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A STUDY OF THE RELATION OF SOME PROPERTIES OF COTTON RAGS TO THE STRENGTH AND STABILITY OF EXPERIMENTAL PAPERS MADE FROM THEM

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ABSTRACT

This article is one of a series on the stability of papers made from various fibrous raw materials. The present study is concerned with rag-fiber papers and the factors affecting their stability.

High-grade bond papers were made under carefully controlled conditions in the semicommercial paper mill of the Bureau from cotton rags of the qualities termed in the trade "new" (cuttings from unused textiles from textile and garment factories) and "old" (used textile materials, principally from homes). Unsized, engine-sized, and surface-sized papers were included. For most of the beater sizing, rosin size was used, being precipitated on the fibers in the usual way with papermakers' alum.

The basic rags, the half-stuffs made from them, and the finished papers were analyzed. The usual physical and chemical tests were made on the paper both before and after it had been subjected to an accelerated-aging test. The results demonstrate that stable paper can be obtained from new rags.

The data obtained confirm the general belief that high acidity resulting from excessive use of alum in rosin sizing has a marked deteriorating effect upon paper. The pH value for optimum results, as far as stability is concerned, was approximately 5.0. The degree of sizing at this acidity was also satisfactory.

Of papers of the same acidity, those having the lesser content of rosin were the more stable.

In general, surface sizing did not materially affect the life of base papers of high stability, although it seemed to serve as a protective surface retarding chemical deterioration of the less stable papers.

Initial quality of the fibers cannot be taken as a criterion of the degree of excellence of paper made from them. The study shows that careful processing of raw materials in respect of active chemical components (alum, rosin, etc.) is necessary for the manufacture of stable papers.

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I. INTRODUCTION

This report deals with a study of the effects of cellulosic impurities and of the papermaking processes on the strength and stability of rag papers. It is the third in a series of studies planned to include all the important types of fibrous raw materials commonly used in the manufacture of record papers.¹ The purpose of the investigation is to extend present information relative to the development of optimum qualities in papers prepared from each of the various fibrous raw materials, and the manner and extent to which the quality of the paper is affected by the raw materials and by the variations encountered in processing them. The plan of the investigation as a whole is stated in more detail in the first report.

II. RAG FIBERS USED

Cotton rags of the qualities termed in the trade "new" and "old" were used in making the papers. New rags are cuttings from unused textiles and come largely from textile and garment factories, whereas old rags are used textile materials, and are principally waste products from homes. The rags employed were the grades known commercially as no. 1 white shirt cuttings, unbleached hosiery clippings, unbleached muslin, unbleached shoe cuttings, twos and blues, and no. 1 old whites. They were supplied by a commercial paper mill and had been sorted, cut, and dusted.

The rags were purchased as being representative of the respective grades. Analyses reported elsewhere herein of the various kinds of rags before they were submitted to the paper-making processes and also after they had been boiled, washed, and drawn out of weave (reduced to half-stuff) indicate the degree of cellulosic purity of the fiber and the extent to which the cellulose had been modified or degraded either in preliminary treatment or in actual preparation of the half-stuff.

The rag composition of the beater furnish, that is, the various kinds of half-stuff blended in the beater, is included in the data for each of the paper-machine runs.

III. PAPERMAKING EQUIPMENT

The equipment of the Bureau paper mill is adapted for making paper on a semicommercial scale under practical mill conditions. That employed in the manufacture of the rag papers included a rag cutter; duster; rotary boiler; 50-pound copper-lined wood-tub beater, having manganese-bronze bars and plate, and equipped with a washing cylinder; jordan refiner, with bars of a bronze and steel alloy; 4-plate

¹ For previous reports see *Highly-purified wood fibers as papermaking material*, BS J. Research **7**, 765-782 (1931) RP372; also, *A study of some factors influencing the strength and stability of experimental papers made from two different sulphite pulps*, BS J. Research **11**, 7-23 (1933) RP574.

screen; 29-inch fourdrinier papermaking machine, with wire 33 feet long and having two presses, nine 15-inch dryers, a small machine stack of 7 rolls, and a reel; surface-sizing bath and drying cabinet; and a 5-roll supercalender.²

IV. PREPARATION OF THE HALF-STUFF

The procedure followed in the preparation of the half-stuff was essentially the same as that generally observed in the commercial production of high-grade papers.

1. CUTTING AND DUSTING

Since the rags employed in the tests had already been sorted as to material and color, the only mechanical treatment necessary to prepare them for the chemical cleansing was cutting and dusting.

2. BOILING OR "COOKING"

(a) CHEMICALS USED

The grease, dirt, starch, sizing, or other impurities were rendered soluble or easily removable by boiling the rags in a chemical solution under pressure. The choice of agents generally used to effect these changes depends somewhat upon mill conditions and the grade and kind of paper to be produced. A mixture of lime and soda ash was used in this study.³

Either quicklime (calcium oxide) or hydrated lime (calcium hydroxide) may be used for cooking rags, but quicklime was employed in the present study. The following analysis⁴ shows the composition of the lime,⁵ which was ground to pass through a no. 100 sieve before analysis:

	Percent
Loss on ignition.....	1.9
Insoluble siliceous matter (SiO ₂ , etc.).....	0.5
Iron and aluminum oxides (R ₂ O ₃).....	0.4
Calcium oxide (CaO).....	96.8
Magnesium oxide (MgO).....	not more than 0.4
Carbon dioxide (CO ₂).....	not more than 1.9

The soda ash (Na₂CO₃) was 58 percent sodium oxide.

² Photographs of the equipment employed are included in the following publications: *Carao fiber as a papermaking material*, Tech. Pap. BS 21, 338-341 (1927) T340. *Further experimental production of currency paper in the Bureau of Standards paper mill*, BS J. Research 3, 904-905 (1929) RP121. *Equipment and research work of the Bureau of Standards paper mill*, Paper Trade J. 89, 19, 60-63 (1929).

