

Introduction

The end of 2001 was a period that produced major changes in the security procedures of the United States. The finding of anthrax in letters sent as a terror weapon changed the way the mail was processed. In order to insure the safety of the mail the Post Office decided to use an irradiation procedure to kill any biological warfare agents such as anthrax spores. Initially, this procedure was applied to mail arriving at the mail processing facility serving the Capitol area, with the possibility of expanding to the treatment of all mail. This procedure had unintended consequences.

While electron beam radiation has been used successfully for some time in sterilizing food, the high doses chosen in order to kill virtually all anthrax spores, 50-100 kGy, presented new problems not encountered at the lower doses used for food, 7-20 kGy (1,2). Not long after the start of the irradiation of mail, problems became apparent. Letters were found to be yellowed and often damaged and embrittled. Objects such as photographic materials were damaged. There were reports in the press of gems changing color and stamp and coin collectors became apprehensive after anecdotal reports of damage (3). Objects mailed to museums and archives in the area, including those of the Smithsonian, also were damaged.

The damage to objects could be separated into two categories, that due to the irradiation itself and that due to the thermal effects associated with the process. Radiation doses were higher than normally used because of the need for certainty in combating the threat. The high temperatures reached in the process were most likely due to the mechanical aspects of processing. Radiation doses were expected to be about 50-100 kGy depending upon the number of passes and heating was thought to be a function of thickness of the irradiated bulk packages.

Modern society generates an ever-increasing amount of documentation. People, government and business require that this documentation be preserved for a minimum amount of time. Because of the problems associated with some irradiated mail, archival materials were often copied, resulting in an increase of work and affecting storage space. Since the effects of the changes in mail processing seem to have altered the lifespan of mailed objects, our laboratory investigated some of the effects upon materials used to document the activities of our institution.

Experimental

A large number of postal specimens were available for study (any mail sent to our central Washington DC mailing address). These included paper and photographic materials as well as plastic holders and containers. The electron irradiation procedure used by the post office consisted of combining mail in bundles about 5 inches thick, sealing the bundles in plastic bags, and irradiating

Chapter 20

Irradiation of Mail: Effects on Archival Museum Materials

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One aspect of the response to a biological attack using anthrax spores sent through the mail has been to use electron irradiation to treat the mail. This irradiation procedure has altered the materials and objects in ways that were probably not anticipated. The mail was damaged by both thermal and radiation processes. Business, government, and personal records are all sent through the mail and damage to these records must be assessed for archival reasons. The irradiated paper became discolored and lost its ductility, i.e. became brittle, and components of some ballpoint pen inks were chemically altered. Thermal effects caused the sticking together of pages in books and journals. Photographic images, slides, and negatives were damaged and often destroyed. Objects such as computer disks were also damaged by melting or softening of their plastic components.

them at 10 MeV for a minimum dose of 50 kGy per pass, with each bundle given 2 passes (2). Other test specimens irradiated separately specifically for this study were treated at the Florida Accelerator Services and Technology (F.A.S.T.) Facility, Gainesville, Florida, at 5.2 MeV at 250 microamps for a total dose of approximately 260 kGy. This was anticipated to be 2 - 5 times the dose at postal facilities and although at a lower dose rate, it was expected to give indications of the problems to be encountered.

Tensile tests on paper specimens were performed on screw driven tensile testers as described previously (4). Specimens were cut to approximately 125 mm x 6 mm x 0.15 mm and equilibrated to 30% RH and then run at ambient temperature and 45% RH. Tests were performed on standard envelopes and paper used in the course of business (both irradiated and unirradiated samples) and on irradiated samples of Whatman paper that had been characterized previously.

Ink samples were applied to Whatman papers and allowed to dry for several weeks to minimize the effects of evaporation of ink solvents. Samples were tested by thin layer chromatography (TLC) on silica gel plates using two different solvent systems as described previously (5).

L*a*b* values and changes in color were measured and calculated on a HunterLab Ultrascan spectrophotometer. Most color changes were apparent to the unaided eye.

Paper and plastics were heated in dry ovens at temperatures expected to be encountered in the process of irradiation of mail. By measurement or deduction, the temperatures reached by the specimens during irradiation were determined to be between 80 and 130°C and possibly higher. Ignition of paper and other materials had been reported, implying quite high temperatures. In addition, certain paper specimens were heated in ovens with controlled RH since this has been found to produce aging processes similar to those that occur during natural aging (6).

Moisture uptake experiments were performed in chambers with controlled RH environments and weight measurements were made using a Mettler AT201 balance accurate to 0.01 mg.

