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Changes in Paper Color due to Artificial Aging and the Effects of Washing on Color Removal

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Abstract

The color change of paper aged under various conditions of temperature and relative humidity is studied, and the effectiveness of washing for removing colored degradation products is assessed. Color production occurs in a manner typical for the deterioration of organic materials under conditions ranging from 50–90°C and from 30–80% relative humidity at three specific dew points. The rate of color change and the shape of the color change curves vary with the specific conditions. The best single predictor of color change is dew point.

Color change can be partially reversed by washing, but the degree of reversal decreases with more severe degradation. Those samples with the greatest color change had the lowest percentage of color removed by washing. In addition, the aging conditions affect the degree to which color change can be reversed by washing. Samples aged under different conditions, but with similar color change, have different proportions of soluble colored material.

An increased dew point resulted in increased color production. If the results found for the artificial aging conditions studied apply to room condition, and if the color change results are found to be characteristic of other chemical degradation processes, then dew point would be the best predictor of chemical stability in storage. To minimize deterioration, therefore, the storage environment should be based upon the lowest feasible dew point rather than on the choice of a specific relative humidity.

Keywords

Paper, cotton, cellulose, artificial aging, color, washing, water, dew point

Introduction

Temperature and relative humidity (RH) play very important roles in the aging of paper. They influence both the *rate* at which paper ages and the *way* it ages. The degradation of paper involves a number of types of reactions, primarily hydrolysis and oxidation. The rate at which each reaction occurs can vary independently of the others. Thus, even if the same reactions occur under two different sets of aging conditions, the relative rates of the reactions may be very different. Some of these reactions cause changes in the color of the paper.

Earlier work demonstrated that dry and moist aging produce very different mixtures of soluble degradation products[1,2]. The mixture of products produced during moist aging includes a large proportion of hydrolysis reaction products, while the result of dry aging is both a smaller proportion of hydrolysis products and a smaller total quantity of soluble products.

Knowledge of how environmental conditions influence the aging of paper is important for several reasons. The conservation treatment of aged paper objects is influenced by the condition of the paper and the known or deduced history of its aging. The choice of environmental conditions for storage should be based, in large part, on how the conditions will affect the aging of the paper. Accelerated aging conditions used to evaluate either materials or the effects of treatments should be chosen so that the accelerated aging conditions reproduce natural aging as closely as possible, speeding up the rate of aging without changing the nature of the aging process.

When examined for treatment, the evaluation of artifacts is based on their appearance and feel, of which color is a large part. This is especially so with paper. Color also is the main visual cue to the state of degradation or age of paper. Conservators use a subjective evaluation of color to determine the degree of deterioration and to help in deciding whether washing would be a useful treatment to increase the effective life of the artifact. In a study in which 18 historic papers were washed and evaluated, the subjective perception was that washing increased the "health" of most of the specimens (Vitale, 1992a). Health was correlated with averaged rankings of both the Yellowness Index $_{E313}$ and work (area under stress-strain curve)[3,4].

In recent work, washing was found to alter "as-manufactured" mechanical properties and "dried-in" strains of paper[5,6]. This suggested that while washing is a beneficial treatment it is not without its liabilities. This study, on the other hand, suggests washing is desirable in many cases that would normally be considered marginal because the color of the sheets had not changed dramatically enough to warrant washing.

Relative humidity, temperature, and dew point

In air with any concentration of water vapor, the temperature to which it must be cooled to cause water vapor to condense to liquid is the *dew point*. The dew point specifies the absolute water vapor concentration in the air. Relative humidity is the ratio of this absolute water vapor concentration to the maximum water vapor concentration possible at a specific temperature. The maximum possible water vapor concentration increases with temperature. Air with a specific absolute water vapor concentration (dew point) has a lower relative humidity at a higher temperature.

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Literature

Changes in the color of cellulose have been studied in the past[7,8]. The development of color was associated primarily with the oxidative introduction of an aldehyde group in the anhydro-glucose ring at the #6 carbon or the oxidation to a ketone at either carbon #2 or #3. Arney and Chapdelaine demonstrated that there is a relationship between yellowing and acidity developed during aging, and the change in reflectance at 500 nm is linear both in the presence and absence of oxygen[9]. Spinner has reviewed the source of color reversion in common manufactured papers[10]. Gray has identified a relatively constant activation energy for changes in brightness (TAPPI A-452m-58) for a variety of modern manufactured papers[11]. Hon has presented thorough reviews of possible sources of color and color reversion[12].

