |

| Pigment CI name | Pigment chemical name | Paint marketing name | Structure |
|-----------------|--|--|-----------|
| PB17 | Trisulphonated copper phthalocyanine (1935) | Peacock Blue [discontinued in 2005] | |
| PG7 | Chlorinated copper phthalocyanine (1927, 1938) | Winsor Green BS Phthalocyanine Green Phthalo Green BS Cupric Green Deep Phthalo Green Blockx green | |
| PG36 | Chlorobrominated copper phthalocyanine (1938) | Phthalo Green YS Cupric Green light Bright Green Bamboo Green Winsor Green YS Phthalocyanine Green (yellow shade) | |

Table 1. The structure of the Phthalocyanine blue and Phthalocyanine green pigments.

of photons by the molecules [3]. The excited molecule loses the absorbed energy through initiation, propagation, and termination reactions. In case of acrylates, two processes, chain scission and crosslinking, are competing, depending on the length of the side groups [4].

The carbonyl groups from 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 toward the bulk, depending on the radiation, oxygen diffusion, time of exposure, and the characteristics of the materials exposed to the radiation. The additives present in the paint formulations might interfere with the photooxidative reactions and could act by catalyzing and promoting or preventing photodegradation reactions, depending on their chemical properties and color [6].

In the present chapter, the influence of different types of phthalocyanines, such as Phthalo Blue and Phthalo Green (**Table 1**), on the photostability of acrylic paints [7] 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 aging using a Hg medium-pressure lamp, with spectral range comparable to outdoor solar radiation.

For the identification and characterization of acrylic films could be mentioned some non-invasive techniques, as: infrared spectroscopy Fourier-transformed (FTIR) in the attenuated total reflection (ATR) mode, UV-Vis spectroscopy, gloss and colorimetric measurements, all these techniques being useful for color changes and ageing processes investigations.

Taking into account that Phthalo Blue and Phthalo Green are the trade names for phthalocyanine pigments which are widely found in original modern and contemporary artworks [8], in the present work, phthalocyanines containing copper (CuPc), having Color Index (CI) name Pigment Blue 15 (PB15), and metal-free phthalocyanine (H_2Pc), PB16, are discussed. The PB15 can present polymorphism (PB15:x), and each crystalline form is characterized by different chemical and color properties [9]. The green phthalocyanines are copper-based phthalocyanines which are completely chlorinated (Pigment Green 7) or chlorinated and brominated (Pigment Green 36) (**Table 1**).

2. General aspects about phthalocyanines

In 1935, the Imperial Chemical Industries began to manufacture copper phthalocyanine, and such compounds were introduced in the commerce with the name of “Monastral Fast Blue” at a London fair in November 1935, and from 1936 produced also in the USA, under other names [10]. In 1936 IG Farbenindustrie began to produce copper phthalocyanine at Ludwigshafen, and in the late 1930s, the DuPont Company, at Deepwater Point, New Jersey, began to produce copper phthalocyanine; the Standard Ultramarine and Color Company started its production in 1949 [11]. Particularly, since the end of the Second World War, phthalocyanine pigments became widely used [12]. Commercially, available pigments of different producers (Maimeri, Winsor & Newton, Lefranc & Bourgeois, etc.) containing phthalocyanines PB15:1, PB15:3, and PG7 were chosen and applied on different kinds of supports, as cardboard. Samples of pigment were prepared using acrylic colors. Phthalocyanine molecules (Pc) are composed of four indole units—pyrrole rings linked by nitrogen atoms conjugated with benzene rings. They have an extensively conjugated aromatic chromophore, exhibit UV-Vis absorption spectra with intense $\pi-\pi^*$ transitions [13]. They have an increased aromatic character which explains the intense near-infrared absorption of these compounds. Metalation reduces the electron density at the inner nitrogen atoms and in UV-Vis spectra produces a hypsochromic shift which depends on the electronegativity of the metal.

The stability of metal phthalocyanines is due to formation of four equivalent N → metal bonds involving filling of vacant *ns*, *np*, and $(n - 1)d$ or *nd* orbitals of the cation with electrons of the central nitrogen atoms.

Dyes and pigments are used in the mixture with polymer materials to provide color-changing properties. Under such context, Cu-phthalocyanine dye can help stabilize against degradation but in other situations such as photochemical aging can actually accelerate degradation. The excited Cu-phthalocyanine may abstract hydrogen atoms from methyl groups in the Pc, which increase the formation of free radicals. This acts as the starting points for the sequential photooxidation reactions leading to the degradation of the phthalocyanine [14].

Electron transfer sensitization is a mechanism where the excited Cu-phthalocyanine abstracts electrons from Pc to form Cu-Pc radical anion and Pc radical cations. These species in the presence of oxygen can cause oxidation of the aromatic ring [15].

3. Light effects on pigments

3.1. Photophysical aspects

Light is the electromagnetic radiation released by an external source of energy. Photochemistry uses radiation that has an energy between 1 eV and 1 KeV, corresponding to visible radiation with $\lambda = 400\text{--}700$ nm and ultraviolet radiation with $\lambda = 200\text{--}400$ nm. Radiation used in photochemistry is selectively absorbed by the molecules with which it interacts.

To initiate a photochemical reaction, the formation of an electronically excited state in a molecule is decisive. Such an excited molecule can be regarded as a new species, characterized by properties other than those of the same basic molecule. The excited-state molecule has a certain electronic distribution responsible for the specific chemical reactivity compared to the fundamental chemical state. The essence of an organic photochemical reaction is the activation of the molecules produced by the absorption of a photon. The main processes that occur during the light action on paints are identified in Jablonski diagram (**Figure 1**):

(a) Non-radiative processes, where the excited-state species release the excess of energy as heat by three different processes: *vibrational relaxation (VR)*, through which the excited molecule decreases its vibrational energy within a single electronic state, *internal conversion (IC)*; meaning a transition between two electronic states with the same spin multiplicity, generally followed by vibrational relaxation; and *intersystem crossing (ISC)*, which involves the transition between two electronic states with different spin multiplicity, generally followed by vibrational relaxation.

