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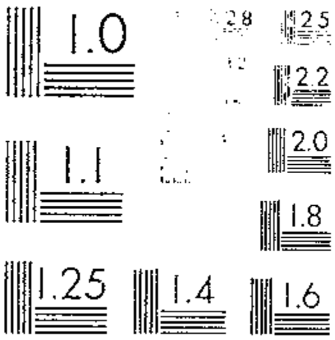

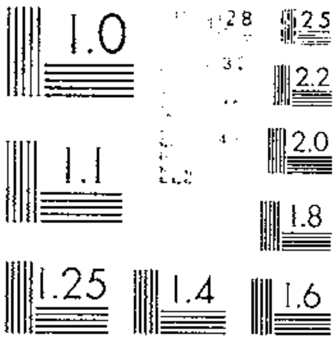

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THE EFFECT OF INORGANIC ACIDS ON THE PHYSICAL PROPERTIES OF WATERLEAF RAG BOND PAPER

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CONTENTS

INTRODUCTION

Acid in paper has long been considered a factor in causing its deterioration. Various investigators have stated that acid in the finished paper may be due to (1) the use of aluminum sulphate in the sizing process, (2) a chemical reaction taking place in the paper after manufacture, or (3) the absorption of acidic sulphur oxides from the atmosphere.

REVIEW OF THE LITERATURE

In 1882 Feichtinger (*7*)[1] reported that paper containing rosin sizing has an acid reaction due to sulphuric acid, which he regarded as injurious to the durability of paper. Wurster (*10*) and Herzberg (*10*), on the other hand, expressed the opinion that when sodium and calcium chlorides resulting from the use of bleaching powder are not thoroughly washed from the pulp and aluminum sulphate is subsequently added, aluminum chloride, a compound which readily gives off free hydrochloric acid, may be formed. Both these authors agreed that small quantities of hydrochloric acid attack cellulose. In 1898 the committee [Great Britain] on the deterioration of paper in discussing the causes of deterioration of rag paper (*6*) said:

> * * * the disintegration may be generally referred to acidity. The acids may have been present in the original paper as made; or may have resulted from reactions going on in the paper itself after making; or lastly may have been due to products of gas combustion.

[1] Italic numbers in parentheses refer to Literature Cited, p. 15.

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Winkler (*18*) treated paper with dilute solutions (1:100 to 1:50,000) of hydrochloric and sulphuric acids and after 3½ years' observation concluded that very small quantities of mineral acids are injurious to paper and that sulphuric acid causes greater deterioration than does hydrochloric acid.

Edlund (*5*) determined the amount of sulphuric acid present as aluminum sulphate, mainly in papers sized with animal sizing, by extracting the paper with warm water and titrating the extract with 0.1 normal potassium hydroxide, using phenolphthalein as indicator. He examined eight samples by this method and found from 0.3 to 1.6 per cent sulphuric acid. Edlund raised the question whether the presence of such large quantities of an acid salt, such as aluminum sulphate, might injuriously affect the durability of paper. Lester (*14*) treated cotton cloth with hydrochloric or sulphuric acid of various strengths and then dried the cloth by ironing. He found that the degree of tenderness caused by the two acids is about the same and concluded that the maximum allowable in cotton cloth appears to be 0.01 per cent of free hydrochloric acid. Coward, Wood, and Barrett (*4*) did some work on the effect of various acids, including hydrochloric and sulphuric, on cotton fabrics. They found that tendering of cotton fabrics in dilute aqueous solutions of acids is roughly parallel to the pH of the solution at constant temperature and is a function of the temperature of the solution. Hall (*9*) reported an investigation conducted at the Government testing institute in Stockholm, Sweden, on the permanence of paper. He concluded that acidity of paper may be caused by rosin sizing and warned against the use of an unnecessary excess of aluminum sulphate in making the rosin size. Hall claimed that the acid number of rosin-sized papers as determined by the Swedish Government testing institute, a method now often used in this country, should not exceed about 20, which corresponds to about 0.08 per cent SO_3. Hoffman (*11*) determined the effect of acidity on the bursting strength of about 24 samples of commercial papers, including wrapping, envelope, and label. He concluded that the higher the acid number of the paper and the lower the pH value of the water extract, the greater in general was the decrease in bursting strength when the paper was artificially aged by heating for 24 hours at 85° C. He did not determine the effect on folding endurance. Hoffman (*11, p. 60*) stated:

> If the acid number of paper is below about 25, as measured by the Swedish Government testing institute's method, the paper does not decrease appreciably in bursting strength when heated at 85° C. for periods as long as 72 hours.

He also concluded from his data that when the pH of the water extract is greater than 4.5 there is no great loss in bursting strength when the paper is heated for 24 hours at 85°. Hoffman, in another article (*12*), expressed the opinion that the acidity caused by the aluminum sulphate used to set the rosin size is an important factor in the deterioration of paper.

