Radiation Physics and Chemistry 125 (2016) 21–26

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Effects of gamma irradiation on deteriorated paper

Marina Bicchieri [a,*], Michela Monti [a], Giovanna Piantanida [a], Armida Sodo [a,b]

[a] Chemistry Dpt. Istituto centrale restauro e conservazione patrimonio archivistico e librario, Via Milano, 76-00184 Roma, Italy
[b] Dip. Scienze. Università Roma Tre Via della Vasca Navale, 84-00146 Roma, Italy

HIGHLIGHTS

- γ-rays irradiation has been proposed to treat cultural heritage objects on paper.
- The effect of low dose γ-rays on paper was investigated.
- Chemical and spectroscopic techniques were used to evaluate the induced modifications.
- Results showed a noticeable degradation of the paper support after irradiation.
- The application to cultural heritage artefacts on paper seems inadvisable.

ARTICLE INFO

Article history:
Received 26 February 2015
Received in revised form
12 February 2016
Accepted 9 March 2016
Available online 10 March 2016

Keywords:
γ-rays
Conservation
Paper
Cultural heritage

ABSTRACT

Even though gamma radiation application, also at the minimum dosage required for disinfection, causes depolymerization and degradation of the paper substrate, recently published papers seemed, instead, to suggest that γ-rays application could be envisaged in some conditions for Cultural Heritage original documents and books. In some of the published papers, the possible application of γ-rays was evaluated mainly by using mechanical tests that scarcely reflect the chemical modifications induced in the cellulosic support. In the present article the effect of low dosage γ-irradiation on cellulosic substrates was studied and monitored applying different techniques: colorimetry, spectroscopic measurements, carbonyl content and average viscometric degree of polymerization. Two different papers were investigated, a non-sized, non-filled cotton paper, and a commercial permanent paper. To simulate a real deteriorated document, which could need γ-rays irradiation, some samples were submitted to a hydrolysis treatment. We developed a treatment based on the exposition of paper to hydrochloric acid vapors, avoiding any contact of the samples with water. This method induces a degradation similar to that observed on original documents.

The samples were then irradiated with 3 kGy γ-rays at a 5258 Gy/h rate. The aforementioned analyses were performed on the samples just irradiated and after artificial ageing. All tests showed negative effects of gamma irradiation on paper. Non-irradiated paper preserves better its appearance and chemical properties both in the short term and after ageing, while the irradiated samples show appreciable color change and higher oxidation extent. Since the Istituto centrale restauro e conservazione patrimonio archivistico e librario is responsible for the choice of all restoration treatments that could be applied on library and archival materials under the protection of the Italian State (http://www.icpal.beniculturali.it/allegati/DM-7-10-2008-Istituto.pdf), it has been evaluated that the modifications induced by γ-rays irradiation are not acceptable as safe conservation treatment (http://www.icpal.beniculturali.it/allegati/Nota_uso_raggi_gamma.pdf).

1. Introduction

Biodeterioration of paper materials is caused by bacteria, fungi and protozoa and, to a smaller extent, by insects and rodents. Library and archival materials may suffer particularly from fungi and insect attack. Preventing and inhibiting their action on paper is a major task in library and archives preservation. Developing new and optimizing existing treatment methods is an ongoing task in conservation science.

* Corresponding author.
E-mail addresses: marina.bicchieri@beniculturali.it (M. Bicchieri), ic-rcpal.chimica@beniculturali.it (M. Monti), ic-rcpal.chimica@beniculturali.it (G. Piantanida), ic-rcpal.chimica@beniculturali.it, sodo@fis.uniroma3.it (A. Sodo).

http://dx.doi.org/10.1016/j.radphyschem.2016.03.005
0969-806X/

Gamma radiation application for paper disinfection purposes has long since been studied (Horio et al., 1963) and long since it has been observed that, for doses strictly above 1 kGy, the treatment induces an immediate strong depolymerization, much more pronounced than the one induced by an accelerated ageing that alternates cycles of controlled temperature and humidity (80 °C, 65%RH) to cycles of ageing under vacuum at ambient temperature (Calvini and Santucci, 1978–1979). Considering that a satisfactory disinfection only happens at irradiation about 5 kGy, the treatment was found unadvisable for paper. However, due to wide range of radiation application in medical sterilization and food disinfestations, the question was reopened in the last decades (Sinco, 2000) and a number of other experiments have been carried out. As far as high dosages effects are concerned, it has been demonstrated by a thorough chemical analysis that serious depolymerization and oxidation is originated on pure cellulose paper and that scission route can be expressed directly as a function of each radiation beam energy (Bouchard et al., 2006). An experiment on gamma irradiation of paper at 1–5 kGy (Adamo et al., 2001) demonstrated depolymerization of cellulose above 2 kGy. However, the same authors reported a possible usage of radiation at 2 kGy, for already damaged paper, since other parameters (pH, tearing resistance, folding endurance) were found not to vary significantly for that dose.