The existing work often is concerned with paper bleaching and color reversion, or the estimation of paper permanence, and uses color measurement units not directly traceable to human perception. These studies generally do not consider the aging of paper beyond the degree of change that would result in the loss of its commercial value. Conservators often deal with art objects or historic artifacts that exhibit a much greater degree of deterioration.

While comments on change in color (brightness, reflectance at a specific wavelength, ΔE CIE L*a*b*, or Yellowness Index) are included in many conservation science articles on paper (among many) the relationship between the change in color ΔE (CIE L*a*b*) and a range of temperatures and relative humidities is still unclear[13,14].

Experimental: aging conditions and duration

Ten samples each of two cotton papers were aged under seven different temperature and relative humidity conditions (See Table I). Samples of each paper were removed from each aging chamber after varying lengths of time; aging of remaining samples continues.

Table I. Conditions and times of aging for the Whatman #1 and CAL cotton paper samples.

Temperature °C	RH %	Dew point °C	Days of aging
90	50	74.0	2, 5, 8, 12, 20, 34, 49, 69, 105, 278
80	77	74.0	2, 5, 8, 12, 20, 34, 49, 69, 105, 278
80	32	55.5	10, 16, 25, 51, 106, 207, 373, 581, 861, 1372
70	50	55.5	10, 16, 25, 51, 106, 207, 373, 581, 861, 1372
60	80	55.5	10, 16, 25, 51, 106, 207, 373, 581, 861, 1372
60	30	36.9	56, 157, 323, 531, 811, 1203
50	50	36.9	56, 157, 323, 531, 811, 1203

The temperature in each chamber was maintained and monitored with a copper onstantan thermocouple (type T) connected to a proportional controller. The relative humidity was maintained by a constant flow of filtered air conditioned to a selected dew point (absolute water vapor concentration) by bubbling it through a water bath maintained at the appropriate temperature. The humidified air from each saturator flowed through parallel heated supply lines to a group of two or three chambers, each maintained at a different temperature higher than the dew point. The relative humidity in each set of chambers was adjusted initially by monitoring the dew point of the humidified air supply with a General Eastern dew point hygrometer, system 1100D with a 1111D sensor. Once set, the relative humidity in each chamber subsequently was monitored with electronic RH sensors, model PC-2101, manufactured by Thunder Scientific Corp., Albuquerque, NM. Temperatures in the sample chambers and water bath were monitored using standard type T thermocouples and digital thermometers.

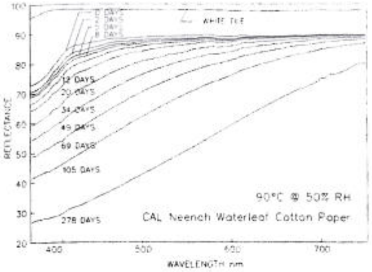

Figure 1. Reflectance spectra, 375–750 nm, of the CAL cotton paper aged at 90°C @ 50% RH (dew point 74.0°C) for 0–278 days with the HunterLab white tile reference standard.

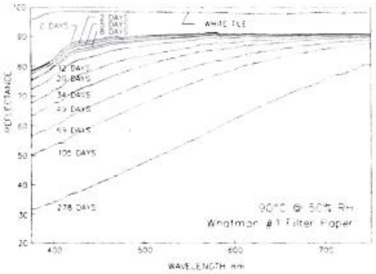

Figure 2. Reflectance spectra, 375–750 nm, of the Whatman #1 filter paper aged at 90°C @ 50% RH (dew point 74.0°C) for 0–278 days with the HunterLab white tile reference standard.

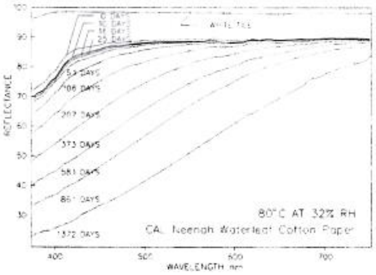

Figure 3. Reflectance spectra, 375–750 nm, of the CAL cotton paper aged at 80°C @ 32% RH (dew point 55.5°C) for 0–1372 days with the HunterLab white tile reference standard.