On the other hand, Baker (*1*) points out that often an excessive quantity of aluminum sulphate is used with tub size and expresses the opinion that it causes rapid deterioration of the paper subjected to an accelerated aging test, as well as of paper in regular use.

Richter (*15, p. 371*) calls attention to the well-known fact that acids in paper cause hydrolysis of the cellulose. He also states:

When the hydrolysis is intensified by increase in temperature or by increase in concentration of acid reagent, the deterioration proceeds rapidly and severe embrittlement occurs.

All these writers agree that mineral acids are injurious to paper or cellulose. All work on the effect of acids on paper that has come to the attention of the writers, however, has apparently dealt exclusively with finished commercial papers that had been sized, or sized and loaded and more or less calendered. In such paper there is obviously more than one factor that may be responsible, in part at least, for deterioration. Apparently no conclusive data have been obtained through a systematic investigation on the durability as measured by folding endurance, bursting strength, and tensile strength of unloaded waterleaf paper which has been treated with definite quantities of single acids or acid salts.

EXPERIMENTAL PROCEDURE

The purposes of the investigation reported in this bulletin were: (1) To ascertain the deterioration, as indicated by loss in strength and discoloration, of waterleaf unloaded all-rag paper treated with very dilute solutions of aluminum sulphate, sulphuric acid, and hydrochloric acid; and (2) to attempt to correlate acidity with deterioration.

For this investigation 13 by 16 inch sheets of waterleaf unloaded white bond paper, all of which were made at the same time on a Fourdrinier machine in a paper mill making high-grade bond paper, were used. Each sheet was soaked in distilled water at room temperature for 15 minutes in order to remove any water-soluble substances, and then dried in air at room temperature. This paper had a relatively high folding endurance, which was not materially decreased by heating for 72 hours at 100° C. The water extract had an average pH value of 7.85. The stock was composed of new white rags in the proportion of 75 per cent linen and 25 per cent cotton. It was free from rosin and glue but contained a trace of starch. The paper weighed 21 pounds per ream of 500 sheets, 17 by 22 inches, had a thickness of 0.0045 inch, and contained 0.2 per cent ash.

The copper number was determined on 1.5 g of the ground sample by the Braidy method (*2*), which directs that the Fehlings solution be replaced by a solution of copper sulphate made alkaline with sodium carbonate and sodium bicarbonate instead of alkaline tartrate. The cuprous oxide was dissolved in molybdophosphoric reagent, and the blue solution was then titrated with standard potassium permanganate to a faint pink color as described by Gault and Mukerji (*8*).

The alpha-cellulose was determined in 5 g of the ground sample by the method described by Burton and Rasch (*3*), modified by filtering through a fritted-glass Jena crucible instead of through a cotton cloth.

The following alpha-cellulose and copper number results, calculated on moisture-free and ash-free basis, were obtained: Unheated paper, 97.2 per cent and 0.64; paper heated for 72 hours at 100° C., 96.5 per cent and 0.81.

Solutions of various strengths of chemically pure aluminum sulphate ($Al_2(SO_4)_3.18H_2O$) and sulphuric and hydrochloric acids were carefully prepared. These solutions were applied to the sheets by allowing one sheet, or subsample, folded to half its original size, to soak for 15 minutes in 500 c c of the solution. The soaking was carried on in a shallow porcelain-lined pan, and the paper was kept completely immersed in the solution during the entire period. At the end of the 15-minute period the sheet was unfolded to its original size and removed from the solution. The excess of the treating solution was shaken off by gently swinging it back and forth several times. It was then placed smooth on a glass plate and allowed to dry in a horizontal position. When dry it was cut in two equal parts. One part of each treated subsample and one untreated control were placed in an electric air oven and heated for 72 hours at 100° C. The other part of each subsample was ground fine enough in a Wiley mill (*17*) to pass through a sieve having circular holes 2 mm in diameter and then placed in sampling bottles for acidity determinations. All heated subsamples were conditioned for at least 48 hours (*13*) at 50 per cent relative humidity and 70° F. Folding endurance and tensile strength in both directions, and bursting strength tests were then made on them. Each result reported in the tables is an average of at least 10 tests. The folding endurance and tensile strength tests were made with the Schopper machines and the bursting strength with the Mullen tester.

A measure of the discoloration of the paper was also made on the heated subsamples by determining the percentage reflection of light with reference to the surface of a magnesium carbonate block. This was measured by means of a polarization photometer. The light source was a magnesium carbonate block illuminated symmetrically by two 500-watt lamps and viewed normally through a monochromatic blue filter. The paper to be tested was fastened over half the magnesium carbonate block so that it covered one-half of the field of view in the photometer. The angular setting for a match was determined three times and averaged. The paper sample and the magnesium carbonate block were then reversed, and the new angle of match was determined three times as before. The percentage reflection was then calculated by multiplying the tangent of the smaller angle of match by the cotangent of the larger angle.

