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AN EXPERIMENTAL EVALUATION OF ACCEPTED METHODS FOR REMOVING SPOTS AND STAINS FROM WORKS OF ART ON PAPER*

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It became apparent that there were great gaps in the literature available on paper conservation, and conflicting recommendations within the existing documents. This lack was quite evident in the area of spot and stain removal. It was impossible to unearth a single source listing the relative harmfulness of suggested methods of bleaching and spot removal, or even to combine data from a number of sources into a coherent whole. The experimental work had not been performed. Therefore, a program of experiments was designed in order to fill this void.

First, the literature was surveyed and many suggested means of spot and stain removal recorded. The list was condensed by choosing the simplest or most precisely described of similar methods to represent the group. Two old ledgers were obtained, the rag paper they contained similar to much of the paper with which the conservator must deal, in bound form in order to reduce the variability of the paper. One of the ledgers contained paper which was relatively white and unaffected by disfiguring influences, while the sheets in the other were degraded in color and strength by foxing and mildew. The better of the two papers was used in tests to measure the deteriorative effect of bleaches and solvents on the strength of the paper, and the permanence of the color change effected by bleaches. The poorer of the two was used to determine the time necessary for bleaching, and the immediate efficacy of the bleaching methods.

Second, thirty methods for spot and stain removal were selected. Eleven of these employed solvents; eighteen used bleaches; and one made use of a surfactant. Each bleaching treatment was carried out on both types of old paper, the whiter one designated paper "A" and the darker one paper "B". The solvents and the surfactant were applied to paper "A" only.

Third, the effects of the treatments were tested by three methods. These were a brightness test, the bursting test, and solubility in hot alkali. Criteria used in the selection of these tests were relevance of the results to longevity and simplicity of employment and interpretation. The tests were carried out on treated papers--2, 10, or 15 replicates as needed--and on control sheets (untreated).

Both types of paper were subjected to the treatment described in the literature, modified if necessary, using paper "B" as an indicator of the end point of the bleaching treatments. That is, the bleach was applied

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simultaneously to papers "A" and "B" and allowed to proceed until paper "B" seemed to have undergone the maximum possible brightening. The treatment of both was then concluded, the papers rinsed, and dried in air. Experimental and control sheets were then artificially aged at 98-99°C, all together in a chamber maintained at 50 per cent relative humidity for 4.93 days. The samples were then subjected to the program of tests previously outlined.

Fourth, the treatments were ranked according to the results of each of the tests. The statistical correlation of the bursting and alkali-solubility tests was calculated. No completely satisfactory statistical method of combining the results of these two tests could be found. However, by consulting the tables, an indication of the relative harm and efficacy of the bleaching methods, and the relative harm caused by solvents, may be obtained.

The following tables list the results of the three tests applied to the experimental papers. They show: rank, treatment number, per cent weight loss in sodium hydroxide (D, E), points bursting strength (psi required to rupture specimen) (C), and brightness values (A, B). It should be borne in mind that the papers treated, aged and subsequently tested were old and, therefore, suffered more from internal variation than would comparable new papers. Hence, the standard deviations for the bursting and the brightness tests, and the ranges for the sodium hydroxide solubility test, are larger than if new papers had been used. However, these difficulties were tolerated in order to measure the relative effect of the various treatments on paper containing decomposition products in order to predict more accurately the effect of each method on paper likely to be subjected to actual conservation treatment.

Wet and dry treatments appear separately in the tables due to the effect of the sizing in the treated papers. "Wet" treatments were those in which the paper was immersed in aqueous solutions, "dry" those in which the solutions were non-aqueous, and the paper was not washed subsequently. Dry-treated samples lost their water-soluble sizing during the alkali-solubility test, thus losing more weight than if the sizing had already been washed out by the previous treatment. The bursting strength for these same "dry" samples is higher, however, since the presence of sizing strengthens paper. Therefore, tables for the dry-treated samples show weight losses higher and bursting strengths greater than tables for wet-treated samples.

Another identifiable source of error in the alkali-solubility test is the presence of acid-soluble loading material in the test paper. The test method employs a wash with weak sulfuric acid. If acid-soluble loading material has not been removed already by acid baths involved in previous treatment, the sample will lose an additional percentage of its weight. The effect of this factor is to produce a weight loss slightly higher for those treatments (H) not involving acid. Conversely, acid-treated samples show lower weight losses (L), but also lower bursting strengths. Therefore, the bursting test seems more reliable in its results for treatments involving acid baths.

Treatments: Bleaches and Solvents

NOTE: All aqueous methods were followed by a one-hour wash in running de-ionized water.

