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RADIOSTERILIZATION OF HISTORICAL DOCUMENTS: THE POTENTIAL EFFECTS OF GAMMA IRRADIATION ON PAPER AND PRINTING INKS

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ABSTRACT

The controlled exposition to gamma radiation is a physical process which can be used for the preservation and recovery of historical documents. Depending on the intrinsic characteristics of the material to be treated, it is necessary to research and stablish, from time to time, the optimum dose rate and total dose, the conditions to eliminate or reduce the biological threat, the equipment and its logistics, the economic aspects and any other impact caused by radiation on the material to be treated. The references indicate that through research it is possible to consolidate the knowledge about gamma radiation emitted from ^{60}Co in order to completely remove or at least greatly reduce infestation by insects or biodeterioration microorganisms. On this work we have used a MDS Nordion self-contained ^{60}Co research irradiator, model Gamacell Excel 220, at Postgraduate Institute of Engineering and Research Alberto Luiz Coimbra, in Rio de Janeiro Federal University. The analysis of the samples submitted to controlled thermal dry aging and to gamma radiation made possible to verify the differences between treated and untreated samples. The results of the chromatic measures indicate that, with the optimum total dose, the gamma radiation treatment does not significantly alter the properties of paper or printing inks. This way, it is possible to conclude that even though the gamma irradiation of historical documents is a complex procedure which demands a detailed study in order to assure its safe application, it is environmentally safer than the use of chemical pesticides.

1. INTRODUCTION

The irradiation technology is being used for a great range of duties from food preservation to medical instruments sterilization and military biothreat decontamination, as for the preservation of cultural heritage which is the scope of this work. According to Butterfield [4], the controlled exposition to ionizing radiation is a physical process which can be used to disinfect, decontaminate, sterilize, preserve or enhance the characteristics of many materials.

The recovery of different materials infected by live organisms through the use of ionizing gamma radiation is being studied throughout the world and it is responsible for the authorization and startup of commercial irradiation facilities. According to Magaudda [7], it is very important that the materials to be treated have known properties, being necessary to study and stablish, from time to time, the right total dose and dose-rate, and the conditions to eliminate and/or reduce the quantity of dangerous microorganisms. It is also important to establish the complexity and logistics of the necessary equipment, the economic aspects and to which extent eventual structural modifications to the treated material can be tolerated.

The research on ionizing radiation applied to books and paper dates back to the 60's, when the resistance to radiation of most types of microorganisms was tested in a context of conservation of materials with cultural value [7]. The deepening of the studies on possible applications of the irradiation technologies for books disinfection suffered a long time lapse due to the popularization of treatments of chemical nature, especially the gaseous fumigation with ethylene oxide, which is efficient against microorganisms and insects [7]. This treatment proved to be affordable and of easy execution.

Through the years, though, the use of these gases proved to be harmful to human health, consequently the technique of gaseous fumigation was banned from many countries turning the ionizing radiation treatment interesting again and promoting new evaluations and the interest of specialists.

Adamo [2] says that through research it is possible to consolidate the knowledge in ionizing gamma radiation emmited from ^{137}Cs or ^{60}Co sources as a path to completely remove or at least significantly reduce the types of degradation on paper known as biodeterioration caused by insects and microscopic fungi.

The results obtained by Butterfield [4], Adamo [2] and Magaudda [7] lead to the conclusion that the ionizing radiation treatment is very efficient on disinfestation against insects and disinfections against microfungi. By the use of the right total dose, so that the mechanical and physical properties of pure cellulose, paper or printing inks do not be significantly affected, it is possible to reduce the vulnerability of these materials to infestation or infection by biodeterioration agents.

Considering that the total dose and its efficiency are linked to the type of material to be treated, it is important to note that the use of the word "sterilization" does not fit adequately, in its place should be used the concept of quantity reduction of biodeteriorating agents below the risk line and, in any way, this reduction should be compatible to the place where the treated materials will be kept after the procedure. As books and documents can be kept and used in non-sterilized places, it better to use the word "recovery" instead of sterilization or disinfection. This way, even smaller total doses should be used eliminating any fear of possible effects induced by gamma irradiation [7].

