2009 International Nuclear Atlantic Conference - INAC 2009
Rio de Janeiro,RJ, Brazil, September27 to October 2, 2009
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-03-8**

GAMMA RAYS IRRADIATION PROCESS ON A RESTORED PAINTING FROM THE XVIITH CENTURY

[*]Marcia M. Rizzo [1, 2], Luci D.B. Machado [3], Paulo R. Rela [3], Yasko Kodama[3]

[1] MRIZZO Laboratório de Conservação e Restauração de Bens Culturais Ltda./SP
Rua Casemiro de Abreu, 191
04624-110 São Paulo, SP
mrizzo@mrizzo.com.br

[2] Instituto de Química da Universidade de São Paulo/SP
Av. Professor Lineu Prestes, 748
05513-9700 São Paulo, SP
mrizzo@mrizzo.com.br

[3] Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
prela@ipen.br
lmachado@ipen.br
ykodama@ipen.br

ABSTRACT

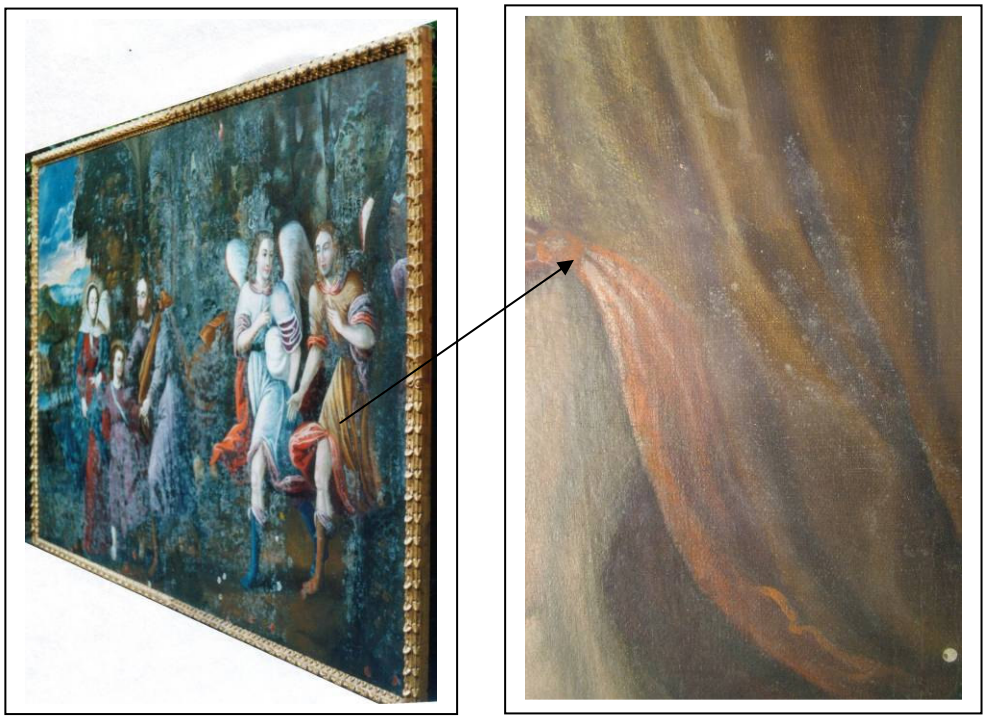
The aim of this work is to emphasize the importance of a previous study of the materials composition and behavior of any art work which will be treated by gamma radiation, as well as to use complementary procedures to prevent recontamination after the treatment, since this is a non residual method. As an example the object of study is a Peruvian painting from the 17th century, which has been restored, contaminated by mould, treated by gamma rays, put in a hermetic acrylic box and showed microorganisms growth after six years. A new treatment was performed using the same process and a complementary method using cloistering with anoxia atmosphere to prevent recontamination.
Before the first irradiation the influence of irradiation process on the original painting and on the materials used in the restoration process were investigated. These data were extremely important in the decision of the use gamma irradiation again on the same art work.
The results obtained allowed concluding that the irradiation with the recommended dose of 6.0 kGy (at the first time) was not sufficient to kill all the fungi specimens in the art work. On the other hand the irradiation with the dose of 6.0 kGy (at the first time) and 9.0 kGy (at the second time), according to the literature, would not damage the restored painting.

