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Comparing Paper Extract to Traditional Toning Materials

Abstract

To repair damaged paper objects it is often necessary to tone the repair material to match the subtle aged tone of the original. Paper extract has been mentioned in some literature as an appropriate toning material. Although not extensively covered in recent conservation literature, the material is being used by conservators. Paper extract is made by evaporating the wash water from aged paper scraps. Two batches of paper extract were made using different qualities of wash water. The first was prepared with distilled water and the second was prepared with water alkalized with Ca(OH)₂ to a pH of approximately nine. A sample of the prepared extract was analysed with gas chromatography mass spectroscopy (GC-MS) and Fourier transform infrared spectroscopy (FTIR) to determine the major constituents. The pH of each sample was determined before and after accelerated ageing using cold extraction and measured with an electronic pH meter. The extract samples were aged artificially together with samples of paper toned with tea, burnt umber acrylic paint, and Vandyke brown watercolour applied to Whatman filter paper. The samples were thermally aged to test the stability of the paper after exposure to these toning materials. Another sample set was light aged to determine to what degree the materials are fugitive to light. The effect of the accelerated aging was recorded using colorimeter readings done before and after ageing. The stability of the paper was measured using the M.I.T. fold-endurance tester. This study had two objectives; the first was to evaluate paper extract's appropriateness as a toning material in conservation and the second was to inform conservators when making decisions about which toning materials to use.

Introduction – Project Impetus and Scope

This paper is based on research conducted at Queen's University as part of the curriculum of the final year of the Master of Art Conservation program. The toning material was introduced to the

author at workshop conducted by Renate Mesmer, Head of Conservation at the Folger Shakespeare Library, Washington, D.C. The information provided by Mesmer was based largely on an article by Piers Townshend head of Paper Conservation, Tate Conservation Department. The use of toning materials, although not as frequent as other materials such as adhesives, is something all conservators will encounter in their practice. Toning materials are used to tone a repair material to integrate a repair with the original and maintain a cohesive overall appearance. In some cases where superficial damage has been done to an object the toning material may need to be applied to the original object. Common toning materials in use today are watercolour paints, acrylics, inks, dyes, in the past materials like tea, coffee, and even beer have been used and reference to their use can be found in conservation literature (Plenderleith, 56). All of these materials have their advantages and disadvantages. A perfect toning material does not exist. The toning material this research is concerned with is a toning material referred to as paper extract. This material has some very brief mention in conservation literature. There is a short entry about it in the Paper Conservation Catalogue in section 26, "Filling of Losses" and there is an article, discussed above by Piers Townshend. In his article, Townshend outlines results from some experiments conducted on paper extract. Townshend concludes that paper extract is a safe and appropriate material to use in conservation treatments. After correspondence with conservators it was discovered that this material may have a very long history with roots in Asian conservation practices. This material is currently being used in Europe and North America. This project has expanded upon Townshend's work and investigates the long term effects of paper extract compared to other toning materials.

Materials

When choosing a toning material there are many things you must take into consideration. Ideally you want a material that has the following characteristics:

Transparency: in order to properly mimic the effect time has on the tone of a paper, a warm tone that comes from within the fibres of the paper, a material that is transparent is required to allow the light to penetrate and reflect off of the paper fibres behind it for a natural look.

Will not change texture: The material should have a matte finish unless the paper to be matched has a glossy coating on it. The material should also not change the working properties of the paper, for example making it stiff and less pliable.

Lightfastness: a material that fades quickly after application would not be desirable.

Reversibility: reversibility is a very important characteristic for all materials used in conservation treatments. Any treatment performed should be easily removed or reversed without damage to the object.

Non-degrading: the life of your object should not be shortened by a treatment or a repair.

