



## Photo-Oxidative Stability of a Series of Red Acrylic Paints

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### ABSTRACT

**P**hoto-oxidative stability of a series of most common red acrylic paints has been investigated. The paints in question were carmine, quinacridone scarlet, alizarin crimson, brilliant red, vermillion and cadmium red hue. Structural changes, discoloration and weight loss of paints film subjected to UV irradiation in an accelerated ageing chamber were measured using FT-IR spectroscopy, colorimetry and gravimetric analysis before and after 400, 800 and 1200 hours of irradiation. The results of FT-IR spectroscopy showed that cadmium, quinacridone scarlet, primary magenta and vermillion involved most structural changes, where the reduction of transmission peak at  $2900\text{ cm}^{-1}$  (symmetric stretching of C-H bond) was noteworthy. Colorimetric measurements indicated the reduction in the absorption of visible light due to photo-degradation of the pigment structure. Furthermore, alizarin crimson and brilliant red have undergone more weight loss compared to the others, which was a result of rapid formation of VOCs. Prog. Color Colorants Coat. 7(2014), 177-185. © Institute for Color Science and Technology.

## 1. Introduction

Polymers based on acrylic and methacrylic esters are widely used in the formulation of varnishes, paints, adhesives, and, more specifically, of protective coatings for different surfaces [1-3]. Acrylic paints, containing suspended pigment in the emulsion of acrylic/methacrylic polymers, are quick-drying paints which have a water-soluble property, whereas after drying convert to a water-resistant film and as a result of this property, acrylic paints do not represent color migration; a typical characteristic in water-reducible paints such as Gum Arabic-based ones [4-6]. Due to the above mentioned characteristics along with the variety, good

working properties and high quality and resistance compared with traditional oil paints, acrylic paints have received extensive use by artists as well as conservators specialized in paintings, wall paintings, paper, wood and other painted cultural materials [7-10].

Paintings, exhibited or stored, are susceptible to environmental factors, and destructions occur with the passage of time. To protect these art works, the reactions of the materials with these destructive factors should be clarified. In this frame, the impact of ultraviolet irradiation, humidity, and temperature on the painting's chromatic structure have been proved of primary

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importance [11, 12]. Considering the increasing application of acrylic paints by the modern artists and conservators, it is necessary to evaluate their stability against destructive factors such as sun light [13, 14].

The process of natural ageing of painting materials could be reproduced in the laboratory only by considering a simplified approach through some kind of simulation with convenient short-term experiments. Lifetime provision and mechanistic studies of the outdoor destruction processes are generally carried out by help of accelerated ageing experiments including UV light and/or temperature studies. The light sources which could be efficiently employed for such purposes should have high power output and the closest resemblance to the solar light spectrum, particularly in the UV range [15, 16].

Durability of acrylic films exposed to UV light has already been investigated and the results show that acrylate units (which are reactive to oxidation and prone to chain-scissions) and long ester groups by promoting cross-linking reactions were the main cause of molecular and structural changes [2, 3]. In a related work, Chiantore and Lazzari have studied structural and molecular changes under condition of accelerated aging and the results showed that molecular weight changes in all samples are due to the chain scission and/or coupling of macro-radicals [3]. The authors concluded that oxidation of polymers are strongly influenced by formation of side groups such as butyl or isobutyl. Also, photo-oxidative stability of acrylic and methacrylic polymers has been investigated by Chinatore et al. [14]. The results showed the high vulnerability of acrylate compared to methacrylate toward photo-degradation. Relevantly, Papliaka et al. [8] have investigated the stability of a series of synthetic pigments towards accelerated ageing using the contemporary binding medium styrene-acrylic copolymer. They have reported that paint layers display greater color difference when exposed to high temperature and humidity than to ultraviolet radiation,

whose effect was not even accelerated by the intense temperature augmentation.

Relevantly, the light fastness declarations of three acrylic colors, i.e. cadmium red, ultramarine blue and chromium oxide green from different companies were investigated before and after UV exposure by Py-GC/MS, FTIR-ATR analyses, and color measurements [17]. The authors have detected different volatile compounds or new chemicals as oxidation products.