In Brazil, the Nuclear and Energy Research Institute (IPEN) from the National Nuclear Energy Commission (CNEN) is the only institution which works with conservation of materials with cultural values on a regular basis, utilizing its ^{60}Co multiproposal irradiator [6]. Others institutions have the potential to research gamma irradiation procedures for fine arts and cultural heritage preservation, with adequate installations and availability of specialists to develop this field of knowledge thus reducing costs in the recovery of books and papers of historic interest.

2. MATERIALS AND METHODS

2.1. Paper samples

Fourteen blocks, with ten sheets each, of standard print paper, size A4 (210 x 297 mm) and 75g/m^2 grains. Twelve blocks were colored printed in a multifunctional equipment brand Ricoh, model Aficio MP C2050 with maximum print resolution of 1200x1200 dpi, in the following colors: cyan (RGB 0,255,255), magenta (RGB 255,0,255), yellow (RGB 255,255,0) and black (RGB 0,0,0).

All the blocks were cut in the same direction to size A6 (105 x 148 mm). The resulting samples were submitted to the following conditions before the chromatic measurements:

i. Control; no treatment.
ii. Gamma irradiation; samples submitted to a total dose of: 0.5; 2.0; 5.0; 10.0 and 15.0 kGy.
iii. Aging; samples submitted to accelerated dry aging for three days (72 h) according to ABNT NBR 14915 (2002) standard.
iv. Gamma irradiation and aging; samples submitted to treatment ii were cut to size A7 (74 x 105 mm) and the resulting samples were submitted to treatment iii.

In all situations the samples were kept in sealed metalized envelopes in order to avoid possible photodegradation.

2.2. Gamma irradiation

Gamma radiation ($6x10^{-3}$ nm to $3x10^{-5}$ nm) is a type of electromagnetic energy with very high frequency ($5x10^{19}$ Hz to 10^{22} Hz) [8]. As a consequence, the radiation affects the atoms which compose the molecules resulting in its excitation or ionization due to this energy increment. In this excited state the molecule produces a multiplying effect causing widespread excitation and ionization. At this time two effects may occur: the excited molecule may dissociate into free radicals or split in two molecules. The free radicals may promote chemical alterations while reacting with other molecules or other radicals in order to form new substances. But, if the radicals recombine, there will be no alteration of chemical order. Even so, radicals can recombine into hydrogen peroxide, a strong oxidizing agent which may promote reactions which, in the case of paper, results in carboxyl groups' formation in cellulose, contributing for its degradation.

Magaudda [7] also suggests that the basic properties of paper are not significantly changed in the case of total doses under 10 kGy. There are divergences which can be explained by dose-rate considerations as the longer the irradiation duration, higher the possibility of interaction with the surrounding oxygen leading to indirect damage. This way, the higher the dose-rate, the lower will be the risk of alteration on paper properties [7].

2.2.1. Irradiator 1 - UFRJ / COPPE

The site of Postgraduate Institute of Engineering and Research Alberto Luiz Coimbra, in Rio de Janeiro Federal University (COPPE/UFRJ) counts with a MDS Nordion, model Gamacell

Excel 220, self-contained ^{60}Co research irradiator. Currently its 1.2 kCi sources provide a maximum gamma dose-rate of 0.83 $kGy.h^{-1}$ in a cylindrical irradiation chamber with a diameter of 15.5 cm and 20.5 cm high. The gamma source consists of 48 cylinders, 21 cm high, containing doubly encapsulated cobalt disposed circularly around the irradiation chamber. An eletromechanic system on the top of the equipment moves the sample inside the irradiation chamber which remains static. The last dosimetric mapping was done in 2005 and indicated a homogeneous distribution of dose rate with variations of ±4% [5].