Recent literature (Otero D'Almeida et al., 2009; Choi et al., 2012; Moise et al., 2012; Nunes et al., 2012; Area et al., March 2014; Michaelsen et al., 2013; Negut et al., 2012) reports positive results in the use of γ rays for library materials conservation. The problem we always remarked in many papers is related to the use of few chemical data but mechanical, optical or biological tests to substantiate the validity of γ rays treatment.

It is to underline that during the first ageing stages -natural or accelerated- there are no significant variations in mechanical properties: degradation evidence is only provided by measuring chemical processes (Porck, 2000; Bicchieri et al., 1993). Oxidation and depolymerization induced by the treatment, in fact, cause carbonyl and carboxyl groups formation, with great impact on paper permanence and durability, even if mechanical characteristics are not affected in the short term.

A paper hosted on Restaurator (Adamo et al., 2007) reports the mechanical, optical and biological evaluation on γ rays effects on the same papers analysed in the present work and chemically pretreated at ICRCPAL (Istituto centrale restauro e conservazione patrimonio archivistico e librario; Istituto Centrale Patologia del Libro -ICPL- at that time) chemistry laboratory using a method developed at our laboratory (hydrolysis induced by HCl vapors as reported in Ref. 17).

In a first moment we decided not to publish our data, supposing that the treatment with γ rays would have been not taken into account by library heritage conservators. We see now the rise of many articles on this topic. Therefore, we decided to add our opinion on the debate.

In our paper, we analyse the chemical and physical effects of γ rays, not only on not-treated papers, but also on pre-hydrolyzed samples, that should simulate an original damaged document. The experiment includes both irradiated and non-irradiated papers and studies them along ageing, by means of chemical, optical and spectroscopic measurements.

2. Materials and methods

2.1. Samples and treatments

Two kinds of paper were used:

- Whatman paper CHR 1 (pure cotton paper, ash-free, not sized)
- Permanent paper manufactured by Cartiere Miliani Fabriano S.p.A. which composition is reported in Table 1 (additives percentage are referred to the weight of the fibrous materials).

Table 1
Permanent paper composition (additives percentage are referred to the weight of fibrous materials).

Bleached sulfite softwood	8.0%
Bleached soda softwood	37.0%
Bleached soda hardwood	55.0%
Calcium carbonate	18.0%
Starch	4.0%
AKD (alkyl ketene dimer)	0.2%
Optical bleacher from stilbene	0.2%
Sodium chloride	0.3%

To obtain samples that would simulate original documents damaged by acids, some papers were exposed to hydrochloric acid (37%) vapors for 20 min then let dry at room temperature. This treatment does not simulate an ageing treatment, but the "original" conditions in which we often find the documents.

Three examples of chemical data on original documents can be found in Table 5

Each group of samples (hydrolyzed Whatman; permanent paper hydrolyzed and untreated) was divided in two portions, one of which underwent to gamma irradiation while the other remained untreated. We report, for comparison, the data obtained from paper made of pure cotton untreated (Whatman) about which, moreover, there is a large amount of literature (Horio et al., 1963; Calvini and Santucci, 1978–1979; Bouchard et al., 2006; Adamo et al., 2001).

The irradiation of paper was carried out at the "Calliope" plant of ENEA (Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile) in its Research Center in Casaccia (Rome), during the same experiment and on the same samples reported in Ref. 17. The chosen dose of radiation declared by ENEA staff was 3 kGy at a 5258 Gy/h rate.

The prepared samples were artificially aged in a climatic chamber at 80 °C and 65% R.H. for 12 and 24 days, according to ISO 5630/3 (ISO 5630/3, 1996).

2.2. Analysis procedures

A Minolta CHROMA METER CR-221 was used to obtain L*a*b* coordinates(ASTM E1347-06, 2011). The color distance parameter $\Delta E=(L^{*2}+a^{*2}+b^{*2})^{1/2}$ expresses the geometric distance of two points in the CIELAB space. Color variation appreciated by human eye corresponds to $\Delta E \geq 4$.

In order to provide insight and a better interpretation of the observed color variation on permanent paper, a series of optical measurements of reflectance R and transflectance T_F (Edwards et al., 1961; ASTM E903-E996) (reflectance R plus transmittance T, measured on the sample suspended in a Spectralon™-Labsphere integrating sphere) was executed in the UV–vis-NIR range (200–1800 nm), both immediately after the irradiation and after accelerated ageing.