Treatment Number	Solutions and Source
1.	Control: Unsoaked aged paper "A".
2.	Control: Soaked (1 hour in distilled water; air dried) aged paper "A".
3.	Control: Unsoaked unaged paper "B".
4.	Control: Soaked unaged paper "B".
5.	4-6% Sodium Hypochlorite on blotters. Unrinsed. Plenderleith, Conservation of Antiquities, p. 78.
6.	Methylene Chloride. Papers saturated; air dried. (Method for all solvents.)
7.	5% Permanganate/1% Orthophosphoric Acid. Banks, "Paper Cleaning," Restaurator, I, 1 (1969) 60.
8.	Tetrachloroethylene.
9.	Xylene.
10.	5% Hypochlorite/3% Sodium Thiosulfate. Bradley, Treatment of Pictures, p. 2.55.
11.	2% Ammonium Hydroxide in Acetone. Bradley, p. 2.531.
12.	Pyridine.
13.	3 litres 2% Sodium Chlorite + 75 ml. Formalin. Gettens, "Bleaching," Museum, XII, 2 (1952) 116.
14.	.5% Permanganate/2% Oxalic Acid. Plenderleith, p. 76.
15.	.5% Hypochlorite/.5% Hydrochloric Acid/2% Sodium Thiosulfate. Plenderleith, p. 76.
16.	10 g. Chloramine-T, 25 ml. Water, 1 litre Methanol. Bhowmik, "Non-Aqueous Method," Studies in Conservation, XII (1967) 116-9; XIII (1968) 156.
17.	Oxalic Acid. 5% aqueous. Plenderleith, p. 79.
18.	Igepal. 4% aqueous CA-630.
19.	Chloramine-T. 10% aqueous. 1 hour.
20.	Sodium Formaldehyde Sulfoxylate. Powdered; applied to damp sheets; washed after 20 minutes. Plenderleith, p. 79.
21.	Used only for test of technique.
22.	Keck Hypochlorite--3 Bath Method. S. Keck, "Method for Cleaning," Technical Studies in the Field of Fine Arts, V, Oct. (1936) 122-4.
23.	Dimethyl Formamide Fumes. M. Weidner. Correspondence.
24.	Hexane.
25.	Toluene.
26.	Acetone.
27.	Dimethyl Formamide.
28.	Benzine.
29.	Methanol.
30.	1 vol. in 60 aqueous Permanganate/1% Potassium Metabisulfite. Flieder, Conservation of Documents, p. 124.

31. 1:1 Ethanol/20 vol. Hydrogen Peroxide. Plenderleith, p. 79.
32. 25 g. Calcium Chloride in 3 litres Water/10% Citric Acid. 1 hour/15 min.
33. 1:2 aqueous 5% Hypochlorite/5% Sodium Metabisulfite. Flieder, p. 115.
34. Hydrochloric Acid. 1% aqueous. Flieder, pp. 128-9.
35. Citric Acid. 10% aqueous. Plenderleith, p. 79.
36. Control: Unsoaked unaged paper "A".
37. Control: Soaked unaged paper "A".

Conclusions

The alcohol and hydrogen peroxide method (#31) seems quite harmful to rag paper, and has relatively little bleaching effect. Its use for ordinary bleaching seems inadvisable. The strong permanganate-hydrosulfite method (#7) also appears harmful, especially when compared with the weaker permanganate method (#14) which caused far less damage. A concentration of permanganate of 0.5% might be considered a maximum. With regard to Chloramine-T, however, comparison of the 10% method (#19) with the 1% in methanol method (#16) will show that the concentration is not critical with regard to effect on strength and chain-length, but brightness is retained better when a higher concentration is employed. Of the hypochlorite methods tested (#15, 22, 23), the method employing hydrochlorite acid as a second bath was least damaging, the Keck multi-bath method (#22) only slightly more harmful, and the metabisulfite anti-chlor method (#33) most deleterious to the properties measured. The latter method, however, produced a pronounced and lasting color change. It might, therefore, be chosen if whitening power is the primary criterion. The blotter hypochlorite method (#5), a dry bleaching method, seems harmful enough to be discarded as an alternative, especially in view of its limited bleaching.

Sodium formaldehyde sulfoxylate (#20) seems to increase paper strength. It is the only method which actually improved the properties of the paper as measured by the alkali-solubility and bursting tests. The method as tested, that is, applied as a powder to the damp paper, did not produce extremely effective bleaching. Some improvement did take place, and reversion was not pronounced. Use of this agent as an aqueous solution was found experimentally to improve its bleaching ability both in uniformity and in degree; the change in effect on strength should be tested. A thorough investigation of this reducing agent, the mechanism by which it acts on cellulose, and concentrations and methods of use, seems a fertile field for future experimental investigation.