Total acidity was determined by a modification of the Minor method (*16*), which directs that the titration with 0.01 normal NaOH be conducted in the presence of the ground paper. The details of the method used in this work were as follows: 1 g of the ground sample was transferred to a 200 c c pyrex glass Erlenmeyer flask, and 100 c c of carbon-dioxide-free distilled water of room temperature and having a pH value of 7 was added. One-half cubic centimeter of phenolphthalein (0.5 g dissolved in 100 c c of alcohol) was added, and a slow stream of carbon-dioxide-free air was allowed to bubble into the solution for five minutes. While a slow bubbling of air was continued, the solution was titrated slowly with 0.01 normal NaOH until a definite pink color was permanent for at least three minutes. A correction was made for a blank determination by using water and phenolphthalein alone. All results, including those obtained on samples treated with hydrochloric acid, were calculated as parts of SO_3 per 100,000 parts of paper.

To determine the hydrogen-ion concentration, 2½ g of the ground sample was transferred to a 250 c c pyrex glass Erlenmeyer flask, and 125 c c of boiling distilled water having a pH of 7 was added. The flask was tightly stoppered and allowed to cool. The solution was then decanted off, and its pH value was determined. The electrometric method, with the quinhydrone electrode, was used for all treated samples, and the colorimetric method, with isohydric indicators adjusted in steps of 0.2 pH, was used for the untreated controls.

Total acidity and pH determination on all subsamples were made in duplicate on different days.

Each treating solution was applied to three different sheets or subsamples at different times in the manner described. In other words, the work was repeated twice. The subsamples having the suffix 1 are considered as set 1. (Tables 2, 3, and 4.) Set 2, which is represented by subsamples having the suffix 2, was not started until the heating, physical testing, and acidity determinations of set 1 were completed. Set 3, represented by subsamples having the suffix 3, was not started until set 2 was completed. This procedure of repeating the work was adopted because it was thought that the average of the triplicate sets would be more nearly correct than if each treatment were run in triplicate at the same time.

RESULTS

The effect of heating the untreated control samples of paper for 72 hours at 100° C., as shown in tests on folding endurance, bursting strength, tensile strength, and reflection of light, is recorded in Table 1. Six untreated sheets were used. Each was heated and tested separately. The effect of chemically pure aluminum sulphate and sulphuric and hydrochloric acids on folding endurance, bursting strength, tensile strength, and color of the paper artificially aged by heating for 72 hours at 100° are recorded in Tables 2, 3, and 4. The results of the triplicate sets are given separately in these tables to show the variation obtained under the same conditions of treating, heating, and testing. The effect of these chemicals on the physical properties is also expressed as percentage variation from the average strength of untreated and heated controls.

TABLE 1.—*Effect of heating for 72 hours at 100° C. on physical properties and color of untreated waterleaf all-rag bond paper*

NOT HEATED

Subsample No.	Folding endurance: Transverse direction	Folding endurance: Longitudinal direction	Folding endurance: Average both directions	Bursting strength	Tensile strength [1]: Transverse direction	Tensile strength [1]: Longitudinal direction	Tensile strength [1]: Average both directions	Variation from strength of unheated controls: Folding endurance	Variation from strength of unheated controls: Bursting strength	Variation from strength of unheated controls: Tensile strength	Acidity, pH of water extract	Reflection of blue light [2]
	Double folds	*Double folds*	*Double folds*	*Points*	*Kg*	*Kg*	*Kg*	*Per cent*	*Per cent*	*Per cent*		*Per cent*
1	579	2,330	1,455	37.5							7.70	83.5
2	875	2,033	1,454	35.9							7.80	87.0
3	604	2,433	1,519	37.5							8.00	83.0
4	403	2,107	1,300	37.6							7.60	85.4
5	644	1,981	1,313	39.0							8.00	88.2
6	734	2,306	1,565	35.0							8.00	86.6
Average	655	2,213	1,434	37.1	4.2	8.1	6.15				7.85	85.6
HEATED												
1-1	782	2,127	1,455	38.3				0	+2.1			84.8
2-1	603	2,358	1,481	39.7				+1.9	+10.6			86.0
3-1	630	2,313	1,472	38.6				−3.1	+2.9			84.2
4-1	524	1,717	1,151	38.0				−11.5	+1.1			87.3
5-1	720	1,726	1,220	38.6				−6.6	−1.0			85.1
6-1	576	2,425	1,501	41.2				−4.1	+17.7			89.1
Average	650	2,111	1,381	39.1	4.6	8.1	6.35	−3.7	+5.4	+3.3		86.1

[1] All tensile strength tests were made on strips 15 mm wide.
[2] Discoloration is indicated by a decrease in the percentage reflection of blue light.