The tests were executed with a Varian Cary 5 with a resolution of 1 nm in the visible spectrum and 3 nm in the Near Infrared (NIR).

On the basis of the reflectance spectra we decided to carry out a series of tests using the transflectance technique that is the stimulation and measure of the visible radiation on samples suspended in the center of an integrating sphere. Working in that way allows collecting entirely the radiation, both transmitted and reflected by the sample, so that it is possible to collect spectra directly and quantitatively correlated to the optical density OpD and

consequently to the absorption of the sample.

The degree of polymerization was measured by extrapolating the intrinsic viscosity [η] from the values of relative viscosity $[\eta]_{rel}$ at zero concentration, according to ASTM D1795 (ASTM D1795-13, 2013).

The average viscometric degree of polymerization (DP) was obtained from Mark-Houwnik Eq. (1):

$$[\eta] = k_\eta DP_\nu^\alpha \quad (1)$$

where k_η and α are constants characteristic of each polymer.

For the cellulose they are (Immergut et al., 1953):

$\alpha = 0.905$ (independent from DP value) and
$k_\eta = 8.07\ 10^{-3}$ for DP up to 300;
$k_\eta = 6.4\ 10^{-3}$ for DP between 300 and 3000.

Each sample was prepared by removing portions of paper from different areas of the sheet. The pieces were then cut in pieces of approximately 1 mm^2 and mixed until complete homogenization.

To measure the carbonyl content we used a method, developed in our laboratory of chemistry (Immergut et al., 1953), based on the redox reaction between carbonyls and 2,3,5-triphenyl-2H-tetrazolium chloride (TTC), after alkaline hydrolysis of the cellulose. The reaction consists in the reduction of TTC to red triphenylformazan, while carbonyl groups are oxidized to carboxyl groups. The amount of formazan formed is directly proportional to the amount of carbonyl groups present, and it is spectrophotometrically determined at 480 nm.

3. Results and discussion

The artificial ageing modifies the chemical and physical properties of the samples. The γ irradiation can induce a further modification that should be extrapolated from the superposition of the two treatments, i.e. ageing and irradiation. To evaluate the last effect we compared the hydrolyzed samples irradiated with those not irradiated at each ageing conditions and the not hydrolyzed not aged samples, irradiated and not, with those aged for 24 days.

3.1. Color change

The chromaticity coordinates L*a*b* identify unambiguously a color. During paper degradation, color changes can happen, that can be exactly quantified by measuring L*a*b* variation.

The results of color coordinates are reported in Table 2. Results are the arithmetic mean of 20 measurements on each sample.

It is evident that gamma rays cause a color variation, even in the short term, which is definitely more pronounced on the pure cotton cellulose paper.

The hydrolyzed irradiated Whatman samples show a color change toward yellow easily appreciable after 12 days of accelerated ageing, whereas the untreated series vary their color only after 24 days of ageing. The permanent samples modify their color to a greyish hue.

On the hydrolyzed permanent papers, the distinction between the two series is somehow more difficult due the fact that hydrolysis affects all components: cellulose, fillers, brighteners and sizes and the data along ageing are compatible.

Regarding the non-hydrolyzed permanent paper, the irradiated samples seem to vary their color more quickly than the non-irradiated ones: the irradiated samples show the first significant variation after 24 days of accelerated ageing, when the non-irradiated samples have still a color hardly distinguishable from the not aged.

The evaluation of chromaticity coordinates was performed by mean of the color distance parameter ΔE (Table 3) that expresses the geometric distance of two points in the Cie L*a*b* space. It should be remarked that a color variation appreciated by human eye correspond to $\Delta E \geq 4$.

In the samples where $\Delta E > 4$ was found, the change must be considered a visible aesthetical impact, and it is clear that such impact is experienced earlier and more in the irradiated series.

Column 0 of Table 3 reports the ΔE of pure Whatman papers (Column A of Table 2) calculated respect to time 0. It shows the variation of chromaticity coordinates only caused by the ageing of the untreated, not irradiated papers.

Column 1 of Table 3 reports the ΔE of hydrolyzed Whatman papers (Column B of Table 2) calculated respect to time 0. It shows the variation of chromaticity coordinates only caused by the ageing of the hydrolyzed papers.

Column 2 of Table 3 reports the ΔE of hydrolyzed irradiated Whatman papers (Column C of Table 2) calculated respect to the value of not irradiated Whatman papers at time 0 (first L*a*b* value of Column B in Table 2). This column shows the variation of chromaticity coordinates due to the superimposition of ageing and irradiation.