However, to the best of our knowledge, the investigations on the photo-stability differences of a series of red acrylic paints are still scarce. So, the aim of this work was to explore the photo durability of a series of red acrylic paints that are commercially available and are widely used by the artists and conservators of paintings and cultural materials. The selected paints including carmine (C.I. PR146, C.I. PR9, C.I. PW6), quinacridone scarlet (C.I. PR112, C.I. PR122), alizarin crimson (C.I. PR206, C.I. PR202), brilliant red, vermilion (C.I. PR112, C.I. PY74) and cadmium red hue (C.I. PR112) were prepared in the form of a thin film, and exposed to the UV light in a photo-ageing chamber. After photo-aging for 400, 800 and 1200 hours, samples were weighed and then analyzed using colorimetry and FT-IR spectroscopy. The results of this study could be directly used by the painters to help them to choose the most light resistible red acrylic paint.

## 2. Experimental

### 2.1. Materials and methods

#### 2.1.1. Materials

A series of six red acrylic paints that are most widely used by the artists and painters were selected and purchased from the suppliers. These paints are mainly the emulsion of red pigment or pigments in an acrylic binder (poly (EA/MMA)) along with some additives. The name and characteristics of these paints are listed in Table 1.

**Table 1:** The name and characteristics of the selected paints.

No.	Commercial name	Manufacturer	Color index number (pigment)
1	Carmine	Maimeri	C.I. PR146, C.I. PR9, C.I. PW6
2	Quinacridone scarlet	Pebeo	C.I. PR112, C.I. PR122
3	Alizarin crimson	Liquitex	C.I. PR206, C.I. PR202
4	Brilliant red	Reeves	-----
5	Vermilion	Ladoga	C.I. PR112, C.I. PY74
6	Cadmium red hue	Winsor&Newton	C.I. PR112

Also, Figure 1 shows the chemical structure of the pigments used in the formulation of these paints.

### 2.2. Sample preparation

Diluted in distilled water, acrylic paints were sprayed on the glass slides (25 mm × 75 mm) and were left for 24 hours in darkness at room temperature to let any trapped solvent evaporate. The thickness of the obtained films, measured by manual micrometer, was  $40 \pm 5$   $\mu\text{m}$ . Weight loss of the samples was measured by a digital balance (precision:  $\pm 0.001$  g). Four series of the samples were prepared to be exposed to UV irradiation for 0, 400, 800 and 1200 hours.

### 2.3. Accelerated photo-aging

A cubic photo-ageing chamber was equipped with two 20 W UV lamp ( $\lambda \sim 254$  nm, Canon, Japan) with a constant irradiation at a power of  $36 \text{ W/m}^2$ . The intensity of the lamps was measured by a Cassy Lab 1.56, Laybold Co. Germany lightmeter. The maximum temperature in the UV chamber during the experiments was around  $32^\circ\text{C}$ . The chamber was also equipped with two fans to ventilate the volatile organic vapors. The distance between the lamp and the samples was adjusted to 22.5 cm.

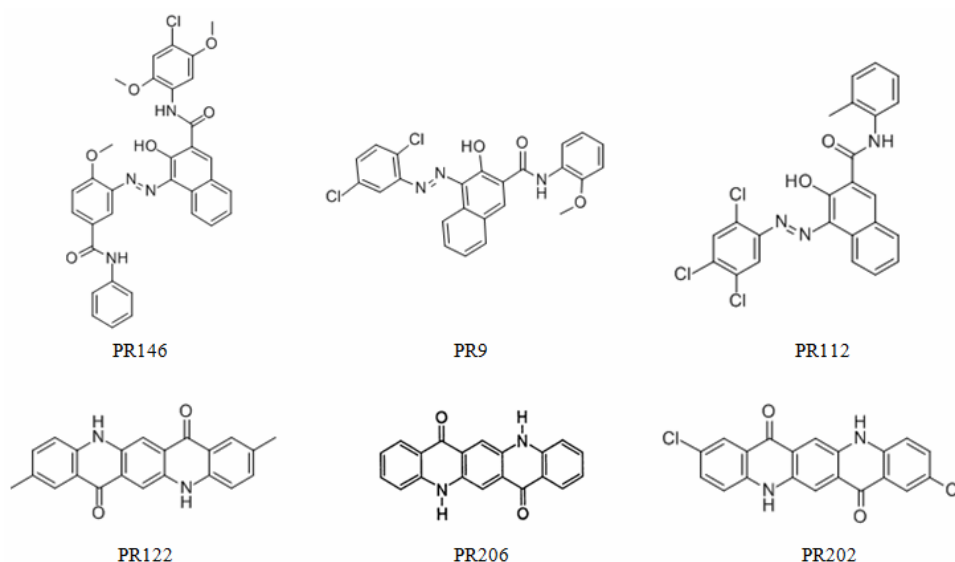
In real conditions, the light is not exposed

continuously and may be at lower intensity. But, in simulated photo-ageing, the samples will be exposed continuously to the lamps. Studies on the simulation of museum conditions by means of accelerated aging showed that in the museum, there is 10 hours/day irradiation, so the result of this simulated photo ageing could be 6 years of natural ageing in a museum with the light of 300 lux or 12 years of natural aging in a museum equipped with 150 lux light tubes [18, 19].