The solvents tested do not vary so widely in harmfulness. However, every solvent tested (S) (#8, 9, 23-29) with the exception of dimethyl formamide liquid (#27) caused more yellowing during aging than the yellowing of the dry control (#1). This effect is interesting and unexpected. However, with respect to strength and alkali-solubility, xylene (#9), methanol (#29),

RANKING

A

Brightness: Aged Paper "A". Wet and Dry Treatments. (10 determinations)

Treatment Number	Mean Value	σ
37* Best	55.5	.79
33	55.4	1.71
10	55.0	2.47
13	53.6	1.15
15	53.2	1.43
19	52.2	1.53
36*	51.6	1.27
34	51.0	1.24
20	50.2	0.82
17	50.1	1.27
22	49.5	1.15
14	48.4	1.06
18	48.1	1.14
35	47.5	1.15
16	47.4	1.01
2*	47.1	1.36
32	45.7	1.09
30	44.4	1.00
27 S	39.9	1.10
7	39.5	1.39
1*	38.6	2.30
26 S	38.1	1.41
9 S	37.4	2.31
29 S	37.1	1.62
23 S	37.0	1.09
5	35.4	1.67
12	34.4	1.82
25 S	33.9	1.67
8 S	33.9	1.33
11	33.3	1.68
6	33.0	1.27
24 S	32.8	0.91
28 S	31.5	0.92
31 Worst	20.9	1.22

B

Brightness: Unaged Paper "B". Wet Treatments Only. (10 determinations)

Treatment Number	Mean Value	σ
33 Best	64.8	2.36
7	63.7	2.06
13	62.9	1.30
10	62.3	3.62
30	54.4	1.46
15	53.6	3.39
22	49.9	4.29
19	49.5	3.70
16	42.3	3.41
14	40.4	2.49
31	35.8	2.29
20	35.4	4.50
32	34.0	4.63
35	32.0	2.55
17	31.2	2.60
4*	31.1	3.62
34	30.8	2.79
5	28.7	2.21
18	27.1	1.79
3* Worst	26.1	2.70

C

Bursting Strength: Pounds Per Square Inch. After Aging. Wet Treatments. (15 determinations)

Treatment Number	Mean Value	σ
31 Worst	12.5	2.92
7	13.1 L	1.39
33	18.5 L	1.63
17	21.8 L	2.52
13	22.0	1.66
32	22.0 L	1.84
30	22.0 L	3.16
22	22.8	2.01
35	23.0 L	2.26
15	23.3 L	2.95
19	25.3	2.60
16	25.4	2.59
14	26.1 L	1.51
34	26.9 L	2.24
10	27.9	2.91
18	28.1	3.04
37*	33.5	3.09
2*	34.3	3.59
20 Best	36.4	5.17

Dry Treatments.

Treatment Number	Mean Value	σ
6 S Worst	24.3	3.75
8 S	24.8	4.98
5	26.1	4.16
27 S	26.9	4.52
23 S	27.1	1.81
11	27.3	5.99
24 S	28.1	3.51
12 S	28.5	6.68
28 S	28.8	1.90
25 S	31.6	3.74
29 S	33.0	3.11
26 S	33.5	4.01
9 S	35.0	3.68
1*	36.1	2.64
36* Best	39.7	1.88

*Treatment Number 1, 2, 3, 4, 36 and 37: Controls.

RANKING

Per Cent Weight Loss in .23N
Sodium Hydroxide, After Aging

D
Wet Treatments:

Treatment Number	Value	Range
31 Worst	29.0 H	1.4
7	26.8 L	1.1
30	22.4 L	0.8
32	22.2 L	0.2
13	21.2 H	1.9
16	20.8 H	0.0
34	20.3 L	0.4
33	20.2 L	4.2
19	20.0 H	0.8
18	19.7 H	0.1
22	19.5 L	0.1
14	19.0 L	0.7
17	18.5 L	1.5
10	18.5 H	0.4
2	18.4	1.9
35	18.4 L	1.4
15	17.8 L	0.1
37	17.4	0.9
20 Best	17.0 H	0.4

E
Dry Treatments:

Treatment Number	Value	Range
5 Worst	28.5	1.4
23 S	25.6 H	0.3
27 S	25.1 H	0.1
24 S	24.8 H	0.5
12	24.6 H	0.0
8 S	24.5 H	0.9
6	24.0 H	1.3
1	23.3	0.4
26 S	23.3 H	0.0
11	23.2 H	1.1
28 S	22.5 H	1.2
25 S	21.8 H	0.5
29 S	21.7 H	0.8
36	21.5	0.6
9 S Best	21.3 H	0.5

toluene (#25), and acetone (#26), seem safe. Hexane (#24), pyridine (#12), and benzine (#28), seem slightly harmful, and methylene chloride (#6) and tetrachloroethylene (#8) seem worse, and should only be employed in cases where no other solvent would be effective.

The test methods themselves seem satisfactory judging by their good correlation. The use of the three methods together seems useful since the factors that modify the results are different for each, thus allowing more correct inferences to be drawn from the tests in combination than could be drawn from only one. The results seem reliable enough for each method, provided the sources of interference are kept in mind.

If some new directions for future work have been suggested here, and if a satisfactory foundation has been laid, the research has been fruitful. Hopefully, the present work will at least give the conservator of paper a concrete basis on which to choose a bleach or solvent for a particular application, and a clearer idea of the long-term results of his choice.