

# *Preparation of Reproducibly Stained Paper Samples for Conservation Research*

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## **INTRODUCTION**

In order to compare effects of various treatments on artists' papers, the conservation researcher must have available enough paper in a uniform condition for many experimental and control samples. If the study is to address effects of treatments on stained paper, procurement of enough similarly discolored paper for the entire experiment may be difficult. Stains in old papers are frequently uneven in intensity or distributed irregularly on a sheet. Usually the material is available in very limited amounts, and the source of the staining and prior treatment of the material is often uncertain. Such conditions limit the usefulness of these papers in comparative studies, because unknown variations in the individual samples could significantly affect their responses to the experimental treatments.

A source of reproducibly stained papers is needed for research in the field of paper conservation techniques. It would be particularly appropriate if the papers consisted of materials, the properties and condition of which were known before the stain was present, e.g., new papers or those that had known storage and treatment history. For example, we required stained samples for a research project on the long term effectiveness of the aqueous light bleaching technique. Thus, we developed a procedure for staining paper that is easily reproduced, so that as many samples as are needed for experimentation could be generated. The samples were stained by contact with newsprint that had been badly discolored under controlled conditions. The stained papers can serve as a model for such conservation problems as acidic mat burn, or discoloration owing to contact with unsealed wood in framing or storage materials.

The detailed procedure for staining "new" artists' or printing papers is described below. The method has been applied to unsized as well as gelatin sized cotton rag papers, and to a modern, mass produced, bast fiber paper intended for printing. The discoloration imparted to these papers is easily detected by eye, and appears unsightly when compared to an unstained sample of the same paper. It can be diminished somewhat by washing the papers in an alkaline bath, and is further decreased by aqueous light bleaching as used in paper conservation treatment.

## **MATERIALS AND INSTRUMENTATION**

### **Materials.**

*a. Papers.* The unprinted newsprint used for staining was Strathmore rough surface newsprint, available in a tablet (#307-814). Four different papers were subjected to stain transfer. Whatman #1 waterleaf paper served as an unsized control for alpha-cellulose papers. Whatman #1 paper which had been bath sized with purified photographic gelatin (See below) was also used. The artists' paper stained was a Whatman 100% cotton alpha-cellulose paper heavily sized with gelatin, which also contained alum and a commercial soap. It was watermarked "J. Whatman 1956," and had been stored in a controlled environment for years. Further details of its manufacture are no longer available [1]. The fourth paper subjected to staining was the newly developed commercial Kenaf paper, made from bast fibers of the crop-grown *Hibiscus cannabinus* plant [2]. This semi-bleached paper was recently described in the Alkaline Paper Advocate [3].

*b. Chemicals.* The photographic gelatin used for sizing was supplied by Sanofi BioIndustries, code no. 41555, lot 54323. Potassium aluminum sulfate was reagent grade. Stock acetic acid was a 5% solution of USP grade. Deionized water was used to prepare all solutions in which the paper samples were immersed.

*c. Supplies.* Unbuffered, waterleaf 100% cotton fiber blotters from Paper Technologies (no. 112) were used for drying paper samples throughout the experiments, and also in assembling the sandwich for transferring stains from the newsprint to the sample papers. The single layer corrugated board used in this sandwich was of archival quality, but the corrugated box board used for supporting the newsprint during discoloration was not. Mylar, 0.005" thick, and 3/16" thick plexiglas, were obtained from local art and plastics shops, respectively. One inch pony clamps were obtained from a local building supply house, and were used without any plastic grips. Whatman #1 paper was bath sized in individual 9 in x 12 in polyethylene trays (dissecting trays) from a laboratory supply house. Felt-lined Gore-Tex was used in rehumidification of dried, sized samples for flattening.

### **2. Instrumentation.**

A Hotpack Temperature-Humidity chamber, Model no. 435304, was used for sample incubation during stain

transfer. Reflectance spectra were recorded on a Diano Matchscan II reflectance spectrometer. The hot plate and remote control magnetic stirrer were standard laboratory equipment obtainable from local supply houses. Surface pH was measured with a Markson model 6170 pH meter equipped with a flat surface Ross style electrode, Orion #8135BN. The instrument was calibrated with Altec 7.0 and 4.0 standard buffers. Bath sizing was performed on the heated surface of a large custom-designed stainless steel sink manufactured for the Textile Conservation laboratory at Los Angeles County Museum of Art. The bottom surface of the sink is maintained at constant temperature by a closed loop water heating and circulation system.

