25 Preservation Technologies
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Mass Deacidification Carrier Fluid Selection to Protect Media

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ABSTRACT

In order to build an alkaline reserve in paper that neutralizes acids already present and protects against acids adsorbed in the future, most mass deacidification processes use a liquid carrier to deliver alkaline particles or solutes. While certain mass deacidification carrier fluids in use today are inert, others are industrial solvents (heptane, hexamethyldisiloxane–HMDSO) that can be flammable and odoriferous. Although vendors using more aggressive fluids screen collections for media compatibility, given the hundreds of thousands of artifacts undergoing mass deacidification yearly, we can expect loss of historic and artistic content.

We have performed several experiments, taking thousands of measurements in the CIELAB color space to quantify the color change of an increasingly large number of relevant media (highlighters, stamp pad ink, colored pencils, markers) on relevant acidic (book and bond) papers. Measuring before and after mechanical action while submerged in relevant mass deacidification carrier fluids in use today (perfluorohexane, heptane, and HMDSO) gauges their susceptibility to color change during treatment. We concluded that perfluorinated hydrocarbons seldom if ever cause noticeable changes in color density of even of the most fugitive media. By contrast heptane and HMDSO induce more changes noticeable to the human eye. Therefore, carrier chemistry is an important though underappreciated criterion in the selection of mass deacidification methods.

INTRODUCTION AND MOTIVATION


Fig. 1. Paper brittle due to acid catalyzed degradation


Fig. 2. PTLP global footprint. Key: Yellow pins – sales offices, red pins – corporate plants, blue pins – national institutions (libraries, archives, universities), green pins – partnerships with private conservation laboratories

Acid catalyzed degradation of paper-based works is a primary threat to their preservation (1, Fig. 1). Given the importance of book and paper-based collections in scholarly communication and historic and artistic works, acid catalyzed degradation is a threat to cultural heritage as a whole. Given the magnitude of the problem, national libraries and archives, as well as private conservation laboratories, install mass deacidification facilities and spray systems to protect their collections or send them to another facility. Today, there are nine mass deacidification installations using the Bookkeeper technology owned by Preservation Technologies, LP (PTLP) on four continents, with new facilities in Korea and Russia built within the last two years (Fig. 2). PTLP also sells Bookkeeper deacidification spray systems and spray dispersion product worldwide (Fig. 3).

Research interest into deacidification is similarly expanding. Articles now appear weekly in publications ranging from core discipline physical science and engineering to popular journals, with the urge to protect cultural heritage surpassing the purely academic interest. Topics have now moved from the validity of the basic approach to how deacidification can be achieved in diverse, challenging artifacts (2). Perhaps the paper-based collections requiring the most caution are those with media sensitive to water or other solvents often used in deacidification. Certain mass deacidification processes feature industrial solvents such as heptane and hexamethyldisiloxane (HMDSO) that are flammable and odoriferous (3). While safety to persons and artifacts is the first question of owners and collections managers prior to approving a deacidification treatment, the effect of mass deacidification solvents on sensitive media is underrepresented in the deacidification literature. In this poster we present new results on color changes (ΔE^*_{ab}) induced in relevant media on naturally aged papers by heptane and HMDSO and the inert perfluorocarbons used by Preservation Technologies, L.P. (Fig. 4).

Fig. 3. Bookkeeper Deacidification Spray System


Fig. 4. Bookkeeper Mass Deacidification of books using magnesium oxide particles (white) suspended in inert perfluorocarbon carrier fluid

MATERIALS AND METHODS

Media selection

Three naturally-aged, acidic, unmarked papers were selected to exemplify papers undergoing deacidification today. A rosin-alum sized paper manufactured ca. 1994 exemplifies acidic machine-made book papers, a bond paper (Southworth Fine Business Paper, 25% cotton, ca. 1992) exemplifies acidic papers found in records, and an acidic newsprint stored in an office environment ca. 5 years in its original roll exemplifies art on newsprint. In addition, new Whatman Grade 2 Filter Paper was added to this study to observe a simplified (pure cellulose paper) system under all conditions.