TABLE 2.—*Effect of aluminum sulphate on physical properties and color of waterleaf all-rag bond paper heated for 72 hours at 100° C.*

Subsample No.	Strength of $Al_2(SO_4)_3 \cdot 18H_2O$	pH of treating solution	Folding endurance after heating: Transverse direction	Folding endurance after heating: Longitudinal direction	Folding endurance after heating: Average both directions	Bursting strength after heating
	Grams per liter		*Double folds*	*Double folds*	*Double folds*	*Points*
Heated control			650	2,111	1,381	39.1
A-1			0	0	0	15.3
A-2	4		1	1	1	20.4
A-3			0	0	0	16.6
Average	4	3.70	0	0	0	17.4
B-1			9	9	9	29.6
B-2	2		11	22	17	27.2
B-3			11	22	17	26.7
Average	2	3.90	10	18	14	27.8
C-1			69	150	110	31.5
C-2	1		78	267	173	36.0
C-3			193	286	240	39.3
Average	1	3.80	113	234	174	35.6
D-1			347	791	569	38.4
D-2	0.4		503	1,050	777	39.0
D-3			369	1,151	760	39.0
Average	.4	4.00	406	997	702	38.8
E-1			387	1,762	1,075	36.8
E-2	.2		640	1,496	1,018	38.0
E-3			305	1,449	922	38.0
Average	.2	4.20	444	1,569	1,005	37.6

TABLE 2.—*Effect of aluminum sulphate on physical properties and color of waterleaf all-rag bond paper heated for 72 hours at 100° C.*—Continued

Subsample No.	Tensile strength after heating			Variation from strength of heated controls			Acidity of unheated paper		Reflection of blue light
	Transverse direction	Longitudinal direction	Average both directions	Folding endurance	Bursting strength	Tensile strength	Total calculated as parts SO_3 per 100,000 parts paper	pH of water extract	
	Kg	*Kg*	*Kg*	*Per cent*	*Per cent*	*Per cent*			*Per cent*
Heated control	4.6	8.1	6.35					7.85	86.1
A-1				−100	−60.9		308	3.91	75.8
A-2				−99.9	−47.8		284	4.01	83.4
A-3				−100	−57.5		296	3.99	86.4
Average	2.8	5.4	4.10	−100	−55.5	−35.4	296	3.97	81.9
B-1				−99.3	−24.3		164	4.04	83.4
B-2				−98.8	−30.4		160	4.19	84.6
B-3				−98.8	−31.7		152	4.15	85.2
Average	3.7	6.8	5.25	−99.0	−28.9	−17.3	159	4.13	84.4
C-1				−92.0	−19.4		88	4.15	85.5
C-2				−87.5	−7.9		84	4.25	84.5
C-3				−82.6	+.5		84	4.24	86.6
Average	4.4	8.2	6.30	−87.4	−9.0	−.8	85	4.21	85.5
D-1				−58.8	−1.8		56	4.36	86.4
D-2				−43.7	−.3		56	4.58	86.7
D-3				−45.0	−.3		60	4.64	89.4
Average	4.3	8.3	6.30	−49.2	−.8	−.8	57	4.53	87.5
E-1				−22.2	−5.9		40	4.72	83.4
E-2				−26.3	−2.8		40	4.91	84.6
E-3				−33.2	−2.8		18	4.87	85.7
Average	4.5	8.2	6.35	−27.2	−3.8	0	33	4.83	84.6

TABLE 3.—*Effect of sulphuric acid on physical properties and color of waterleaf all-rag bond paper heated for 72 hours at 100° C.*

Subsample No.	Strength of H_2SO_4	Folding endurance after heating			Bursting strength after heating	Tensile strength after heating		
		Transverse direction	Longitudinal direction	Average both directions		Transverse direction	Longitudinal direction	Average both directions
	Grams per liter	*Double folds*	*Double folds*	*Double folds*	*Points*	*Kg*	*Kg*	*Kg*
Heated control		650	2,111	1,381	39.1	4.6	8.1	6.35
F-1	0.4004	0	0	0	10.5			
F-2		0	0	0	8.8			
F-3		0	0	0	8.0			
Average	.4004	0	0	0	9.1	1.6	2.1	1.85
G-1	.2452	8	13	11	25.2			
G-2		21	31	26	31.0			
G-3		1	1	1	25.0			
Average	.2452	10	15	13	27.1	3.3	7.0	5.15
H-1	.1226	348	984	666	39.2			
H-2		272	667	470	39.0			
H-3		198	664	431	41.0			
Average	.1226	273	772	523	39.7	4.3	8.2	6.25
I-1	.0613	465	1,548	1,007	39.4			
I-2		524	1,589	1,057	39.0			
I-3		366	1,295	831	40.0			
Average	.0613	452	1,477	965	39.5	4.4	8.2	6.30
J-1	.0306	501	1,848	1,175	38.6			
J-2		487	1,655	1,071	39.6			
J-3		499	1,709	1,104	40.7			
Average	.0306	496	1,737	1,117	39.6	4.3	8.2	6.25

TABLE 3.—*Effect of sulphuric acid on physical properties and color of waterleaf all-rag bond paper heated for 72 hours at 100° C.*—Continued