## EXPERIMENTAL PROCEDURES

### 1. Discoloration of newsprint.

Sheets of Strathmore rough surface newsprint were placed on a piece of corrugated box board, covered with mylar, and placed in full sun for a total of 24 hours, accumulated between ca 9:30 am and 4:30 pm over several days. The integrated spectral irradiance in northern Los Angeles County, where exposure took place, does not vary markedly with time of day and year, as long as the sky is cloudless, and the sun is fairly high in the sky. Newsprint sheets exposed to sun during October, November, February, May and July were used in these experiments. The same side of the newsprint faced the sun during the entire exposure.

Newsprint was also discolored by exposure to near ultraviolet light from a 36 watt fluorescent bulb in a Blak-Ray fixture (Ultra-Violet Products, Inc., South Pasadena, CA) suspended approx 12 inches above the paper. A total exposure time of 21 hours over several days was required to cause a discoloration similar to that caused by sun exposure. The paper and fixture were surrounded by cardboard to avoid inadvertent exposure of personnel to the uv light.

Following sun exposure, two sheets of newsprint were placed, exposed sides facing each other, on aluminum foil on a rack in an oven at  $70 \pm 5^\circ\text{C}$ . A tray of diluted acetic acid (ca 10 ml 5% in 500 ml  $\text{H}_2\text{O}$ ) was placed on the floor of the oven, and the newsprint left for 3 hr. The oven was cooled to room temperature and the acetic acid removed. The oven was then reheated to  $70 \pm 5^\circ\text{C}$ , dry. The cycling was repeated once more, with water in the oven. By this time the newsprint appeared very yellowed, with a slight orange or beige cast, but was still not very brittle or cockled. The pH of the unstained newsprint was  $5.7 \pm 0.1$ . Following sun exposure it had fallen to  $4.9 \pm 0.1$  and, after cycling in the oven, to ca 4.6.

### 2. Transfer of stain to sample papers.

Sample papers cut to the desired size were sandwiched between sheets of the stained newsprint, with the sides of

the newsprint which were originally toward the sun now facing the sample paper. This combination was sandwiched between double layers of waterleaf blotter, the dimensions of which were slightly larger than the newsprint sheets. Several such 'sandwiches' can be stacked. The entire stack was placed between sheets of archival corrugated board. Plexiglas was used for the outermost layers of the assembly, which was held firmly together with pony clamps. For a stack ca 8.5" by 17", six pony clamps were used. Each sandwich in this stack contained two 7.5" x 8" pieces of sample paper. The final dimensions of a particular stack will depend on the size of the paper samples being stained, and the size of the newsprint sheets used. See Figure 1 for an exploded view diagram of an assembly which contains one stain transfer sandwich.

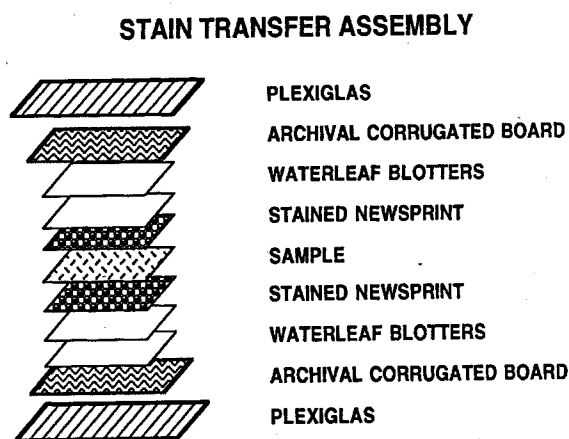


Figure 1. Assembly for transferring stain from discolored newsprint to experimental paper sample, exploded view. The assembly is held together by pony clamps. See text for other details.

The assembly was placed in a humid aging oven equilibrated at  $70^\circ\text{C}$  and 50% relative humidity, and incubated for 12 to 14 days. A repeat incubation with fresh stained newsprint may be required to transfer an obvious stain to a very hard sized paper. (See below.) Because the sample papers were essentially being artificially aged in order to transfer stain from the acidic material, it was necessary to prepare a set of control samples which were only artificially aged, without any stain transfer. This was accomplished at the same time as the stain was transferred, by including sample papers sandwiched between sheets of new Whatman #1 waterleaf paper in the assembly. Although this doubled the size of the experiments, it was an essential control measure for subsequent investigations of the effects of treatments to lessen the stain.

