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Effects of gamma rays on a restored painting from the XVIIth century

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Abstract

The subject of this study is a Peruvian painting from the 17th century, which has been recently restored and then contaminated by mould. It received different unsuccessful treatments. Therefore, radiation process was suggested as an alternative once it is an effective technology for decontamination and conservation purposes. The aim of this study is to investigate the influence of irradiation process on the original painting and on the products used in the restoration process. These products were irradiated with ^{60}Co gamma rays applying doses in the range of 6–25 kGy. The polymeric materials were characterized by thermal analysis techniques before and after irradiation. The colour of the pigments irradiated and non-irradiated were compared by spectrophotometric analysis. Small samples removed of the original painting were also irradiated and investigated. The results obtained until now allowed concluding that the irradiation with the appropriated dose of 6.0 kGy, according to the literature, will not damage the restored painting.

Keywords: Gamma radiation; Decontamination; Artwork conservation

1. Introduction

One of the biggest problems found in the conservation of a cultural property is to prevent and control the microbial contamination. In South America, which has a tropical climate with high temperature and relative humidity, it is very common to find artworks with a growth of mould. For a special Peruvian painting from the 17th century, that had been recently restored, followed by a hard contamination of mould growing close to 70% of its area, the gamma irradiation appears as a feasible alternative for biological decontamination and conservation. But it is well known that it can interact with the molecular structure of the material changing its characteristics, especially those related to the colour of pigments and chemical and physical properties of the polymers.

2. Experimental

2.1. Painting description

Title: "Sacred Family with Angels"; author: attributed to Leonardo Flores; age: 17th century; dimensions: 1.9 m × 3.0 m; origin: Peru/South America; technique: tempera over canvas. The painting arrived at the conservation laboratory without framework, rolled up, torn, with a significant lost of the support (canvas) and of the painting layer. It had some improper patches and it was repainted in some areas. It did not have varnish—as almost all Peruvian paintings—and it had some dirt adhered directly to the painting layer (Fig. 1a).

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This painting was restored according to the appropriated procedures and materials (Fig. 1b).

2.2. Painting restoration materials

2.2.1. Polymers

The polymers used in restoration processes are: (a) micro-crystalline wax, (b) Paraloid B72 (acrylic resin) from Rhom and Haas; BEVA 371 from Adam—an adhesive developed specifically for restoration purposes which contains, (c) A-C Copolymer 400 (VAC c.15%) from Allied Chemical, (d) Larapol K-80 (ketone resin) from BASF, (e) Elvax 150 (VAC c.33%) from DuPont, (f) Cellolyn 21 (phthalate ester of abietyl alcohol) from Hercules, and (g) Paraffin oil free 65°C m.p. (Berger, 1976; Horie, 1996).

2.2.2. Retouching paints

All retouching paints used were made of pigments plus acrilic resin medium from Lefranc & Borgeois and Maimeri and are listed in Table 1, with the manufacturer code.

Fig. 1. Peruvian painting from the 17th century "Sacred Family with Angels": (a) before restoration and (b) after restoration.

2.3. Identification of biological contamination

After restoration, micro-organisms infected the painting. In order to identify the contaminants present in the artwork, a simple approach was taken. Almost all colonies consisted of fungi, and microscopical observation of conidiophore structures revealed the presence of Aspergillus sp. as well as Penicillium sp.

2.4. Choosing radiation doses

According to the literature, the appropriated gamma radiation dose to eliminate the identified microorganisms is 6 kGy. Then, small samples of the original painting and all materials used in the restoration process were submitted to three subsequent irradiation process using gamma radiation to get the doses: 6 kGy—recommended to decontamination in this case, 10 kGy—above what some colour modification has been detected before and 25 kGy—standard dose for sterilisation (Belyakova, 1961; Tomazello, 1994).

Table 1
Pigment colour comparison by Grey scale method

Sample	6 kGy	10 kGy	25 kGy
Original painting			
Black	5	5	4–5
Cerulean blue	5	5	4–5
Yellow ochre	5	5	4–5
Mars red	5	5	5
Pale brown	5	5	5
Grey	5	5	5
Restoration paints			
083.1—Cadmium yellow	5	5	4–5
242—Naples yellow shade	5	5	4–5
243—Yellow ochre	5	5	5
244—Mars yellow	5	5	4–5
245—Raw sienna	5	5	4–5
246—Burnt sienna	5	5	5
247—Red ochre	5	5	5
248—Mars red	5	5	4–5
249—Raw umber	5	5	5
251—Vandyke brown	5	5	5
256—Breughel red	5	5	4–5
258—Crimson lake	5	5	4–5
259—Permanent violet	5	5	4–5
260—Bayex violet	5	5	4
262—Hoggar blue	5	5	5
263—Viridian	5	5	4
264—Armour green	5	5	4–5
265—Hooker's green	5	5	5
266—Green Ox. chromium	5	5	5
267—Transparent brown	5	5	4–5
271—Cadmium vermilion	5	5	4–5
273—Cobalt blue	5	5	4–5

2.5. Investigating the effects of radiation in the colour of samples

Small samples of the original painting were taken from the painting border, trying to cover as most as possible the different pigments existent in this art work and also having in mind the South America pigments identification done by others scientists (Selder et al., 1999; Abad, 2000). All retouching paints used in the restoration process were tested too. The colour wavelength of all samples were measured by a Datacolor SF 600 spectrophotometer before and after irradiation. All the spectra were compared. The changing colour was evaluated by American Association of Textile Chemists and Colourists (AATCC) evaluation procedure 1/Grey scale for colour changing.