The weight loss of the paint films was determined gravimetrically at the defined intervals. A Helios- $\alpha$  Thermo Spectronic spectrophotometer was used to measure the discoloration rate of the samples in the characteristic wavelength of each paint maximum absorbance. FT-IR spectra of the samples were also recorded in transmission mode before and after defined intervals using Jasco 680-plus FT-IR spectrometer with  $4 \text{ cm}^{-1}$  resolution in the range of  $4000\text{--}400 \text{ cm}^{-1}$ .

## 3. Results and discussion

The photo-durability of a series of red acrylic paints including six commercial paints were studied by means of an accelerated photo-ageing chamber. Three different analysis methods, i.e. FT-IR spectroscopy, colorimetry and gravimetric analysis were used to evaluate the effect of UV light on thin films of the selected paints.



**Figure 1:** Chemical structure of the pigments used in the acrylic paints formulation.

### 3.1. FT-IR spectroscopy

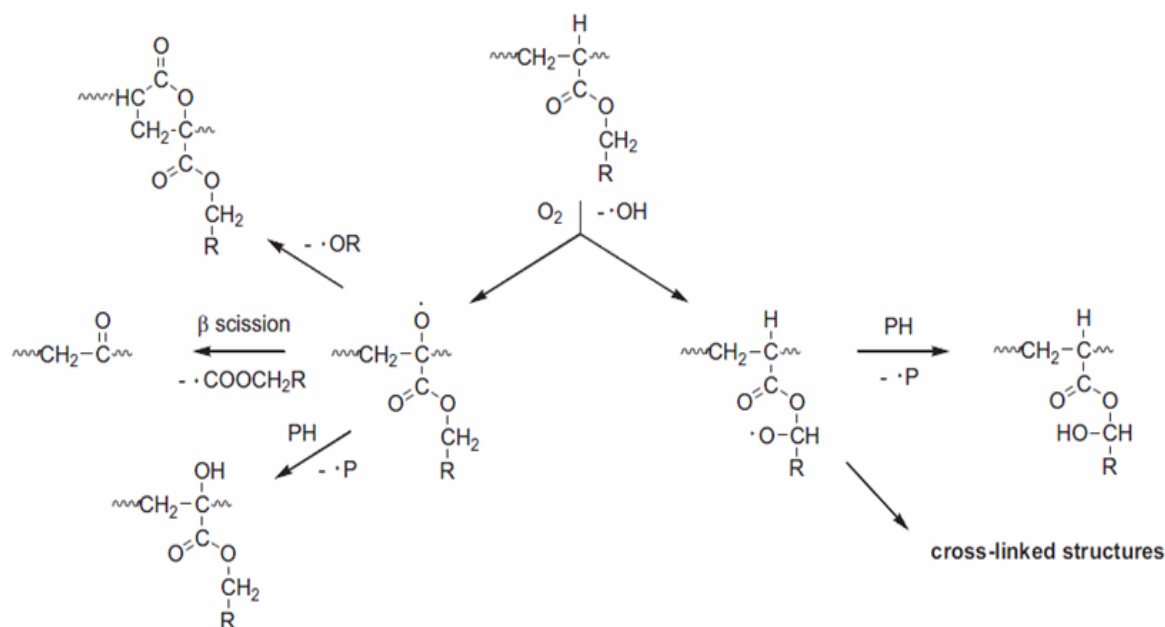
The FT-IR spectra of the selected paints were recorded to follow the structural changes of the paints under UV irradiation. The FT-IR spectra of paint films show that hydroxyl groups (mostly alcohols and peroxides) are responsible for the appearance of broad band at 3250  $\text{cm}^{-1}$  [20].