To determine the appropriateness of paper extract as a toning material, prepared samples will be compared to three other traditional toning materials: tea, watercolour and acrylic paint. Tea is a natural dye and has been recommended for conservation treatments in the past (Plenderleith, 56). Tea is translucent but is naturally acidic. Watercolour is a common toning material and is translucent, and with the addition of a barrier layer of methylcellulose is purported to be reversible. The pigment Vandyke brown from Winsor & Newton's Cotman watercolour series has been chosen for its AA lightfastness rating (Extremely permanent). According to Winsor & Newton's rating system, Vandyke brown is transparent to semi-transparent, is a staining colour and has a rating of ASTM 1, permanent for artists' use. Vandyke brown is an organic pigment. Acrylic paints are also considered appropriate for use in conservation. Raw Umber is extremely permanent and received the same rating as Vandyke brown pigment. Raw umber is an inorganic pigment. Synthetic dyes are also used occasionally in art conservation. The advantage of dyes is that dyed paper can be used with any solvent/adhesive system (Norton, 42) and because there is no binder, the colour will not be affected by solvent/adhesive systems. The working properties of the paper after the dye has been applied are retained. Synthetic dyes were not used in this research for the following reasons: the only way to match a given colour is by making a chart consisting of samples of dyed paper of known weight, intensity and dye mixture (Norton, 39). This is a time consuming process. Most dyes are acidic. Acidic materials will deteriorate paper upon aging. Dyes are not reversible and may only be applied to repair material but not to the original object.

Paper extract is made by washing old degraded paper in an aqueous bath and boiling down this wash water to concentrate the water soluble material discolouring the paper. This material can be mixed with water and applied to a repair paper or to the actual object. It was expected that paper extract will be composed of the degradation products of cellulose; these would include products yielded by both hydrolytic and oxidative degradation; de-polymerized cellulose which would include simple sugars and carboxyl groups. When paper degrades there are two major mechanisms for this process. These are: hydrolytic degradation, usually catalyzed by acids, and oxidative degradation usually catalyzed by light. Hydrolytic degradation refers to cleavage at the glycosidic linkage between the ¹C carbon and oxygen by an acid. If carried to completion the final product will be glucose, a monosaccharide. A gas chromatography-mass spectroscopy analysis completed at the University of Northumbria by Bronwyn Ormsby, now a Conservation Scientist at Tate Britain, found that a sample of paper extract prepared by Townshend contained arabinose, xylose, glucose and traces of other monosaccharides. Hydrolysis is not oxidative or colour-producing but it increases the number of sites on the cellulose polymer that are open to oxidation (Casey, 1980). For oxidative degradation, most auto-oxidative processes are random and lead to the introduction of carbonyl and carboxyl groups at various positions in the anhydro-D-glucose units of cellulose (Casey, 1980). These oxidation products are what cause the discolouration of paper as it ages. The major constituents of paper extract are assumed to be monosaccharides like glucose and carboxyl groups like carboxylic acids.

An important impetus for this project was to determine if extract is damaging to paper. Because hydrolysis of cellulose is catalyzed by acids, adding an acidic material to paper could potentially be very destructive. The rate of degradation of cellulose caused by acid hydrolysis is dependent upon the concentration of acid present. The extent of degradation is a function of the length of time to which the artefact is exposed to a certain concentration of acid. If the pH of this paper extract is low, applying it to a paper object could result in hydrolytic mechanisms that will cause a profound drop in the degree of polymerization of the cellulose (Burgess, 1983). If paper extract contains acidic compounds, chances are it will be harmful to paper in the long term. The purpose of this research was to determine whether paper extract is an appropriate material to use in conservation treatments.

Preparing Paper Extract

Because it was not known what mass of paper extract would be washed out of the paper, a wide variety of aged paper was combined in order to be certain a measureable and usable amount of extract was obtained. The intention was to have enough extract to do analysis on as well as enough to tone 40 samples for artificial aging. Two types of paper extract were made. Equal parts of each paper source were measured out so that the compositions of the paper were identical for each type of extract. The first batch of extract was made using distilled water as the wash water. The second used wash water alkalized to pH 9 with calcium hydroxide. Paper extract was expected to be acidic and the second type of extract was made to ascertain whether alkalizing the extract was possible and to observe any effect it would have.