³ In previous experimental tests in the Bureau mill using caustic soda as the digesting chemical, papers of excellent quality were obtained. Caustic soda was not included in the present study, however, on advice of commercial papermakers, who thought its use unnecessary. It is not commonly used in cooking rags because its use is dangerous to workmen when mills are not properly equipped. Recent work by Edwin R. Laughlin, *Observations relative to the physical and chemical changes taking place in the cooking of new white rags*, Paper Trade J. 97, 17, 39-53 (1933), gives interesting data on the effects of different chemicals in the cooking of rags, including caustic soda and a comparison of calcium and magnesium limes.

⁴ Made by Chemistry Division, National Bureau of Standards.

⁵ The lime conforms to the chemical requirements of Bureau of Standards Circular C96, Recommended Specifications for Quicklime and Hydrated Lime for Use in the Cooking of Rags for the Manufacture of Paper.

(b) COOKING PROCEDURE

The constant factors for each cook were as follows:

Weight of bone-dry fiber.....	106 pounds.
Volume of water.....	52.5 U. S. gallons (231 in. ³)
Initial temperature.....	70 to 80° F.
Duration of initial temperature.....	1 hour.
Time for raising to cooking temperature.....	1 hour.
Cooking temperature.....	250 to 260° F.
Duration of cooking temperature.....	5 hours.
Cooking pressure.....	30 to 40 pounds.

The no. 1 white shirt cuttings, no. 1 old whites, and twos and blues were each cooked separately. The unbleached hosiery, muslin, and shoe cuttings were mixed in equal parts and cooked together.

The amounts of chemicals used in the cooking liquor were varied according to the kind of rags being treated. For the new rags, 3 percent of lime and 1 percent of soda ash, based on the bone-dry weight of the rags, were employed; for the no. 1 old whites, 6 percent of lime and 1.5 percent of soda ash; and for the twos and blues, 8 and 2 percent, respectively. These percentages were recommended by a commercial paper company making high-grade rag papers.

In preparing the lime solution a portion of the total amount of water, 52.5 gallons, was used to slake the lime; the balance of the water and the soda ash were later added and thoroughly mixed with the slaked lime. The mixture was run through a no. 60 screen to remove sand, splinters of wood, coal particles, or other foreign material as it was charged into the boiler.

3. WASHING

When the cook was completed the boiler pressure was relieved and the liquor was allowed to drain off overnight. The cooked rags were then transferred to the beater and washed until the effluent was clear, to remove the cooking liquor and the loosened impurities. One-half of a cook constituted a beater charge. Fresh water was added continuously during the washing.

The time required for washing was about two hours for the no. 1 whites and the hosiery clippings, muslins, and shoe cuttings; about three hours for the no. 1 old whites and the twos and blues. The amount of water used was about 30 gallons per pound of new rags and about 45 gallons for the old. The temperature of the wash-water was 75 to 85° F.

After the washing had continued for about one-half hour, or until the water discharged from the washer was fairly clear, the roll was partially lowered to the bed plate and the pressure was increased by lowering the roll at intervals thereafter during the washing process to further cleanse the rags and gradually brush them out of weave into threads and the threads into fibers.

4. BLEACHING

After the rags were reduced to half-stuff, an oxidizing agent was added to change the residual coloring materials or impurities into soluble or colorless substances. Bleaching powder, calcium hypochlorite, containing 35 percent of available chlorine, was the oxidizing agent used. The powder was thoroughly mixed with water and after being agitated for some time was allowed to settle. The clear liquor was then drawn off, analyzed, and subsequently used as needed.

The amount of bleaching powder required to attain the desired degree of whiteness varied with the color of the rags. The amount used, based on the bone-dry weight of the rags, was, for no. 1 white shirt cuttings, 0.1 to 0.2 percent; for unbleached hosiery clippings, muslin, and shoe cuttings, 0.3 to 0.5 percent; for no. 1 old whites, 1.0 percent; and for twos and blues, 2.0 percent.

The bleaching operation was begun in the washer (beater used as washer) and completed in the drainer. Before the bleach liquor was added to the half-stuff in the washer, water was removed from the washer to increase the concentration of the half-stuff. The bleach liquor was then slowly added and the stock was circulated for one hour. The temperature in the washer during this interval varied from 85 to 105° F. The washer contents were then dropped into the drainer, as was also the fresh water subsequently used in washing out the beater, and left for one-half hour before the valve was opened and the water permitted to drain off. No acid or other material was added to accelerate the bleaching operation.

The bleaching was followed by washing to remove residual chemicals and the soluble products of the bleaching action. The half-stuff in the drainer was covered with fresh water and thoroughly mixed, and allowed to stand for one hour before the drainer valve was opened. The process was later repeated and the half-stuff left to drain. All traces of active chlorine were removed in the washing, therefore no antichlor was used.

The divisions of the rags used in cooking—no. 1 white shirt cuttings; unbleached hosiery, muslin, and shoe cuttings; no. 1 old whites; and twos and blues—were maintained throughout all the processes. The corresponding lots of bleached half-stuffs were kept separate until blended in the beater.

5. LOSSES DURING PREPARATION OF HALF-STUFF

The total loss in weight of the various rags used in the preparation of the half-stuff—boiling, washing, and bleaching—based on the bone-dry weight of the rags, was as follows: no. 1 white shirt cuttings, 10 to 11 percent; mixture of the unbleached rags (hosiery, muslin, and shoe cuttings), 13 to 15 percent; no. 1 old whites, 15 to 18 percent; and twos and blues, 18 to 21 percent.

V. PAPERMAKING PROCESSES

1. BEATING

The method of beating the half-stuff to prepare it for forming a sheet on the paper machine followed very closely that described in a previous publication.⁶ The characteristic feature of the method was the very gradual lowering of the beater roll.

Before the furnish was added to the beater, the roll was raised off the plate in order to give clearance to the lumps of half-stuff. The tub was partially filled with water, half-stuff from the drainers was introduced, and additional water was run in until the desired concentration was obtained. After some circulation of the furnish the roll was gradually lowered, by definite amounts and at fixed intervals,

⁶ Research on the production of currency paper in the Bureau of Standards experimental paper mill, Tech. Pap. BS 21, 96-97 (1926) T329.

to brush out the fibers and reduce them to optimum length. The various positions of the roll and the time intervals for each during the beating of a furnish are given in table 1 for both new and old rags, and are representative of the beating procedure.

