D. ERHARDT
C.S. TUMOSA
D. VON ENDT
A.-S.M. EL-EASELY

COLLATERAL DAMAGE: ANTHRAX, GAS, AND RADIATION

Smithsonian Center for Materials Research and Education, Suitland, MD

ABSTRACT In response to acts of bioterrorism, chemical and radiation treatments have been employed to kill suspected pathogens. These treatments are effective in killing the microorganisms, but are potentially damaging to surrounding objects and materials. The chemical treatments usually involve oxidizing agents such as the gas chlorine dioxide or solutions, gels, or foams of various peroxides or chlorine bleaching agents. Electron irradiation of mail produces damage both directly and by the heating induced during treatment. For example, polystyrene slide mounts have softened and warped, and stacks of papers have adhered together and transferred printing and images. Tensile measurements on irradiated paper show a substantial (up to 80%) loss in the ability of the paper to be deformed. Chemical analysis of the paper shows a large increase in hydrolytic and oxidative soluble degradation products compared to controls. The irradiated paper is both brittle and discolored.

INTRODUCTION The fall of 2001 saw terrorism on a scale not previously seen in the U.S. in modern times. Among the problems encountered were a series of anthrax-contaminated letters sent to a number of locations including the offices of two senators. This resulted in the contamination of the Hart Senate Office Building and its mail-handling center, as well as mail sorting locations starting from the point of origin of the letters. Because of the scale of contamination, gaseous fumigation with chlorine dioxide was proposed as the method of decontamination for the Senate building. However, because of the aggressive oxidizing nature of this gas, there was concern about the possible effects on artwork and sensitive technical equipment as well as personal items such as photographs in the building. Tests of exposure to a number of quickly prepared test samples showed that damage such as fading of inks, dyes, and photographs did indeed occur. Mitigation of the problem by such techniques as treatment with Oxone or hydrogen peroxide was also considered.

Chemical treatments to mitigate biohazards have include the traditional agents such as hypochlorite bleaches, peroxide-based agents such as that developed at Sandia National Laboratories for chemical and biological warfare agents, and Oxone, a DuPont product whose active ingredient is potassium peroxymonosulfate. All of these compounds and formulations are potentially damaging to many of the materials in the objects encountered in offices and museums.

Because of such concerns, it was ultimately decided that chlorine dioxide would be used to decontaminate only the most heavily contaminated areas of the Hart Building. Other surfaces throughout the building were decontaminated using other techniques, including a peroxide foam. Valuable materials, including artwork, were bagged, sealed, and taken to another site where methods such as vacuuming with HEPA filters were used to decontaminate them. However, none of these reagents and treatments are unsuitable for the treatment of mail.

Eventually, the decision was made to sterilize all mail that was present in the closed mail handling facility, as well as all subsequent mail that normally would have passed through it. Electron beam irradiation was chosen for this purpose. This process is routinely used for food items with no apparent problems. The results for mail were quite different, probably because of the higher total dose, 50–100 kGy, versus the 7–20 kGy typically used to kill spores or the even lower doses used to kill insects. The methods, dosage, and conditions chosen resulted in severe yellowing and embrittlement of papers, melting of plastics, and blocking of manuscripts. Chemical analysis and measurements of changes in color and mechanical and physical properties verify the damage, and confirm reports that the irradiated mail reaches temperatures well over 100°c. These effects have serious implications for museum objects and samples, and will affect decisions regarding the archival nature of irradiated documents.

METHODS

Tensile Tests and Paper Specimens Tensile tests were performed on screw driven tensile testers as described previously (Mecklenburg and Tumosa, 1991). Samples of paper were approximately 125 mm × 6 mm × 0.15 mm. 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.

Irradiation of Test Specimens Postal specimens were estimated to be irradiated at 10 MeV for a minimum dose of 50 kGy per pass and with at least two passes (McKnight, 2002). Some specimens were from routine mail routed through our own Washington, D.C., address. Other samples prepared specifically to evaluate the effects of irradiation were mailed to our Washington address from our Maryland facility and evaluated on their return. Other test specimens prepared before the use of irradiation for mailed specimens began were irradiated at an agricultural irradiation facility at 5.2 MeV at 250 microamps for a total dose of 257 kGy. This was anticipated to be two to five times the dose received at postal facilities.

Chemical Testing for Glucose Formation A sample of paper (about 1 g) was extracted with stirring in 25 ml of water for two hours. The extract was filtered, separated into 5-ml aliquots, and 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. Then 0.1 ml hexamethyldisilazane and a drop of trifluoracetic acid are added. The *per*-trimethylsilylated supernatant is analyzed by gas chromatography on a DB-17HT column with FID detector starting at 50°c and immediately rising to 330°c at 10°c/min. Sugars are identified by comparison of retention times with standards, or by analysis by GC/MS. The basic method was described previously (Erhardt and Mecklenburg, 1995).