Fig. 5. Media used in this study

Altogether, 21 different media were applied to the four papers named above, creating a large sample set (Fig. 5). These media include those about which our customers routinely enquire to ensure that they are compatible with our deacidification process. These include red and green stamp pad ink and yellow highlighters. In addition, several diverse media were added that customers have not asked about explicitly, but that we anticipate in collections undergoing deacidification. These include pastels and colored markers. For clarity, we refer to the marking of all samples as "inking" despite this diversity of media.

Inking of papers


Fig. 6. Test samples and their placement on the measurement platform

Paper samples were cut to 15.00 ± 0.05 mm x 120 mm using a JDC Precision Sample Cutter 150M-10 (Thwing-Albert) to ensure consistent placement within the jig (Fig. 6). Papers were inked manually with an ink density to represent that of collections (not to conform to a specific reference). For media with line widths shorter than the spot size (8mm diameter), lines were drawn close together on the sample to avoid uninked areas but may not appear uniform across the surface. While an effort was made to achieve uniform ink density across the inked area, effects from the paper non-uniformity, application method, and capillary action/edge effects are present. These factors required that each sample (having a specific paper, ink, and carrier fluid exposure) be produced in triplicate.

Visible spectrophotometer

All reflective colors of surfaces measurements were collected using a Minolta CR-300 Chroma Meter (Fig. 7, 8 mm-diameter measurement area, diffuse illumination, 0° viewing angle, specular component included) and recorded as $L^*a^*b^*$ values (4).


Fig. 7. Minolta CR-300 Chroma Meter, measuring platform, test sample, and jig

Measurement technique

As explained above, samples could not be expected to be uniform either within the spot size or across the inked area despite an effort to achieve this. Therefore, samples were measured before and after exposure in the same location (in the center of the inked area) in triplicate to determine measurement repeatability/uncertainty. For each replicate measurement the sample and spectrometer were repositioned using a jig (Fig. 7).

In order to rigorously assess the effects of mass deacidification carrier fluid exposure to color change, variation in ink density across the sample set had to be taken into account. Therefore, each sample was produced in triplicate as described above.

Sample exposure

Samples were exposed to mass deacidification carrier fluids HMDSO, heptane, and perfluorohexane (all 98+%) in 500 mL media bottles (300 mL fluid, 5 hrs.) under uniform mechanical action using a Roller Dog BIG24 (Fig. 8) without heating. Samples were exposed to the fluids as vended without the addition of alkaline particles or solutes.

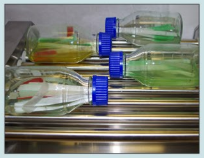
Fig. 8. Samples under carrier fluid exposure condition

RESULTS AND DISCUSSION

Measurement uncertainty

To determine the uncertainty of the measurement technique, one standard deviation for each triplicate measurement of the same sample was averaged over the entire sample set ($N = 1480$) in its initial condition. For the lightness and color channels, L^*, a^*, *and* b^*, this gives 0.5 ± 1.2, 0.5 ± 1.1, and 0.7 ± 2.8, respectively. As described above, papers were inked to represent collections (and not to conform to a reference) so the samples were compared among themselves. Averaging ΔE^*_{ab} between the 1st and 2nd, 2nd and 3rd, and 1st and 3rd replicates gives 1.4 ± 3.2.

Uniformity of inking uncertainty

To add the uncertainty due to replicate sample preparation, one standard deviation for one measurement of each of three samples was averaged over the entire sample set ($N = 1480$) in its initial condition. For the lightness and color channels, L^*, a^*, *and* b^*, this gives 3.2 ± 3.6, 2.4 ± 3.0, and 2.9 ± 4.2, respectively. To perform the analogous color difference analysis as above, averaging ΔE^*_{ab} between the 1st and 2nd, 2nd and 3rd, and 1st and 3rd samples gives 7.3 ± 8.5. Because a commonly accepted just noticeable difference (JND) of ΔE^*_{ab} is 2.3 (5), on average there will be a just noticeable difference between samples of the same formulation. Nevertheless, we can observe significant color changes induced by carrier fluid exposure, and in some of these the difference between carriers is significant, all else being equal.