To prepare the extract, raw material was gathered, the sources included: the paper glued to the back of a framed print and a framed watercolour painting being treated in the paper lab at queens. The paper was very brown but the date of framing was unknown. Another source was from pages of scrapbooks, one scrapbook from 1881 and another from 1967. There were two newspaper clippings that had been taped up in the labs at queens and been there for a very long time. Raw material was divided equally to make two separate batches of extract. The final mass was 294.5g of paper for each batch of extract made. Paper was torn and cut into small squares

Figure 1 paper scraps soaking in water to dissolve discoloured degradation products.



amount of discolouration removed. This step is illustrated in figure 1. After paper scraps were thoroughly saturated and wash water was discoloured the paper scraps were removed and the wash water was filtered and evaporated over heat. To prevent the material from scorching, once it had evaporated to a very dark concentrated liquid it was poured into a shallow tray and allowed to evaporate further until a solid material remained. This is shown in figures 2 and 3.

about 4 cm² and soaked in water and heated to maximize the





Figure 2 close up of evaporated extract

Figure 3 Evaporated paper extract in plastic photo tray.

This process was repeated for both batches. To remove it from the trays the material was reconstituted with 75 ml of water. It was this concentrated liquid that was used for analysis and for artificial aging samples.

Experimental: Sample Preparation, Artificial Aging, and Analysis

Before samples for artificial aging were prepared, the material was analysed using gas chromatography. A sample from the distilled water extract and the alkalized water extract was taken from the reconstituted extract batches. The samples were analysed at the Analytical Services Unit at Queen's University. The distilled water extract sample was analysed using gas chromatography with a flame ionization detector (GC-FID).The analyte for the GC-FID was obtained through liquid extraction in dichloromethane. The concentrated liquid extract (1 ml) made with distilled water was mixed with 5 ml of dichloromethane; the mixture was shaken and allowed to settle out. The analyte was taken from the clear bottom layer. The sample (2 μ l) was injected on a 30m GC_{SPBI} column with helium as a carrier gas. The resulting chromatogram showed promising peaks and further analysis was done using gas chromatography – mass spectroscopy (GC-MS).

Analysis was performed on the paper sources to determine the type of pulp used in the making of the paper and to determine the lignin content. A sample was taken from each source of aged paper. A temporary slide was made from each sample in order to perform a Herzberg Stain test. The Herzberg test is able to distinguish between natural pure cellulose, mechanically processed lignocelluloses and chemically processed lignocelluloses. A clump of fibres from the sample was placed on a glass microscope slide. The cover slip was placed on top of the fibre particles and a drop of prepared Herzberg staining solution was applied to the edge of the slide cover with an eyedropper. The stain was drawn under the slipcover by capillary action. The slide was then observed with Nikon SkT polarized light microscope. The above process was repeated with phloroglucinol to detect the presence of lignin in the unknown samples. The temporary fibre slide was analyzed using a Nikon SkT polarized light microscope at four different magnifications: 40, 100, 200 and 400 times magnification. The characteristics of the paper fibres were characterized using plane-polarized light. Crossed polarized light was used to determine whether the fibres were isotropic or anisotropic and to characterize their extinction behaviour. Digital micrographs were taken to record these observations.

Sample Preparation

Samples were cut from a roll of Whatman No. 1 chromatography paper 4.0 cm wide. The sample set for relative humidity and temperature aging is 4.0 cm x 15.0 cm. A sum of five repeats of each of the five toning materials was cut in this size for thermal aging and another five repeats of each for a control set. The light aging samples are 4.0 cm x 11.0 cm to fit into the sample holders for the Q-Sun light aging chamber. Five repeats of the five toning materials was also cut for light aging trials with another five repeats of each for an additional control sample for a total of 50 samples. A total of 100 samples was aged and analysed for this research project.