(b) Radiative processes. The excited-state species release the excess of energy as electromagnetic radiation. There are two known processes: *fluorescence (F)*, as spontaneous emission of radiation upon transition between two electronic states with the same spin multiplicity, and *phosphorescence (P)*, known as a spontaneous emission of radiation upon transition between two electronic states with different spin multiplicity.

(c) Other deactivation processes, identified by photochemical or photophysical reactions which compete the excited-state molecules.

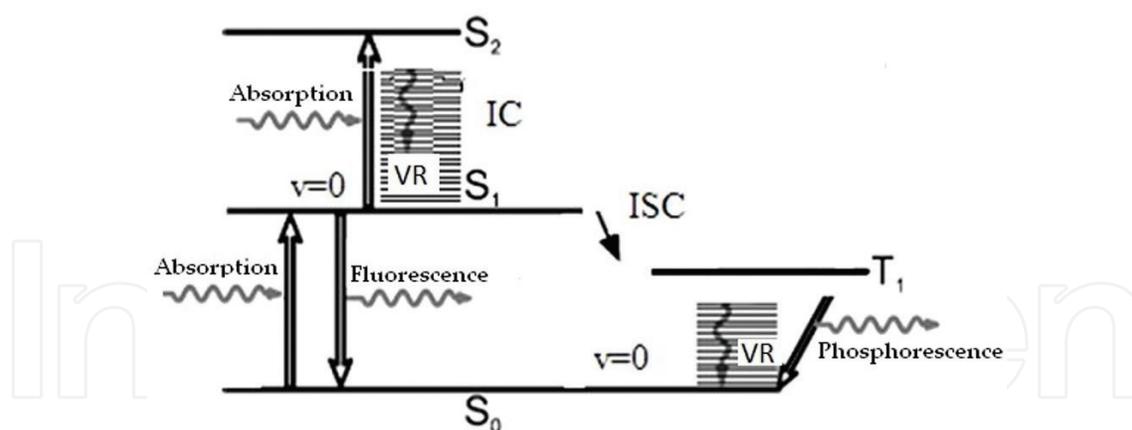


Figure 1. Jablonski diagram.

3.2. Photooxidation reaction

The photooxidation is a degradation of a compound in the presence of oxygen or ozone. The initiation of photooxidation reactions is due to the existence of chromophore groups in the molecules. For example, in a polymer case, by photooxidation, aldehydes, ketones, and carboxylic acids along or at the end of polymer chains are generated. The photooxidation reaction induces a chemical change that reduces the polymer's molecular weight. The material will become more brittle, with a reduction in its tensile, impact, and elongation strength. Also, a discoloration and loss of surface smoothness accompany photooxidation. High temperature significantly increases the effect of photooxidation.

The photooxidation reactions include chain scission, cross-linking, and secondary oxidative reactions, which obey the following process steps that can be considered [16], as follows (Figure 2):

1. Initial step: Free radicals are formed by photon absorption.
2. Chain propagation step: A free radical reacts with oxygen to produce a polymer peroxy radical ($\text{POO}\bullet$). This reacts with a polymer molecule to generate polymer hydroperoxide (POOH) and a new polymer alkyl radical ($\text{P}\bullet$).
3. Chain branching: Polymer oxy radicals ($\text{PO}\bullet$) and hydroxy radicals ($\text{HO}\bullet$) are formed by photolysis.
4. Termination step: Cross-linking is a result of the reaction of different free radicals with each other.

From mechanistic point of view, during the photooxidation two main reaction types occur (Figure 3):

Type I mechanism: a photosensitizer (PS) in its singlet or triplet excited state reacts with a substrate via (a) electron transfer or (b) hydrogen abstraction to yield free radicals, which will readily react with oxygen to form peroxide radicals and in turn start a radical chain reaction. These radicals react with oxygen to form reactive organic species (ROS).

Type II mechanism: in this process, the sensitizer in its excited state (commonly in its triplet state) transfers its energy to ground-state molecular oxygen, giving rise to the PS in its ground state and singlet oxygen (1O_2), a very reactive oxygen species. On type II reaction, an energy transfer during a collision between the excited photosensitizer and molecular oxygen occurs, as it is reported in the literature's report. Usually, a photosensitizer, not degraded through photobleaching by 1O_2 or other processes, can produce 10^3 – 10^5 molecules of singlet oxygen [19].

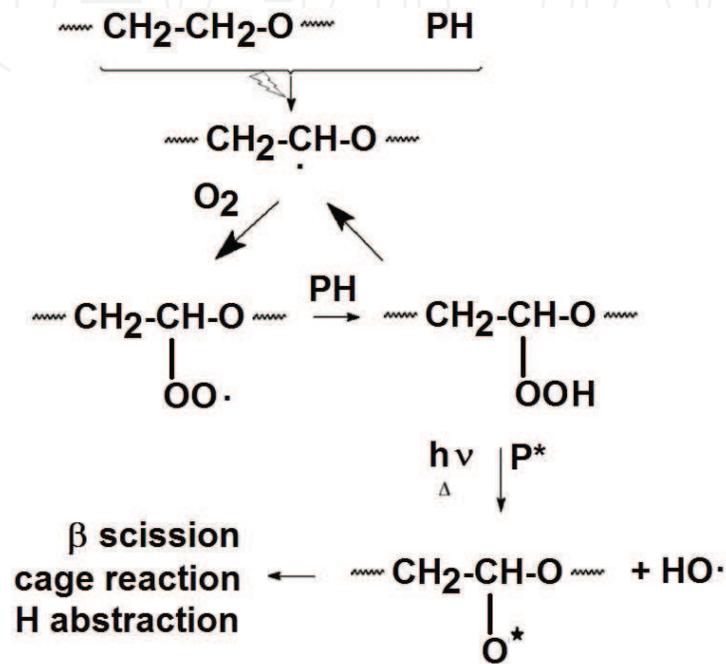


Figure 2. Adopted after [17, 18].

