THE EFFECT OF OZONE ON CELLULOSE STRENGTH:

Considering Ozone for the Removal of Odour from Paper Artifacts

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BACKGROUND

• Odours left in artifacts from fire and flood can be very difficult to remove, especially from complex structures such as books, for which aqueous treatments are not always appropriate.

• Exposure to ozone gas (O_3) is an effective treatment for removing odours from paper artifacts; it is used by disaster restoration companies for batch treatments of books and documents. Objects are placed in a contained chamber with a corona-discharge ozone generator, and exposed to ozone gas for a period of several days; objects are monitored periodically with a "smell test" to determine when the treatment is finished.

• Conservation literature discourages the use of ozone for treatments because oxidation is a key chemical reaction causing deterioration in most materials. It has been proven to cause fading of organic colourants in pigments and dyes; in cellulose oxidation accelerates deterioration by lowering the degree of polymerization by breaking cellulose chains.

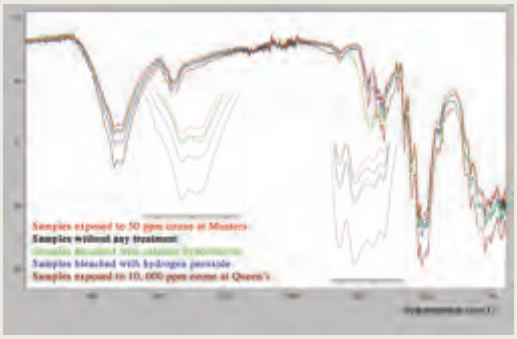
• Most research on ozone focuses on environmental ozone affecting collections in urban areas, but these results cannot be reliably extrapolated to indicate the effects of higher concentrations or shorter doses. It is uncertain exactly how much damage may be caused by a strong but brief exposure as used for odour elimination.

• This research aims to establish whether or not the amount of deterioration caused by ozone treatment for the purpose of eliminating odour is prohibitively harmful to cellulose.

MATERIALS

Samples	Ozone	Chemical Testing
Whatman Filter Paper #40 used for all samples.	Munters: Total Zone TZ-2 model	Hydrogen peroxide, calcium hypochlorite
Three tests completed on each type of treated paper, results averaged.	Queen's: Hankin Ozotec Type S, Model 3	Copper sulfate, carbonate-bicarbonate, phosphomolybdic acid, potassium permanganate.

RESULTS



FTIR spectroscopy – Unexpected results as bands in 3330 and 1025 regions show increase in –OH and C-OH stretching, indicating oxidation, in all samples *except* the O_3 exposure from Munters, which shows a decrease but no carbonyl groups. Oxidation from H_2O_2 and $Ca(ClO)_2$ appears in reverse of what was expected. Queen's O_3 samples show marked increase in –OH and also a small shoulder indicating carbonyl groups.

Paper Treatment	Control	$Ca(ClO)_2$	H_2O_2	50 ppm Ozone	10, 000 ppm Ozone
Average Copper number	0.67 (+/- 0.07)	0.72 (+/- 0.14)	0.80 (+/- 0.06)	0.89 (+/- 0.10)	5.08 (+/- 0.12)

Copper number – Again the H_2O_2 and $Ca(ClO)_2$ results are the reverse of expected, indicating H_2O_2 is causing more oxidation. Copper number of O_3 samples from Munters is only slightly higher than those of bleaching. Copper number of Queen's O_3 samples is significantly higher, as expected.

EXPERIMENTAL

Oxidation Exposure:
Paper samples were exposed to various strengths of oxidizing agents, including bleaches and ozone gas, to provide a range of levels of deterioration for comparison.

Oxidant	Strength	Duration	Description
Hydrogen peroxide H_2O_2	2% in deionized water	15 minutes	Mild bleach which inflicts a small but acceptable level of damage.
Calcium hypochlorite $Ca(ClO)_2$	2% in deionized water	30 minutes	Harsh bleach known to cause severe oxidation in cellulose.
O_3 at levels for odour elimination	50 ppm	63.5 hours	Exposed at Munters MCS (disaster restoration company) facilities in commercial treatment conditions
O_3 at extremely high levels	10, 000 ppm	12 hours	Exposed in Queen's Department of Chemical Engineering

Ozone Apparatus and Pot Containing Samples

Paper Samples Disintegrated into Pieces for Testing

Copper Number Testing:
TAPPI T-430 Test for the Copper Number of Pulp, Paper, and Paperboard employed to detect oxidation damage. "Copper number is defined as the number of grams of metallic copper resulting from the reduction of $CuSO_4$ by 100g of paper fibres… oxidized cellulose is capable of reducing certain metallic ions to lower valence states, and these reactions… can serve to detect damage to cellulose."

Summary of Procedure:
• 1.5g of the paper disintegrated into pieces measuring approx. 5 mm square.
• Paper immersed in a solution of copper sulfate and carbonate-bicarbonate, and flask suspended in boiling water bath for 3 hours.
• After 3 hours, paper washed & filtered, filtrate collected and titrated with $KMnO_4$.
• Amount of $KMnO_4$ to titrate the solution used in calculation to determine copper number of paper.

Flasks in Boiling Water Bath

Washing and Filtering

Titration

CONCLUSIONS

The results appear to indicate that exposure to O_3 for the purpose of odour elimination is only slightly more damaging to cellulose than a mild oxidizing bleach. Test results are, unfortunately, showing some inexplicable deviations from what was expected, and therefore the bleaching exercises intended to offer comparison are perhaps not entirely reliable. More copper number testing of samples treated with oxidizing agents of known strength would be advised in order to rank the oxidative damage inflicted by O_3. Nonetheless, the research has offered an important insight into the levels of oxidation caused by exposure to O_3 gas, and it suggests that O_3 treatment for odour might be considered a viable option for paper artifacts. It must be noted however, that this research pertains only to cellulose and any composite artifacts containing sensitive pigments or dyes should not be subjected to O_3 treatment without further evaluation.

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