2.6. Thermal characterisation of polymeric materials

All polymeric materials used in the restoration process were characterised by thermal analysis techniques as thermogravimetry (TG) and differential scanning calorimetry (DSC) before and after irradiation with gamma rays. Thermogravimetric measurements were performed using a Shimadzu Corporation thermobalance TGA50 at 20°C/min heating rate, from the room temperature reached up to 600°C, under air flow of 50 ml/min. The calorimetric measurements were performed using a Shimadzu Corporation DSC 50 at 10°C/min heating rate, in the range from −90°C to 300°C depending on the sample, under N_2 atmosphere.

3. Results and discussion

The comparisons of all pigments paint colour before and after irradiation are expressed as numbers in the "grey scale", which are presented in Table 1. In this scale, number 1 means a great colour modification and number 5 means no modification. The data show that there is no significant changing in the colour of all samples as a function of the radiation, even after been submitted to dose of 25 kGy.

On the other hand, the interaction of the ionizing radiation with the polymeric materials may cause cross-linking and degradation of the chain, what modifies the important chemical and physical parameters as thermal stability, glass transition temperature, crystallization, and melting point of thermoplastic polymers. Figs. 2 and 3 present the thermal behaviour of the polymers used in the restoration process of the original picture. Every sample is represented by two curves concerning to the non-irradiated samples (a until g) and the sample irradiated with dose of 25 kGy (a' until g'). In the TG curves (Fig. 2), it can be observed the thermal decomposition of the polymeric material by its weight loss as a function of temperature. No significant modifications are observed in the stability after the irradiation process.

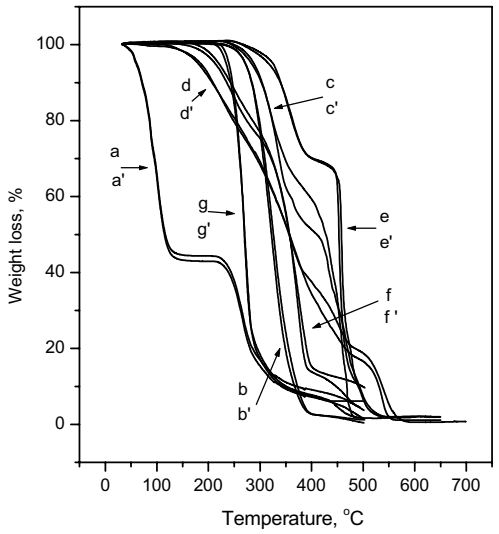

Fig. 2. Thermogravimetric curves, TG, of polymeric materials cited on the text (a until g) before and (a' until g') after irradiation.

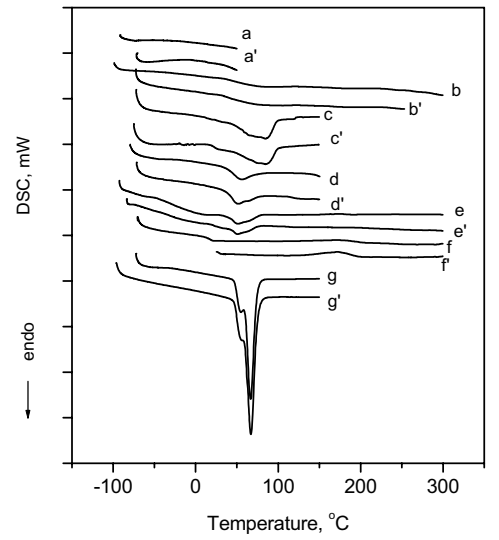

Fig. 3. Differential calorimetric curves, DSC, of polymeric materials cited on the text (a until g) before and (a' until g') after irradiation.

By comparing the DSC curves of the polymers before and after irradiation (Fig. 3), it can be observed that the radiation doses applied do not affect the properties of the materials studied. Therefore, the curves b and b' from Fig. 3 show the glass transition of the acrylic resin at the temperature of 63°C. Therefore, there is no

evidence of cross-linking promoted by the radiation. The curves c/c', d/d', e/e' and g/g' show the endothermic melting peaks of the corresponding samples that were not changed after the irradiation. The samples represented by the curves a/a' and f/f' do show neither through transitions of enthalpy nor through specific heat variations in the conditions and over the range of temperature investigated.

4. Conclusion

The results obtained until now allowed concluding that the irradiation of the picture with dose of 6 kGy will not damage the restored painting immediately, from the point of view of pigments and polymers themselves. No significant colour modification could be detected in these processes. In addition, the highest radiation dose applied (25 kGy) does not cause permanent modifications in the physical and chemical structure of the investigated polymers. However, since a painting is a complex system with a lot of interfaces, the authors are now studying the possibility of the irradiation on molecular changing as a starting agent of a heterogeneous catalysis that could deteriorate the artwork at long term, in order to exclude as most as possible any induced deterioration mechanism.

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