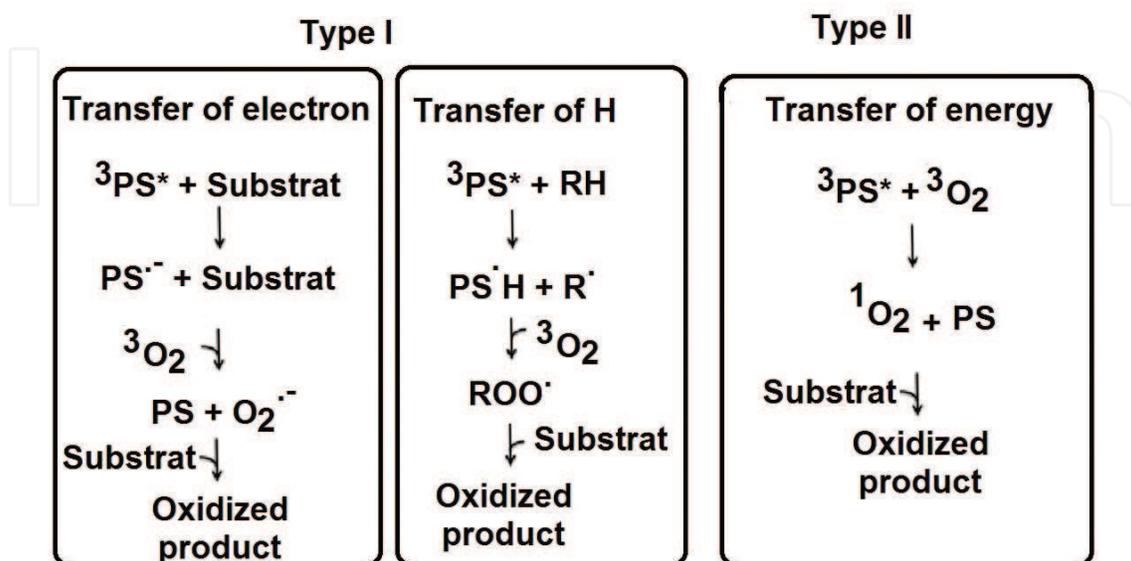


Figure 3. Mechanism of the photo-oxidation reaction.

4. Mechanism of phthalocyanine oxidative photobleaching

The main factors, which affect the photobleaching, are:

- Triplet excited state with long-lived triplet states and high triplet quantum yields induce a higher rate of photobleaching [20].
- Radiation type, the ultraviolet light being more effective in promoting phthalocyanine photobleaching than Q-band excitation [21].

The presence of oxygen favors the bleaching of metallic phthalocyanines (MPcs) predominantly due to photooxidation [22]. The oxygen concentration in oxygen-saturated solutions is $[O_2] = 10^{-3}$ – 10^{-2} mol/l. The reaction between ${}^3Pc^*$ and oxygen is diffusion-controlled reaction, so that it is very rapid ($k_{O_2} = 10^9$ – 10^{10} l/(mol. s)). A **type I photooxidation reaction** occurs only if $k_A[A]$ has a value of 10^6 – 10^7 s $^{-1}$. If k_A or $[A]$ has small values, then **type II reaction** occurs (if oxygen is present in small concentration). If k_A has a great value, then **type III reaction** occurs (the oxygen is completely absent in the system).

4.1. Photooxidation study case

The tested compounds in this chapter were Phthalo Blues (CI names PB15:1, PB15:3, PB15:6, and PB16) and Phthalo Green (PG7) with the chemical structure shown in **Table 2**; all these structures have been exposed to irradiation with polychromatic light generated by a Hg medium lamp 375 nm.

| Acrylic paints | Market name | Pigment |
|----------------|-------------------|--|
| 143 | Phthalo Blue | Phthalocyanine Blue PB15 |
| 159 | Primary Blue | Phthalocyanine Blue PB15 |
| 718 | Metallic Blue | Titanium dioxide-coated mica PW6; Phthalocyanine Blue PB15 |
| 335 | Emerald Green | Arylamide Yellow 10G PY3; Phthalocyanine Green PG7 |
| 375 | Sap Green | Arylamide Yellow 5GX PY 74; Phthalocyanine Blue PB15 |
| 719 | Metallic Green | Titanium dioxide-coated mica PW6; Phthalocyanine Green PG7 |
| 154 | Phthalo Turquoise | Phthalocyanine Blue PB15; Phthalocyanine Green PG7 |
| 343 | Hookers Green | Phthalocyanine Green PG7; Iron oxide PR101; Arylamide Yellow 5GX PY 74 |
| 386 | Phthalo Green | Phthalocyanine Green PG7 |

Table 2. The composition of the tested acrylic paints.

The tested samples are shown in **Figure 4**.

A low photostability of Phthalo Green compared with Phthalo Blue has been observed, similar with the photodegradation study of the Heliogen Blau 6900 and Heliogen Grün L8730 standard solutions (**Figures 5 and 6**).