TABLE 1.—*Schedule of roll settings for beating*

New rags			Old rags		
Beating interval		Position of roll ^a	Beating interval		Position of roll ^a
hr	min		hr	min	
0	0	+10 ^b	0	0	+10 ^b
0	5	+10 ^c	0	5	+10 ^c
0	15	+6	0	15	+6
0	45	+5½	0	45	+5½
1	15	+5	1	15	+5
1	30	+4½	1	30	+4½
1	45	+4	1	45	+4
2	00	+3½	2	00	+3½
2	15	+3	2	15	+3
2	30	+2½	2	30	+2½
2	45	+2	3	00	+2
3	00	+1½	3	30	+1½
3	15	+1	4	00	+1
3	30	+½	4	30	+½
4	30	+½	5	00	+½
5	30	0	5	30	+½
6	30	0			
7	30	-½			
8	00	-½			

^a Expressed in turns of the handwheel with which the position of the roll relative to the bedplate is changed. At zero setting the bedplate is just barely cleared. One turn of the handwheel raises or lowers the roll 0.008 inch.

^b Lighter-bar up.

^c Lighter-bar down.

The duration of the beating and freeness readings indicating the rate at which water flowed through or from the pulp sample are given for each paper-machine run in table 4. The freeness data are for the stuff (beaten half-stuff) at the time of running into the stuff chest at the completion of the beating. The concentration of fiber in the test samples was 0.2 percent and the temperature 80° F.

For more detailed description and discussion of the beating technic the reader is referred to the Bureau's Technologic Paper T329,⁷ pages 96 to 102.

2. PAPER-MACHINE OPERATION

From the stuff chest the stuff was pumped in a continuous stream through the stuff box and the jordan refiner to the paper machine. Pumping the stock from the jordan directly to the paper machine is considered better practice than discharging it into a machine chest and subsequently withdrawing it as needed. By the former method, changes in the character of the stock indicated as desirable by conditions at the screen, on the paper machine, or in the finished sheet can be effected rapidly by suitable adjustments of the jordan.

The operation of the paper machine was carefully controlled during the tests. For additional details of the operation see Bureau Technologic Paper T329, pages 102 and 103.

⁷ See footnote 6.

3. SIZING

Practically all the commonly used varieties of rag papers are sized to improve the writing or printing quality, or various other properties. For some of the papers manufactured in this study, sizing agents were introduced into the beater and precipitated on the fibers (beater sizing); and in some experiments the surface of the paper also was impregnated with a sizing material after manufacture (surface sizing).

(a) BEATER SIZING

Rosin and starch were each used as sizing agents. The rosin size contained about 33 percent of free rosin, and was precipitated on the fibers in the beater with aluminum sulphate (papermaker's alum) in the usual manner. The starch was a commercial beater starch prepared by an oxidation process, and was used in accordance with current commercial practice as far as possible.

In preparing the starch mixture one part of starch was allowed to soak for about one-half hour in five parts of cold water, after which time the mixture was warmed to between 170 and 175° F, while stirred continuously. It was kept at this temperature until the starch had swollen to the proper extent, and then was cooled. When used with rosin size, the starch was added to the beater after the rosin size and before the addition of the alum. When used alone, the starch was added at the same stage of the beating.

(b) SURFACE SIZING

For surface sizing, glue and starch were each used. The glue was a high-grade hide glue with 331-grams jell strength, 87-millipoises viscosity, and 6.2 pH value.⁸ The sizing bath was a 4-percent solution containing alum, and was maintained at approximately 130° F. The paper was passed through the heated solution, then between a pair of squeeze rolls to remove excess sizing solution, and dried in a festoon drier at a temperature of 110 to 120° F. The desired finish was imparted to the paper by supercalendering.

The procedure for surface sizing with starch was essentially the same as that for sizing with glue, except that no alum was added. A commercial starch prepared by a process of oxidation was used. In preparing the sizing solution, one part of starch was allowed to soak for one-half hour in four parts of cold water, and the mixture was then heated to 170° F. When proper swelling had taken place, sufficient water was added to make a 4-percent solution.

VI. TEST METHODS

The physical and the chemical tests were made in accordance with the official paper-testing methods⁹ of the Technical Association of the Pulp and Paper Industry. The pH was determined electrometrically, using a quinhydrone electrode.

⁸ Division of Tests and Technical Control, U. S. Government Printing Office, Washington, D.C.

⁹ Copies of the methods can be secured from the Technical Association of the Pulp and Paper Industry, 122 East 42nd Street, New York, N.Y.

The relative stability of papers cannot be determined by analysis of the original papers alone. Too little is definitely known of the effect of any given combination of components on the aging of paper. Therefore the pertinent physical and chemical tests were applied not only to the original papers but to samples that had been submitted to an accelerated-aging test as well. This test is made at the Bureau by exposing specimens of paper to air at a temperature of 100° C for 72 hours, and then determining to what extent the paper has been altered in folding endurance, tearing strength, alpha cellulose content, and copper number. A marked decrease in alpha cellulose (unmodified cellulose) content and increase in copper number (a measure of degraded cellulose) are considered indicative of deterioration. A high degree of resistance to change in the heat test, particularly with respect to folding strength and alpha cellulose content, as well as copper number, are regarded as favorable indications of permanence. For further details of this test the reader is referred to previous discussions of the method.¹⁰ Although the test is only empirical and the time relation to natural aging is not known, Rasch and Scribner¹¹ found that results obtained by the test corroborated those obtained after a 4-year period of natural aging in differentiating the stability of papers.

VII. ANALYSES OF RAGS AND HALF-STUFFS USED

Analyses showing the purity of the various grades of rags used and the half-stuffs made from them are given in tables 2 and 3. The fiber samples were converted into disintegrated form before being submitted to the alpha cellulose and copper-number tests.