Discoloration of carrier fluid

Fig. 9. Carrier fluids after exposure, heptane (center), HMDSO (right), and perfluorohexane (left)

First evidence of mass deacidification carrier fluids heptane and HMDSO to solubilize sensitive media may be seen in figure 9, where heptane (center), and HMDSO (right) have become visibly discolored relative to perfluorohexane (left) exposed to identical inked samples.

Color change due to carrier fluid exposure

ΔE^*_{ab} values were calculated from one measurement each of all three samples, paying careful attention to error propagation. Values were calculated from the first measurement of each target, the second, and third, to identify any measurement error. Average ΔE^*_{ab} between the initial condition and the exposed sample for each sample formulation averaged over the entire sample set is 10.6 for heptane, 7.2 for HMDSO, and 4.8 for perfluorohexane. In several instances, there is a significant and appreciable difference between the same sample formulations exposed to different fluids. This may be seen in the results we obtained for an oil pastel (Fig. 10), where the average ΔE^*_{ab} is higher for all heptane and HMDSO formulations than perfluorohexane, and in heptane significantly higher than perfluorohexane in all formulations but one. Although there is a wider distribution in the data for an oil paint (Fig. 11) there is nevertheless a significantly higher ΔE^*_{ab} for HMDSO than perfluorohexane, and significantly higher ΔE^*_{ab} for heptane than HMDSO in the alum-rosin samples. Finally, for the soft pastels (Fig. 12) average ΔE^*_{ab} values for all formulations are higher than the other carriers, and significantly higher for the Southworth and Whatman papers.

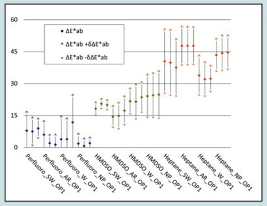

Fig. 10. ΔE^*_{ab}, plus and minus one standard deviation, before and after exposure (5 hrs.) of oil pastel on Southworth Fine Business Paper (_SW_), alum-rosin sized paper (_AR_), Whatman Grade 2 Filter Paper (_W_), and newsprint (_NP_) to mass deacidification carrier fluids as marked

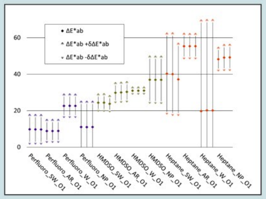

Fig. 11. ΔE^*_{ab}, plus and minus one standard deviation, before and after exposure (5 hrs.) of oil paint on Southworth Fine Business Paper (_SW_), alum-rosin sized paper (_AR_), Whatman Grade 2 Filter Paper (_W_), and newsprint (_NP_) to mass deacidification carrier fluids as marked

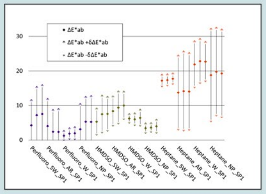

Fig. 12 ΔE^*_{ab}, plus and minus one standard deviation, before and after exposure (5 hrs.) of soft pastel on Southworth Fine Business Paper (_SW_), alum-rosin sized paper (_AR_), Whatman Grade 2 Filter Paper (_W_), and newsprint (_NP_) to mass deacidification carrier fluids as marked

CONCLUSIONS

In this study of color changes in relevant sensitive media due to exposure to mass deacidification carrier fluids in use today, we conclude the following:

- Although hand-inked samples differed from each other (on average) more than a just noticeable difference (JND) of $\Delta E^*_{ab} = 2.3$, in many samples a statistically significant color change was observed following carrier fluid exposure.
- Color change, as measured by ΔE^*_{ab} from highest overall to lowest overall, were heptane, followed by hexamethyldisiloxane (HMDSO), and perfluorohexane.
- In several sample formulations, ΔE^*_{ab} is significant and noticeable to the human eye.

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