For all tested samples, measurements of gloss degree and optical parameters (ΔE_x^* and Δb_x^*) were performed. The variation of these parameters was also measured during the photodegradation process with polychromatic light irradiation provided by an artificial light source similar to solar radiation spectrum. After analyzing the obtained results, it was possible to assign that the gloss degree decreases gradually after irradiation with polychromatic radiation (at the samples 375, 335, 154, 343, and 386), while at the other samples (718, 719, 143, 159),

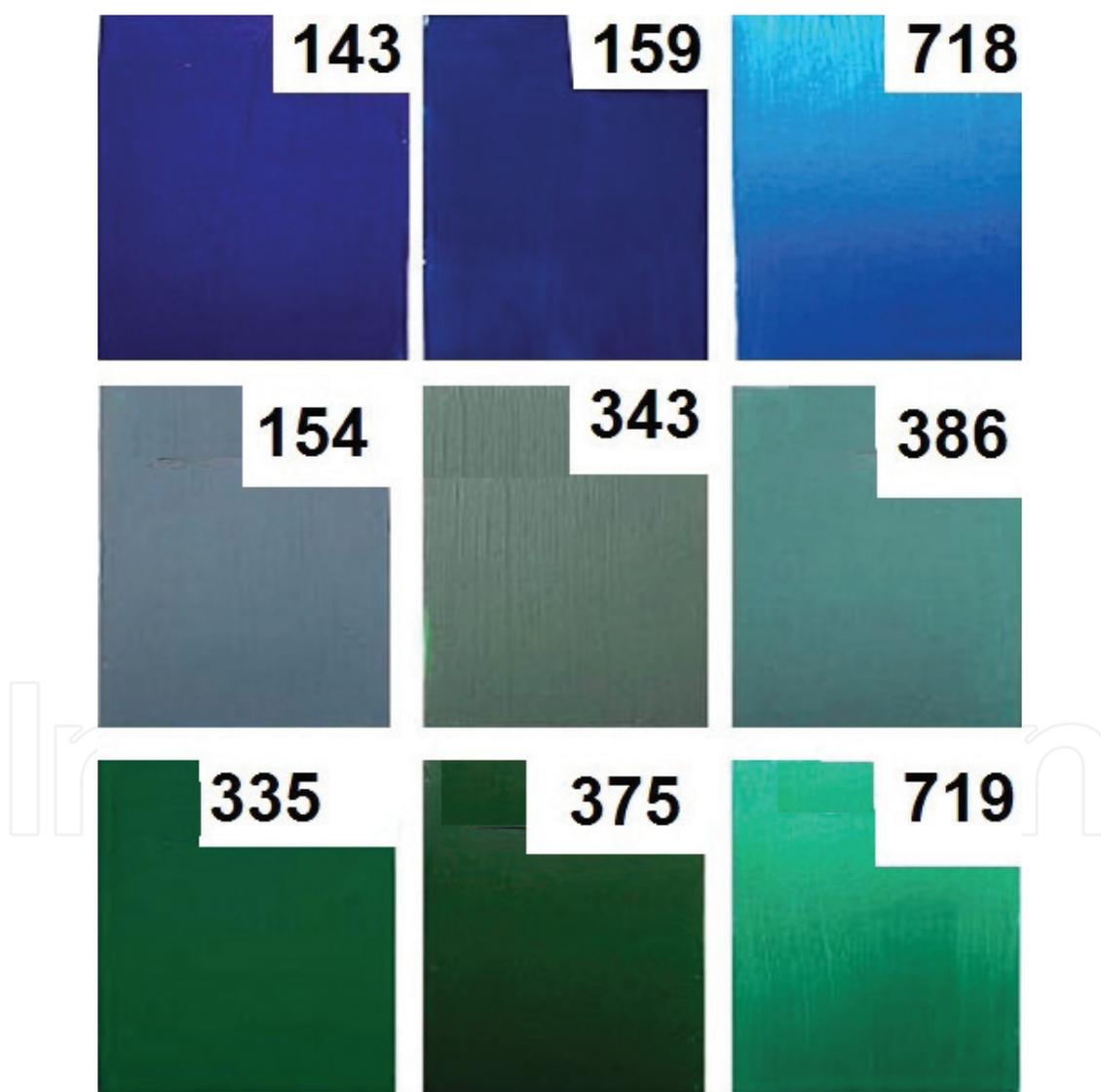


Figure 4. The cardboard painted with blue and green pigments.

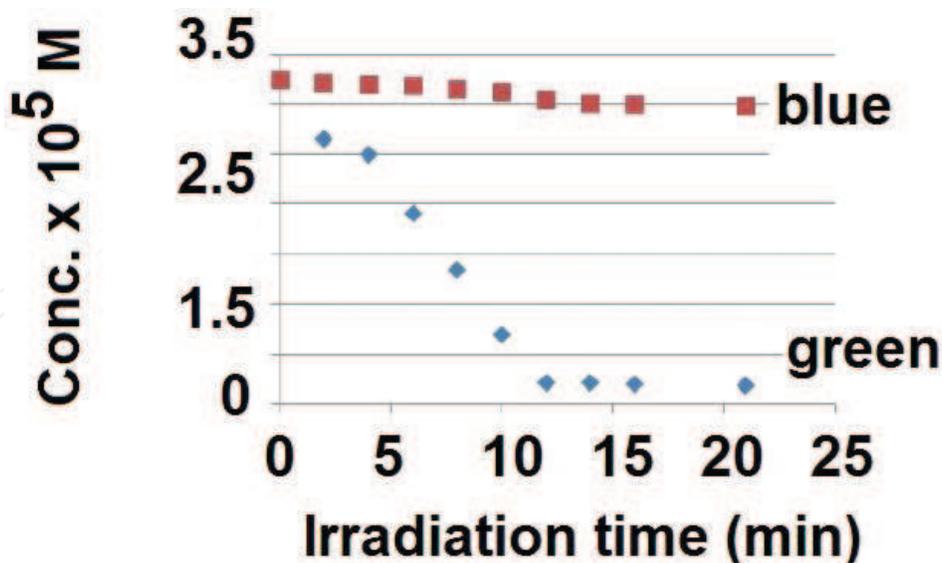


Figure 5. Photodegradation kinetics of Heliogen Blue 6900 and Heliogen Grün L8730 standard solutions.