As proposed in scheme 1, the oxidation of polymers in the paint samples may occur via the addition of oxygen molecules in the air to the tertiary radicals formed by absorbing the liable hydrogen of acrylic units [2]. On the other hand, ester side chain can undergo other reactions that produce insoluble intermediates. Unstable secondary hydro peroxides are easily destroyed and produce alkoxy radicals which are decomposed through cross-linking reactions due to high mobility of chains connected to butyl group [2].

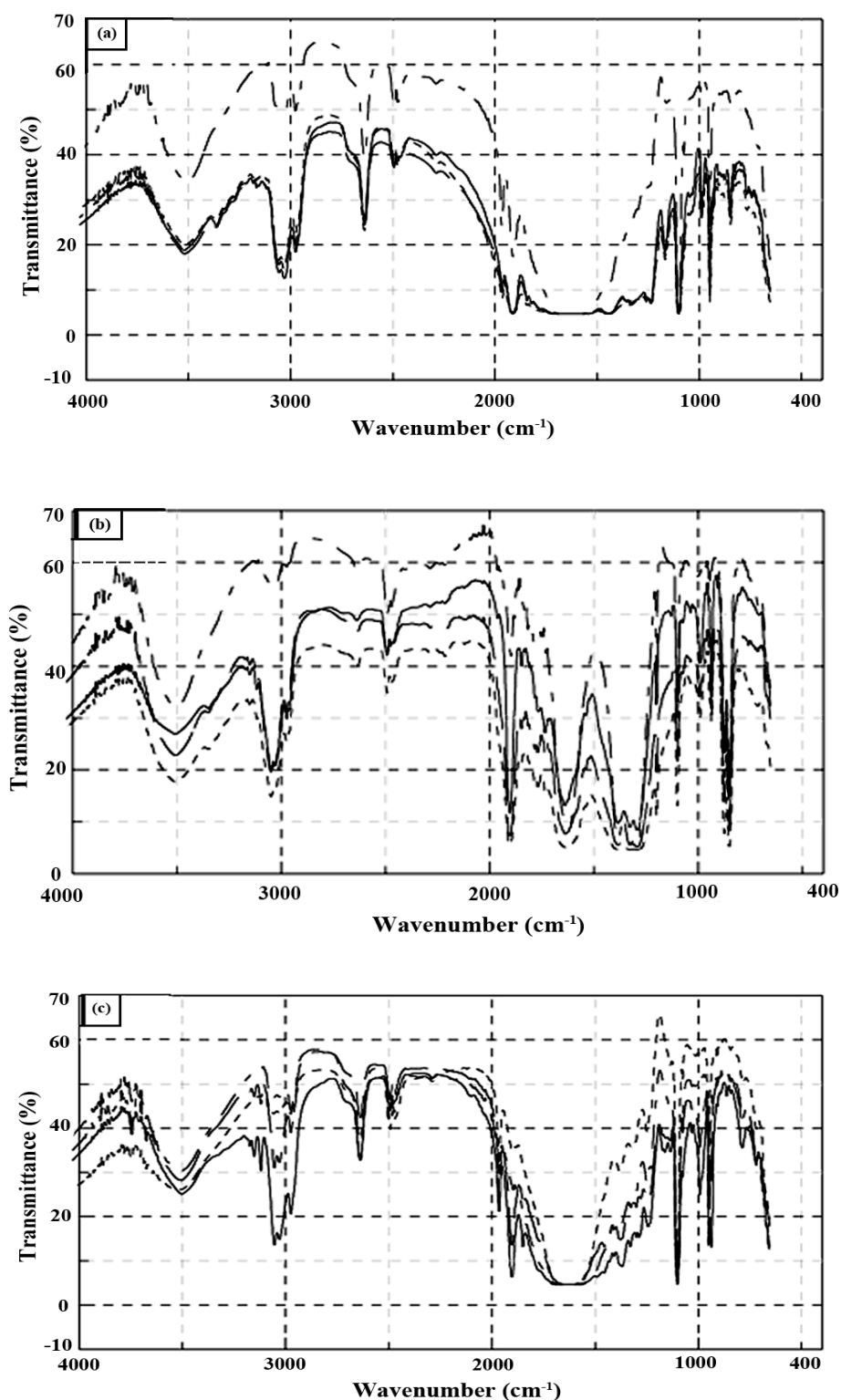
In the FT-IR spectra of the samples irradiated for 400 hours intervals, it may be deduced that only the intensity of transmission peaks is reduced (Figure 2). This could be due to the photo-destruction of acrylic resin used in the formulation of the paints. It means that during the first 400 hours of irradiation, the

pigments do not exhibit any structural changes. In the case of carmine, quinacridone scarlet, vermilion and cadmium red hue, FT-IR spectrum shows a notable reduction at 2900  $\text{cm}^{-1}$  after 1200 hours of the irradiation, as shown in Figure 2.