TABLE 2.—Chemical-test data on rags used

Types of rags	Alpha cellulose content	Copper number	Ash
	<i>Percent</i>		<i>Percent</i>
Hosiery clippings.....	98.2	0.18	0.44
Muslin.....	91.3	3.57	.62
Muslin after being washed with boiling water.....	96.9	.20	.1
Shoe cuttings.....	90.9	.73	2.75
No. 1 white shirt cuttings.....	97.3	.32	3.33
No. 1 old whites.....	90.9	1.28	.74
Twos and blues.....	89.0	1.67	1.37

It will be noted in table 2 that the muslin rags originally had a high copper number, no doubt due to filler or loading material in the cloth. The material was apparently easily removed however, since, after being washed with boiling water, the rags had a high alpha cellulose content and a low copper number. The new rags were higher in cellulosic purity and were stronger than the old rags. Old rags are inherently less strong and of lower cellulosic purity because of the usage and repeated laundering of them.

¹⁰ Accelerated-aging test for paper, BS J. Research 7, 465-475 (1931) RP352. Also, *Estimating stability of paper by heating*, Paper Trade J. 95 4, 28-30 (1932). Also, for previous reports, see *Highly-purified wood fibers as papermaking material*, BS J. Research 7, 765-782 (1931) RP372; *A study of some factors influencing the strength and stability of experimental papers made from two different sulphite pulps*, BS J. Research 11, 7-23 (1933) RP574.

¹¹ *Comparison of natural aging of paper with accelerated aging by heating*, BS J. Research 11, 727-732 (1933) RP620.



FIGURE 1.—*New rag fiber*, $\times 100$.
(Stock from head box, machine run no. 1,013.)



FIGURE 2.—*Old rag fiber, $\times 100$.*
(Stock from head box, machine run no. 1,032.)

The values given in table 3 show the degree of purity of the half-stuffs and the extent of modification of the cellulose in their preparation. The relative quality of the rags is reflected in the half-stuffs and, as will be seen later, in the papers made from them.

TABLE 3.—*Chemical test data on bleached half-stuffs made*

Half-stuff	Cook number	Alpha cellulose content	Copper number	Ash
		<i>Percent</i>		<i>Percent</i>
Hosiery, muslin, and shoe cuttings	440	96.7	0.26	0.14
Do.....	441	97.1	.22	.16
Do.....	446	97.2	.19	.19
Do.....	451	97.7	.21	.15
Do.....	452	97.3	.22	.12
No. 1 white shirt cuttings	439	96.0	.34	.14
Do.....	442	96.1	.24	.12
Do.....	445	96.2	.29	.10
Do.....	449	96.3	.25	.10
Do.....	450	96.8	.25	.18
No. 1 old whites	458	90.8	.67	.48
Do.....	460	90.9	.76	.33
Do.....	462	91.2	.67	.44
Do.....	466	91.0	.76	.23
Twos and blues	457	86.1	1.46	.38
Do.....	459	85.3	1.60	.25
Do.....	461	87.4	1.20	.69
Do.....	463	84.3	1.70	.19

VIII. DATA ON PAPERS MADE

Data relative to the beater furnish, beating time, and condition of the beaten stock for each paper-machine run, and various measurements on the papers are given in table 4.

After preliminary runs (nos. 991 to 993), in which beating time was varied to determine the optimum beating conditions, an eight-hour beating, with the method of roll manipulation given in table 1, was adopted as suitable to produce a high-grade commercial-type writing or bond paper from the new rags. This time was used for practically all subsequent runs on new rags. As a result of previous work in the Bureau mill on old rags, five and one-half hours was used for them.

The condition of the fibers at the head box, that is, as the stock was ready to go over the wire of the paper machine, is shown in the photomicrographs, figures 1 and 2. Figure 1 is representative of the stock prepared from new rags, and shows the fibers to be long, clean, and well brushed out. It will be noted that this condition was not destroyed by the jordanning. Figure 2 shows the fibers of the stock prepared from the old rags to be shorter, more broken, and less fibrillated, as would be expected. The photomicrographs were made at a magnification of 100 diameters.

1. UNSIZED PAPERS

A series of runs of unsized papers in which the amount of alum added was varied were made to determine the effect of acidity on the stability of the papers. Tests were made on both original and heat-treated samples to determine the probable permanence of the papers. The test data are given in table 4, but the relative effects

of increasing amounts of alum are shown more clearly in figures 3 and 4. The measurements on the heat-treated samples show that the

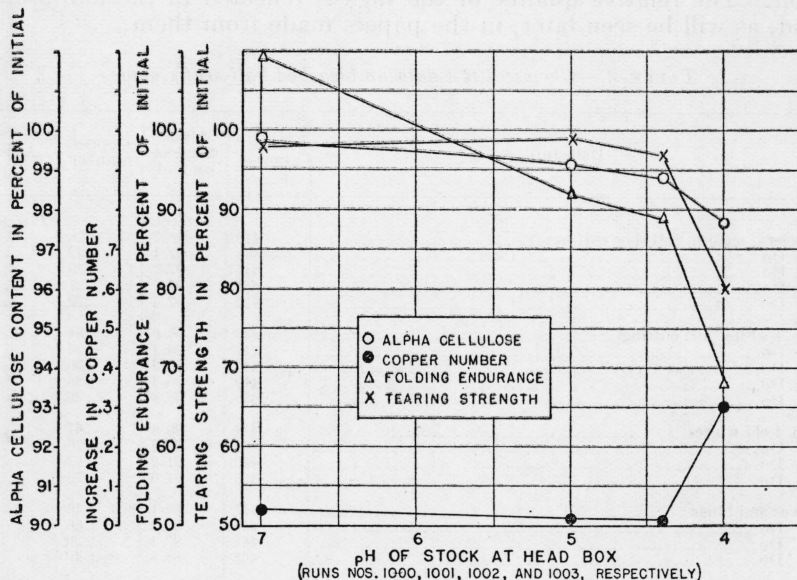


FIGURE 3.—Effect of acidity on stability of unsized new-rag papers.

folding endurance, tearing strength, and alpha cellulose content decrease as the acidity increases, and that the copper number in-