The same calculations, with the same meaning, have been performed to obtain the data reported in the other columns of Table 3. We underline that in Table 3 the reference value for columns 3 and 4 is the first L*a*b* value of Column D in Table 2, while for columns 5 and 6 it is the first L*a*b* value of Column F in Table 2.

Observing the last row in Table 3, it is evident that the yellowing of the only aged Whatman paper is far less intense than the other samples.

Table 2
Color coordinates of irradiated and not irradiated papers as a function of ageing.

Ageing	L*a*B*	WH	HY-WH		Permanent paper		HY Permanent paper	
(days)	coord.	A: no γ	B: no γ	C: γ	D: no γ	E: γ	F: no γ	G: γ
	L*	97.15 ± 0.10	96.14 ± 0.17	95.30 ± 0.47	93.60 ± 0.11	92.48 ± 0.15	93.71 ± 0.16	93.94 ± 0.56
0	**a***	−0.42 ± 0.03	−0.31 ± 0.04	−0.36 ± 0.05	+1.56 ± 0.09	+1.82 ± 0.09	+2.01 ± 0.07	+1.85 ± 0.03
	b*	+0.68 ± 0.06	+0.94 ± 0.11	+3.53 ± 0.57	−2.39 ± 0.11	−3.02 ± 0.12	−3.52 ± 0.14	−3.18 ± 0.15
	L*	96.56 ± 0.10	95.02 ± 0.24	93.79 ± 0.50	93.11 ± 0.11	91.88 ± 0.03	91.49 ± 0.22	91.13 ± 0.43
12	**a***	−0.51 ± 0.02	−0.22 ± 0.04	+0.10 ± 0.08	+1.00 ± 0.04	+1.20 ± 0.03	+1.10 ± 0.05	+1.23 ± 0.09
	b*	+2.05 ± 0.17	+2.95 ± 0.24	+5.51 ± 0.36	+0.68 ± 0.10	+0.33 ± 0.08	+2.14 ± 0.18	+2.64 ± 0.13
	L*	96.44 ± 0.12	92.85 ± 0.85	92.89 ± 0.31	92.97 ± 0.11	90.99 ± 0.12	86.90 ± 0.13	87.43 ± 0.77
24	**a***	−0.51 ± 0.02	+0.07 ± 0.18	+0.25 ± 0.08	+0.97 ± 0.03	+1.01 ± 0.03	+1.91 ± 0.03	+2.06 ± 0.04
	b*	+2.10 ± 0.06	+5.49 ± 0.75	+6.49 ± 0.30	+1.25 ± 0.08	+2.84 ± 0.11	+8.32 ± 0.13	+7.12 ± 0.18

WH = Whatman; HY = hydrolyzed; no γ = not irradiated; γ = irradiated.

Table 3
ΔE of samples. On each series, the non-irradiated, non-aged sample is taken as the reference.

Accelerated ageing (days)	WH	Hydrolyzed Whatman paper		Not Hydrolyzed permanent paper		Hydrolyzed permanent paper	
	0	1: Not irradiated	2:Irradiated	3: Not irradiated	4:Irradiated	5: Not irradiated	6:Irradiated
0	–	–	2.72 ± 1.04	–	1.31 ± 0.65	–	0.44 ± 0.54
12	1.49 ± 0.11	2.30 ± 0.66	5.16 ± 0.83	3.16 ± 0.33	3.24 ± 0.29	6.15 ± 1.02	6.72 ± 0.86
24	1.59 ± 0.12	5.63 ± 0.93	6.46 ± 1.14	3.74 ± 0.38	5.87 ± 0.37	13.66 ± 2.17	12.36 ± 0.99

3.2. Optical measurements

Color coordinates visualization can be easy when a single coordinate is subjected to the main variation, as in the Whatman samples case. It is less obvious when the three of them vary at the same time. The hydrolyzed permanent paper was, as previously stated, mostly affected by the chemical hydrolysis of the fibrous and non-fibrous materials, producing a very complex system; the non-hydrolyzed permanent paper has a less complicated behavior and offers an interesting case study.

Color change relevant to the preservation purposes can be well and easily explored by mean of spectroscopic analysis.

The whole reflectance spectra of the permanent papers (Fig. 1) show that the treatment and the ageing do not affect the NIR range (800–2000 nm) whereas in the visible range (400–800 nm) the presence of fluorescent optical brighteners gives rise to peaks in the permanent paper spectra, completely different from the flat one of a new Whatman paper.

In the same figure it can be observed that the reflectance spectrum of the permanent paper shows a 20% lower intensity albeit, to the naked eye, it appears whiter than the Whatman, because the visual aspect of the paper is mainly due to the fluorescence effect of the brighteners.