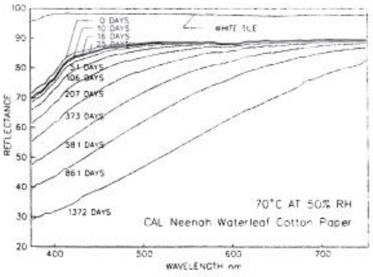

Figure 4. Reflectance spectra, 375–750 nm, of the CAL cotton paper aged at 70°C @ 50% RH (dew point 55.5°C) for 0–1372 days with the HunterLab white tile reference standard.

Washing

Approximately 2.5 in^2 portions of selected samples were washed in ultrapure deionized water for one hour, drained for 1–2 minutes and dried between blotters at a pressure of 690 Pa (0.10 psi). The deionized water was processed through Hydroservices Corporation mixed-bed and activated charcoal columns. In-pipe water quality was 18.1 megaohms at 20°C. No pH measurement was made, due to the inaccuracy of such a measurement caused by the absorption of atmospheric carbon dioxide and reference electrode solution.

Ultrapure water, in relation to other common water types, has been shown to have little or no effect on the mechanical and chemical properties of historic and modern paper[15,16]. This suggests that the effect of washing with ultrapure water should not be different than other types of water for removing soluble components, and that it has no specific effects which would alter the chemistry or interfiber bonds of the paper uniquely.

Color Measurements

The reflected spectrum (375–750 nm) of each sample was measured using a Hunter Lab Ultrascan spectrometer with a D65 light source, 10° viewing angle, 0.375 in^2 sphere opening, in the RSIN mode (reflected specular light included). The entire spectral curve was recorded, and CIE 1976 $L^*a^*b^*$ values and the ASTM Yellowness Index $_{E313}$ were calculated. Measurements taken from five different spots on each sample were averaged and the standard deviations calculated. The differences in total color, ΔE, as well as ΔL^*, Δa^* and Δb^* were calculated for each aged sample relative to the control sample[17]. The ΔE for the aged and washed samples was calculated relative to the washed control. The ΔE determination for the difference between washed minus aged was calculated relative to the aged version of the washed sample.

Spectral reflectance from 375–750 nm was calculated as an average of the same five spectral readings for each aged, and aged and washed specimen. Selected examples of the spectral reflectance have been plotted in the same figure along with the HunterLab Instrument Standard D8 #7566 (2/88, Reston, VA) white tile standard. Small humps, peaks and other features are evident in these samples that do not appear in the spectra of the white tile.

The CIE 1976 $L^*a^*b^*$ scale is a human perception based, color axis system for defining a specific color by its location on three axes: a vertical axis and two intersecting perpendicular axes. L^* measures lightness/darkness along the vertical axis, with 0 being black and 100 being white. The a^* axis measures redness-greenness, with positive values indicating redness, and negative values indicating greenness. Similarly, b^* values measure blueness-yellowness, with positive b^* values indicating yellowness and negative b^* values indicating blueness.

Materials

Two types of paper were used: (1) a waterleaf cotton paper prepared by Neenah Paper Company (Appelton, WI) for the Conservation Analytical Laboratory (CAL) and (2) Whatman #1 filter paper. The research paper from Neenah is a staple cotton fiber unsized sheet which is 0.004″ thick. Fiber analysis (conducted by the Institute of Paper Science and Technology, IPST, formerly Institute of Paper Chemistry, IPC) determined that the paper is 91% cotton seed hair pulped from cotton knit cuttings in sodium hydroxide liquor, with 2.2% softwood and 6.7% hardwood, both pulped using predominantly the Kraft process.

The Whatman #1 filter paper is made from high alpha cellulose cotton linter pulp beaten and formed to 0.0069″ thickness for an 11 micron particle capture size. No acid or alkaline wash or wet strength additives are used. Ash content is listed as 0.06%; cation content is 185 ppm Ca, 160 ppm Na, 7 ppm Mg, 5 ppm Fe; and anion content is 130 ppm Cl and 15 ppm S.

Results of aged (only) specimen data

Figures 1 and 2 plot the change in reflectance spectra for the CAL cotton and Whatman #1 specimens aged at 90°C@50%RH. The changes in the spectra

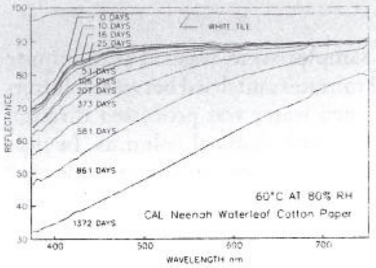

Figure 5. Reflectance spectra, 375–750 nm, of the CAL cotton paper aged at 60°C @ 80% RH (dew point 55.5°C) for 0–1372 days with the HunterLab white tile reference standard.