### 3. Other Experimental Procedures.

a. *Bath sizing of Whatman #1 paper.* Samples of paper

were cut 7.5" x 8". A 2.0% solution (weight:volume) of photographic gelatin was prepared by softening the gelatin in deionized water at room temperature with constant slow stirring for ca 30 min. The suspension was then heated in a water bath to 45 - 50°C, and stirred until the gelatin dissolved. This solution was kept at ca 35°C in a water bath on a large hot plate. A 0.10% solution (weight:volume) of  $KAl(SO_4)_2$  was also prepared in deionized water, and heated in the same bath. Enough solution to size 6 to 8 paper samples was prepared at one time. Polyethylene trays for individual sizing of the samples were spread out on a heated surface maintained at ca 35° C. A piece of Reemay was placed in each tray. 140 ml of each of the two heated solutions was poured into a tray and stirred. A piece of paper was quickly placed in the tray and submerged for 3 min. It was removed on the Reemay, drained briefly, and transferred to a sheet of mylar on top of a piece of plexiglas, also on the heated surface. Another piece of mylar was placed on top of the sized sample, then another plexiglas sheet. A cylindrical shaped weight was rolled rapidly across the plexiglas in the area of the sample, in two perpendicular directions. This step took the place of pressing a stack of sized papers in a press, and ensured that each sheet was treated in an identical manner, i.e., that all were kept warm and pressed at the same stage in the process before they began to dry. The sized paper was transferred from the mylar to a nylon screen, which had been stretched across a frame. The frame also rested on the heated surface. Sample papers were sized one sheet at a time. The sized samples were allowed to air dry before being removed from the screen. They were humidified between sheets of Gore-Tex and then dried and flattened in a blotter and plexiglas press under moderate weight (less than 0.1 psi). They remained in the press at least overnight.

*b. Colorimetry measurements.* Reflectance spectra were recorded on a Matchscan II spectrophotometer in four different places on each side of each sample. The samples were backed by a white tile. A calibrated white tile was used as the reference. CIE lab  $L^*$ ,  $a^*$ , and  $b^*$  values were calculated for a D65 light source and a 10° observer. Specular reflectance was excluded. The data reported below for the Whatman papers are averages of the eight (recto plus verso) scans. These papers showed no significant differences between recto and verso values. The Kenaf paper has a distinct sidedness, so recto and verso values are reported separately.

*c. Sizing assay.* Small pieces of the sized papers were analyzed for gelatin using a modification of the TAPPI standard procedure for the qualitative determination of glue in paper [4]. Sanofi photograde gelatin was used as a standard. The modified procedure was found to give useful semiquantitative results, and will be published elsewhere.

## RESULTS

Examples of reflectance spectra for sized Whatman #1 samples are shown in Figure 2. Qualitatively similar results were obtained for the other papers. However, a second incubation in the humid oven with fresh newsprint was required to cause an easily visible discoloration of the hard sized Whatman 1956 artists' paper. For all the papers, the stained samples look distinctly discolored to the naked eye and have the lowest reflectance values. Staining attenuates the reflectance most markedly in the blue region of the visible spectrum.

CIELab tristimulus values for all papers were calculated automatically from the reflectance data and parameters of the instrument. They are summarized in Table I. It can be seen that  $b^*$ , a measure of blueness or yellowness, is the parameter most sensitive to the discoloration caused by the staining process. Although the artists' paper (Whatman 1956) and the modern paper (Kenaf) have the most color before staining, the greatest increase in yellowness occurs in the Whatman #1 and bath sized Whatman #1 papers upon stain transfer (Figure 3a). This may be due to resistance to stain transfer by the heavily sized Whatman 1956 and Kenaf papers. Measurement of gelatin content showed that the Whatman 1956 paper contained approximately 3.5 times