Tea Samples

Distilled water (500 ml) was brought to a boil. Five 2 g tea bags of Lipton's Yellow Label tea were added to the boiling water and allowed to steep for ten minutes. The tea was applied to the strips as prepared.

Paint samples

To 100 ml of distilled water, 0.5 g Vandyke brown from Winsor & Newton's Cotman watercolour series was added and stirred until dissolved. The acrylic sample material was prepared in the same manner with 0.5 g of Golden Acrylic raw umber.

Extract samples

The concentrated liquid obtained after dissolving the evaporated extract in 75 ml of distilled water was diluted 1:1 with equal parts of concentrated extract water and distilled water.

For each sample set, a drop of the appropriate toning material was placed on a large piece of flat glass. For the 11.0 cm samples, 1.0 ml of each sample was applied to the glass with a syringe. For the 15.0 cm samples, 1.5 ml of each sample was applied to the glass in the same manner. The Whatman paper strip was placed on top of the drop and capillary action allowed for an even absorption and distribution of toning material into paper. This process was repeated for all samples and toning materials. Figure 4 shows one from each sample set of each toning material.

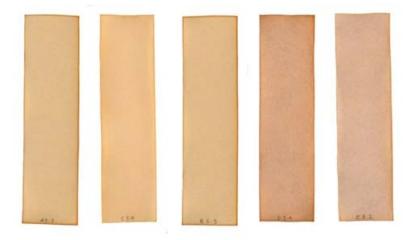


Figure 4 Prepared samples from left to right are: paper extract prepared with distilled water, extract prepared with alkaline water, tea, watercolour, and acrylic

Instrumentation and Analysis

Thermal aging samples were aged in a Despatch temperature and relative humidity chamber for 21 days at 85°C and 65% relative humidity. Light aging samples were aged in Q-sun light aging chamber with an irradiance sensor of 420 nm and a UV filter WINDOW:Q which produces a spectral power distribution equivalent to noon summer sun coming through window glass. The irradiance was set to 1.00 W per m² and the samples were aged at 50 °C for 144 hours. The microfade testing was done by Season Tse senior conservation scientist at the Canadian

Conservation Institute with an Oriel Microfade Tester. Changes to the aging samples were detected using three methods of analysis. Changes in colour were monitored detected colourimetry. Chemical changes were monitored by measuring pH and physical changes were evaluated using a fold endurance test. Changes occurring during micro-fading were monitored by the micro-fader itself. The micro-fading tester operates by inducing fading from visible light on very small test areas on an object. It is able to perform accelerated aging tests very quickly and non-destructively on a very small scale. The micro-fading tester is essentially a spectrophotometer, measuring the visible reflectance spectra of the sample areas. The key difference is the intense light source, a xenon arc light emitting about 7 million lux, which causes fugitive colours to fade measurably in an exposure length of as little as five minutes (Whitmore, 1999).

Colourimetry

For analysing the thermal aging samples colourimeter readings were taken with a Minolta CR-300 hand-held colourimeter. Measuring in the L*a*b* colour space, the colourimeter was used to record the average of readings taken on each of the five repeats of each sample group and control group. The readings were recorded before aging, and after aging. For the light aging samples the readings were recorded before aging, after aging and every forty-eight hours during 144 hours of aging.

Fold Endurance

Thermal aging was done to determine the long term stability of material toned with paper extract and the other toning materials. The physical stability of the samples was tested with the MIT fold endurance tester. Aged samples were compared to un-aged controls. The MIT paper fold endurance tester folds a 150 mm x 15 mm sample through an angle of 135° in both directions at a rate of 175 ± 25 double folds per minute until the sample is severed at the fold. The samples were cut to 15 mm x 150 mm with a TMI Twin Blade Model No. 22-34-15. The samples were tested using a 1 pound (0.45 kg) tension.