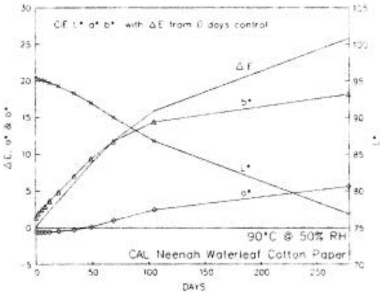

Figure 6. The CIE 1976 L*, a*, b* and ΔE (from 0 days, control) data for the CAL cotton paper aged at 90°C @ 50% RH (dew point 74.0°C) for 0–278 days. Note the second y axis for L* on right.

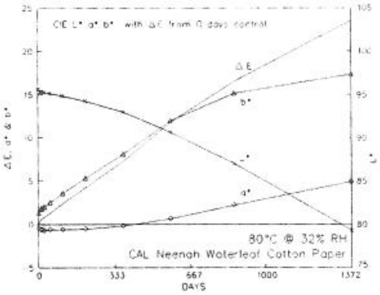

Figure 7. The CIE 1976 L*, a*, b* and ΔE (from 0 days, control) data for the CAL cotton paper aged at 80°C @ 32% RH (dew point 55.5°C) for 0–1372 days. Note the second y axis for L* on right.

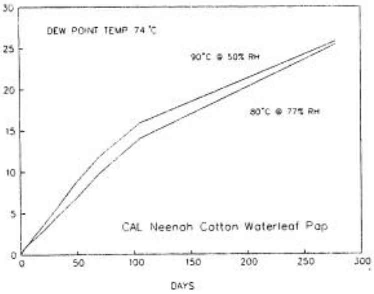

Figure 8. ΔE for the CAL cotton paper at dew point 74.0°C, 90°C @ 50% RH and 80°C @ 77% RH, aged for 0–278 days; note the near-parallel behavior.

that occur upon aging are typical of those obtained for all conditions (see Figures 3–5). The shoulder on the curve of the unaged papers (0 days) between 395–450nm disappears as the aging process proceeds. Note that this feature does not appear in the spectral curve for the HunterLab WHITE TILE that is included in all figures. There are also features between 555–620 nm that also disappear during the aging process. In the spectra for samples aged longest in Figures 1 and 2 (278 days), new features appear around 380 nm, 420 nm and in the range 670–750 nm. While these features cannot now be attributed to a specific process or degradation product, it can be stated that two papers of different composition (cotton linters vs. cotton staple fibers) show the same loss and introduction of features. Note that the red (shorter wavelength) end of the spectrum changes less than the blue (longer wavelength) end. The increased absorption in the blue end of the spectrum causes the paper to appear yellower and darker. This is most clearly seen when ΔE, L*, a*, and b* are plotted together, as in Figures 6 and 7.

Figures 3, 4, and 5 plot the reflectance spectra curves for the CAL cotton paper at 80°C@32%RH, 70°C@50%RH and 60°C@80%RH (55.5°C dew point) for the 0–1372 day aging series. The resemblance is remarkable, both within the 55.5°C dew point group and between the Whatman #1, 90°C@50%RH, samples in the 74.0°C dew point series (see Figure 2) and the 55.5°C dew point group.

When L*a*b* and ΔE values are plotted together in Figures 6 and 7 (CAL cotton 90°C@50%RH and 80°C@32%RH) the b* (yellowness-blueness) value appears to control the trend of the ΔE plot. Note, also, that under these conditions at approximately 49 and 373 days of aging, respectively, the a* value becomes positive and has a significant influence on the ΔE curve.

Figure 8 plots ΔE for the 74.0°C dew point group (90°C@50%RH and 80°C@77%RH) of the CAL cotton paper from 0–278 days of aging. The plots are remarkably similar both in shape and slope, increasing linearly at first and then tailing off.

Figure 9 plots ΔE for the 55.5°C dew point group (80°C@32%RH, 70°C@50%RH and 60°C@80%RH) of the CAL cotton paper for the 0–1372 day aging period. Although they deviate slightly during the initial stages of aging, the three curves become nearly parallel for the rest of the aging period. Note that curves for 70° and 80° exhibit the S-shaped curve (induction time, autocatalytic, steady state, and autoretardation) discussed by Feller[18].