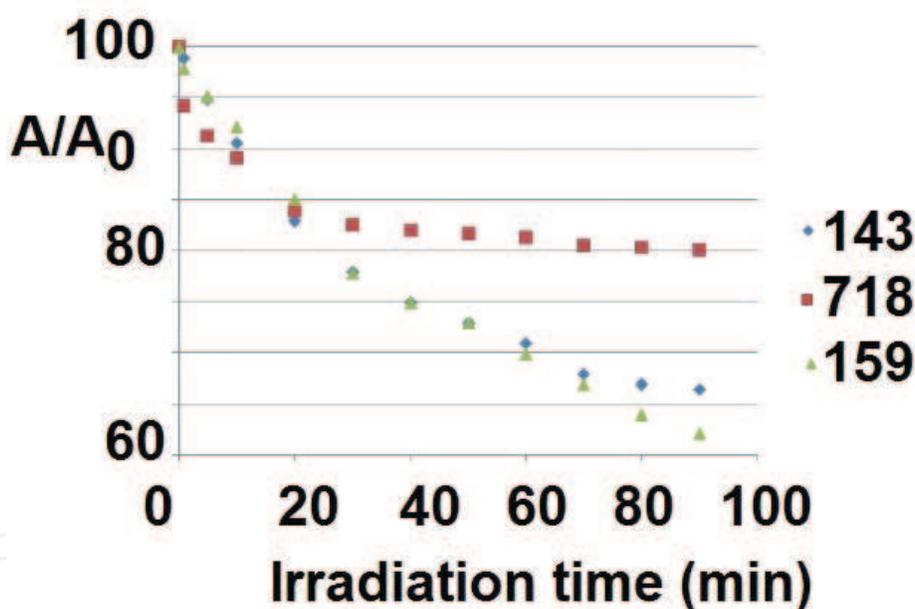


Figure 6. Photodegradation kinetics of some acrylic paints.

there is a significant decrease in this parameter recorded in the first 30 min, followed by a new slight increase of gloss degree. In the case of acrylic paints containing TiO_2 and micas, a decrease of the gloss parameter after the first 30 min of irradiation was observed, most probably due to the role of TiO_2 , recognized as photocatalyst which generates OH radicals and, in this case a good contributor to photocatalytic degradation processes (Figures 7 and 8). In the case of the paints that contain arylamide yellow, a limited stability of these paints is observed, due to this pigment light sensitivity. This behavior is proven by a low increase gloss index for the paints that contain arylamide yellow (Figure 7).

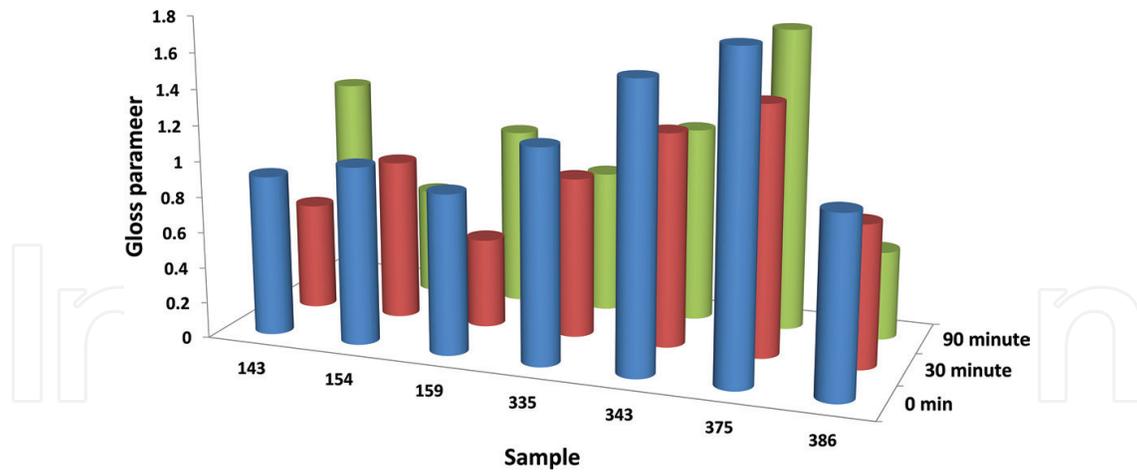


Figure 7. Gloss parameter variation.