Subsample No.	Variation from strength of heated controls			Acidity of unheated paper		Reflection of blue light
	Folding endurance	Bursting strength	Tensile strength	Total calculated as parts SO_3 per 100,000 parts paper	pH of water extract	
	Per cent	*Per cent*	*Per cent*			*Per cent*
Heated control					7.85	86.1
F-1	−100.0	−73.1		104	3.65	72.2
F-2	−100.0	−77.5		74	3.95	60.6
F-3	−100.0	−79.5		84	3.76	67.2
Average	−100.0	−76.7	−70.0	87	3.79	66.7
G-1	−99.2	−35.5		69	4.11	78.7
G-2	−98.1	−20.7		52	4.28	83.0
G-3	−99.9	−36.1		60	4.16	84.0
Average	−99.1	−30.7	−18.9	60	4.18	81.9
H-1	−51.8	+ .3		52	4.44	82.8
H-2	−66.0	−.3		48	4.52	86.7
H-3	−68.8	+1.9		40	4.41	84.0
Average	−62.1	+1.5	−1.6	47	4.46	84.5
I-1	−27.1	+.8		44	4.99	85.3
I-2	−23.5	−.3		36	4.75	83.0
I-3	−39.8	+2.3		32	4.61	87.5
Average	−30.1	+1.0	−.8	37	4.79	85.3
J-1	−14.9	−1.3		25	5.10	85.6
J-2	−22.4	+1.3		28	4.98	84.2
J-3	−20.1	+4.1		28	5.16	84.2
Average	−19.1	+1.3	−1.6	27	5.08	84.7

TABLE 4.—*Effect of hydrochloric acid on physical properties and color of waterleaf all-rag bond paper heated for 72 hours at 100° C.*

Subsample No.	Strength of HCl	Folding endurance after heating			Bursting strength after heating	Tensile strength after heating		
		Transverse direction	Longitudinal direction	Average both directions		Transverse direction	Longitudinal direction	Average both directions
	Grams per liter	*Double folds*	*Double folds*	*Double folds*	*Points*	*Kg*	*Kg*	*Kg*
Heated control		650	2,111	1,381	39.1	4.6	8.1	6.35
K-1	0.1823	0	0	0	14.3			
K-2		0	0	0	15.0			
K-3		0	0	0	16.2			
Average	.1823	0	0	0	15.2	2.6	5.1	3.85
L-1	.0912	3	4	4	21.1			
L-2		5	7	6	30.0			
L-3		1	2	2	22.0			
Average	.0912	3	4	4	24.4	3.5	6.5	5.00
M-1	.0156	298	740	519	36.3			
M-2		242	816	529	37.0			
M-3		325	854	590	41.0			
Average	.0156	288	803	546	38.1	4.2	8.2	6.20
N-1	.0228	490	1,678	1,084	38.3			
N-2		427	1,491	959	39.0			
N-3		505	1,855	1,180	39.0			
Average	.0228	474	1,675	1,075	38.8	4.3	8.3	6.30

TABLE 4.—*Effect of hydrochloric acid on physical properties and color of waterleaf all-rag bond paper heated for 72 hours at 100° C.*—Continued

Subsample No.	Variation from strength of heated controls			Acidity of unheated paper			Reflection of blue light
				Total calculated as—			
	Folding endurance	Bursting strength	Tensile strength	Parts HCl per 100,000 parts paper	Parts SO_3 per 100,000 parts paper	pH of water extract	
	Per cent	*Per cent*	*Per cent*				*Per cent*
Heated control						7.85	86.1
K-1	−100.0	−63.4		47	52	4.24	81.0
K-2	−100.0	−61.6		51	56	4.39	78.6
K-3	−100.0	−58.6		33	36	4.45	85.2
Average	−100.0	−61.1	−39.4	44	48	4.36	81.6
L-1	−99.7	−40.0		36	39	4.37	83.1
L-2	−99.6	−23.3		40	44	4.44	85.7
L-3	−99.9	−43.7		44	48	4.47	83.6
Average	−99.7	−37.0	−21.3	40	44	4.43	84.1
M-1	−62.4	−7.2		36	39	4.66	85.5
M-2	−61.7	−5.4		35	38	4.68	83.1
M-3	−57.3	+4.9		31	34	4.68	85.8
Average	−60.5	−2.6	−2.4	34	37	4.67	84.8
N-1	−31.5	−2.0		29	32	4.86	87.0
N-2	−30.0	−.3		33	36	4.92	83.7
N-3	−14.6	−.3		26	29	5.04	87.3
Average	−22.2	−.8	−.8	29	32	4.94	86.0

The total acidity figures are given as parts of SO_3 per 100,000 parts of paper, the pH figures are values obtained on the water extract of the paper, and the percentage reflection of light is a measurement of the change in color of the sample.

Figure 1 shows the effect of the chemicals used on folding endurance of the paper heated for 72 hours at 100° C. Figures 2 and 3 show the effect of the same chemicals on the bursting strength and tensile strength. Only the average results of the triplicate sets are shown in the graphs.