Figure 10 plots ΔE for the 36.9°C dew point group (60°C@30%RH and 50°C@50%RH) for the 0–1203 day period. Though very little change in color (note the ΔE scale) has occurred after 1203 days of aging (1.5 ΔE), there is some indication that these two plots also will reach parallel paths after a small initial deviation.

Figures 11 and 12 show the combined ΔE data for all aged series in the CAL cotton and Whatman #1 groups. Note that the results for both papers are almost identical. The Whatman #1 samples show a slightly more pronounced and longer induction period. The slightly darker values that the CAL cotton samples aged the longest have attained may be the result of a shorter induction period.

Aged & washed specimen data

Figures 13, 14 and 15 plot the data and Table II lists the changes in ΔE after washing for the three dew point groups of the CAL cotton paper. It can be seen in the data for the high dew point group that only a small portion (1.9–2.4 units) of the color change is reversed by washing after 69 days of aging and an even smaller reversal, 0.9–1.8 units, is realized after 278 days of aging (See fig. 13). Note that the aged, and washed & aged samples symbols (with dotted line tracing the difference) in the figures are superimposed over the aged curves for the purpose of providing a reference.

It can be seen in Figure 14 that washing the samples in the 55.5°C dew point group results in relatively constant absolute changes in ΔE. On average, there is a larger change in the 55.5°C group than for the 74.0°C dew point group

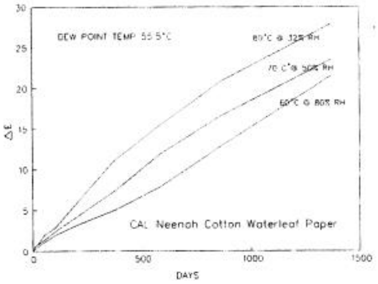

Figure 9. ΔE for the CAL cotton paper at dew point 55.5°C, 80°C @ 32% RH, 70°C @ 50% RH and 60°C @ 80% RH, aged for 0–1372 days; note the parallel behavior in the later stages of this aging period.

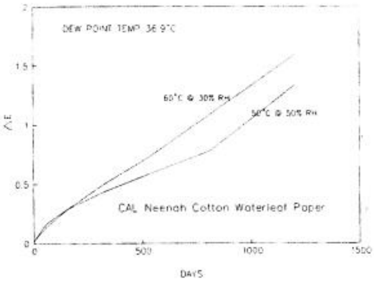

Figure 10. ΔE for the CAL cotton paper at dew point 36.9°C, 60°C @ 30% RH and 50°C @ 50% RH, aged for 0–1203 days; note the parallel behavior in the later stages of this aging period.

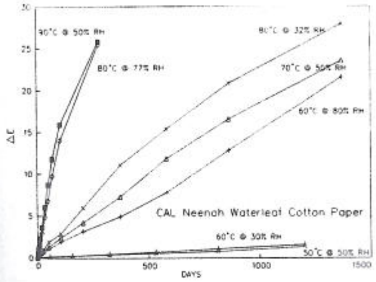

Figure 11. ΔE of all the dew point groups (74.0°C, 55.5°C and 36.9°C) for the CAL cotton paper; note distinct grouping by dew point and similarity to Whatman #1 filter paper data.

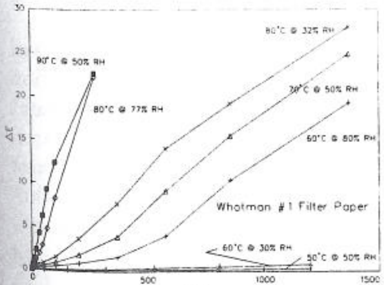

Figure 12. ΔE of all dew point groups (74.0°C, 55.5°C and 36.9°C) for the Whatman #1 filter paper. Note the grouping by dew point.

Table II. ΔE before (aged) and after washing, difference and percent difference of selected CAL cotton paper samples.