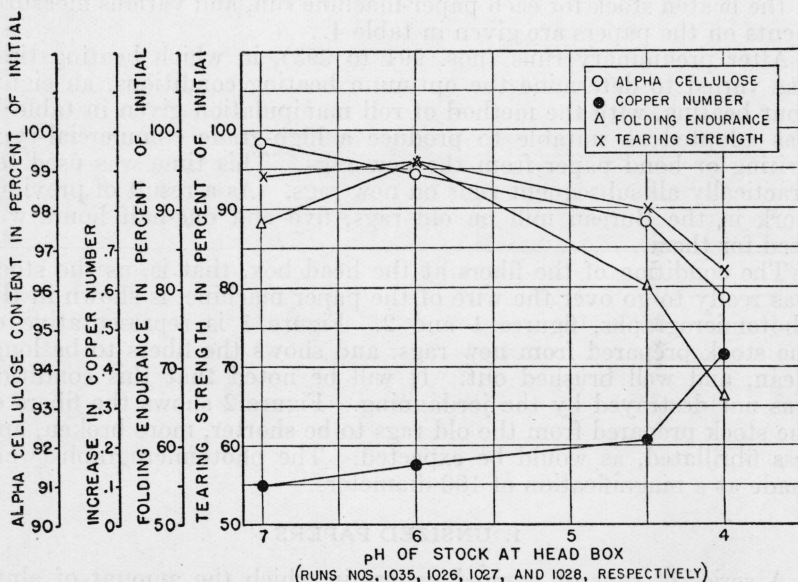


FIGURE 4.—Effect of acidity on stability of unsized old-rag papers.

creases. Figure 9 indicates that the addition of alum alone does not decrease the initial folding endurance of the paper, however.

TABLE 4.—Data on unsized, beater-sized, and surface-sized rag papers

PAPERS MADE FROM NEW RAGS

Run number		Beater furnish					Beating interval	Freehess		Surface-sizing solution				Physical tests of papers ^a														Chemical tests of papers										Heat tests of papers ^a								
Paper machine	Surface sizing	Fiber composition		Sizing materials (amount based on dry fiber)				After beating	At head box	Acid-ity of stock at head box	Glue	Starch	pH value	Weight: 25 by 40 inches, 500 sheets	Bursting strength	Ratio of bursting strength to weight	Thick-ness	Folding endurance ^a		Tensile properties				Tearing strength		Water resistance				Sizing materials				Acidity			Alpha cellu-lose	Copper number	Folding endurance in percent of initial strength	Tearing strength in percent of initial strength	Decrease in alpha cellulose content	Increase in copper number				
		Un-bleached rags; twos and blues ¹	Shirt cuttings; old whites ¹	Rosin	Starch	Alum												Machine direction	Cross direction	Breaking load ^a		Elongation at rupture		Machine direction	Cross direction	Opacity	Dry-in-dicator method, 21° C	Curl method, 21° C	Ash	Resin	Glue	Starch	Extract, Kohler-Hall method	Fiber suspen-sion	pH of extract											
																				Machine direction	Cross direction	Machine direction	Cross direction																							
		Percent	Percent	Percent	Percent	Percent	Hours			pH	Percent	Percent		Pounds	Points ³	Percent	Inch	Double folds	Double folds	Kilo-grams	Kilo-grams	Percent	Percent	Grams	Grams	Percent	Seconds	Seconds	Percent	Percent	Percent	Percent	Percent ⁷	Per-cent ⁷		Percent										
991	271	50	50				9	42	14		4		±4.5	57.0	32	56.1	0.0036	2,900	1,400	7.5	4.3	3.5	8.0	105	95	78																				
991														55.5	54	97.4	.0035	4,400	4,000	11.0	6.0	4.8	10.2	98	95	77	24	21	.24	.28	2.06															
992		50	50				7	78	26		4		±4.5	56.4	31	55.0	.0036	3,500	1,100	7.1	4.3	3.0	7.0	109	114	77			.11	.20																
992	272													56.7	58	102.1	.0035	4,400	5,200	10.1	6.6	4.4	9.4	96	100	74	10	12	.26	.20	2.27															
993		50	50				13	66	30		4		±4.5	53.2	31	58.3	.0035	4,300	2,000	6.8	3.9	3.0	8.0	128	126				.10	.20																
993	273													58.0	61	105.0	.0035	5,500	5,400	11.6	6.8	4.4	9.9	107	110	74	11	10	.22	.20	2.74															
995		100					14	32	21					59.2	35	59.0	.0035	6,300	2,400	8.0	4.2	3.5	10.0	155	138				.12	.20																
998	274	100					9	52	25		4		±4.5	58.2	36	61.8	.0037	5,200	2,300	8.2	4.5	3.0	8.0	126	126	76			.37	.23																
998														59.1	55	94.8	.0034	5,700	5,000	11.6	6.0	4.2	10.0	121	119	71	16	18	.22	.23	1.57															
1,015	284	100		2		1.5	9	62	31	±5.0				56.6	30	53.0	.0036	2,700	720	7.3	4.3	3.0	7.5	134	126	79	14	11	.54	2.12																
1,015											4		±4.5	57.7	50	86.5	.0033	5,200	3,500	9.4	5.8	4.5	10.2	117	116	76			.76																	
996A		100					10	52	23					57.1	34	59.5	.0037	4,200	2,100	7.4	4.4	2.5	7.0	108	111	78			.09	.22																
996B		100				1.5	10	52	23	±5.0				54.1	30	55.5	.0035	2,400	930	6.9	4.1	3.0	7.0	102	98	78			.42	.22																
999		100					7	68	31					56.6	33	58.3	.0038	3,000	820	7.4	4.2	2.5	7.5	104	103	80			.42	.22																
1,014		100		2		1.5	7	66	30	±5.1				56.5	31	54.9	.0037	1,200	440	6.9	4.4	2.9	7.0	112	113	81	13	10	.82	2.05																
1,014	285										4		±4.5	58.4	50	85.6	.0035	3,200	1,600	9.7	6.1	4.3	8.7	98	96	79	21	21	.40	1.70	1.60															
1,001		50	50			.6	8	53	26	±5.0				56.6	32	56.5	.0036	4,000	1,200	7.5	4.1	2.2	7.9	115	112	79			.27	.15																
1,001	275										4		±4.5	57.9	57	98.5	.0035	4,800	4,100	11.4	6.1	5.0	9.4	100	106	78	15	14	.38	.15	2.39															
1,002		50	50			1.2	8	54	24	±4.4				58.1	32	55.0	.0037	3,900	1,500	7.4	4.2	2.9	7.9	121	118	76			.27	.14																
1,002	276										4		±4.5	59.8	57	95.4	.0035	4,700	4,600	11.8	6.3	5.1	9.4	112	119	77	19	17	.23	.14	2.06															
1,003		50	50			2.1	8	53	28	±4.0				58.1	32	55.0	.0036	3,600	1,400	7.4	4.2	2.8	7.7	117	121	77			.32	.15																
1,003	277										4		±4.5	59.0	55	93.2	.0036	4,300	4,500	11.0	6.3	4.7	9.6	103	114	78	22	21	.23	.15	2.01															
1,004		50	50	2		.9	8	62	28	±6.1				56.0	31	55.4	.0035	2,400	1,100	7.0	4.5	2.5	7.2	113	121	79	16	10	.29	1.87																
1,004	278										4		±4.5	57.8	50	86.5	.0036	4,500	3,430	9.3	5.7	3.6	7.4	104	114	78	25	23	.41	1.87	1.46															
1,005		50	50	2		1.1	8	58	28	±4.9				57.2	32	56.0	.0036	2,500	740	7.4	4.4	2.7	7.0	122	120	79	22	15	.33	1.96																
1,005	279										4		±4.5	58.9	46	78.0	.0035	3,400	2,400	9.5	5.8	3.8	7.2	107	122	74	28	24	.43	1.96	1.63															
1,006		50	50	2		1.7	8	58	32	±4.4				55.6	32	57.5	.0037	1,900	580	7.3	4.6	2.9	7.2	103	107	80	21	15	.30	1.92																
1,006	280										4		±4.5	59.7	52	87.0	.0035	3,200	2,100	9.9	5.8	4.6	7.5	111	111	75	27	21	.44	1.93	1.52															
1,007		50	50	2		2.9	8	62	28	±4.0				55.6	31	55.7	.0036	1,500	590	7.0	4.0	2.2	6.2	114	116	81	14	10	.33	1.88																
1,007	281										4		±4.5	57.9	52	90.0	.0035	3,500	2,500	10.1	6.0	4.0	7.1	106	117	75	29	24	.46	1.88	1.83															
1,008		50	50			.6	8	59	28	±5.0				55.7	39	70.0	.0035	4,800	3,600	8.5	5.2	2.9	8.8	102	114	75	4	3	.14	.22				1.16												
1,008	282										4		±4.5	58.8	61	103.8	.0035	4,800	5,000	11.7	6.2	4.7	8.7	107	117	73	27	21	.48	.22	2.03															
1,009		50	50	1	5	.9	8	65	30	±5.0				55.1	41	74.4	.0036	3,200	3,030	8.2	5.2	3.0	8.0	112	120	73	12	10	.16	.74				1.05												
1,009	283										4																																			

