THE EFFECT ON BALLPOINT PEN AND MARKER INKS OF CHEMICAL AND ELECTRON BEAM REMEDIATION TECHNIQUES FOR BIOLOGICAL WARFARE AGENTS

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INTRODUCTION

Recent terrorist acts, including the mailing of anthrax containing letters in late 2001 emphasized the importance of the neutralization or remediation of biological warfare agents. The letters contaminated the facility handling the mail and the offices of the recipients. In addition, contamination spread to other pieces of mail. Various strategies were considered to solve the contamination problem. These were eventually reduced to electron irradiation of the mail and chemical treatment of the facilities. Procedures were developed with neutralization of the biological threat as the highest priority. The effects of the remediation techniques on the mail, the buildings, and objects within the buildings though taken into consideration, were of secondary concern. This present research is designed to address this issue.

The electron beam irradiation of mail, primarily legal size envelopes or smaller, was instituted immediately. The chemical and thermal effects of this process became apparent after only a short time (1).

The chemical treatments considered for the facilities and objects inside them included three common oxidizing agents, Oxone™, hydrogen peroxide, and sodium hypochlorite (bleach). Oxone™ is a triple salt of potassium peroxymonosulfate and is a mild oxidizing agent. In addition, it produces chlorine if chloride is present, enhancing its biocidal effect. Hydrogen peroxide and sodium hypochlorite are commonly used disinfectants that are effective against a range of chemical as well as biological agents (2).

The retrieval of information contained in treated documents, both immediately and after archiving, will undoubtedly be necessary. Therefore, the effects of these oxidants and radiation treatments were studied.

EXPERIMENTAL

Specimens of ballpoint pen and marker inks were created by applying writing to either Whatman 1 or Whatman 3 papers. These were allowed to dry in the dark for several weeks to avoid solubility problems encountered with freshly applied inks since the chemical remediation agents would be applied in aqueous solution. Previous testing had shown differences in ink solubility over time with water. The sources of the inks and markers are listed in Table 1.

Electron beam irradiation was performed at 5.2 MeV at 250 microamps for a total dose of 257 kGy. This is 2 to 5 times the anticipated dose expected for letters sent through the postal system.

The chemical reagents tested were: a 1% Oxone solution, a 3% hydrogen peroxide solution and a 1:10 dilution of sodium hypochlorite (5.8%). Since the reagents are all aqueous, controls included both untreated and water treated specimens. The testing itself was performed by immersion of the specimens in the reagent for 30 minutes. This is the most aggressive method of contact between the reagent and the substrate and

was used in order that any possible effects would be seen. The chosen time represents the time frame in which a reagent is expected to be effective within a military context (2).

Thin layer chromatography (TLC) was performed with either Whatman 3 MM paper or silica gel 60 on glass plates as substrates. Two solvent systems were used: ethyl acetate, absolute alcohol, deionized water 70:35:30, and n-butanol, absolute ethanol, deionized water 50:10:15. Both are as described by Brunelle and Pro (3). Inks were extracted with either acetone, pyridine or ethyl acetate.

RESULTS

1. Electron Irradiation

Electron irradiation of the ink specimens on Whatman paper did not show any perceptible differences in the ink colors. The paper turned yellow and became increasingly yellow with time. On TLC analysis 7 of the 26 inks showed changes. These changes are summarized in Table 2.

TABLE 2
Samples Which Were Altered By Electron Irradiation

Samples	Changes in Ink Components
Skilcraft US gov. fine; blue	new blue component
Skilcraft felt tip; blue	new blue component
Skilcraft marker; blue	new pink component
Skilcraft marker; red	new red component
Papermate med. pt.; blue	new blue component
Bic round stic medium; blue	new blue component
Schwan stabilo; red	altered mobility of components

2. Treatment by Immersion

A. Water

Of the specimens which did not dissolve, all of the inks were either unchanged or slightly diminished in intensity because of solubility of the ink components. This data provides a baseline to evaluate the tests with the oxidizing reagents. Solubility was found to be a problem with freshly applied inks and even after several weeks, 6 samples dissolved readily.

B. 1% oxone solution

In addition to the solubility effects observed in section 2A, three samples showed obvious changes in their color on the paper. These were the Papermate med. pt; blue, and the Skilcraft US gov. fine; blue which shifted in color to a blue-green, and the Schwan stabilo; red, which turned orange.

C. 3% hydrogen peroxide

The effects of immersion in 3% hydrogen peroxide were the same as immersion in water alone.

D. 1:10 dilution of sodium hypochlorite (bleach) 5.8%

This is by far the most aggressive reagent/technique of those studied. The only unaffected samples were the Skilcraft US gov. med.; green and the Col-erase 1272; brown. The remainder either dissolved or changed color.

CONCLUSIONS

The forensic analysis of inks after document remediation for chemical or biological warfare agents can be problematic. Especially surprising was the alteration of ink composition after electron beam irradiation. The presence of extra spots of similar color to the original ink were detected after TLC analysis . These could lead to an inappropriate exclusion.

The rather drastic changes seen on treatment with aqueous oxidizing agents was expected but the changing of color of certain inks could lead to an *a priori* exclusion which isn't warranted.

TABLE 1
Sample Origin and Color for Inks Tested by Electron Irradiation

Skilcraft med.; blue
Skilcraft US gov. med.; green
Skilcraft US gov. fine; blue, black
Skilcraft; green
Skilcraft US gov.; red
Skilcraft felt tip; blue
Skilcraft markers; green, red, blue, black, yellow
Papermate metal roller fine; black
Papermate metal roller micro; blue
Papermate eraser-mate; red
Papermate med. pt.; blue, red
Schwan Stabilo; red
Pentec Hybrid gel roller; black
Eberhard Faber; black
Bic Round stic med.; blue
Sharpie ultrafine point; black
Sharpie fine point; red, black, blue
Col-erase 12722; brown

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REFERENCES
1. Erhardt, D., C. S. Tumosa, D. von Endt and A-S. M. El-Easley. "Collateral Damage: Anthrax, Gas, and Radiation". *International Biodeterioration & Biodegradation* (2003) [in press].

2. Raber, E. and R. McGuire. "Oxidative decontamination of chemical and biological warfare agents using L-Gel". *Journal of Hazardous Materials* (2002) 93(3):339-352.

3. Brunelle, R. L. and M. J. Pro. "A Systematic Approach to Ink Identification". *Journal of the AOAC* (1972) 55(1):823-826.

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