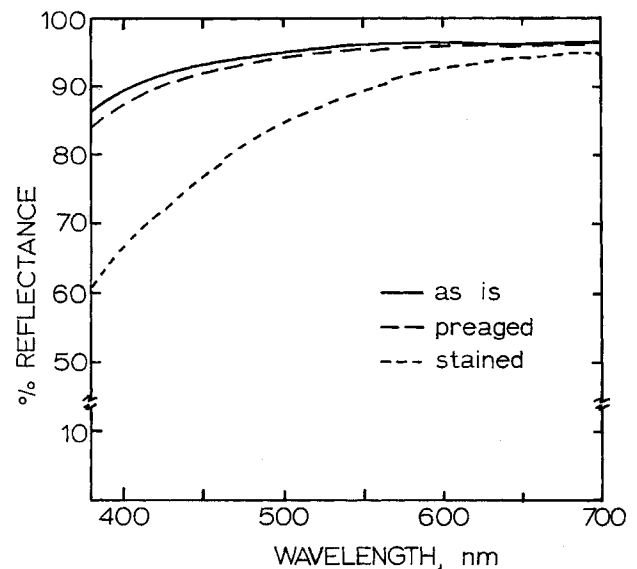


Figure 2. Reflectance spectra for bath sized Whatman #1 paper samples treated as indicated.

as much gelatin by weight as the bath sized paper. Also, twice as much humid oven aging was required to transfer a noticeable stain to the Whatman 1956 paper.

Aging alone did not have a significant effect on the yellowness of the unsized paper, and had only a very slight effect on the Kenaf paper. However, the gelatin sized papers were significantly yellowed by aging alone.

**TABLE I**  
**CIE LAB TRISTIMULUS VALUES FOR PAPER SAMPLES**

PAPER	AS IS			AGED <sup>a</sup>			STAINED <sup>b</sup>		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
Whatman #1	98.28±0.05	-0.41±0.06	1.72±0.07	98.06±0.04	-0.27±0.05	2.01±0.08	94.90±0.09	0.60±0.01	7.81±0.20
Sized <sup>c</sup> Whatman #1	98.30±0.02	-0.36±0.02	1.78±0.05	98.08±0.05	-0.40±0.03	2.46±0.09	95.59±0.05	0.0±0.05	8.82±0.02
Whatman 1956	96.16±0.06	-0.91±0.04	7.85±0.10	95.15±0.05	-0.20±0.02	9.88±0.19	94.41±0.05	-0.05±0.05	11.88±0.13
Kenaf, r v	90.01±0.05	1.72±0.05	10.18±0.15	89.72±0.18	1.84±0.02	10.35±0.16	88.72±0.13	1.97±0.06	11.26±0.10
	89.50±0.11	1.83±0.05	11.81±0.15	88.83±0.15	1.98±0.02	12.38±0.20	87.96±0.15	2.24±0.01	12.97±0.18

a. Humid oven at 70°C and 50 % relative humidity, in contact with new Whatman 1 paper (See text for further details).  
 b. Humid oven at 70°C and 50 % relative humidity, in contact with prestained newsprint (See text for further details).  
 c. Bath sized with solution of 1% photographic gelatin and 0.05% potassium aluminum sulfate in deionized water (See text for procedure).

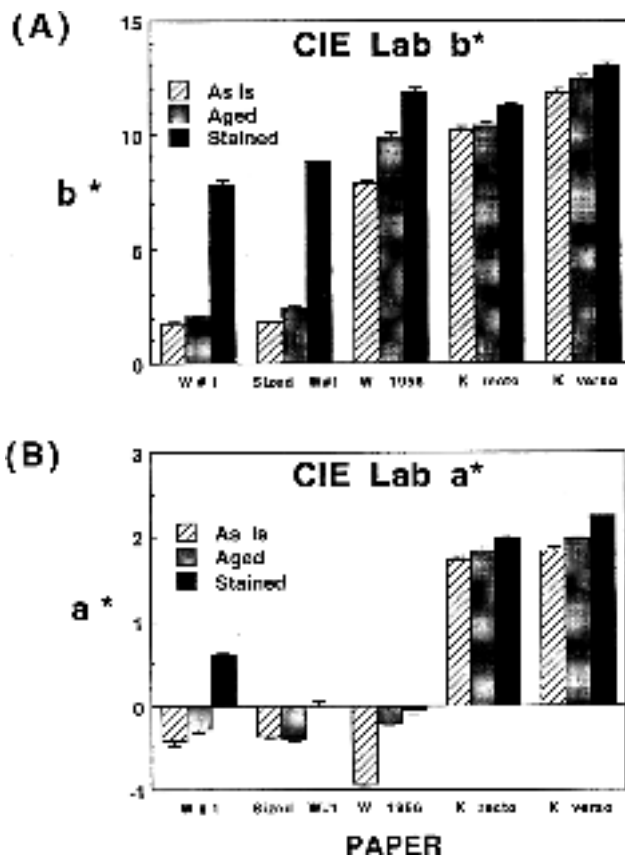


Figure 3. CIE Lab b\* and a\* for Whatman (W) and Kenaf (K) paper as is, aged, or stained, as described in text. Data are averages +/- SD for measurement at 8 places on each sample (W) or 4 places on each side of each sample (K).