Series	Days of aging	ΔE aged	ΔE washed	Difference	Percent change
90°C@50%RH	0	0	0.19	0.2	NA
	69	11.74	9.34	2.4	21%
	278	25.79	23.94	1.8	7%
80°C@77%RH	69	9.75	7.90	1.9	19%
	278	25.42	24.45	1.1	4%
80°C@32%RH	373	11.10	7.31	3.8	34%
	581	15.38	12.06	3.4	22%
	861	20.80	17.23	3.6	17%
70°C@50%RH	373	7.32	4.44	2.9	39%
	581	11.84	8.16	3.7	31%
	861	16.55	13.40	3.2	19%
60°C@80%RH	373	4.96	3.43	1.5	31%
	581	7.81	5.49	2.3	30%
	861	12.80	10.90	1.9	15%
60°C@30%RH	1203	1.59	0.72	0.9	55%
50°C@50%RH	1203	1.34	0.68	0.7	49%

(2.9 units vs 1.75 units). The 80°C@32%RH and 70°C@50%RH changes range from 2.9 to 3.8 units and those for the 60°C@80%RH group range from 1.5 to 2.3 units. These amounts are larger percentages of the original color change than for the 74.0°C dew point group. This is so, even when samples that experienced about the same degree of color change are compared.

Figure 15 shows that for the 36.9°C dew point samples, about half of the color change is reversed by washing. Since the total color change in these samples is much smaller (1.5 vs. 5–25 units) than in the other groups the results cannot be compared directly.

Figures 16 and 17 show the spectral reflectance, 375–750 nm, data for selected samples before and after washing. Change occurs primarily in the yellow region.

Production of color

Color changes in both types of paper depend on time, temperature and relative humidity. Plots of the total color change, ΔE, are remarkably linear during much of the aging process. The shape of many ΔE plots exhibits an S-shaped curve typical of the deterioration of organic materials, as described by Feller[19]. In some plots, within the first few days a very fast but short-lived deterioration, inception period, can be observed. This is followed by a relatively slow induction period. A period of rapid increase after induction demonstrates an autocatalytic type of behavior. Prolonged steady state behavior, the linear portion of the curve, follows. None of the curves reached a termination point, but most show the declining rate indicative of autoretardation.

Deviations from linearity occur during the initial stages and after long periods of aging. The early stages of the plots for the Whatman #1 55.5°C dew point series are typical of autocatalytic behavior (an increasing slope followed by a steady rate), and the later stages of the plots for the 74.0°C dew point series are typical of autoretarded behavior (a slope that decreases over time). The nonlinearity during the initial stages of aging can be due either to the effects of reactions that occur only during this period or because the amounts of intermediate reaction products had not yet built up to equilibrium (steady state) concentrations. The decrease in rate during the later stages of aging can be due to either the color of the paper approaching a limiting value or to the decrease of reactants that generate the colored products.

The complexity and variability of the ΔE curves, along with the appearance of some humps and features in the visible light reflected spectra and disappearance of others during aging, indicate that the production of color is not a single

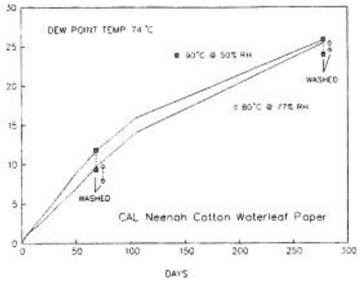

Figure 13. ΔE for the deionized water washed CAL cotton paper specimens following aging at 90°C @ 50% RH and 80°C @ 77% RH, for 69 and 278 days respectively, superimposed over the aged (only) data. Note that longer aging results in decreased loss of color as a result of washing.

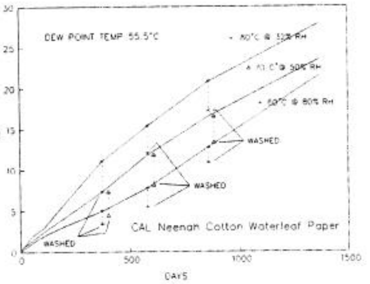

Figure 14. ΔE for the deionized water washed CAL cotton paper specimens following aging at 80°C @ 32% RH, 70°C @ 50% RH and 60°C @ 80% RH for 373, 581 and 861 days respectively, superimposed over the aged (only) data.

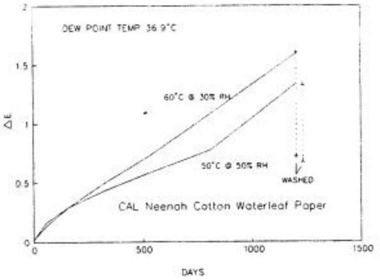

Figure 15. ΔE for the deionized water washed CAL cotton paper specimens following aging at 60°C @ 30% RH and 50°C @ 50% RH, for 1230 days respectively, superimposed over the aged (only) data.

reaction or process. This is confirmed by the fact that changing the temperature and changing the relative humidity affects the shapes of the curves differently.