Thermal Treatments Plastics were heated in dry ovens at temperatures expected to be encountered in the irradiation of the mail between 80 and 130°c. Paper specimens were treated in both dry ovens and ovens with a controlled relative humidity. Control of relative humidity ensures a process more like that of natural aging (Erhardt and Mecklenburg, 1995).

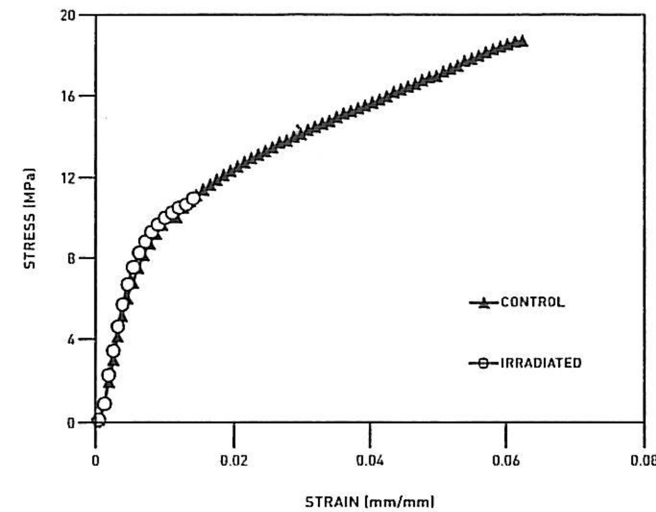
Color Tests Color changes were calculated from standard L*a*b* measurements obtained with a HunterLab Ultrascan spectrophotometer.

RESULTS Plastics received in an altered state were identified by Fourier transform infrared spectroscopy and examined for heat damage. Test specimens were heated to determine the temperature ranges required for similar damage. The largest number of plastic specimens received through the mail was based on polystyrene. This included the clear windows on business envelopes, slide mounts for 35-mm slides, and the bodies of 3½-inch computer disks. Continuous heating of similar materials for up to 30 min at temperatures of up to 100°c showed only slight changes in dimension or stiffness. Above 100°c changes became more apparent and by 110°c changes were drastic. Deformation occurred due to softening and relaxation of casting strains and sometimes due to handling. Softening above 100°c is commonplace for polystyrene materials (Roff and Scott, 1971).

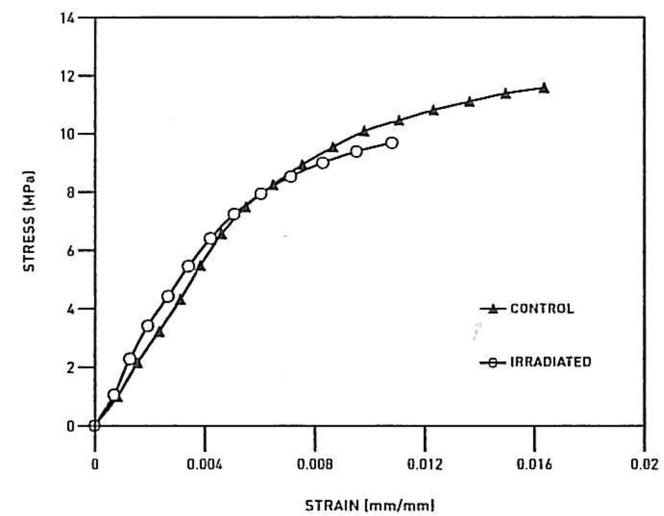
The most obvious effects on paper are changes in color. The changes are a distinct yellowing, which was found to be slight immediately after irradiation but increased in intensity with time. Color measurements, L*a*b*, for a typical paper showed distinct darkening and a color shift to the yellow in the irradiated sample. The decrease in L* (L* = −1.13) is indicative of a general darkening. The large increase in b* (b* = 4.68) is due to increased yellowness. There was little change in a* (−0.29).

Stress-strain testing of paper samples showed that irradiation greatly reduces the strength and extensibility of paper. Figure 1 shows stress-strain curves for paper from identical business envelopes, one of which was irradiated by the Postal Service. [FIG. 1] The paper is typical of business envelopes made from recycled fibers. The extensibility of the irradiated paper (the amount of strain, or stretching, required to break it) has been reduced from 6.2% to 1.3%. The strength of the paper (stress to break) has also been reduced, from 19 MPa to 11 MPa. Interestingly, the stiffness of the paper (slope of the initial stress-strain curve) is essentially unchanged—the paper is not stiffer, just weaker. In this case, it is the loss of extensibility that results in the impression that the paper is more brittle. Figure 2 shows stress-strain plots for Whatman paper samples, a control sample, and a sample irradiated to 257 kGy. [FIG. 2] While the loss in strength and extensibility is not as great as for the envelope paper, the overall effect is similar. It is expected that the Whatman paper would be more stable than the recycled paper of the envelope.