This way, it was possible to proceed the irradiations for the necessary time in order to reach the proposed total dose for each sample according to the following table:

Table 1: Exposition time for each sample in Irradiator 1.

Sample	Irradiation time (min)	Total irradiation time (min)	Total Dose (kGy)
1	36,1	36,1	0,511
2	(1) + 108,4	144,5	2,047
3	361	361	5,114
4	722	722	10,23
5	(3) + (4)	1083	15,34

2.3. Accelerated dry aging

Exposition of paper to aggressive environments, such as high temperature for a period of hours, may support info about physical or chemical alterations to the structure of paper which normally would take years to occur in standard conditions.

According to Butterfield [4], the degradation of cellulose is very sensible to humidity. Comparing the accelerated aging with the natural aging indicates that a certain amount of humidity is necessary. This way, the accelerated dry aging is much less sensible than the accelerated aging in a humid environment. Though, the accelerated dry aging is simpler to be done and it was considered sufficient to indicate variations after different treatments.

This way, the accelerated dry aging was done at 105ºC±0,1ºC according to ABNT NBR 14915 standard, using an oven with vent circulation, brand Ethik, for 3 days (72h). The samples were put inside the oven at 24,7º C and 62,7% of relative humidity, than it was stablished a $5ºC.min^{-1}$ temperature ramp. After 72h the relative humidity had stabilized and downed to 47,8%.

2.4. Chromaticity measures

The aging of cultural heritage with paper in its composition occur due to cellulose degradation resulted from the action of external agents such as: humidity, UV radiation, pollutants and microorganisms, normally acting at the same time. The process of degradation may be summarized as a combination of two correlated chemical reactions, the acidic hydrolysis of the glycosidic chains in cellulose, which reduces the length of the polymeric chain resulting in a loss of mechanical resistance. And the oxidation of cellulose with the subsequent development of various by-products. Among these oxidation by-products are the carbonyl groups responsible for the yellowish color of aged paper.

The yellowish color seen on aged paper is mainly caused by the presence of chromophores in cellulose which absorbs in the highest portion of the visual specter (the blue and violet region) reflecting the yellow and red portions.

To verify the color differences between samples, the histograms of each channel (Red, Green, and Blue) were analyzed. Each of these colors has its tonal band individually defined while the RGB histogram represents the sum of all bands.

In image processing the data processed are shades of grey (digital numbers or DNs) correlated with the pixels of an image. The histogram is one of the most common ways to represent the distribution of DNs in an image, and possibly the most adequate in digital image processing. It represents the information about how many pixels each possible value of DN may have (which varies from 0 to 255 in an 8 bit image), or which proportion of the image corresponds to each value of DN [9].

Histograms are known as Probability Density Function (PDF). And that means that, statistically, the histogram represents the probability to find a DN of a specific value in the image [9].

Another important point is that histograms represent digital data also called discrete. This way, the distribution of intensities is represented by discreet columns, which cannot be broken or divided, and represented by whole numbers (in opposition to fractional numbers). This concept assumes true importance when it needed to operate with contrast in images [9].

When working with an image histogram it is possible to instantly observe some of its characteristics. The shape of the histogram gives info such as the average intensity and the scattering of DN values; the last giving the magnitude of the contrast: the more scattering takes place along the DNs axis, higher the contrast in an image [9].

The chromaticity measurement was done using a “mask” of 37 mm x 105 mm in black A4 paper, where the sample to be analyzed was positioned. This configuration aimed to stablish a standard measure in all histograms avoiding the possibility of interference by the equipment due to lamp luminosity variations.

This way, the chromaticity measurements were done using HP Photosmart C4480 multifunctional equipment with a maximum scanner resolution of 1200x1200 dpi and converting the images into histogram with Image J software, version IJ 1.46r as shown in figure 1. Following that, the digital data was opened with Peak Fit software, version 4.11, in order to read and quantify each band in two distinct sectors: from 50 to 150 pixels stablishing the control mean value in each image; and from 350 to 450 pixels, which is the sector of interest in the analysis of contrast.