Brighteners, in fact, absorb light in the UV rang and then re-emit it in the blue portion of the visible spectrum. This mechanism let appear whiter to the human eye the object treated with the optical brighteners.

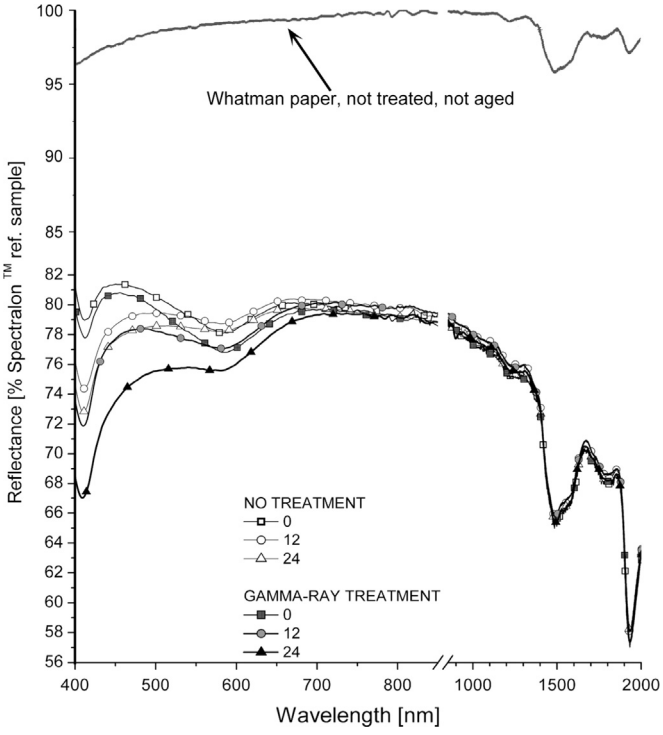

Fig. 1. Vis–NIR reflectance spectra of permanent paper. For comparison the spectrum of not aged and not treated Whatman paper is reported.

Fig. 2 enhances the visible range for a better visualization of the ageing and irradiation effects: along time, a greater color change is observed for the irradiated samples in comparison to the non-irradiated. This change appears as a decrease of the fluorescence peak, showing that γ-rays have an impact on brighteners, fillers and sizes.

The transflectance measurements (T_F=transmittance T+reflectance R), are directly related to the optical density (OpD= $-\log (T+R) = -\log T_F$), i.e. to the absorption of radiations by the sample.

In fact a decrease of transflectance corresponds to an increase of the radiation absorbed by the sample.

The transflectance measurements, reported in Fig. 3, show a decrease of transflectance between 400 and 600 nm, after 24 days of accelerated ageing. This corresponds to an increase of absorption in the blue region and to a shift towards yellow of the investigated sample. A weak, very broad band between 600 and 700 nm is observed in the irradiated sample and corresponds to the more pronounced fluorescence variation, shown in Fig. 2.

The modification of the whole spectrum is greater for the irradiated samples in respect to the only aged ones. They also present a different slope in the range 400–550 nm. Results in Fig. 3 are the average of 10 measurements made on each sample.

3.3. Cellulose average degree of polymerization (DP)

Four concentrations of paper solutions were used to obtain the values of intrinsic viscosity for each kind of paper/treatment; for each concentration four measurements were performed and values reported in Table 4 are corrected for the water content of paper.

Whatman paper is made of pure cellulose, while the permanent paper contains also other materials including fillers, sizing and optical brighteners. Therefore the experimental errors on DP of permanent paper are greater than those affecting Whatman paper measurements. However it is possible to compare the results and to evidence the differences between irradiated and not irradiated consistent samples.

The hydrolysis treatment was extremely traumatic for the Whatman paper, immediately inducing a decrease of DP from 1000 to 115. DP values are practically unaffected by ageing treatment, that, on the contrary, if prolonged could promote a little DP increase due to formation of hydrogen bonds between cellulose fragments. This means that chains linked *via* hydrogen bonds appear longer than the individual fragment and this causes an apparent increase in DP, due to the fact that the viscosity of the paper solutions depends not only on the length of the single chain, but also on the steric hindrance.

By analysing the DP data we note that 24 days of ageing do not substantially modify the DP of all the not hydrolyzed and not irradiated papers. Conversely, the irradiated samples show a lower average DP value already at zero time. The DP difference between not hydrolyzed, not irradiated paper at 0 time and the not hydrolyzed irradiated paper at 24 days shows a decrease of 185 DP units with an approximate loss in weight of 28860 units.