Determinations of glucose and xylose concentrations were performed on some specimens. A sample of paper (about one gram) was extracted with stirring in 25 ml of deionized water for at least 2 hours. The extract was filtered, separated into 5 ml aliquots, and then evaporated under vacuum. The residue was derivatized as follows: 0.1 ml STOX, a commercial reagent containing hydroxylamine hydrochloride and O-phenyl-β-D-glucopyranoside (internal standard) in pyridine, is added to the residue of one of the aliquots and heated at 70°C for 1 hour to convert carbonyl groups and any cyclic hemiacetals to the oximes. 0.1 ml hexamethyldisilazane and a drop of trifluoroacetic acid is added. The *per*-trimethylsilylated supernatant is analyzed by gas chromatography on a DB-17HT column with flame ionization detection. The chromatograph is programmed to start at 50°C and then rise to 330°C at a rate of 10°C per minute.

Sugars were identified by comparison of their retention times with standards as well as by GC-MS. The procedures have been described previously (6).

Results

Polystyrene

Polystyrene is a component of many postal envelopes and was found to be a good indicator of damage. The "windows" of business envelopes were often deformed and in some cases contracted to small brittle fragments. The contractions were due to the release of "casting" strains within the windows. Experiments with similar materials showed that there was little damage at temperatures below 100°C even for an extended period of time, e.g. 30 minutes. Where these fragments were in contact with printing they often reproduced in miniature the printing beneath. Computer disks of polystyrene sent through the mail were found to be deformed in some cases. Simulations that involved heating disks, windows, photographic mounts, etc., showed that temperatures of at least 80 to 110°C were needed to replicate the damage seen in many postal specimens. Damage in postal specimens was not universal, however, and probably depended on their location in the irradiated bundles. Reducing the thickness of the irradiated packages will minimize damage due to thermal effects (2).

Spunbonded Olefin

Envelopes made from spunbonded olefin were also received in conditions indicative of high temperature. These materials will permanently deform at temperatures above 107°C and will melt at 135°C (7). Journals mailed in packages made of these materials were stuck to the envelope, probably due to a combination of effects from both changes in the inks present on the journal cover and the softening of the envelope itself. Heated envelopes exhibited a softening range of 118 - 130°C.

Photographic Emulsions

Photographic emulsions were found to be at risk given the high temperatures reached during the irradiation process. Cracking and separation of the emulsion was noted on transparencies and in some cases blackening and powdering as well. Polystyrene slide mounts were found to be deformed in many cases. Tests on similar materials indicated that the temperatures reached were over 100°C.

Ballpoint pen inks were analyzed after irradiation and found to be relatively stable in color. One surprising finding was that on TLC analysis some of the blue pen inks had a new more rapidly moving component similar in color to the bulk color of the ink. While not of immediate practical concern, this may have some forensic implications.

Printing inks and photocopy toners in particular were found to adhere to adjacent pages of photocopies, journals and magazines. This is probably due primarily to softening of the resin binders at temperatures similar to those that affect polystyrene. However, wrinkling and tide lines indicative of the effects of liquid water also were observed. Liquid water probably resulted when water driven out of the hottest regions of the bundles condensed in cooler areas. The combination of softened ink binders and moisture condensed in cooler areas lead to severe "blocking" or sticking problems. This has become a serious problem at the Smithsonian Institution Libraries and elsewhere.

Paper

The most obvious effect on paper is the change in color. The change is a distinct yellowing and muting of color which is slight immediately after irradiation but which intensifies with time. Color measurements, $L^*a^*b^*$, for a typical paper six weeks after irradiation showed a general distinct darkening ($\Delta L^* = -1.13$) and a color shift to the yellow ($\Delta b^* = 4.68$). There was a small change in a^* , ($\Delta a^* = -0.29$). Yellowing occurred whether or not the paper had any lignin content. Mail that had been irradiated could be identified almost universally when compared to unirradiated mail.

Significant physical changes to irradiated paper, particularly in the mechanical properties, could be determined. Whether these changes were due to thermal effects, radiation, or a combination of both were investigated.

Samples of Whatman #1 MM paper were sent through the mail or were irradiated elsewhere. Whatman #1 MM paper is a rugged paper, which is primarily a β -linked glucose polymer (α -cellulose) with no hemicellulose or lignin. Even at a high dose of 250+ kGy the Whatman paper remained strong and somewhat ductile although measurements showed some loss of ductility. A tensile test of the irradiated paper versus an unirradiated paper is shown in Figure 1. As the strain-at-break decreases to less than 0.01 (i.e. 1%) the ability of the paper to be folded, deformed, or manipulated becomes increasingly less. The irradiated paper becomes more susceptible to damage.

