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APPLICATION OF GAMMA RADIATION FOR RECOVERY OF PAPERS INFECTED BY FUNGI: CASE STUDY ABOUT SÃO LUIZ DO PARAITINGA

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ABSTRACT

The material studied in this work was flooded in the city of São Luiz do Paraitinga, SP, Brazil on January 2010 during a record flood suffered by the river that pass through the region. The documentary collection belonging to the City Hall underwent emergency drying and recovery treatments including irradiation with gamma rays to the destruction of various cellulosic fungi. Seven record books with many pages in blank and presenting severe fungal and mold infestation were provided by the Public Archive of the State of São Paulo, in charge of the damaged official documents, as samples for the present investigation on the effects of gamma radiation in the recovery and preservation of paper supported collections that are victims of biological contamination. This study represents a very rare possibility of working with a real object of actual use, which suffered a real disaster, and not with material prepared in laboratory and subjected to a forged flood situation.

1. INTRODUCTION

The documentary, bibliographical and artistic collections on paper support are usually constituted by a great diversity of materials. In its composition, there are mainly papers of different characteristics, related to the time of its manufacture and use.

At present, the main raw materials used for the production of printing and writing papers are pine or eucalyptus wood pulp, or the mixture of both. Fillers and additives are added to give specific characteristics to the various applications of contemporary papers.

Adequate methods of housing and access, environmental control, constant cleaning, correct packaging, use of suitable materials for exposure, air quality control, disaster prevention (floods or fire) are key elements for preservation of these kind of cultural heritage, as they help to prevent or to stop damages, prolonging the survival of these materials. However, collections are often exposed to inadequate conservation conditions for a variety of reasons, suffering from disasters such as wars, fires and floods, as well as periods of inadequate storage [1].

In Brazil, climatic characteristics, the lack of adoption of comprehensive integrated preservation policies and the lack of resources add up, leading the collections to face the many maintenance difficulties [2] and suffering irreversible losses. Due to the predominant tropical climate in most of the territory, which presents high temperatures and relative humidity (RH), one of the major problems encountered in the conservation of Brazilian cultural heritage is the prevention and control of contamination by microorganisms, insects and rodents [2].

Among the factors of degradation in cultural goods, fungal attacks occur with great incidence and are the ones that cause greater difficulties of combat and later control. It is observed that temperature conditions between 25ºC and 30ºC, relative air humidity greater than 70% - conditions present in most of the Brazilian territory - and pH between 4 and 6 favor the development of most fungi [3]. Fungi can occur in both acidic and alkaline papers [4].

All the cultural materials in general have a great diversity of nutritious elements for the development of microorganisms, by the different materials that compose them. Among these materials present in the collections, paper is one of the preferred substrates for the development of fungi because it is a rich source of nutrients and water [5]. Paper provides nutrients from carbonaceous sources of cellulose, chlorides, salts and adhesives. Fungi feed on these substances and grow, in conjunction with the conditions listed above. In this process, they excrete organic acids (oxalic, fumaric, acetic, lactic), enzymes, pigments, vitamins, amino acids, certain purines, toxins and other volatile organic compounds, which are deposited in the support. Cellulose undergoes chemical degradation by enzymatic oxidation or by acid hydrolysis and biodeterioration [1,5]. As a result, paper is physically and mechanically damaged.

In this sense, combating the fungi proliferation of paper can be accomplished through curative processes - chemical or otherwise - all of which present some difficulty or disadvantage in terms of effectiveness or implantation. The challenge, therefore, is to define a treatment that is effective in combating fungus contamination and that can be applied without compromise on the ethical issues involved in the preservation universe, especially those related to the maintenance of the maximum possible of the original characteristics of the present works in these collections. Cultural material must be recovered without being able to suffer more damages [6]. In this context, gamma ray processing has also been studied for combating infections in mobile cultural goods due to their efficiency in reducing the microbial.

The most appropriate immediate actions for the conservation of archival documents depend on three aspects [7]: removal of the cause of the deterioration; interruption of the process of destruction in progress; and retrieval of objects of cultural value in the sense of enabling them to perform in the sense of making them able to play their socio-cultural function again, the main motive of preservation.

In this context, the treatment with gamma rays has presented possibilities of efficient and comprehensive applications, although still controversial in the universe of the preservation of cultural goods, given the irreversibility of the process.

On the other hand, irradiation has been presented as the most efficient method to kill fungi, as it can eradicate spores much more efficiently than any chemical treatment considered toxic or even prohibited, freezing or anoxic atmosphere. The radiation dose should be sufficient to reduce the population of agents that cause biodeterioration to below the risk limit. Studies have reported that doses below 6 kGy are efficient for most fungal infections. Nevertheless, the negative effect such as depolymerization of the cellulose molecule does not significantly affect the basic properties of a good printing paper [7-9].