These responses suggest that the gelatin size itself may be yellowed somewhat upon two to four weeks of humid oven aging.

The data for  $a^*$ , a measure of the redness or greenness of the papers, show that only the Whatman 1956 paper undergoes a large shift to the red upon aging (Figure 3b). However, both sized and unsized Whatman #1 papers are reddened markedly upon transfer of the stain. Interestingly, the unsized paper is made redder by stain transfer than are the sized Whatman papers. This could be due to transfer of more red chromophore to the unsized cellulose furnish, and/or to a reaction involving the gelatin in the sized papers which creates a chromophore with absorption characteristics that counteract the shift to the red caused by the stain.

Color difference values, DE, were calculated from the CIE Lab tristimulus values for all the papers and are given in Table II. The greatest color differences were caused by staining the unsized and sized Whatman #1 papers. The Whatman 1956 paper was most changed by aging alone. The Kenaf paper, although the most highly colored initially, underwent by far the least change in appearance upon staining. Two weeks of aging caused no greater difference in this paper than it did in the Whatman #1 papers.

## DISCUSSION

The procedure described above has been successfully used to cause a distinct and even discoloration of various types of papers. Preliminary trials had indicated that in order to achieve uniform and efficient stain transfer, the sample paper must be in contact with the stained newsprint *in a humid atmosphere* at an elevated temperature. The extent of discoloration may depend on the amount and type of sizing and other additives in the paper used, as well as on the length of time the paper is in contact with the discolored newsprint. Two to four weeks were sufficient for the papers in this study.

If adequate sunlight is not available, the newsprint can be discolored by exposure to near ultraviolet light from a

fluorescent fixture such as a Blak-Ray lamp. The time of exposure required will depend on the intensity of the light source. It may be similar to the amount of time used for sunlight exposure. Care must be taken to ensure even exposure of the entire area of the sheet of newsprint if this method is used.

Some tensile properties of the Whatman papers were measured. The strength, stiffness and brittleness of the samples that had been aged or stained for two weeks differed negligibly from those of the untreated samples. However, the Whatman 1956 paper, which had been incubated in stain transfer sandwiches twice as long, showed significant changes in these tensile properties. These observations suggest that the staining of the papers may have been superficial during the shorter incubation period. The fibers and sizing in the interior of the sheets may not have been altered significantly by incubation in the oven, or by reaction with the substances that migrated from the stained newsprint into the paper. Thus, unless repeated oven incubation is used, the staining procedure might not provide samples that are appropriate models for old papers with significant mechanical and chemical degradation of their fibers.

The staining process does provide an excellent model for a paper that has been stained by acidic material over a relatively short time period. For example, the procedure provided samples appropriate to our investigation of the long term effectiveness of aqueous light bleaching when used to reduce this type of stain. A report of this study will appear elsewhere (manuscript in preparation).

## NOTES

1. Dr. David Martin, Whatman, Ltd., London, personal communication.
2. Strelis, I. and R.W. Kennedy, 1967. *Identification of North American Commercial Pulpwoods and Pulp Fibres*, University of Toronto Press, p. 61.
3. Alkaline Paper Advocate, 1992. "Sample papers enclosed in newsletter." 5(5):35-36.
4. TAPPI Standard Procedure T504 om-84, "Glue in

TABLE II  
COLOR DIFFERENCES

PAPER	$\Delta E$ (aged - as is)	$\Delta E$ (stained - as is)	$\Delta E$ (stained - aged)
Whatman #1	8.39	7.04	6.66
Sized Whatman #1	8.72	7.55	6.84
Whatman 1956	2.38	4.48	2.14
Kenaf recto	0.36	1.70	1.36
Kenaf verso	0.89	1.97	1.08

Paper," qualitative determination.

#### **ACKNOWLEDGEMENTS**

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