There was no appreciable yellowing of the unsized papers in the 72-hour heat treatment at 100° C.

Although there was a difference in the folding endurance in the machine and cross directions of the experimental papers made from new rags, this condition appears to be common to all papers made from cotton rags, as is also generally the case with other fibers. The commercial unsized papers tested showed the same lack of uniformity. The surface sizing, however, tends to even the folding endurance in the two directions of the sheet.

The folding endurance of some of the heat-treated papers was greater than that of the corresponding original papers. This has been noted by other observers also, not only for heat-treated papers but for papers after natural aging as well. The cause of this seeming inconsistency is probably that the papers were tested too soon after being made; they had not had time to reach a state of equilibrium.

In general, the agreement between the pH values of the water from the stock at the head box and of the extract of the finished paper was fairly good. The greater differences were noted around the neutral point; closer checks were obtained at the lower pH values. Since the completion of the tests it has been found that around the neutral point, better agreement is obtained with a glass electrode. In future work a glass electrode will be used when the pH approaches 7.

2. BEATER-SIZED PAPERS

In studying the effect of rosin size on the properties of the rag papers a number of machine runs were made in which the amounts of alum and rosin size used were varied, while the factors involved in the mechanical operation of the beater and paper machine were kept constant. The pertinent papermaking data and the results of tests on the papers produced are given in table 4.

The results of the runs, in which the amount of rosin was varied but the acidity kept practically constant, are shown in figures 5 and 6. The curves indicate that the presence of any appreciable amount of rosin—over 1 percent for new rags; less for old—caused a very decided increase in copper number and decrease in alpha cellulose content on oven aging. There was some decrease in folding endurance and tearing strength of the papers made from new rags, but the initial folding endurance and tearing strength of the papers from old rags were so low that the decrease for the heat-treated samples was not pronounced.

The test data on the runs, in which the amount of rosin was kept constant at 2 percent and the amount of alum was varied, are shown graphically in figures 7 and 8. The curves show that as acidity increased, folding endurance and tearing strength of the heat-treated samples decreased moderately, whereas there were decided changes in the copper number and alpha cellulose content. All the rosin-sized papers were yellowed by the heat treatment, the amount of color change increasing with increasing amounts of alum.