The pH readings were taken according the TAPPI standard cold extraction method. The TAPPI method involves soaking 1.0 g +/- 0.01 g of the paper sample cut into tiny 5 -10 mm squares. 70 ml of distilled water was added to the samples and they soaked for 3 hours before readings were taken with an OMEGA PHB-212 Micrprocessor pH meter. The distilled water used for the test had a pH of about 6.75. During the cold extraction, while the samples were soaking in the distilled water, it was observed that some of the toning materials were soluble in water before aging and not after aging. The tea, and extract samples were soluble before aging, and the watercolour and acrylic samples were insoluble. After aging, the tea became insoluble but the paper extract remained soluble. It was observed that of all the materials paper extract appears to be the most reversible.

Results and Discussion

GC-MS Results

The results from the GC-MS analysis can be seen below in figures 1 and 2. Figure 1 shows the chromatogram for the paper extract sample made from paper soaked in distilled water. The retention times of the major peaks are labelled on the chromatogram. The peaks were identified by comparing the mass spectra of each major peak to known mass spectra. When comparing the peak at retention time 9.05 minutes to the National Institute of Standards and Technology (NIST) database an identification was made with a very high probability of vanillin. The most abundant peak at retention time 12.37 min was identified with high probability to be acetovanillone a compound structurally related to vanillin. The third most abundant peak at time 9.52 min indicated dimethyl phthalate. The fourth most abundant peak at 10.50 minutes indicated a high probability of isovanillic acid.

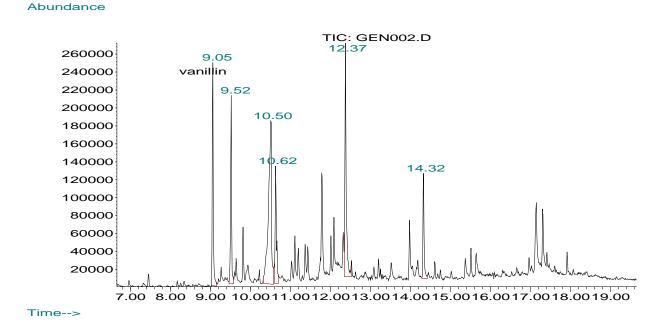
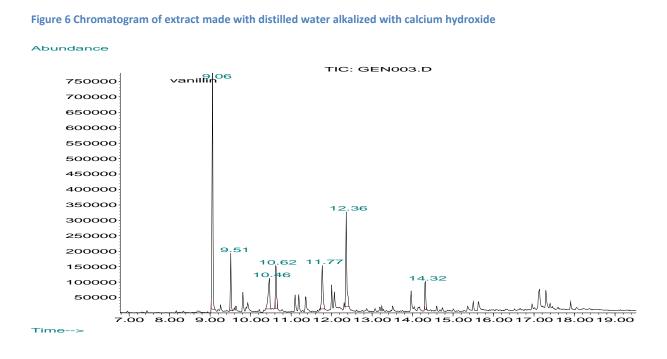


Figure 5 Chromatogram of paper extract made with distilled water.

Figure 2 shows the chromatogram of the extract made with distilled water alkalized with calcium hydroxide. This chromatogram shows similar results; the four most abundant peaks were identified as vanillin, dimethyl phthalate, isovanillic acid and acetovanillone. The only difference in the two chromatograms was the alkalized extract had a much higher abundance of vanillin.



The presence of vanillin was researched further. It was discovered that artificial vanilla extract has been made from lignin. This identification was confirmed in an article by Jose Luiz Pedersoli Junior. He lists the water soluble lignin degradation products vanillic acid, vanillin and ferulic acid. The presence of these lignin degradation products confirms the contribution of lignin to the degradation and development of acidity in paper.