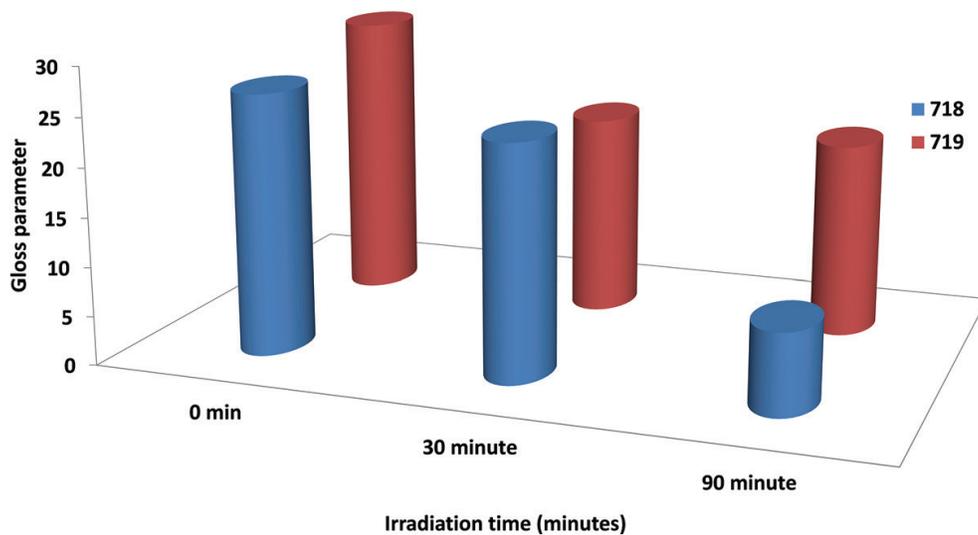


Figure 8. Gloss parameter variation in case of acrylic paints containing TiO_2 and micas.

The same trends are recorded for the ΔE_x^* and Δb_x^* optical measurements, **Figures 9 and 10** for ΔE_x^* and **Figures 11 and 12** for Δb_x^* .

With regard to the change of the sample yellowness ($\Delta b^* = |b_f^* - b_i^*|$), the following classes are specified: stable for $\Delta b^* \leq 3$ points of absolute increase, moderately stable for $\Delta b^* > 3$ and $\Delta b^* \leq 8$ points of absolute increase, and unstable for $\Delta b^* > 8$ points of absolute increase. In this way, at the samples 143, 159, 718, and 719 (samples that contains TiO_2 , micas, arylamide yellow), the yellowness corresponds to an increase of the instability ($\Delta b^* > 8$), obeying the abovementioned rule, while for the samples 375, 335, 154, 343, and 386 ($\Delta b^* > 3$ and ≤ 8), the yellowness corresponds to a moderate stability, as shown in **Figures 11 and 12**. For all the paints, subsequent light exposure resulted in a more severe degradation with large deterioration in optical properties. However, this tendency is the same as for Δb^* parameter: moderately stable for all the samples, except the samples 143, 159, 718, and 719, with a high instability.

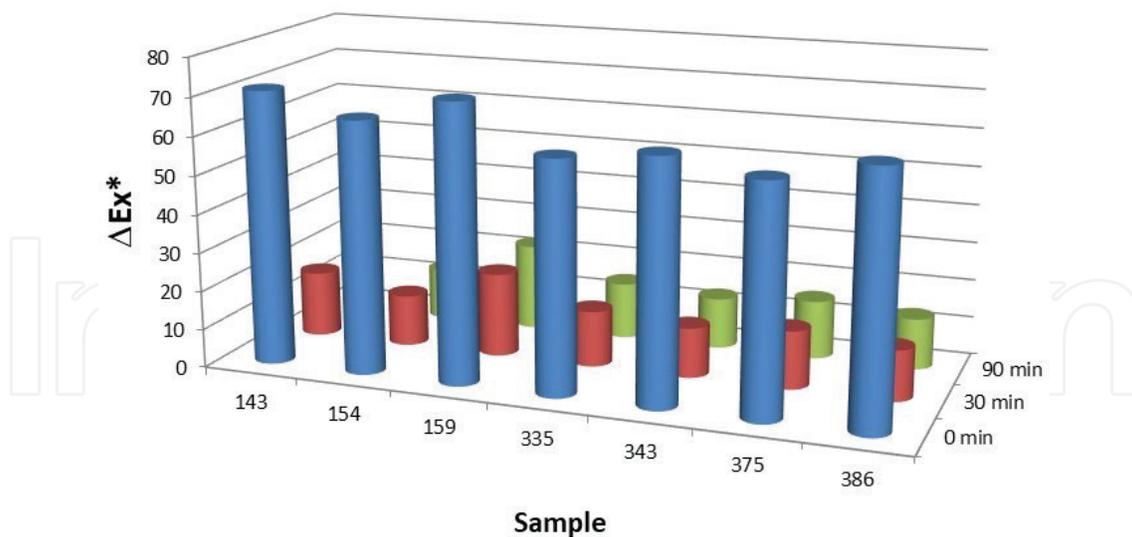


Figure 9. Changes of ΔE_{x^*} for irradiated samples at different times.

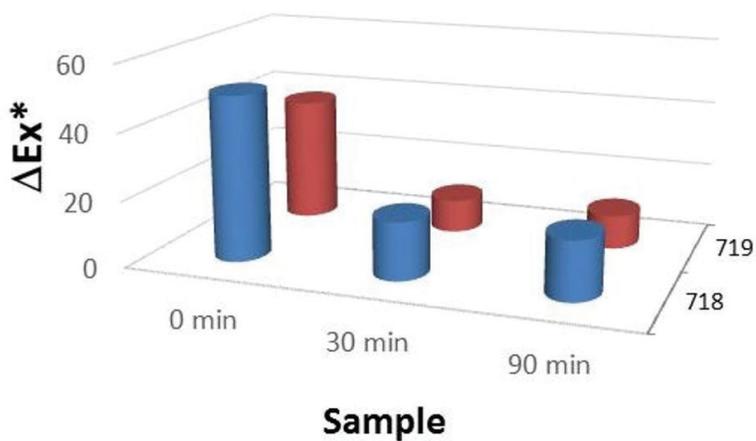


Figure 10. Changes of ΔE_{x^*} for irradiated metallic samples at different times.