Oxidation of C-H bonds (appeared at 2800-3000  $\text{cm}^{-1}$  region) could be the main reason of this reduction [21]. It should be noted that these paints represent also maximum discoloration due to the accelerated aging; hence, it can be assumed that the spectral changes may also be attributed to the destruction of the pigments chemical structure. So, the significant difference around 1500-1700  $\text{cm}^{-1}$  after aging in cadmium red hue spectra could be attributed to the destruction of C=O bonds (1700  $\text{cm}^{-1}$ ) of PR112 pigment. Similarly, the decrease of peak intensity around 1330-1500  $\text{cm}^{-1}$  in carmine spectra is due to the breaking of C=C bonds of aromatic rings (1450-1500  $\text{cm}^{-1}$ ) presented in PR146 and PR9 pigments. Moreover, the destruction of C=O bonds (1700-1800  $\text{cm}^{-1}$ ) in PR112 pigment causes a considerable decrease around 1800-2000  $\text{cm}^{-1}$  at vermilion spectra.



**Scheme 1:** Simplified mechanism of oxidation of acrylic copolymers (PH and  $\cdot\text{P}$  are the symbols of phenyl and phenyl radical, respectively) [2].



**Figure 2:** FT-IR spectra of (a) carmine, (b) quinacridone scarlet, (c) vermillion and (d) cadmium red hue before (solid line) and after 400 (dashed line), 800 (short dashed line) and 1200 hours (dash-pointed line) of UV irradiation.

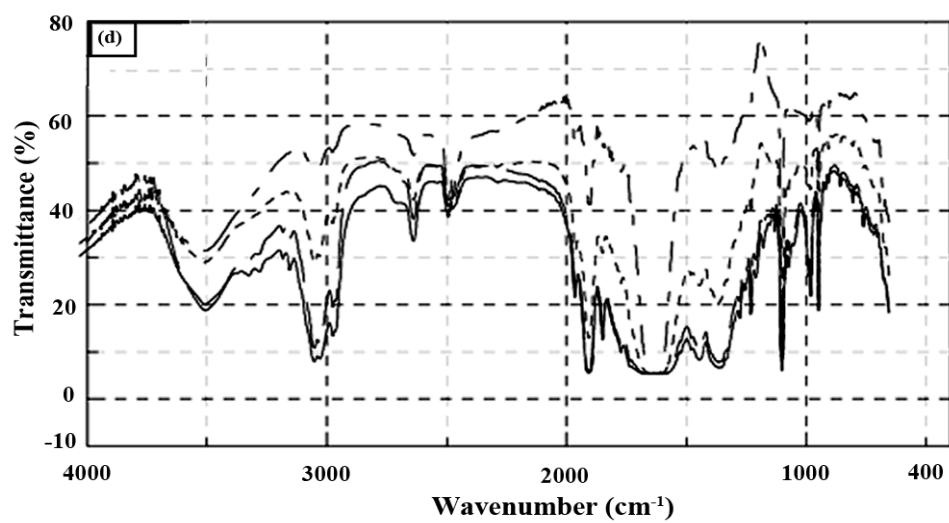
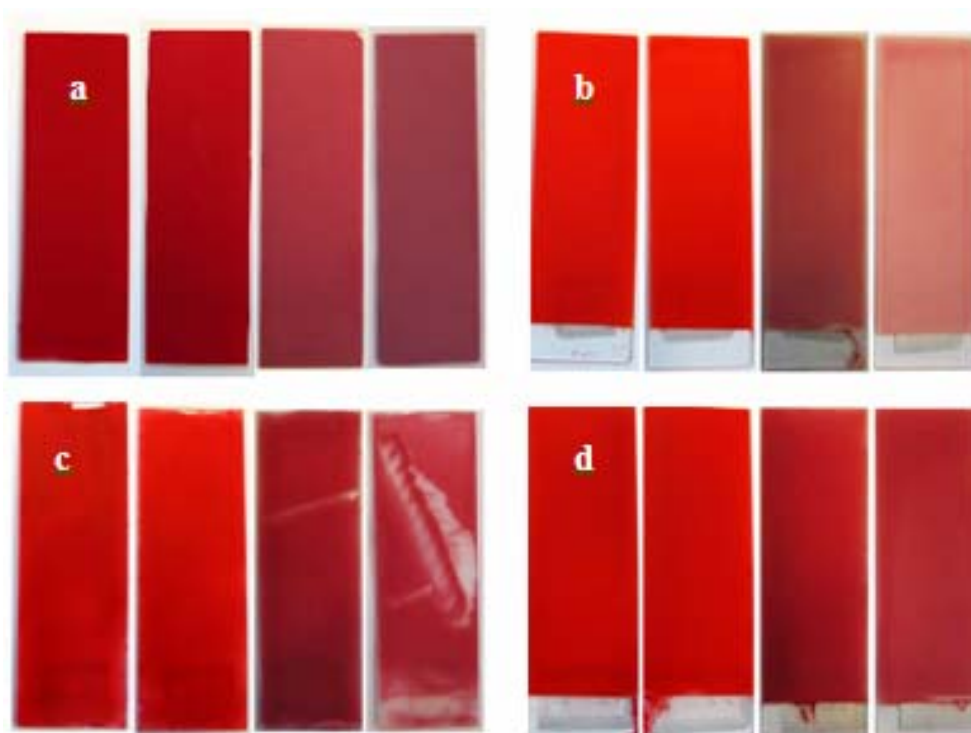