The changes in the mechanical properties of business paper sent through the mail were even more drastic. These papers, which are less rugged than the Whatman paper, have often been found to be damaged and torn when received. If the loss of ductility becomes severe then the movement of the business paper through the postal machinery and other handling could lead to the observed rips

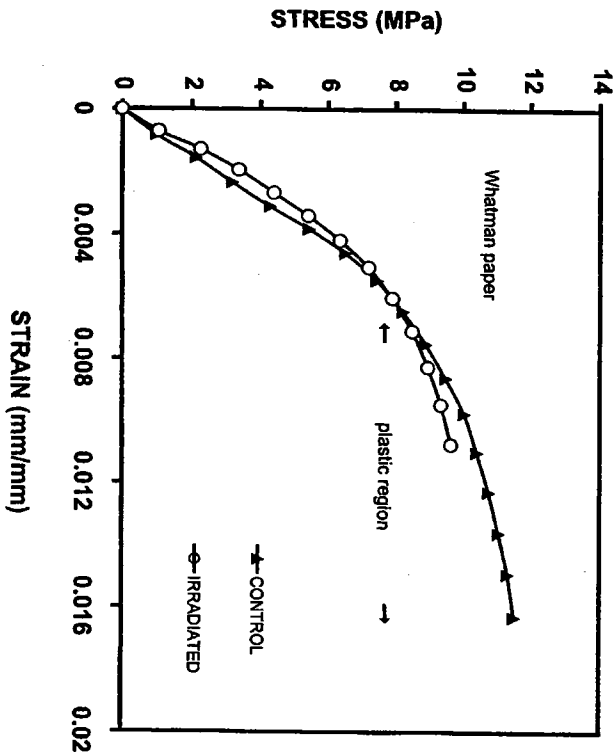


Figure 1. The stress-strain plot for two samples of Whatman paper in the same direction. One specimen was irradiated to a total dose of 257 kGy. There is a loss of ductility which if continued increases the possibility of damage on handling.

and tears. Figure 2 shows the stress-strain plot illustrating the loss in ductility of a business envelope sent through the postal system as compared to an unirradiated envelope. It can be seen that the paper has lost almost all of its plasticity, the ability to tolerate large strains by permanently deforming. It does retain its elasticity as is noted in the initial linear portion of the stress-strain curve. At these lower strain values the paper can be deformed without permanent change. Even though this paper was initially quite tolerant of large strains, it has now reached a point where it is susceptible to damage through handling or folding. This does represent an extreme in damage and is not representative of all mail that is irradiated. It is meant to demonstrate the potential for damage under the most adverse conditions.

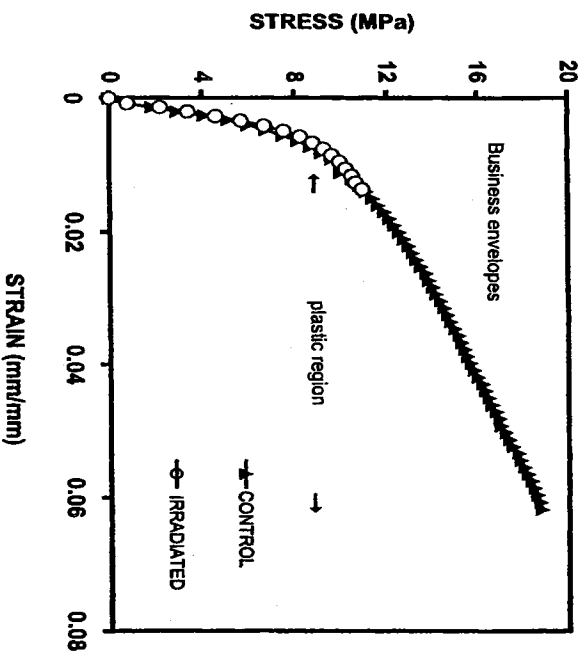


Figure 2. The stress strain plot for two business envelopes, one irradiated when sent through the mail and the other a control. The loss of ductility in the irradiated envelope is severe and represents an extreme of damage to mailed objects.

There are also significant changes that occur chemically. These changes are different from those seen in the control papers, or papers that have undergone natural or accelerated aging.

The chemical consequences of the irradiation of paper may be seen in the comparison of degradation products as illustrated in the gas chromatogram in Figure 3. Differences in the profiles of extracts of the control and irradiated specimens are apparent. Aqueous extracts of irradiated papers showed a significant increase in the amount of extractable, soluble material. This soluble material represents degradation products since unirradiated paper has only small amounts of soluble components. The degradation product distribution of the irradiated samples is very different from the distribution one finds on examining naturally aged papers.