Color change and deterioration reactions

While this report does not contain the results of degradation by-product analysis (in process) some preliminary conclusions can be drawn. The presence of water plays a large part in the development of color as indicated by the fact that an increase in relative humidity has a significant effect on the rate of color production. In going from 30–80% RH at 60°C, both the moisture content of the paper and the water vapor concentration in air increase 2.7 times while the equilibrium reaction rate increases about 14-fold. Going from 32–77% RH at 80°C increases the moisture content of the paper and the water vapor concentration of the air by roughly the same factor, 2.4 times, but this results in only a 6-fold increase in rate. Both of these values are greater than would be expected based upon a linear dependence of the reaction rate on either relative humidity or moisture content, i.e., a 2.4-fold to 2.7-fold increase in rate. The larger relative increase in the reaction rate at the lower temperature indicates that the overall process of color change is more dependent on water content at lower temperatures.

Changing the temperature from 50°C to 90°C at constant relative humidity (50%) produces a 120-fold increase in the rate of color production. Changing the temperature from 70°C to 90°C at 50% RH produces a 9-fold increase in rate.

Increases in relative humidity and temperature result in greater color production, but a smaller percentage of that color can be removed by washing. The amount of color removed by washing for samples with a ΔE of about 10–11 is halved (3.8 vs. 1.9) for the increase in relative humidity from 32% RH to 77% RH at 80°C. For an increase in temperature from 70–90°C at 50% RH, the amount of color removed by washing (for samples with a ΔE of about 12) decreases by about one third (3.7 to 2.4).

Application to storage

The most striking feature of the graphs is the clustering of the curves into three distinct groups based on the dew point of the air flowing through the chambers. The curves within each of the three groups differ from each other by less than they differ from curves of other groups. This is the combined result of two opposing effects. If the temperature is raised at constant dew point then the relative humidity decreases. These two changes (higher temperature, lower relative humidity) produce opposing effects.

An increased temperature means that all molecules of the reactants have a greater average energy, and specifically that a higher proportion of them have the amount of energy necessary for a reaction to occur. Raising the temperature at constant relative humidity should increase the rate of all reactions that are occurring. This can be seen by comparing pairs of curves with different temperatures but the same relative humidity, e.g., 60°C@80%RH and 80°C@77%RH; the 80°C@77%RH conditions result in an increase in the rate of production of color.

Relative humidity is directly related to the activity (effective concentration) of water. A relative humidity of 100% is the equilibrium water vapor concentration over liquid water. A relative humidity below 100% thus represents the water vapor concentration over a liquid with an "equivalent" concentration of water, i.e., 50% water in alcohol solution. Thus one finds, for instance, that the amount of water vapor absorbed in paper is directly related to relative humidity rather than to the absolute water vapor concentration of air. There is 5.7 times as much water vapor in the air at 90°C@50%RH than there is at 50°C@50%RH, but the amount of absorbed water in paper is approximately the same, only 1.15 times greater at 90°C than at 50°C at 50% RH[20]. Lowering the relative humidity at constant temperature reduces the amount of water absorbed in paper. Less water results in reduced rates of those reactions which are dependent upon water. The effect of lowering the relative humidity can be seen by comparing the

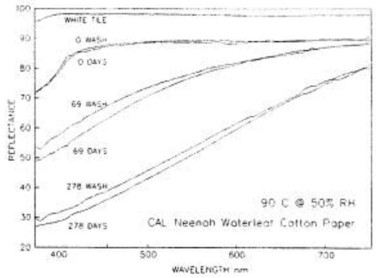

Figure 16. Reflectance spectra, 375–750 nm, for the CAL cotton paper specimens which were washed in deionized water following aging at 90°C @ 50% RH for 69 and 278 days respectively, with the HunterLab white tile reference standard.

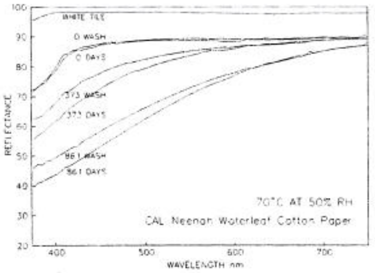

Figure 17. Reflectance spectra, 375–750 nm, for the CAL cotton paper specimens which were washed in deionized water following aging at 70°C @ 50% RH for 373 and 861 days respectively, with the HunterLab white tile reference standard.