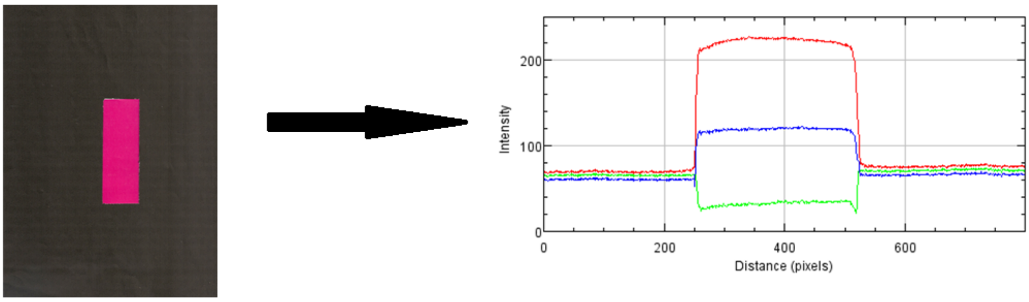

Figure 1 – Composition of the magenta sample (irradiated at 10 kGy in irradiator 1) with its following histogram. The ordinate varies from 0 to 255, and shows the intensity of the contrast in each band. The abscissa shows the quantity of pixels in each image.

3. CALCULATIONS

To determine if there is a significant difference between the results of chromaticity in the samples submitted to gamma irradiation with (IV) and without (II) accelerated dry aging, compared to the untreated control sample (I), the linear regression equation of the graph shown in figure 2 was obtained, where the ordinate varies with the intensity of the relative contrast in each band, and the abscissa varies with the total dose (in kGy) to which the sample was submitted.

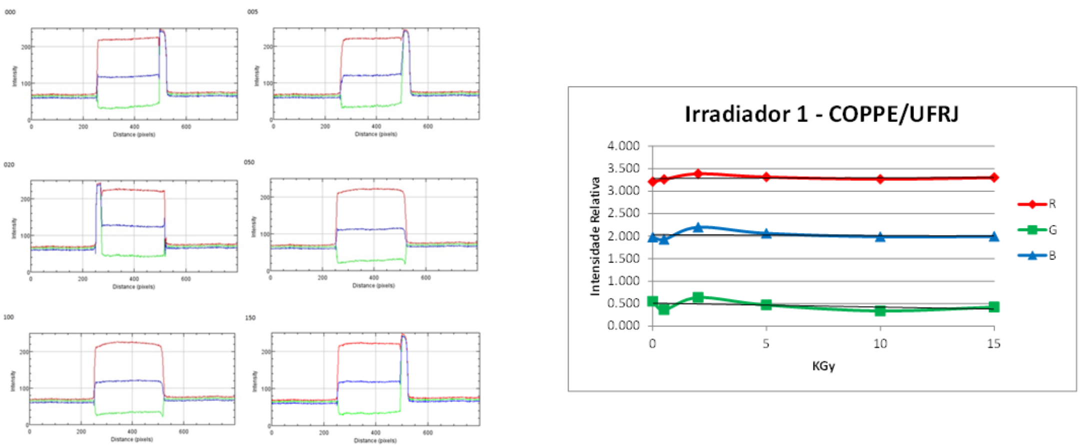

Figure 2 – Composition of all histograms of magenta samples (irradiated in irradiator 1) with the following composition graph where the ordinate shows the intensity of the relative contrast, and the abscissa shows the total dose to which the sample was submitted.

The value of intensity of the relative contrast for each sample submitted to a determined total dose was calculated as the mean value of contrast in each band from 350 to 450 pixels divided by the mean value of contrast in the respective band in the reference sector (from 50 to 150 pixels), through the following Equation 1:

$$I_R = \frac{\bar{I}_{350:450}}{\bar{I}_{50:150}} \tag{1}$$

Where:

I_R = the value of intensity of the relative contrast
$\bar{I}_{350:450}$ = the mean value of contrast in each band from 350 to 450 pixels
$\bar{I}_{50:150}$ = the mean value of contrast in the reference area from 350 to 450 pixels

This way, the lowest the value of the slope, smaller the contribution of gamma radiation in the variation of contrast for a specific color in each of the three bands.