In general, the initial folding endurance of the rosin-sized papers was less than that of the unsized papers. The initial folding strength of the rosin-sized papers (sized with 2 percent of rosin) decreased as the amount of alum was increased (see fig. 9). That is, with the

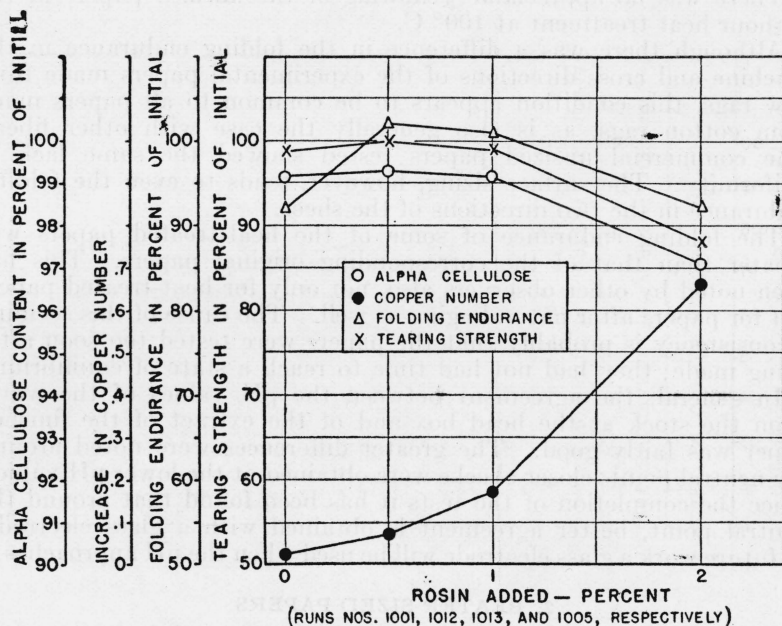


FIGURE 5.—Effect of rosin (pH of stock constant) on stability of new-rag papers.

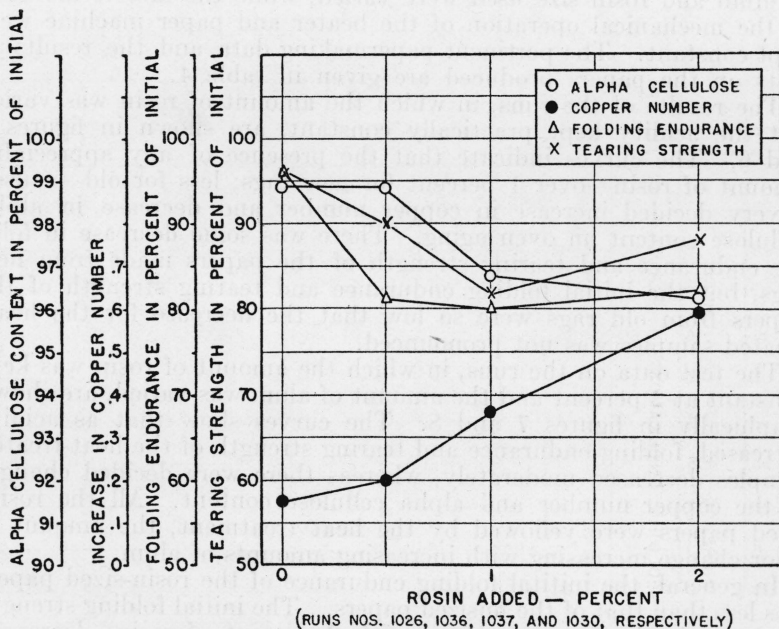


FIGURE 6.—Effect of rosin (pH of stock constant) on stability of old-rag papers.

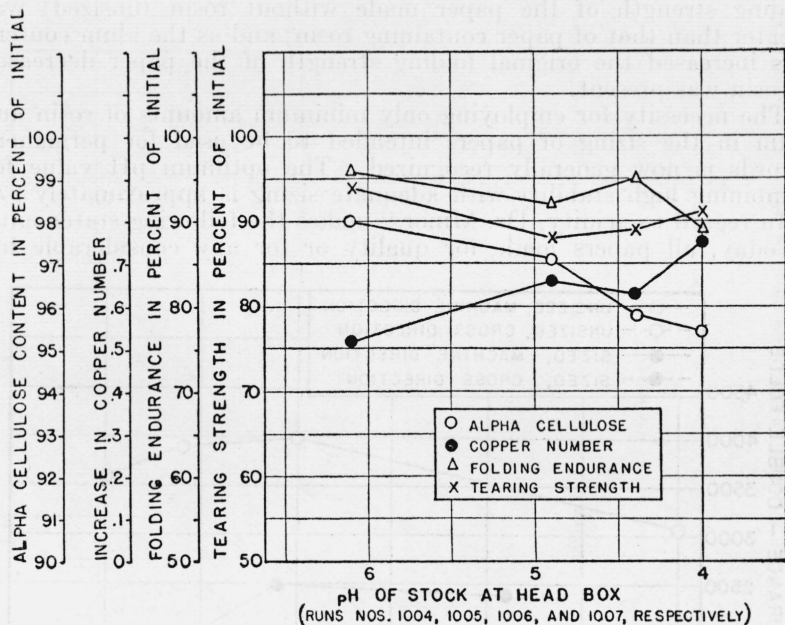


FIGURE 7.—Effect of acidity on stability of rosin-sized (2 percent of rosin) new-rag papers.

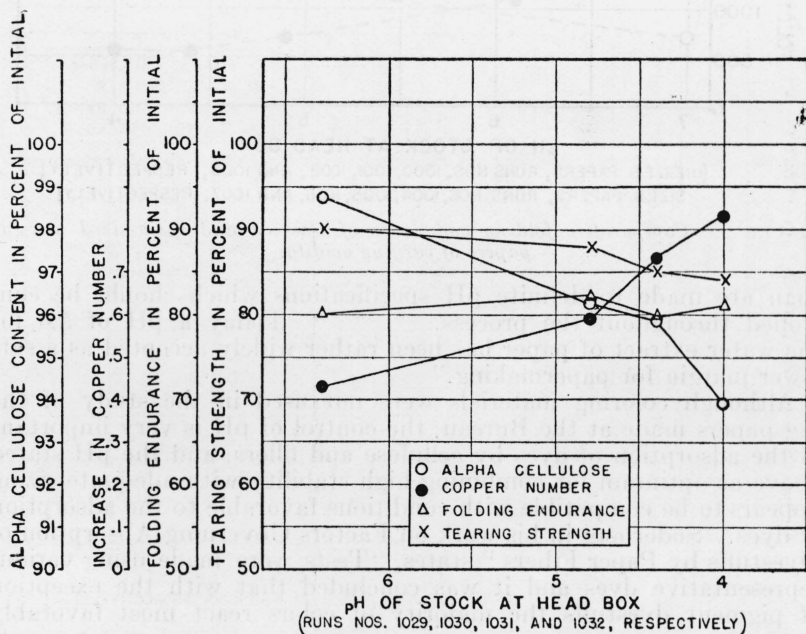


FIGURE 8.—Effect of acidity on stability of rosin-sized (2 percent of rosin) old-rag papers.

same rag stock and the same beater roll manipulation, the original folding strength of the paper made without rosin (unsized) was greater than that of paper containing rosin; and as the alum content was increased the original folding strength of the paper decreased if rosin was present.