However, it should be emphasized that irradiation does not make the material sterile nor does it prevent recontamination of the collection by new infestations. Therefore, studies should consider the dose limit that the documentary and bibliographic supports could endure, especially if they need to undergo a new treatment, since the effects of radiation are cumulative.

The present work intends to study the effects of gamma rays irradiation process on samples of official documents paper based from the city of São Luiz do Paraitinga, São Paulo State, Brazil that had undergone a severe flood at January 2010 (Fig 1) and were contaminated by fungi in the sinister event, in order to study the recovery and preservation of national collections from biological contamination.

Fig.1: São Luiz do Paraitinga flood

This fact allowed the use of the material as a very rare source of research, for the investigative deepening in a real sample space and enabling the execution of destructive tests for paper characterization. Conducting destructive tests on archive documents, books, library or memorial collections is a fairly remote possibility for obvious reasons, since it is quite unusual to find material that allows this procedure, especially having passed through a real and therefore not a simulated event of flood.

So, this work aims to follow the surface changes of papers damaged by natural flooding at São Luiz do Paraitinga by colorimetric analysis before and after exposition to different gamma radiation doses.

2. MATERIALS AND METHODS

2.1 Materials

Blank paper sheets of seven books of records or minutes of the Public Prosecutor's Office from the city of São Luiz do Paraitinga, São Paulo State, Brazil were analyzed throughout this work (Fig.2). Few paper sheets of these books contain information stores on them but hundreds of sheets were blank. The removal of the blank sheets of these books was authorized by those responsible for their guard at the time, the Public Archive of the State of São Paulo - APESP.

The sheets containing written information were digitized, properly packaged, identified, and then returned to the Public Prosecutor's Office. This kind of book was commonly used in the twentieth century. The paper sheets of each book were made with the same technique and underwent the same flood damage, since they are bound together.

Fig.2: Books from the Public Prosecutor's Office after flood

2.2 Methods

2.2.1 Gamma radiation treatment of papers

The samples of paper were irradiated with gamma rays from a cobalt-60 source, in the compact multipurpose irradiator at the Radiation Technology Center - CTR, Institute for

Nuclear and Energy Research, National Nuclear Energy Commission, IPEN- CNEN, Brazil.

Based on the previous fungi identification results, the doses of 8 kGy, 16 kGy and 25 kGy were determined, controlled by dosimeters. The minimum dose was established based on the most radioresistant fungus identified in the samples, and the maximum dose predicts the need for a new irradiation in case of the papers recontamination. The initial samples, taken as references, were irradiated with consecutive dose ranges to complete 8 kGy, 16 kGy and 25 kGy.

2.2.2 Determination of color and brightness

For color and brightness measurements, a BYK Spectroguide portable spectrophotometer and Sphere Gloss meter with simultaneous index of brightness at 20° was applied. These measurements were taken on mud and black and purple fungal patches in initial samples and samples irradiated with several doses in the range from 8 kGy to 25 kGy. The studied spots were selected in not patterned area, to avoid the interference of the color of the lines on the result of color parameters. Additionally, the stains were as homogeneous as possible. Such criteria, which are necessary for a coherent and precise measurement, have greatly limited the number of possible areas of measurement. Mud stains and fungi were classified qualitatively in intense, medium and low intensity (Fig.3). The color is represented by three-dimensional coordinates CIELab system (ASTM D2244-11) that consists of a grey axis L* (lightness from L*= 0 corresponding to black and L*= 100 related to white color), a* axis from red (+a*) to green (-a*) and b* component from yellow (+ b*) to blue (-b*) coloration. The brightness measure, G, was made according to ASTM D2457-08.