DISCUSSION OF RESULTS

As the results obtained on the three sets of samples treated at different times with the same solution are in fairly good agreement with respect to the effect on the folding endurance, bursting strength, and tensile strength, only the average of the three sets given in the tables and graphs are considered in this discussion.

Where the pH of the water extract of the paper treated with aluminum sulphate, sulphuric acid, or hydrochloric acid is plotted against the percentage decrease in folding endurance (fig. 1), the curves show that the papers which were treated with aluminum sulphate and sulphuric acid and which yielded water extracts of the same pH value suffered essentially the same deterioration, whereas those treated with hydrochloric acid were subject to decidedly greater deterioration for the same pH of the water extract when the pH of the extract was below 4.80.

Where the total acidity values are plotted against the percentage loss in folding endurance, bursting strength, and tensile strength (figs. 1, 2, and 3), the curves show that hydrochloric acid causes a greater deterioration than does sulphuric acid, whereas the total titratable acidity of aluminum sulphate, as was to be expected, is not nearly so harmful to the paper as is the equivalent quantity of free sulphuric acid.

UNTREATED CONTROL

Table 1 shows that the pH of the water extract of the six sheets of untreated paper ranged from 7.60 to 8 and averaged 7.85.

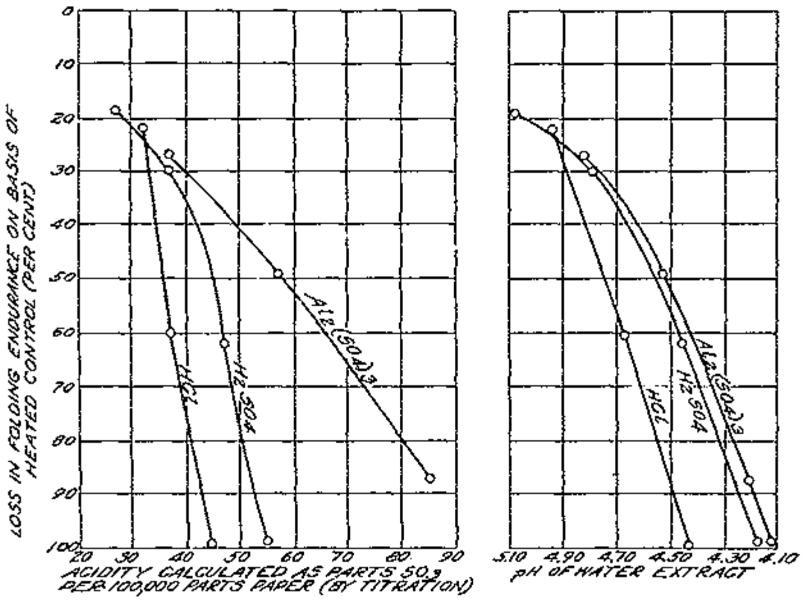

FIGURE 1.—Effect of $Al_2(SO_4)_3$, H_2SO_4, and HCl on folding endurance of waterleaf paper heated for 72 hours at 100° C.

The untreated control sheets showed practically no change in folding endurance, bursting strength, or tensile strength after being artificially aged by heating from 72 to 336 hours at 100° C.

The average folding endurance of the unheated controls was 1,434 double folds, the average tensile strength was 6.15 kg, and the average bursting strength was 37.1 points. After the paper was heated at 100° C. for 72 hours the average folding endurance, tensile strength, and bursting strength were 1,381 double folds, 6.35 kg, and 39.1 points. Paper heated for 336 hours had a folding endurance of 1,338 double folds, a tensile strength of 6.25 kg, and a bursting strength of 40.5 points.

Heating for 72 hours caused no perceptible change in the color of the untreated paper. The percentage of light reflected by the unheated controls ranged from 83 to 88.2, averaging 85.6, and the heated controls ranged from 84.2 to 89.1, averaging 86.1, which is practically the same as for the unheated controls.

Table 1 also shows the variation in folding endurance and bursting strength that may be expected between the various sheets of paper used in the experiments. The average folding endurance of the unheated controls ranged from 1,300 double folds on subsample 4 to 1,565 double folds on subsample 6, and the bursting strength ranged from 35 points on subsample 6 to 39 points on sub-

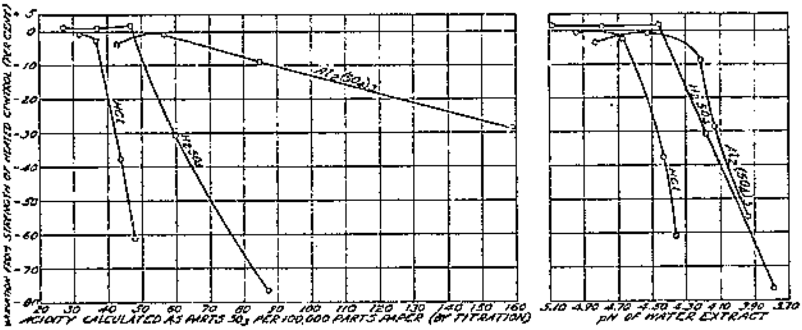

FIGURE 2.—Effect of $Al_2(SO_4)_3$, H_2SO_4, and HCl on bursting strength of waterleaf paper heated for 72 hours at 100° C.

sample 5. The variation between the heated portions of the same sheets was about the same as that of the unheated portion. The average folding endurance of the heated controls ranged from 1,151 double folds on subsample 4–1 to 1,501 on subsample 6–1, and the bursting strength ranged from 38 points on subsample 4–1 to 41.2 on subsample 6–1.