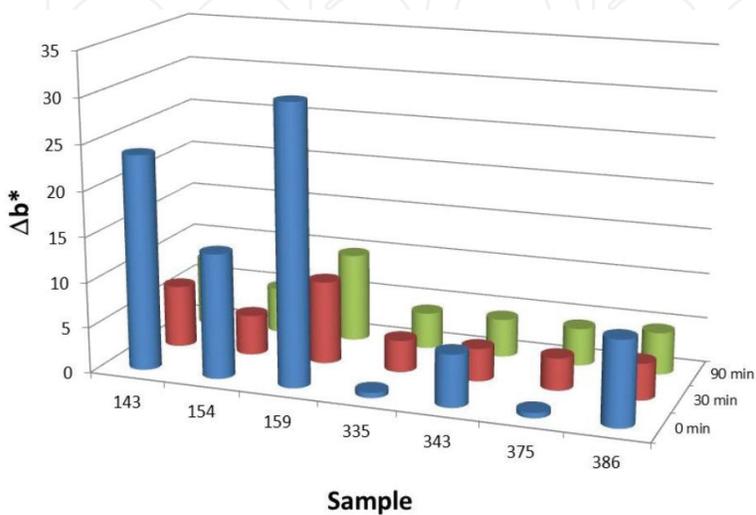


Figure 11. Changes of Δb_{x^*} for irradiated samples at different times.

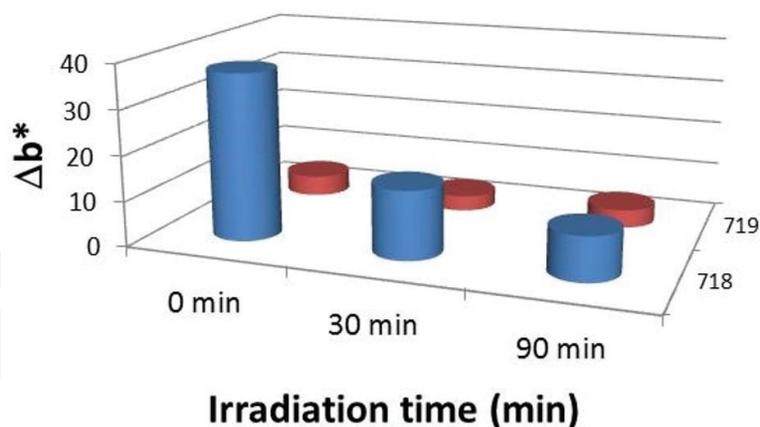


Figure 12. Changes of Δb^* for irradiated metallic samples at different times.

During the irradiation with polychromatic light, in the UV–Vis spectra of these pigments, either in solution or painted on cardboard, some minor changes evidenced in the spectral region between 480 and 840 nm could be observed, as follows:

- An insignificant decrease of Heliogen Blau 6900 absorbance, both at 660 and 860 nm, concomitant with a small increase of absorbance at 472 nm (Figure 13).
- A strong decrease of Heliogen Grün L8730 absorbance, visible both for Soret band from 447 nm and for the bands from 690 and 805 nm, most probably due to the high number of chlorine atoms present as substituents in the pigment structure, responsible for new generated species. The irradiation with Hg lamp (which contains a high level of UV radiation) causes dissociation of the *chlorine substituents*, leading to free radical formation [23] and new species visible by the new wideband from 495 nm (Figure 14).
- This behavior is exhibited for the cardboard painted with Heliogen Grün L8730, the spectral changes and absorbance decrease being observed most predominantly in the visible area (the absorption bands from 690 and 805 nm); in the near UV area, the changes attributed to Soret band are not visible, due to the presence of TiO_2 in the paint composition, this metallic oxide being responsible for the wide and not defined band from this area (Figure 15).

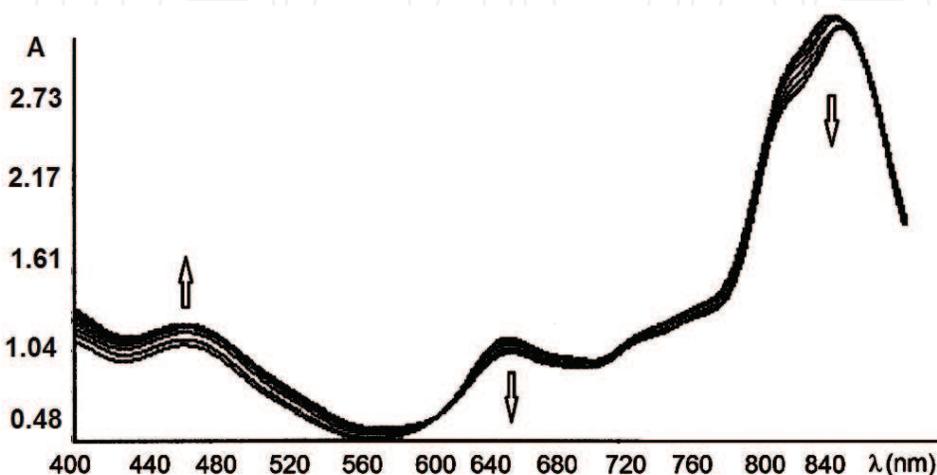


Figure 13. Spectral changes of Heliogen Blau 6900 in solution during light irradiation.