A definite decrease tendency, along time, can be observed for

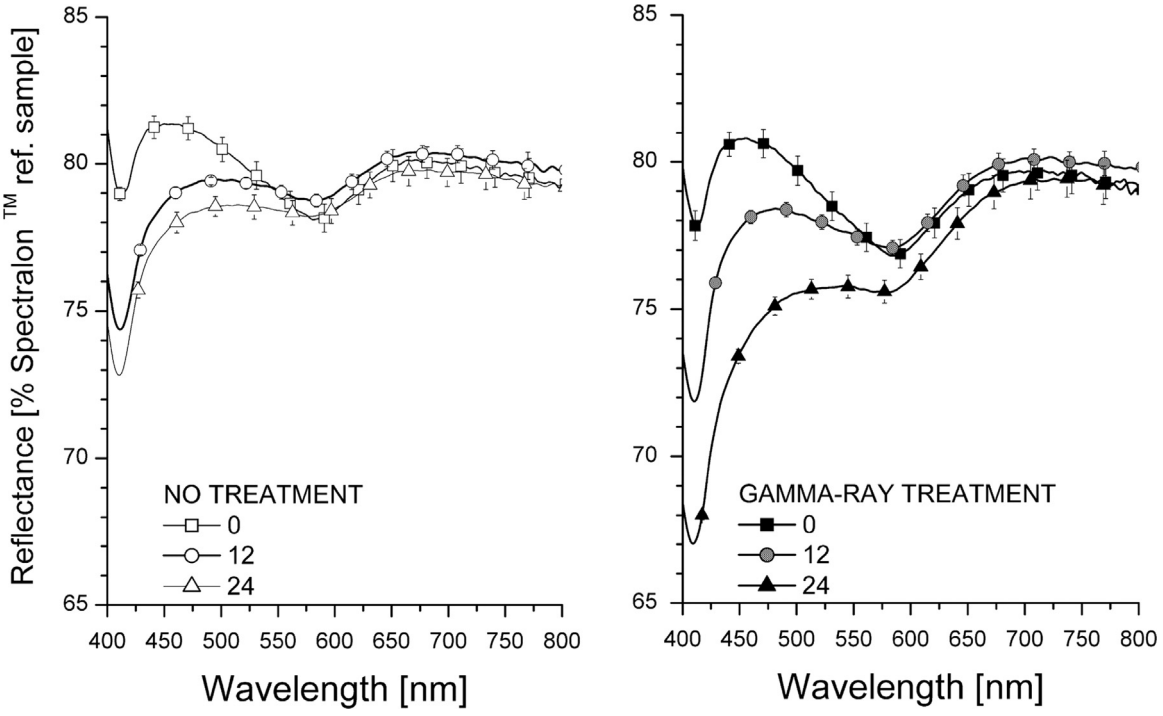

Fig. 2. Visible reflectance spectra of permanent paper.

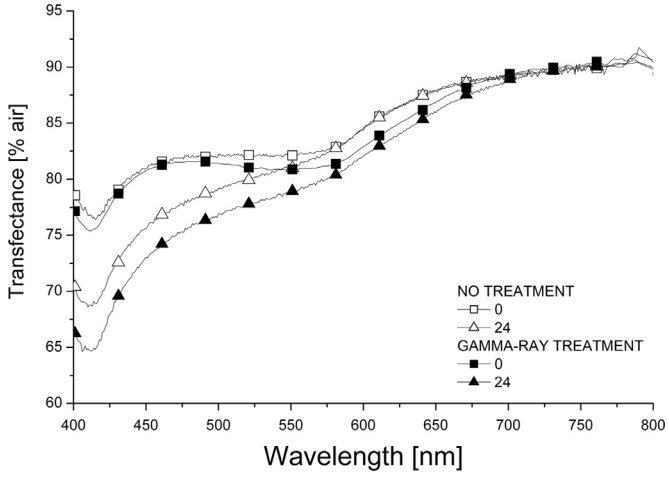

Fig. 3. Visible transflectance spectra of permanent paper aged 0 and 24 days, gamma irradiated and not.

hydrolyzed permanent paper and the DP values of the irradiated samples are considerably lower, at 0 and 12 days, than the values of corresponding non-irradiated paper.

Hydrolysis is a very dramatic treatment, but it simulates real measured conditions, as can be see by comparing the values reported in Table 5 with those in Tables 4 and 6.

After 24 ageing days the LODP (Levelling Off Degree of Polymerization) is almost reached for both the hydrolyzed samples, but with different kinetic patterns. The term LODP refers to the fact that a sample of cellulose is rapidly reduced to a relatively constant value upon being subjected to severe hydrolysis. The most important and evident effect is the decrease of DP at zero time for all the samples, before and after irradiation.

Table 5
Results of chemical analyses on original samples.