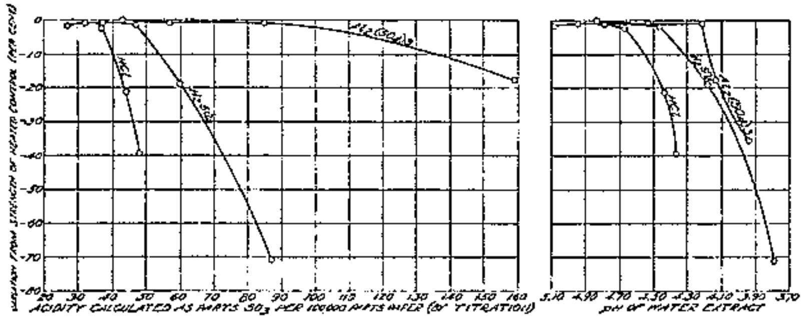

FIGURE 3.—Effect of $Al_2(SO_4)_3$, H_2SO_4, and HCl on tensile strength of waterleaf paper heated for 72 hours at 100° C.

EFFECT OF ALUMINUM SULPHATE

The results of the tests with aluminum sulphate are shown in Table 2.

4 G PER LITER

The average pH value of the water extract from the subsamples treated with a 0.4 per cent solution of $Al_2(SO_4)_3 \cdot 18H_2O$ was 3.97, and the total titratable acidity was 296. On artificial aging by heating for 72 hours at 100° C, the folding endurance decreased

100 per cent, the bursting strength decreased 56 per cent, and the tensile strength decreased 35 per cent. The percentage reflection of light of the heated portion was 81.9. This subsample was slightly darker than the untreated and heated controls.

2 G PER LITER

The pH of the water extract from the paper was 4.13; the total titratable acidity was 159. The folding endurance decreased 99 per cent, the bursting strength decreased 29 per cent, and the tensile strength decreased 17 per cent. The percentage reflection of light of the heated portion was 84.4. This subsample was not visibly darker than the controls.

1 G PER LITER

The pH of the water extract from the paper was 4.21, and the titratable total acidity, 85. The heated subsamples decreased 87 per cent in folding endurance, and 9 per cent in bursting strength. The tensile strength remained practically the same as that of the untreated and heated controls. The percentage reflection of light was 85.5, or practically the same as that of the controls.

0.4 G PER LITER

The pH of the water extract from the paper was 4.53, and the total titratable acidity was 57. The folding endurance decreased 49 per cent, but the bursting strength, tensile strength, and reflection of light remained practically the same as those of the controls.

0.2 G PER LITER

The pH of the water extract from the paper was 4.83, and the total titratable acidity was 43. The folding endurance decreased 27 per cent; the bursting strength decreased 4 per cent, which was well within the experimental error; and the tensile strength remained the same as that of the controls. The percentage reflection of light was 84.6.

EFFECT OF SULPHURIC ACID

Table 3 shows the results of the tests with sulphuric acid.

0.4904 G PER LITER (0.01 N.)

The average pH of the water extract from the subsamples treated with sulphuric acid was 3.79, and the total titratable acidity was 87. The folding endurance decreased 100 per cent, the bursting strength decreased 77 per cent, and the tensile strength decreased 71 per cent when the paper was heated for 72 hours at 100° C. The percentage reflection of light of the heated portion was 66.7. This portion was considerably darker than the untreated and heated controls.

0.2452 G PER LITER (0.005 N.)

The pH of the water extract from the paper was 4.18, and the total titratable acidity was 60. The folding endurance decreased 99 per cent, the bursting strength decreased 31 per cent, and the tensile strength decreased 19 per cent upon heating for 72 hours at 100° C. The percentage reflection of light of the heated portion was 81.9. This subsample was slightly darker than the controls.

0.1226 G PER LITER (0.0025 N.)

The pH of the water extract from the paper was 4.46, and the total titratable acidity was 47. The decrease in folding endurance was 62 per cent, but the bursting strength, tensile strength, and reflection of light remained practically the same as those of the controls.

0.0613 G PER LITER (0.00125 N.)

The pH of the water extract from the paper was 4.79, and the total titratable acidity was 37. The folding endurance decreased 30 per cent, but the bursting strength, tensile strength, and reflection of light remained practically the same as those of the controls.

0.0306 G PER LITER (0.000625 N.)

The pH of the water extract from the paper was 5.08, and the total titratable acidity was 27. The decrease in folding endurance was 19 per cent, but the bursting strength, tensile strength, and reflection of light remained about the same as those of the controls.