Microscopy of Paper Sources

Digital micrographs were taken under plane-polarized light, before and after the fibres were stained with the Herzberg stain. The Herzberg stain is a chemical indicator used to distinguish between natural pure cellulose, mechanically processed lignocelluloses and chemically processed lignocelluloses. The observations from polarized light microscopy examination and Herzberg Stain are summarized below in table 1. Observations of the phloroglucinol lignin test are recorded in table 2.

Sample	Presence of lignin	Cellulose type	
1	None	Natural pure cellulose	
2	None	Natural pure cellulose	
3	None	Natural pure celluloses, lignocelluloses,	
		and chemically processed lignocelluloses	
4	Present	Mechanically processed wood fibres	
5	Present	Mechanically processed wood fibres	
6	Present	Mechanically processed wood fibres	

Table 1 Summary of Analysis on the Composition of Paper Sources

Sample 1, 2 and 3 tested negative for the presence of lignin. Sample 1 and 2 had similar results for the Herzberg stain which indicate that they are natural pure cellulose. According to the Herzberg stain sample 3 appears to be a mixture of natural pure celluloses, lignocelluloses and chemically processed lignocelluloses.

Samples 4, 5 and 6 tested positive for the presence of lignin. All three contain wood fibres according to observations under magnification, samples 5 and 6 have torn and broken fibres

indicating a mechanical pulping process. Sample 4 also indicates a mechanical treatment due to the yellow colour developing after staining.

Sample Number	Observations	Conclusion
1	Fibres were stained a pale yellow colour.	No lignin is present in sample.
2	Fibres were stained a pale yellow colour.	No lignin is present in sample.
3	Fibres were stained a pale yellow colour.	No lignin is present in sample.
4	All fibres were stained a bright fuchsia	Sample contains lignin.
	colour	
5	Half the fibres turned pink	Sample contains lignin.
6	About one third of the fibres were stained	Sample contains lignin.
	pink.	

Visual Observations of Thermal Aging Samples

Figure 3 shows a composite photograph of the samples before and after thermal aging. The colour changes in the extract samples and the tea samples are the most apparent. A darkening of paper colour is an indication of acidity and as a result a deterioration of the paper stability.



Figure 7 before aging images are above, after thermal aging images are below

Colourimetry

The results of the readings, before and after aging were compared to determine whether a significant colour change has occurred using the equation: $\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$. A (ΔE^*) larger than one will indicate a change in colour

that is visible to the human eye. A change of this degree would be considered outside of an acceptable degree of change. The average of ΔE^* values were calculated from the ΔL^* , Δa^* and Δb^* calculated from the difference of the L*a*b* readings.

Thermal Aging Results

The ΔE^* readings from the thermal aging trial were plotted and can be seen in figure 8. According to the results the samples stained with the paper extracts and the tea darkened after thermal aging and the watercolour and acrylic samples faded. The largest colour change occurred in the tea stained samples with an average overall colour change with a ΔE^* value of 26.08. Even the control groups of the tea stained samples, where there was no accelerated ageing, darkened noticeably during the experimental period. The samples with the next largest colour change were the distilled water extract samples ($\Delta E^*= 24.97$), followed by the alkalized water extract ($\Delta E^*= 19.57$). The samples that faded upon exposure to high heat and humidity faded and had the following overall colour changes: watercolour ($\Delta E^*= 2.07$) and acrylic ($\Delta E^*= 1.10$)