4. RESULTS AND DISCUSSION

In all cases the chromatic measurement of paper samples was divided in two blocks: non irradiated and irradiated samples not submitted to accelerated dry aging, with its linear regression equations for each band shown in table 2; and non-irradiated and irradiated samples submitted to accelerated dry aging, with its linear regression equations for each band shown in Table 3.

Table 2 - The linear regression equations of the graphs obtained for each color, of non-irradiated and irradiated samples not submitted to accelerated dry aging.

COLORS	R	G	B
YELLOW	y = 0.0016x + 3.611	y = 0.0011x + 3.6871	y = 0.0009x + 0.1205
WHITE	y = 0.0007x + 3.6861	y = 0.0007x + 3.8485	y = -0.0003x + 4.1844
CYAN	y = 0.0014x + 0.189	y = -0.0026x + 2.1878	y = -0.004x + 3.4064
MAGENTA	y = 0.0015x + 3.2803	y = -0.0087x + 0.5094	y = -0.0019x + 2.0323
BLACK	y = -0.0118x + 0.6014	y = -0.0112x + 0.6518	y = -0.0112x + 0.6736

Table 3 - The linear regression equations of the graphs obtained for each color, of non-irradiated and irradiated samples submitted to accelerated dry aging.

COLORS	R	G	B
YELLOW	y = 0.0011x + 4.4972	y = -0.003x + 4.6693	y = 0.0008x + 0.3844
WHITE	y = -0.0004x + 5.2186	y = -0.0017x + 5.684	y = -0.0064x + 6.8984
CYAN	y = -0.0002x + 0.2082	y = -0.0089x + 2.6244	y = -0.0146x + 3.9431
MAGENTA	y = 0.0084x + 4.2978	y = 0.0023x + 0.8482	y = -0.0057x + 3.0712
BLACK	y = -0.0111x + 0.9084	y = -0.011x + 1.0006	y = -0.0086x + 1.0657

From the results shown in Tables 2 and 3 it can be seen that gamma irradiation alone does not result in color alteration of all the samples tested. A more significant alteration in the sample printed in black indicates a slightly higher loss of contrast both in samples submitted or not to accelerated dry aging, but this alteration is still marginal.

From the results shown in Table 4 it can be seen that accelerated dry aging caused severe alterations in contrast. It should be specially noted the 329.47% difference in the blue band of the yellow samples and the 65.11% difference also in the blue band of the white samples. This alteration indicates the presence of chromophores in cellulose absorbing in the highest portion of the visual specter and, thus, giving the characteristic yellowish color of aged samples.

Table 4 – Comparison of the value of intensity of the relative contrast between non irradiated samples.

	R	G	B
YELLOW			
I	3.613	3.687	0.104
III	4.494	4.682	0.447
difference	24.39%	26.99%	329.47%
WHITE			
I	3.688	3.848	4.182
III	5.222	5.689	6.904
difference	41.62%	47.83%	65.11%
CYAN			
I	0.193	2.249	3.442
III	0.210	2.672	3.985
difference	8.64%	18.77%	15.77%

MAGENTA			
I	3.207	0.551	1.974
III	4.162	0.802	3.043
difference	29.77%	45.55%	54.18%
BLACK			
I	0.580	0.629	0.651
III	0.906	0.999	1.064
difference	56.35%	58.82%	63.51%

Control I – no treatment. Treatment III – accelerated dry aging.

5. CONCLUSIONS

The damage originated by accelerated dry aging was much larger than that induced by gamma irradiation.

Irradiated and control samples experienced similar damage when subjected to accelerated aging.

No synergistic effects were observed between irradiation and aging.

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