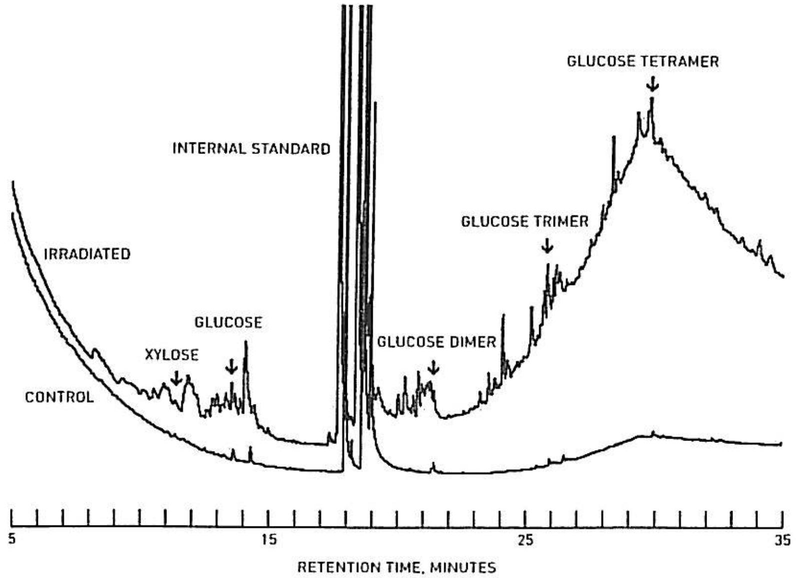
Gas chromatographic analysis of aqueous extracts of the envelope paper samples showed a significant increase in the amounts of extractable material in irra-



[1] Stress-strain curves for samples of initially identical mailed business envelopes, one unirradiated and one irradiated. The strength and extensibility are both reduced, but the stiffness (initial slope of the curve) is unaffected.



[2] Stress-strain curves for samples of Whatman paper, one unirradiated and one irradiated to 257 kGy. The effects are similar to those in Fig. 1, but less drastic.



[3] Gas chromatograms of the *per*-trimethylsilylated oxime derivatives of the extracts of unirradiated and irradiated business envelopes. Small amounts of xylose, glucose, and glucose oligomers, compounds typically formed during natural aging, are seen. However, uncharacteristically large amounts of other compounds (the unlabelled peaks) are also formed.

diated samples. [FIG. 3] Unirradiated fresh paper contains only small amounts of soluble material. The increase in soluble material in the irradiated samples represents decomposition products. However, the mixture of products formed due to irradiation is quite different than what is found in typical naturally aged samples. The primary degradation process during natural aging is hydrolysis, and the typical product mixture includes xylose, glucose, and glucose oligomers (short chain polymers) resulting from hydrolysis at different points along the cellulose chain. Other compounds including products of oxidation and chain scission are also present, but in smaller amounts. The irradiated samples do show increased amounts of the hydrolysis products, but also significant amounts of other compounds. The hydrolysis products were probably formed before the water absorbed in the paper at ambient conditions was driven off by heating. The other products are formed either through scission reactions directly caused by irradiation, or by thermal scission or oxidation resulting from the greatly increased temperatures.

DISCUSSION The electron irradiation of mailed items causes both thermal and radiation effects that create damage not generally associated with the usual postal processes. In the procedures in use at the time of this work, mail up to 5 in. in thickness is placed in plastic bags, sealed, and irradiated, usually with two passes to ensure a minimum dose throughout the mass of mail. The changes are due to the irradiation combined with the resulting high temperatures and the effects of moisture being driven from the materials by the heating.

These effects of electron irradiation were often obvious. Paper is quite yellowed and brittle and plastics are melted or deformed. There were early reports of melted and burnt mail and even color changes in gems (Reese, 2001). Measured temperatures during irradiation have reached 130°C. This leads to various physical changes such as sticking and contraction of common materials (McKnight, 2002).

Because the heating of the packages of mail is uneven, moisture driven from the hottest regions of the blocks of mail by temperatures above 100°C can condense in cooler areas. The resulting liquid water can cause blocking or adhesion of paper, running of inks and dyes, and tide lines. In conjunction with the melting of resins in printed materials, this leads to inseparable masses of paper, particularly in the case of journals.

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EDITED BY
ROBERT J. KOESTLER
VICTORIA H. KOESTLER
A. ELENA CHAROLA
FERNANDO E. NIETO-FERNANDEZ

ART, BIOLOGY, AND CONSERVATION: BIODETERIORATION OF WORKS OF ART

The Metropolitan Museum of Art, New York