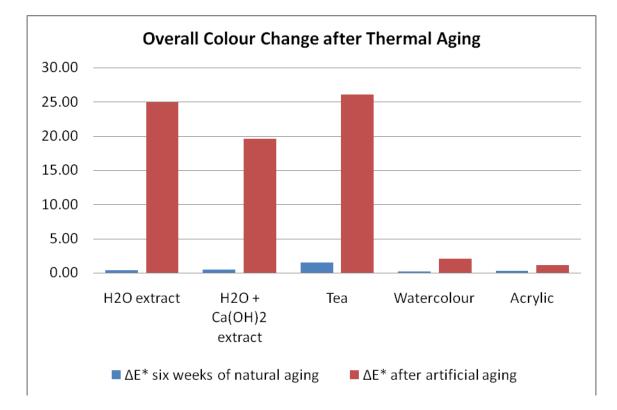


Figure 8 Colour Change after Thermal Aging

Light Aging Results

The ΔE^* readings were plotted and can be seen in figure 9. According to the results tea had the greatest colour change. The tea samples darkened upon exposure to light and even the control groups darkened noticeably during the experimental period. Watercolour and acrylic samples did not have a noticeable colour change with ΔE^* values less than one. The extract samples faded noticeably. Figure 41 shows the overall colour changes that occurred upon exposure to light over a 144 hour period.

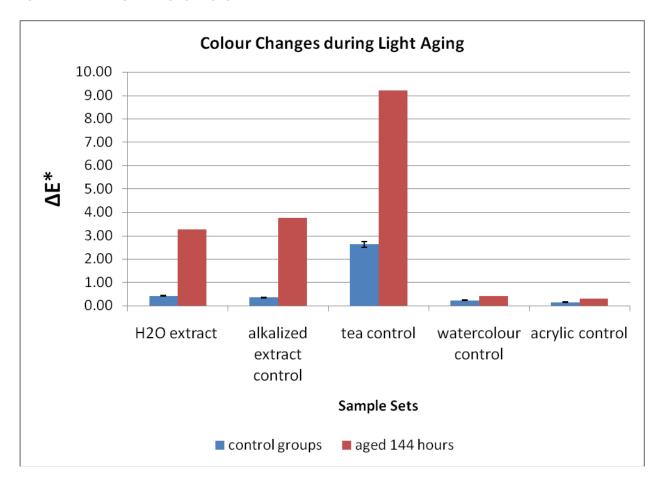


Figure 9 Colour Changes during Light Aging

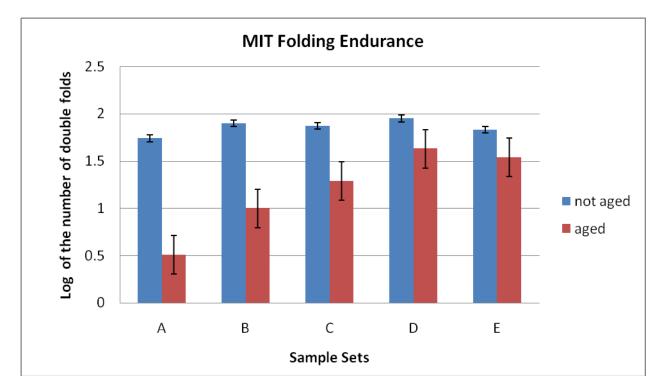
Microfade Tester Results

The following results were obtained by senior conservation scientist Season Tse at the Canadian Conservation Institute. During 20 minutes of exposure to the Oriel Microfade Tester (O-MFT) light spot, the averaged rate of colour change for the two paper extract samples were slightly faster than that of Blue Wool 3 (BW3). The Blue Wool Standards were created by the International Standards Organization (ISO) to gauge the extent of fading caused by exposure to light. Blue Wool 1 fades very easily while Blue Wool 8 does not fade. Pigments and dyes can be classified by comparison to these standards (Patkus, 2007). The tea sample is slightly slower that BW3 and the acrylic and watercolour samples showed almost no colour change during 20 minutes of exposure. These results showed that the two extract samples and the tea sample would be classified as high sensitivity to light.

Results of Folding Endurance

The number of double folds was recorded and results were displayed using the log10 of the number of double folds. The rationale behind reporting the log10 fold is discussed In the TAPPI standard T 511 om-88. It states that the greatest source of test variability is that the folding stresses are applied to a very small area of the paper. The failure occurs at this point and not necessarily at the weakest point. The fold test also operates cumulatively causing the reduction in strength after each fold to be approximately exponential. The log10 of the fold number provides a better way of displaying the results. The results from the MIT folding endurance test are reported in Figure 10. Un-aged samples show fairly uniform fold endurance. After artificial aging the greatest loss in fold endurance occurred in the extract made with distilled water. The acrylic and watercolour samples maintained their fold endurance the best while the tea and alkalized water extract had moderate loss in fold endurance results.