EFFECT OF HYDROCHLORIC ACID

The results of the tests with hydrochloric acid are given in Table 4.

0.1823 G PER LITER (0.005 N.)

The average pH value of the water extract from the subsamples treated with this solution was 4.36, and the total titratable acidity was 48. The folding endurance decreased 100 per cent, the bursting strength decreased 61 per cent, and the tensile strength decreased 39 per cent upon artificial aging by heating for 72 hours at 100° C. The percentage reflection of light of the heated portion was 81.6. This subsample was slightly darker than the untreated and heated controls.

0.0912 G PER LITER (0.0025 N.)

The pH of the water extract from the paper was 4.43, and the total titratable acidity was 44. The folding endurance decreased 100 per cent, the bursting strength decreased 38 per cent, and the tensile strength decreased 21 per cent. The heated paper showed no visible discoloration, the reflection of light being 84.1 per cent.

0.0456 G PER LITER (0.00125 N.)

The pH of the water extract from the paper was 4.67, and the total titratable acidity was 37. The folding endurance decreased 61 per cent. The bursting strength, tensile strength, and reflection of light remained practically the same as those of the controls.

0.0228 G PER LITER (0.000625 N.)

The pH of the water extracts from the paper was 4.94, and the total titratable acidity was 32. The decrease in folding endurance was 22 per cent, and the bursting strength, tensile strength, and reflection of light remained practically the same as those of the controls.

CONCLUSIONS AND SUMMARY

Experiments were conducted to show the effect of small quantities of aluminum sulphate and sulphuric and hydrochloric acids on the folding endurance, bursting strength, tensile strength, and color of waterleaf all-rag bond paper artificially aged by heating for 72 hours at 100° C.

The folding endurance, bursting strength, tensile strength, and color of the untreated paper heated for 72 hours at 100° C. remained essentially the same as those for the unheated paper. The differences that occurred in these experiments are within the limits of error of the method of test.

Small quantities of aluminum sulphate, sulphuric acid, or hydrochloric acid in paper caused its rapid deterioration. The deterioration increased as the quantities of these chemicals were increased. Hydrochloric acid caused greater and more rapid deterioration than did sulphuric acid or aluminum sulphate when the pH values of the water extract or the total titratable acidity were the same.

When the pH of the water extract from the paper treated with these chemicals was 5.10, the loss in folding endurance on heating was less than 20 per cent. By extrapolation it appears that the loss at a pH of 5.50 would be approximately 10 per cent.

When the total titratable acidity of the paper was less than 20 (calculated as parts SO_3 per 100,000 parts paper), the loss in folding endurance of the heated paper was less than 20 per cent.

When the pH of the water extract from the paper treated with aluminum sulphate, sulphuric acid, or hydrochloric acid was greater than 4.20, 4.40, and 4.60, respectively, the loss in bursting strength on heating was less than 10 per cent.

When the total titratable acidity of the paper treated with aluminum sulphate, sulphuric acid, or hydrochloric acid was less than 85, 50, and 38, respectively, the loss in bursting strength of the heated paper was less than 10 per cent.

When the pH of the water extract from the paper treated with aluminum sulphate, sulphuric acid, or hydrochloric acid was greater than 4.20, 4.30, and 4.55, respectively, the loss in tensile strength of the treated paper was less than 10 per cent.

When the total titratable acidity of the paper treated with alumium sulphate, sulphuric acid, or hydrochloric acid was less than 135, 55, and 40, respectively (calculated as parts SO_3 per 100,000 parts paper), the loss in tensile strength of the heated paper was less than 10 per cent.

The folding endurance, bursting strength, and tensile strength rapidly and progressively decreased as the pH value of the water extracts of the treated samples decreased from the figures given in the preceding paragraphs, and as the total titratable acidity increased from the figures given above.

The folding endurance of the paper was decidedly more affected by acidity, whether expressed as pH of the water extract or as total titratable acidity, than was the bursting strength or the tensile strength.

Of the three tests employed, folding endurance yielded the most significant results as to the effect of mineral acids on this paper. It appears to be the only one of the three necessary to make in studying the deterioration of paper by acids.

An observable discoloration of this paper occurred on heating (1) when it contained sufficient aluminum sulphate to give a water extract having a pH of about 3.95, (2) when it contained sufficient sulphuric acid to give a water extract having a pH of about 4.15, or (3) when it contained sufficient hydrochloric acid to give a water extract having a pH of about 4.35. The paper containing these chemicals and having a pH somewhat higher than these figures showed no visible discoloration, whereas the paper having a pH value somewhat less than these figures showed a pronounced discoloration.

Although no relation has been established between the deterioration of paper under the experimental and actual service conditions, it seems reasonable to assume that in general such a relation exists. Acids and acid salts, even in the small proportions used in these experiments, exert a slow deteriorating effect on paper, which may not be observable for many years.

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