Figure 2: Continued.



**Figure 3:** The color value dissipation of (a) carmine, (b) quinacridone scarlet, (c) vermilion and (d) cadmium red hue in (left to right) 0, 400, 800 and 1200 hours of UV irradiation.

### 3.2. Colorimetry

Discoloration of the paints thin film as a result of accelerated photo-ageing could be studied by comparing the irradiated samples of the paint at different intervals. Results indicated in Figure 3 show that the color value of carmine and quinacridone scarlet dissipated after 1200 hours of photo-ageing, while vermilion and cadmium red hue were more resistant against this accelerated ageing process.

This could be due to the chemical nature of the pigments presented in the paints formulation. PR146 have two carbonyl groups that facilitate the destruction of azo chromophore. On the other hand, PR122 presented in quinacridone scarlet formulation is a quinacridone pigment and therefore, is more vulnerable to photo-aging.

To quantify the discoloration of the paint samples under the irradiation of UV light, a specific amount of the irradiated paint was soaked in chloroform and then, the absorbance of the solution was measured in the

characteristic wavelength of the paints (~550 nm) (Figure 4). Here again, carmine and quinacridone scarlet represent maximum discoloration whereas vermilion and cadmium red hue are more UV-resistant. This discoloration is mainly due to the photo-oxidation of pigments presented in the formulation of the paints.

### 3.3. Weight loss measurements

To investigate the amount of weight loss, the paint samples were weighed before and after 400, 800 and 1200 hours of UV irradiation.

The results, shown in Figure 5, revealed that alizarin crimson and brilliant red have the most weight loss. This was due to the fast destruction of PR206 and PR202 pigments with quinacridone structure, presented in the formulation of alizarin crimson. In contrary, the apparent formation of low molecular weight volatile compounds was practically negligible in cadmium red hue; the most UV-resistant paint in the current study.