Figure 10 MIT Folding Endurance



Cold Extraction pH Results

The results of the cold extraction pH readings can be seen in Figure 11. Before thermal aging the lowest pH readings occurred in the tea group of samples. The alkalized water extract had the highest pH before aging. After aging, the highest pH occurred in the acrylic samples and the lowest pH occurred in the distilled water extract samples.

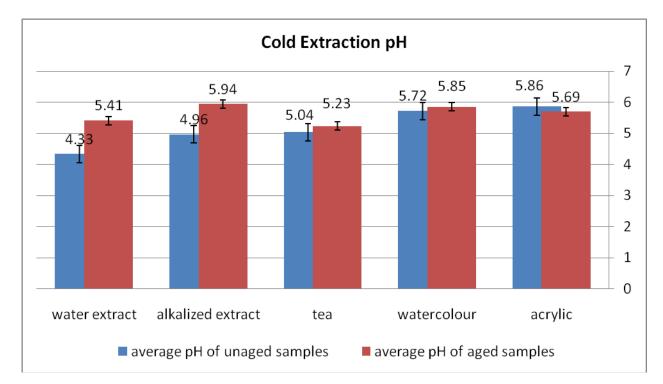


Figure 11 Cold Extraction pH

Observations of solubility

During cold extraction, while the samples were soaking in the distilled water, it was observed that some of the toning materials were soluble in water before aging and not after aging. The tea, and extract samples were soluble before aging, and the watercolour and acrylic samples were insoluble. It was observed that of all the materials, paper extract appears to be the most reversible. The results of the solubility before aging are depicted in Figure 12 and after aging in Figure 13.

Figure 12 Samples soaking in distilled water before accelerated aging.



Figure 13 Samples soaking in distilled water after accelerated aging.



Conclusions

Paper extract has some positive characteristics. Paper extract is transparent and matches the tone of aged paper exactly. It absorbs into the paper substrate and maintains the paper's matte appearance. Paper extract is more lightfast than tea and it is the most reversible of all the materials tested. Another advantage to paper extract may be that a colour shift as the repair ages may not be as visible. As shown in the aging trials, watercolour and acrylic both faded. After a few years when the surrounding paper has aged, but the repair has faded, these repaired areas will become quite apparent and will likely need to be re-done. The use of paper extract may prevent this dramatic colour shift. These characteristics make paper extract a very attractive material to use for toning. Before choosing paper extract an important result of this investigation must not be overlooked. Paper extract degrades the paper substrate upon accelerated aging. The paper samples became more brittle and were significantly discoloured after artificial aging. According to the analysis done to the paper extract materials and then paper sources of the extract, the main culprit behind the deterioration upon aging seems to be lignin. Half the papers used as the raw material for the extract tested positive for lignin. The GC-MS results found a high abundance of lignin and its degradation products. Although the results show the content of lignin in the paper extract is contributing to the degradation of the samples during aging, there is a notable improvement in folding endurance and discolouration when the alkalized extract results are compared to the nonalkalized extract results. Further research should be conducted to test whether an adequate alkaline buffer can be added to the extract to make it archival or to test whether the extract can be applied to material that has been de-acidified with an alkaline buffer. Extract made from paper that is lignin free should also be tested to compare artificial aging results with the lignin containing sample results. After analyzing the results of this research, the conclusion can be made that paper extract is not the best choice for a toning material, as paper extract has been shown to degrade the paper substrate with accelerated aging. Although having better aging characteristics than tea, a commonly used toning material, the best choice remains to be either watercolour or acrylic paint.

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