Provenance	Composition	DP	C=O	pH ± 0.02
ICPL 19th century	65% chemical sulpahte hard-wood, 35% mechanical pulp from softwood; sized with rosin.	450 ± 10	6.0 ± 0.4	4.95
A.S. Roma 17th century	100% bleached hemp; sized with starch	230 ± 18	11.2 ± 0.7	2.86
A.S. Cagliari 18th century	90% bleached hemp, 10% flax; sized with gelatin	190 ± 25	38 ± 4	2.50

(ICPL= Patologia del Libro; A.S.=State Archive).

3.4. Carbonyl groups content

Sampling procedure was the same applied for the average viscometric degree of polymerization. Five measurements were executed for each kind of paper, treatment and ageing period.

Table 4
DP values as a function of treatments and ageing.

Ageing (days)	WH ± 2%	Hydrolyzed Whatman paper ± 2%		Not Hydrolyzed permanent paper ± 10%		Hydrolyzed Ppermanent paper ± 10%	
		Not irradiated	Irradiated	Not irradiated	Irradiated	Not irradiated	Irradiated
0	1100	115	94	576	445	625	495
12	980	148	90	531	441	405	230
24	920	132	118	582	391	203	192

(Not hydrolyzed, not irradiated Whatman paper has DP=1100 ± 2%).

Table 6
Carbonyl groups content as a function of irradiation and artificial ageing.

Ageing (days)	WH ± 0.5%	Hydrolyzed Whatman paper ± 2%		Not Hydrolyzed permanent paper ± 3%		Hydrolyzed permanent paper ± 3%	
		Not irradiated	Irradiated	Not irradiated	Irradiated	Not irradiated	Irradiated
0	0.50	14.2	20.2	2.2	3.1	30.2	38.5
12	0.84	12.7	22.5	3.4	3.4	31.5	41.4
24	1.09	17.9	29.2	2.7	3.0	33.7	43.6

Results reported in Table 6 are the arithmetic mean of the obtained values, corrected for the water content.

Measurements confirm the negative effect of gamma ray irradiation (increase of oxidized functions), in particular for the hydrolyzed paper.

Erratic results for the permanent untreated paper both irradiated and not at 12 ageing days should be related to inhomogeneity of the used paper sample.

4. Conclusions

This study focused on the investigation of the chemical behavior of cellulosic substrates subjected to gamma irradiation, which has been suggested and used, as a treatment for biodeteriorated paper objects. No mechanical tests were carried out because our previous studies evidenced that the paper permanence and durability are more effectively related to microscopic structural modification (Bicchieri et al., 1999; Piantanida et al., 2005; Bicchieri et al., 2006; Missori et al., 2006) in the cellulose molecule than in the macroscopic mechanical variations.

Mechanical data on the same samples (permanent paper as described in Table 1) are reported by other authors (Adamo et al., 2007).

The study made it evident that gamma irradiated papers are more damaged than the non-irradiated counterparts. Moreover, with the increasing of the ageing time gamma rays treatment causes an overall yellowing of all the considered paper sheets.

The yellowing is more intense for permanent paper than for Whatman, presumably because of the effect of artificial ageing coupled with hydrolysis and irradiation on fillers and brighteners that are particularly sensitive to ionizing radiation. Spectroscopic measurements showed, in fact, a reduction of the fluorescent states, responsible of the whiter appearance of paper.

The comparison between irradiated materials and the non-irradiated ones shows that in the former the carbonyl groups content is remarkably higher than in the latter, which corresponds to a lower average degree of polymerization. The experiments confirmed what already expressed in a survey on preservation science (Porck and Teygeler, 2001): gamma radiation application, even at the minimum dosage required for disinfection, causes depolymerization and degradation of the paper substrate and therefore cannot be recommended[2].