Keywords: Gamma radiation, biological 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. South America has a tropical climate with high temperature and relative humidity. Because of these conditions, it is very common to find artworks with a growth of mould. Microorganisms degrade and as consequence modify the aesthetical appearance of art work using it as a substratum [1]. For a special Peruvian painting from the 17th century, that had been restored, followed by a hard contamination of mould growing close to 70% of its area (Fig.1), the gamma irradiation was used as alternative for biological decontamination and conservation. The art work was treated and put inside a hermetic acrylic box.

Six years latter it showed the beginning of the fungi growth again and the treatment with gamma radiation was proposed once more. But a painting is a complex system made by successive layers, each one composed by a lot of different materials. And it is well known that gamma radiation can interact with the molecular structure of the material changing its characteristics, especially those related to the color of pigments and chemical and physical properties of the polymers.



(a) (b)

Figure 1. (a) 1st time contamination: fotography with raking light took in angle to show almost 70% of the Peruvian painting covered by fungi some time after restoration. (b) 2nd time contamination: detail of the painting, showing the beginning of a new fungi growth in the painting layer.

2. EXPERIMENTAL

2.1- Painting description:

Title: "Sacred Family with Angels"; author: attributed to Leonardo Flores; age: 17th century; dimensions: 1.9 m x 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. This painting was restored according to the appropriated procedures and materials.

2.2 -Painting restoration materials

Polymers: The polymers used in restoration processes were: (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. [2] [3].
Retouching paints: All retouching paints used were made of pigments plus acrylic resin medium from Lefranc & Borgeois and Maimeri.

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*. For more details of these procedures, see reference [4].

2.4- 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 [5] [6]. All retouching paints used in the restoration process were tested too. The colours wavelengths 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 AATCC (American Association of Textile Chemists and Colourists) Evaluation Procedure 1/Grey Scale for Colour Changing [4].

2.5- Thermal characterization of polymeric materials

All polymeric materials used in the restoration process were characterized 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 [4].

2.6- First time irradiation process

According to the literature, the appropriated gamma radiation dose to eliminate the identified micro-organisms 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 [7] [8].

Before the irradiation procedure, the art work was cleaned. All the apparent fungi residues were took out by mechanical process, just to rescue the aesthetical appearance of the artwork. Because it is well know that this procedure doesn't eliminate the infestation. The painting was put inside an acrylic box, hermetically closed in order to prevent recontamination after the irradiation. The acrylic box with the painting was accommodated in a wood box lined with expanded polystyrene (Fig. 2). This entirely system was irradiated.

Figure 2. The back side of the painting with acrylic protection inside of the wood box lined with expanded polystyrene being observed before the first irradiation.

2.7- Checking the acrylic box leakage

When the painting showed fungi colonies on the surface again, first of all the acrylic box sealing was checked.
The method used was: by a small role in the back side of the acrylic box, helium gas was forced inside and all perimeters susceptible of leakage were tested by a portable Sniffer probe, Leak Detector, Spectron 3000s, Edwards (Fig. 3).

Figure 3. Checking the leakage of helium gas from the acrylic box by a Sniffer probe.

The helium gas is weightless than oxygen and it is easier to it to escape if there is any passage. After the check up of the system leakage the acrylic box was opened.

2.8 - Second time irradiation process

The studies of the painting materials behaviour made before the first time irradiation allowed us to decide the properly second time dose gamma radiation. The new gamma radiation dose used was 9 kGy totalizing 15 kGy, under what some modification in pigments or in polymers was found [4].

Both the box and the painting were cleaned again. All the apparent fungi residues were took out by mechanical process. The painting was put inside the acrylic box again, hermetically closed in order to prevent recontamination after the irradiation. But at this time the atmosphere inside the box was changed. Two roles with controlled valves were made in the diagonal extremes of the back side of the box. By them, the argon gas was injected inside the box creating an anoxic atmosphere with positive pressure. This micro atmosphere without oxygen is not favourable for the growth of the kind of fungi found in the painting [9] [1]. The argon gas is heavier than oxygen, therefore it is expected that it is more difficult to any molecule of oxygen go into the box, if any leakage happens. The valves will permit the future maintenance of the modified atmosphere by a regular change of the argon gas.

All the irradiation process was repeated with the new dose selected. The painting was irradiated at the IPEN irradiator (Fig.4).

Figure 4. View of the outside of the IPEN irradiator.