80°C@77%RH curve with the 80°C@32%RH curve. Lowering the relative humidity to 32% decreases moisture content of the paper from 7.0% to 2.9%, to 40% of its 77% RH value, while the rate of reaction decreases to less than 20% of its value at 77% RH[21]. Thus, the reaction rate decreases with the decreases in RH and moisture content, though the relationship is not linear.

If the dew point is kept constant as the temperature is raised, then the relative humidity is lowered. This occurs in the change from 60°C@80%RH to 80°C@32%RH. Increasing the temperature tends to increase the rates of all reactions, but the lower relative humidity tends to decrease the rate of water dependent reactions. It turns out that for color change these two effects nearly cancel each other out. Thus the plots within each of the three groups are similar. This, of course, is only because the relationships between the rate of color change and the temperature and relative humidity are such that the increase due to the increased temperature and the decrease due to the decreased relative humidity happen to be about the same. Larger differences would be obtained in a system in which the degradation process had a different degree of dependence on the temperature or relative humidity. A reaction in which water played no part, for instance, would have the same rate at different relative humidities if the temperature were held constant, and would speed up with increased temperature no matter what the relative humidity.

Color change for these samples can be relatively accurately predicted (especially the slopes of the linear portions of the plots) within the range of conditions studied from the *dew point only*, without knowing either the temperature or relative humidity. For instance, the 70°C@50%RH curve would provide a relatively accurate prediction of color change for any of the aging conditions with a dew point of 55.5°C. Knowing only the temperature or the relative humidity does not allow such accurate predictions.

If, and this is by no means certain, such results are found to extend to other aspects of the aging of paper, such as other chemical reactions and mechanical and physical properties, then the implications for the storage of paper are profound. Fifty percent relative humidity is widely recommended and maintained in many museums, archives, and libraries. Chemical considerations argue for a lower relative humidity to reduce the rate of the water dependent aging processes. Physical and mechanical considerations argue for higher values of relative humidity to prevent damage caused by the fact that paper is stiffer and more brittle at lower relative humidities. Building engineering HVAC (heating, ventilation, and air conditioning) considerations place a limit on the dew point temperature (somewhere above freezing) that can be maintained within a conventional building (not a cold storage facility). To minimize color change (and possibly other types of chemical degradation), a higher priority should be placed on maintaining a low dew point rather than a specific relative humidity. Once the dew point is chosen then the temperature can be adjusted up or down to achieve a relative humidity that is acceptable based on physical considerations such as stiffness or brittleness, and other considerations such as human comfort.

These results indicate that a low dew point minimizes color change. Further work on the chemical and physical changes that have occurred in these paper samples is planned and should help to determine whether the conclusions derived from the color change results also apply to other degradation processes.

Effects of washing

The washing data demonstrate that the amount of soluble material contributing to color change varies with the degree of deterioration and the conditions that cause it. Samples with greater deterioration (higher ΔE) lose a lower proportion of acquired color than samples with less deterioration. The darker the color prior to washing, the smaller the percent color change that results from washing.

Samples that have been aged under different conditions which seem to have experienced the same "amount" of color change as indicated by similar values of ΔE contain different proportions of soluble colored material indicating that they have aged "differently." For example, in samples with a ΔE of about 12, washing removed 2.4 ΔE units of the color in the 90°C@50%RH, 69 days sample while in the 80°C@32%RH, 373 days and 70°C@50%RH, 581 days samples the loss was 3.7–3.8 ΔE units; about 50% more color lost in the lower dewpoint samples.

Conclusions

- Color changes occur in both types of paper, and the rate of change varies with the conditions of temperature and relative humidity. Plots of the total color change, ΔE, are remarkably linear in the middle stages of color production. Many ΔE plots exhibit an S-shaped curve typical of the deterioration of organic materials.
- The production of color during artificial aging has a complex mechanism, which consists of more than one reaction and is dependent upon a number of environmental factors.
- Dew point is the best predictor of the rate of color production.
- An increase in temperature from 50°C to 90°C causes a 120-fold increase in the equilibrium rate of color production.
- An increase in relative humidity from 30% to 80% (at 60°C or 80°C) results in a 6-fold to 14-fold increase in the equilibrium rate of color production.
- When washed, samples with greater color do not lose the same proportion of acquired color as samples with less deterioration; darker samples lose less color. It appears to be desirable to wash paper with small amounts of color change, as well as those which are regularly considered for such treatment.
- In selecting storage conditions to *minimize color change*, a higher priority should be placed on choosing the lowest possible dew point rather than a specific temperature or relative humidity.

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