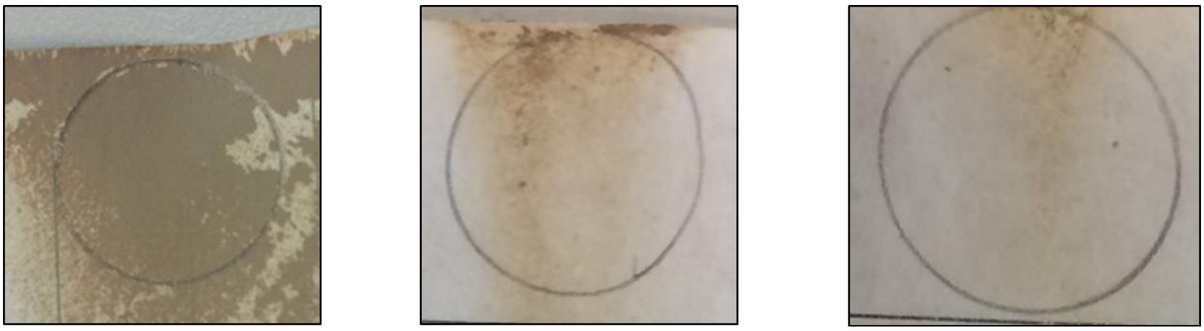

Fig.3: Intense, medium and low intensity mud stains

3. RESULTS AND DISCUSSION

Gamma rays irradiation is considered a cold treatment and can be applied in thermosensitive materials such as paper. The irradiated material does not require quarantine. Radiation has high penetration power, ensuring the processing of objects that contain cavities of difficult permeation or access to gases, such as books. It is effective in combating fungi because it also eliminates spores.

In the present work, previous results from identification of the fungi genera present in the flooded samples of paper were considered. The identified genres were: *Aspergillus* spp, *Penicillium* spp, *Nigrospora* spp, and *Trichoderma* spp. *Aspergillus* and *Penicilium* present similar radioresistance, and greater than that of *Trichoderma* and *Nigrospora*, at any stage of growth and development. The dose considered as the reference for decontaminating treatment with gamma radiation applied a fungi infected paper is 6 kGy [8]. Based on this information, the dose of 12 kGy to be applied in the samples was defined. As one of the objectives of the work is "to study the process of irradiation with gamma rays, characterizing their effects on paper, with a view to the recovery and preservation of national collections victims of biological contamination" and also to analyze the need of new irradiation treatment, it was decided to double the reference dose to evaluate the resistance "limit" of the paper that went through a real incident, defining it, as stated above, at 12 kGy.

The gross results of the color readings were tabulated by books and respective doses, for the calculation of delta E and delta G, which is the quantity that allows quantifying the differences between colors and brightness, respectively, for each spot after irradiation with different doses of absorbed radiation.

The average of measured color data are shown in table 1.

Table 1 Color measurements

	Non-irradiated			8 kGy				16 kGy				25 kGy			
Stain	L*	a*	b*	L*	a*	b*	ΔE*	L*	a*	b*	ΔE*	L*	a*	b*	ΔE*
Purple	86.9	-0.12	0.60	91.5	-0.20	0.65	0.72	86.5	0.09	1.08	1.10	85.9	-0.66	1.55	1.95
Mud	84.4	2.04	12.83	83.4	1.64	12.65	1.93	83.5	1.62	12.96	1.93	84.1	1.67	12.69	1.71
Black	91.2	0.45	4.41	89.3	0.19	4.10	1.81	89.3	-0.05	6.49	2.01	88.4	0.78	6.94	2.26

Note: The figures presented in table 1 are results of the average of data obtained.

The values of a* (green-red) present a very small tendency to change to the red color as the dose increases. The exception occurs in purple stain, which follows the inverse of this trend by going to the green axis.

The data of b* (blue-yellow) show a similar behavior, indicating very slight yellowing as a function of to the increasing of gamma radiation dose. However, some results sometimes follow a tendency for blue, sometimes for yellow.

The values of L* (lightness) did not show significant variation in any of the applied doses, demonstrating that the radiation did not alter the properties related to darkening or bleaching of the analyzed spots.

ΔE* defines the total color difference among the 8 kGy, 12 kGy and 25 kGy doses and the non-irradiated samples, respectively. Results have shown that no significant variation in color occurred.

The average of G* results are presented in table 2, as a function of gamma rays absorbed doses.

Table 2 Average brightness data (G)

Stain	NI	8 kGy	16 kGy	25 kGy
Purple	2.90	2.93	2.95	2.93
Mud	2.31	2.37	2.41	2.43
Black	3.06	3.11	3.14	3.07

The same discussion from L* (lightness) data can be applied to G* (brightness), indicating that the radiation did not alter the brightness properties.

4. CONCLUSIONS

The results obtained by the L *, a *, b * and G * readings at the specified doses in all books showed minimal changes in stain colors.

The mud spots were those that presented a slightly larger alteration than those of purple or black fungus, although notably reduced. The radiation application process did not degrade them significantly.

Mold stains also showed insignificant changes in the various doses applied. Such stains are results of the mold metabolism, when it excretes pigments, among other products. In this way, regardless of whether or not the fungi are active or alive, the paper will remain stained. Gamma radiation from Co-60 was not able to alter the studied pigments even when applied at the 25 kGy absorbed dose.

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