3. RESULTS AND DISCUSSION

All detailed data of the investigation of the painting materials and the conservation materials used in the painting done before the first treatment can be found in the ref. [4] and are summarized in the two following paragraphs:

The comparisons of all pigments paint colour before and after irradiation are expressed as numbers in the "grey scale". In this scale, number 5 means no modification while number 1 means a great colour modification. No modification was found in any sample irradiated with 6 or 10 kGy. And little modification (between 4 and 5 in the scale) was found in some colours with 25 kGy. Therefore 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 [4].

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. The thermal behavior of the polymers used in the restoration process of the original picture was studied by TG as well as DSC.
By comparing the curves of the polymers before and after irradiation it can be observed that the radiation doses applied do not affect the properties of the materials studied. Therefore, there is no evidence of cross-linking promoted by the radiation [4].

The possible recontamination of the painting caused by some fail in the seal of the acrylic box was checked by a Sniffer probe and no leakage was found. The system was intact. There is no evidence of that some news specimens entered in the system to caused a new growth of the colonies.

4. CONCLUSION

The results obtained until now allowed concluding that the dose of 6 kGy do not killed all the fungi specimens in the painting. Since the fungi population was huge, probably some spore was not eliminated in the first irradiation process and germinated years later.
In addiction this experience showed how important is to perform a previous study of materials composition and behaviour of any object that will be irradiated. It showed also that a complementary way to prevent recontamination should be used, like a controlled atmosphere, since this is not a residual method. There is a limit to repeat this treatment because the quantities of the radiation doses in the same object are cumulative. For all these reasons it is very important to keep a detailed report with the art work for future conservations interventions.

On the other hand, the irradiation of the painting with dose of 15 kGy (6 kGy in the first time plus 9 kGy in the second time) 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.
However, since a painting is a complex system with a lot of interfaces, the authors are continuously studying the possibility of the irradiation molecular changing as a starting agent of a heterogeneous catalysis what could deteriorate the artwork at long term, in order to exclude as most as possible any induced deterioration mechanism.

ACKNOWLEDGEMENTS

To MSc. Anselmo Feher for the leakage measurements.

REFERENCES

1. M.M. Rizzo, (2008). "Physical-Chemical characterization of waxy sculptures materials from the Museum Alpino". Master Thesis, Graduate Program in Chemistry,IQ/USP, SP
2. G.A. Berger "Formulating adhesives for the conservation of paintings." In: *Conservation and restoration of pictorial art*. Brommelle and Smith (eds.), Butterworths-IIC, London, p. 169-181 (1976).
3. C.V. Horie, *Materials for conservation: organic consolidants, adhesives and coatings.* Hartnolls Ltd., Bodmin, Cornwall, (1996). (Reprinted).
4. M.M. Rizzo, L.D.B. Machado, S.I. Borrely, M.H.O. Sampa, P.R. Rela, J.P.S. Farah, R.I. Schumacher, "Effects of gamma rays on a restored painting from the XVIIth century", *Radiation Physics and Chemistry*, **63**, pp. 259-262 (2002).
5. G. Abad, "Green, red and yellow pigments in South America painting" (1610-1780), personal communication with the author (2000).
6. A. Seldes, J. E. Burucúa, M. S. Maier, G. Abad, A. Jáuregui, G. Siracusano, (1999). "Blue pigments in South America painting" (1610-1780), *JAIC*, Number **38** : 100-123
7. L.A. Belyakova "Gamma-radiation as a disinfecting agent for books infected with mould spores." *Microbiology*, **29**, 548-550 (1961).
8. M.G.C. Tomazello (1994). "A aplicabilidade da radiação gama no controle de fungos que afetam papéis". Doutor Thesis, IPEN-CNEN/SP, USP
9. C. Selwitz, S. Maekawa, (1998) *Inert Gases in the Control of Museum Insect Pests,* The J. Paul Getty Trust Ed.
10. G.. Magaudda (2004) "The recovery of biodeteriorated books and archive documents through gamma radiation: some considerations on the results achieved", *Journal of Cultural Heritage,* **5** 113–118
11. M. Silva, A.M.L. Moraes, M.M. Nishikawaa, M.J.A. Gattic, M.A.V. Alencard, L.E. Brandão, A. Nóbrega(2006) " Inactivation of fungi from deteriorated paper materials by radiation" *International Biodeterioration & Biodegradation,* **57** 163–167 Elsevier