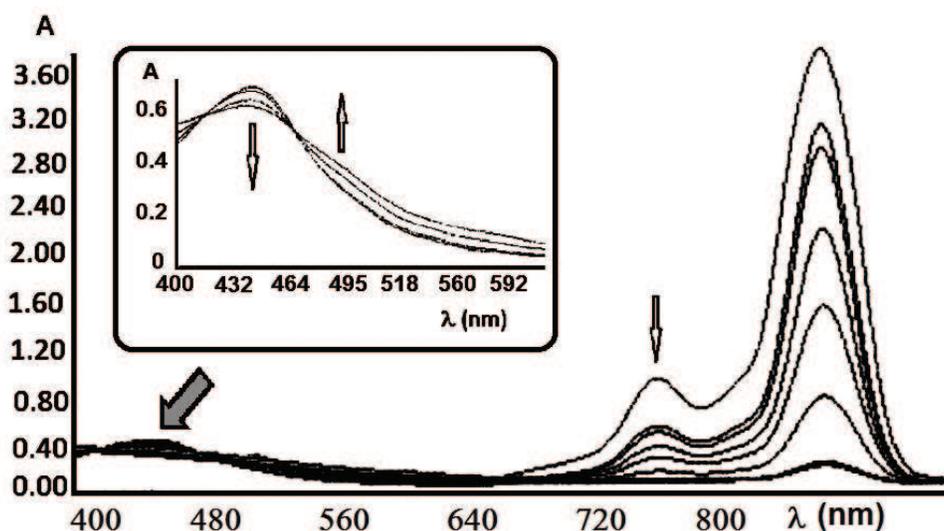


Figure 14. Spectral changes of Heliogen Grün L8730 in solution during light irradiation.

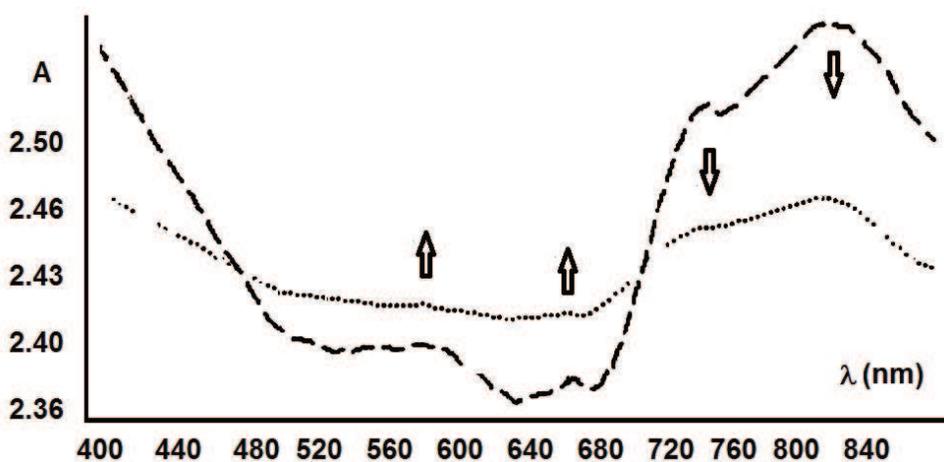


Figure 15. Spectral changes of cardboard painted with Phthalo Green during light irradiation.

If the Pc oxidative photobleaching occurs via singlet oxygen species, the unsaturated bonds of phthalocyanine chromophoric system are oxidized [24], singlet oxygen being responsible for the phthalocyanine photobleaching [25]. There are some limited studies about photobleaching of MPcs in solution; because of its complex reaction, the product isolation is very difficult; and the final photooxidation products are obtained in insufficient amount (phthalimides and phthalonitriles) [26, 27]. Similar results have been described for porphyrin structures, which are related compounds with phthalocyanines [28–30]. Formation of highly toxic hydrogen cyanide upon ruby laser irradiation of the tattoo pigment Phthalocyanine Blue has been reported [31] (Figure 16).

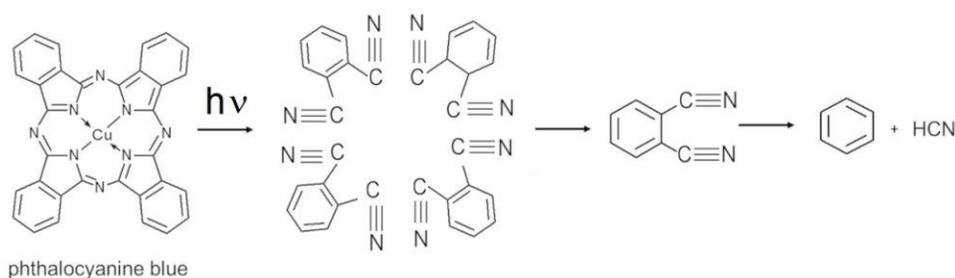


Figure 16. Decomposition pattern of Phthalocyanine Blue (PB15:3) based on the pyrolysis and laser irradiation.

5. Conclusions

By means of the abovementioned experiments, the following has been observed:

- In solution the green pigment is more degradable than the blue pigment.
- In acrylic paints containing these pigments, the photodegradation is more intense in the first 20–30 min of irradiation; after that, depending on the presence or absence of other compounds (TiO_2 , micas, etc.), an increase of the optical parameters is observed.

Since the photodegradation results for pigments and acrylic paints are not fully correlated, some additional studies are needed in order to elucidate the photodegradation mechanism and products.

However, it is necessary to strictly observe that some protective measures regarding the uncontrolled exposure of paintings using these acrylic paints are necessary, in order to avoid the irreversible degradation processes of artworks.

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Conflict of interest

The author(s) declared no potential conflicts of interest.

Author informations

R. M. Ion, A. Nuta, A. A. Sorescu, and L. Iancu contributed equally to this work.

Author details

Rodica-Mariana Ion^{1,2*}, Alexandrina Nuta¹, Ana-Alexandra Sorescu¹ and Lorena Iancu^{1,2}

* Address all correspondence to: rodica_ion2000@yahoo.co.uk

1 ICECHIM, Evaluation and Conservation of Cultural Heritage, Bucharest, Romania

2 Materials Engineering Doctoral School, Valahia University, Targoviste, Romania

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