References

⟨http://www.icpal.beniculturali.it/allegati/DM-7-10-2008-Istituto.pdf⟩.
⟨http://www.icpal.beniculturali.it/allegati/Nota_uso_raggi_gamma.pdf⟩.
Horio, M., Imamura, R., Mizukami, H., 1963. Effects of gamma irradiation upon cellulose. Bull. Inst. Chem. Res. Kyoto Univ. 41 (1), 17–38.
Calvini, P., Santucci, L., 1978–1979. Alcuni dati sugli effetti dell'irradiazione gamma sulla carta, Boll. ICPL XXXV, 55–62.
Sinco, P., 2000. The use of gamma rays in book conservation. Nucl. News, 38–40.
Bouchard, J., Méthot, M., Jordan, B., 2006. The effects of ionizing radiation on the cellulose of woodfree paper. Cellulose 13, 601–610.
Adamo, M., Brizzi, M., Magaudda, G., Martinelli, G., Plossi-Zappalà, M., Rocchetti, F., Savagnone, F., 2001. Gamma radiation treatment on paper in different environmental conditions: chemical, physical and microbiological analysis. Restaurator 22 (2), 107–131.
Otero D'Almeida, M.L., de Souza Medeiros Barbosa, P., Guerra Boaratti, M.F., Borrely, S.I., 2009. Radiation effects on the integrity of paper. Radiat. Phys. Chem. 78 (7), 489–492.
Choi, J.I., Chung, Y.J., Kang, D.I., Lee, K.S., Lee, J.W., 2012. Effect of radiation on disinfection and mechanical properties of Korean traditional paper, Hanji. Radiat. Phys. Chem. 81 (8), 1051–1054.
Moise, I.V., Virgolici, M., Negut, C.D., Manea, M., Alexandru, M., Trandafir, L., Zorila, F.L., Talasman, C.M., Manea, D., Nisipeanu, S., Haiducu, M., Balan, Z., 2012. Establishing the irradiation dose for paper decontamination. Radiat. Phys. Chem. 81 (8), 1045–1050.
Nunes, I., Mesquita, N., Cabo Verde, S., João Trigo, M., Ferreira, A., Carolino, M.M., Portugal, A., Botelho, M.L., 2012. Gamma radiation effects on physical properties of parchment documents: assessment of D_{max}. Radiat. Phys. Chem. 81 (12), 1943–1946.
Area, María C., Calvo, Ana M., Felissia, Fernando E., Docters, Andrea, Miranda, María V., 2014. Influence of dose and dose rate on the physical properties of commercial papers commonly used in libraries and archives. Radiat. Phys. Chem. 96, 217–222.
Michaelsen, A., Pinzari, F., Barbabietola, N., Piñar, G., 2013. Monitoring the effects of different conservation treatments on paper-infecting fungi. Int. Biodeterior. Biodegrad. 84, 333–341.
Negut, C.D., Bercu, V., Duliu, O.G., 2012. Defects induced by gamma irradiation in historical pigments. J. Cult. Herit. 13 (4), 397–403.
Porck H.J., 2000. Rate of paper degradation. The predictive value of artificial ageing tests. European Commission on Preservation and Access, Amsterdam.
Bicchieri, M., Bortolani, M., Veca, E., 1993. Characterization of low-molecular-weight polyvinyl alcohol for restoration purposes. Restaurator 14, 11–29.
Adamo, M., Magaudda, G., Rocchetti, F., 2007. The effect of γ-radiation on acidified and artificially aged paper. Restaurator 28 (4), 227–238.
ISO 5630/3:1996: Paper and Board-Accelerated ageing-Part 3. Moist heat treatment at 80 °C and 65% Relative Humidity.
ASTM E1347-06, 2011. Standard Test Method for Color and Color-Difference Measurement by Tristimulus Colorimetry.
Edwards, D.K., Gier, T.J., Nelson, K.E., Roddick, R.D., 1961. Integrating sphere for imperfectly diffuse samples. Appl. Opt. 51, 1279–1288.
ASTM E903-E996: Standard Test Method for Solar Absorbtance, Reflectance, and Transmittance of Materials Using Integrating Spheres.
ASTM D1795-13, 2013: Standard Test Method for Intrinsic Viscosity of Cellulose.
Immergut, E.H., Randy, B.G., Mark, H.F., 1953. Recent Work on Molecular Weight of Cellulose. J. Ind. Eng. Chem. 45 (11), 2483–2490.
Bicchieri, M., Bella, M., Sementilli, F., 1999. A quantitative measure of borane tert-butylamine complex effectiveness in carbonyl reduction of aged paper. Restaurator 20, 22–29.
Piantanida, G., Bicchieri, M., Coluzza, C., 2005. Atomic fmrce microscopy characterization of the ageing of pure cellulose. Polymer 46 (26), 12313–12321.
Bicchieri, M., Sodo, A., Piantanida, G., Coluzza, C., 2006. Analysis of degraded papers by non-destructive spectroscopic techniques. J. Raman Spectros. 37 (10), 1186–1192.
Missori, M., Mondelli, C., De Spirito, M., Castellano, C., Bicchieri, M., Schweins, R., Arcovito, G., Papi, M., Congiu Castellano, A., 2006. Modification of the mesoscopic structure of cellulose in paper degradation. Phys. Rev. Lett. PRL 97 238001-1-238001-238004.
Porck H.J, Teygeler R., 2001: Preservation Science Survey: An Overview of Recent Developments in Research on the Conservation of Selected Analog Library and Archival Materials. European Commission on Preservation and Access, Amsterdam.