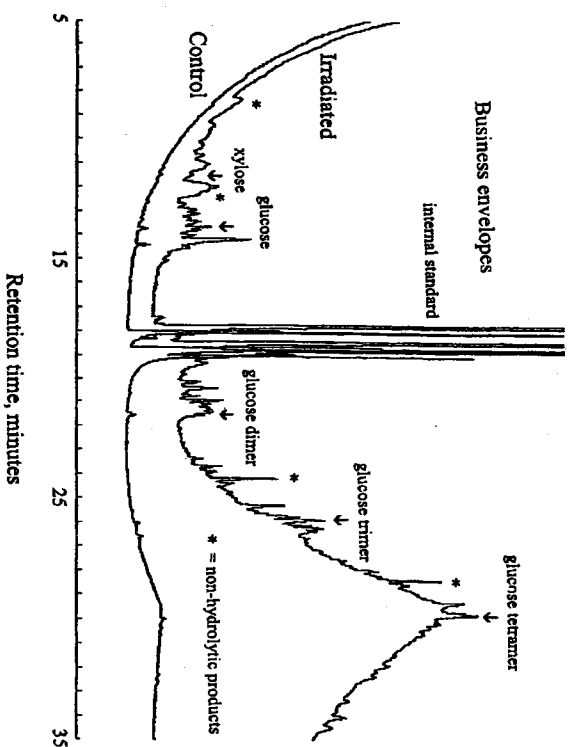


Figure 3. Comparison of the gas chromatograms of the per-trimethylsilylated oxime derivatives of extracts of unirradiated and irradiated paper sent through the mail. Typical amounts of the products of natural aging are seen in the unirradiated sample while increased amounts of xylose, glucose and glucose oligomers as well as other compounds are seen in the irradiated sample.

The primary degradation process during natural aging is hydrolysis, and the typical soluble products found on analysis of naturally aged papers include

xylose, glucose and a series of glucose oligomers resulting from hydrolysis at different points along the cellulose chain. Hydrolysis of the hemicellulose found in papers containing wood pulp also yields xylose and some glucose as well. Smaller amounts of other compounds including products of oxidation and chain scission are also present, but in smaller amounts. The control paper has only minor amounts of these compounds as would be expected in a "new" sample. The irradiated samples show increased amounts of hydrolysis products, but these are overshadowed by the production of other compounds from other reaction paths. One may postulate that the hydrolysis products were formed at high temperatures before the original ambient water was driven out by heating. "Tide lines" found on some mailed items showed that there was water present beyond that normally contained in the paper. The condensation of water in some regions of the packets is due to uneven heating of the bundles, which drives moisture to the cooler regions. The other products are formed either through scission or free radical reactions directly caused by irradiation, or by thermal scission or oxidation resulting from the greatly increased temperatures.

To determine changes in moisture uptake at high relative humidity, thermally treated and irradiated papers were compared with paper sent through the mail. Paper heated to 105°C in a dry oven (less than 2% RH) crosslinks and loses its ability to take up moisture at high RH, e.g. 100% RH. Whatman paper previously heated at 105°C for 1 hour takes up 10% less water than unheated paper. The same paper irradiated to approximately 260 kGy dose by an electron beam took up 51% less water. Whatman paper mailed to our facility through Washington DC showed a reduction in the ability to take up water of 43%. Since it is doubtful that high temperatures would be sustained for over one hour during the irradiation process, this change in the paper would be primarily due to the electron beam and induced free radical reactions.

Discussion

The treatment of mail by electron beam irradiation can create damage by both thermal and radiation effects. In the procedures in use at the time of this work, small mailed items were packaged in bundles up to five inches thick sealed in plastic bags, and then irradiated usually with two passes to insure a minimum dose of 50 kGy throughout the bulk sample. The overall effects observed by the postal patron are due to high temperatures, electron beam irradiation, and some moisture effects.

Mailed paper was found to have yellowed and embrittled, and address windows either deformed or contracted. Printed materials may be stuck together either from softening and melting of ink binders or from the movement of

moisture within the irradiated package. Plastic materials such as slide mounts or computer disks may be seriously deformed.

Because the heating of the packages of mail causes moisture to migrate, water can be driven from the hottest portion of the block of mail and condense in the cooler regions, especially on the inner surface of the plastic bag. The resulting movement of water can cause blocking or adhesion of paper, the running of inks and dyes, and the formation of tide lines. In conjunction with the softening of resins in printed materials this can lead to inseparable masses of paper, particularly in the case of journals.

Changes in the thickness of the irradiated packages and lower total doses will lower the temperature and reduce the possibility of thermal damage and associated moisture damage.

Pending the adoption of methods that can reduce both the biological hazard and damage to mailed items, items that cannot or should not be irradiated are shipped by other means. Archival materials such as paper are being duplicated where practical.

Acknowledgments

The authors would like to thank Walter Hopwood and Caroline Solazzo for technical assistance and Dr. Burrell J. Smittle, Division of Plant Industry of the Florida Department of Agriculture and Consumer Services, Gainesville, Florida for irradiation of some samples.

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