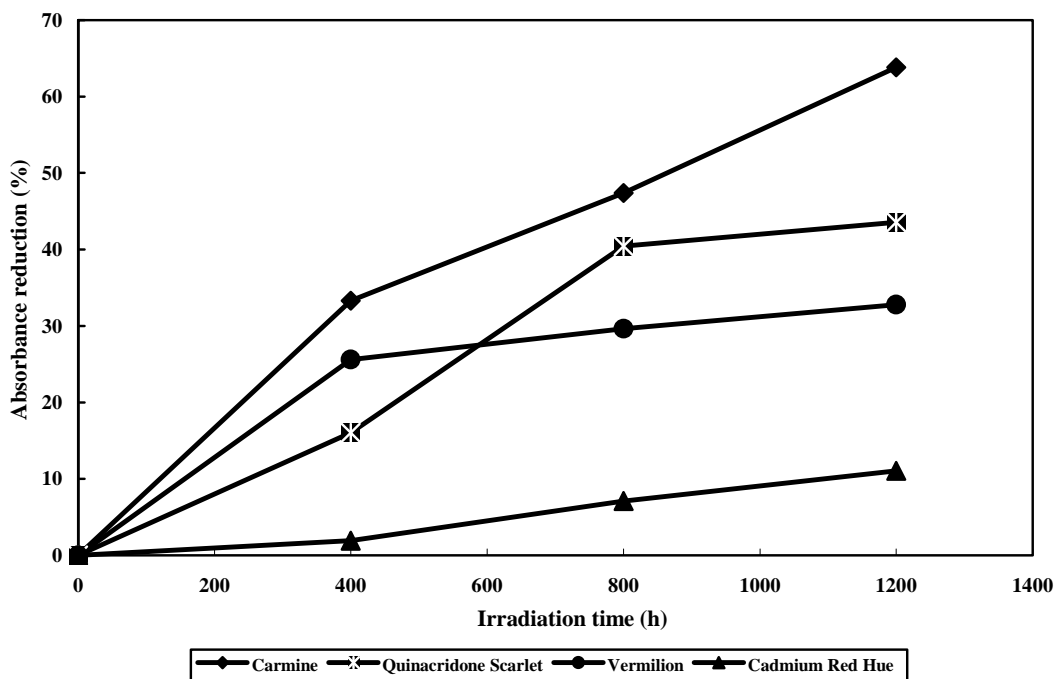


Figure 4: Absorbance reduction of the dissolved paint samples in chloroform as a function of irradiation time.

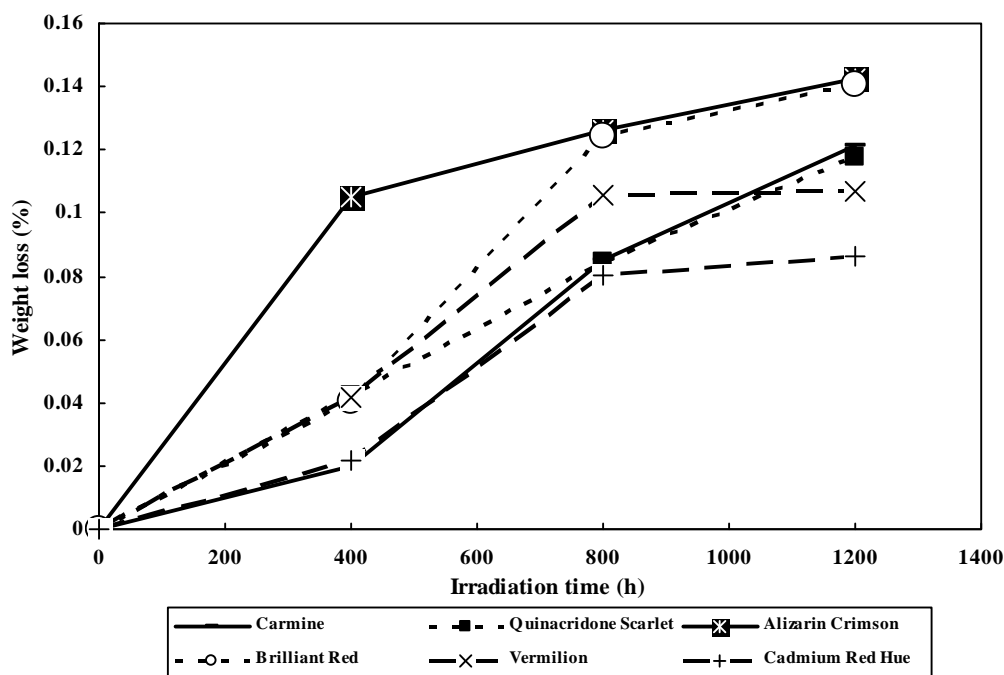


Figure 5: Weight loss of the paint films as a function of irradiation time.

#### 4. Conclusions

The results indicated that photo-oxidative stability is different in the selected red acrylic paints which may be due to different acrylic binder or pigments used in the formulation of the paints. FT-IR spectroscopy analysis showed that carmine and quinacridone scarlet have undergone the maximum structural change that was attributed to different pigment structures used in the formulation of the paints. Furthermore, carmine and quinacridone scarlet showed notable reduction in color values due to photo-degradation of used red

pigments. Finally, it was observed that alizarin crimson and brilliant red have maximum weight loss compared to other samples which can be speculated to the formation of volatile organic compounds. The weight loss of cadmium red hue, the most UV-resistant paint in the current study, was practically negligible.

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