The necessity for employing only minimum amounts of rosin and alum in the sizing of papers intended to be used for permanent records is now generally recognized. The optimum pH value for combining high stability with adequate sizing is approximately 5.0.

In regard to acidity, Dr. Minor¹² makes the following statements: "Today, all papers made for quality or for any considerable life

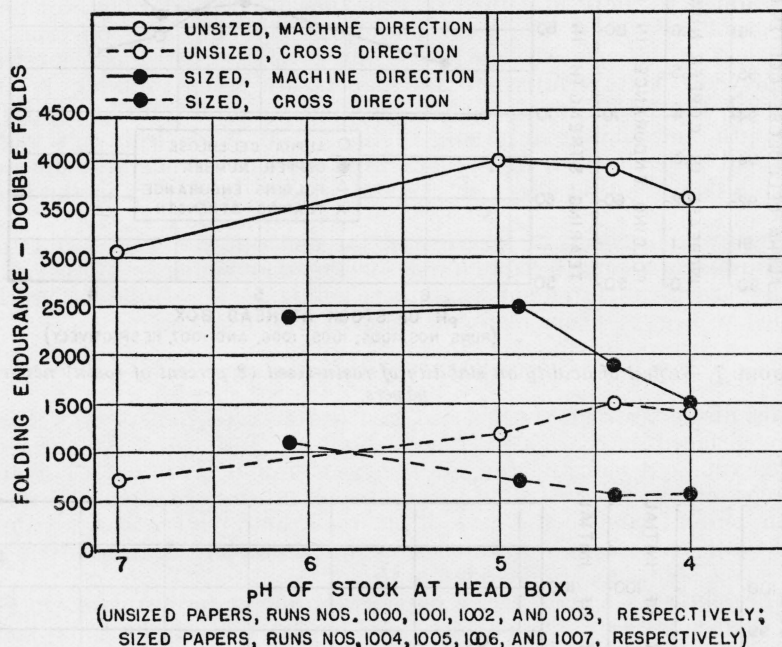


FIGURE 9.—Comparative folding endurance of unsized and rosin-sized new-rag papers of varying acidity.

span are made to definite pH specifications which should be controlled throughout the process. * * * Today a pH of 5.0 for the water extract of paper has been rather widely accepted as a safe lower margin for papermaking."

Although coloring materials were not used in the study of the rag papers made at the Bureau, the control of pH is very important in the adsorption of dyes by cellulose and fillers, and the pH stated above as optimum for combining high stability with adequate sizing appears to be compatible with conditions favorable to the adsorption of dyes. Soderberg in his work on Factors Governing Absorption of Dyestuffs by Paper Fibers¹³ states, "Tests were made using various representative dyes and it was concluded that with the exception of pigment dyestuffs the majority of colors react most favorably

¹² Jessie E. Minor, *Chemical control in paper manufacture*, Paper Trade J. 90, 20, 45-48 (1934).

¹³ Paper Trade J. 97, 21, 39-45 (1933).

to an acid condition of from pH 4.5 to 5.5 produced in the presence of rosin size and aluminum sulphate. Speaking generally, anything below the range mentioned produced a deadened shade, while above the 5.5 figure the colors were not entirely absorbed." Roberts¹⁴ found that the pH values at which different dyestuffs show maximum color strength vary considerably, and that no one pH can be established for all groups of dyestuffs. The optimum pH values given for the different colors tested were, however, between 4.6 and 6.0, with the greater number between 5.0 and 5.7, which are satisfactory values as far as permanence of the finished paper is concerned.

Beater starch, manufactured commercially by an oxidation process, was added to the beater for two runs, nos. 1,008 and 1,009, for new rags, and two runs, nos. 1,033 and 1,034, for old. For one run in each case rosin size was not used, and for the other 1 percent was employed. Data relative to the papers are given in table 4. In general, the starch increased the bursting strength, tensile breaking strength, and folding endurance of the papers made from new rags, but had little effect on those made from the old. The starch did not have a deteriorating effect on the stability of the papers in the heat test.

Clay was included in the furnish for one run, no. 1,041, and the measurements on the paper made are further evidence of the generally accepted statement that inert mineral fillers may be safely added to beater furnishes for permanent record papers.

3. SURFACE-SIZED PAPERS

Results of tests on the unsized and beater-sized papers after they were surfaced sized are also given in table 4. In most of the surface-sizing runs a 4-percent glue solution was employed, but a 4-percent starch solution also was used for one group of three papers of varying rosin content, and in the case of old rags three papers were treated with an 8-percent glue solution as well. Complete data relative to the sizing solutions are included in the table.

The relative stability of the papers was not materially affected by the surface sizing. The surface-sized papers showed the same general trend as the base papers, but to a lesser degree. As the amount of alum in the rosin-sized papers, or the rosin content of the paper, was increased, the deterioration of the surface-sized paper increased also.

The relative stability of the surface-sized and the base papers is shown graphically in figures 10 and 5, respectively, for one group of papers of varying rosin content. The stability of the surface-sized papers as measured by the heat test was in the same general direction as that of the base papers before being surface sized, although the surface sizing seems to have served as a protective material and to have retarded the change in alpha cellulose content and copper number.

The foregoing shows that careful processing of raw materials and purity of fiber in respect of active chemical components are necessary for the manufacture of stable papers. Resistance of paper to deterioration from internal causes is not sufficient to insure its stability

¹⁴ *Paper dyeing*, Paper Ind. 15, 6, 313-315 (1933).

however. The conditions of its use and storage are as important as the initial quality of the paper. For discussion of external deteriora-

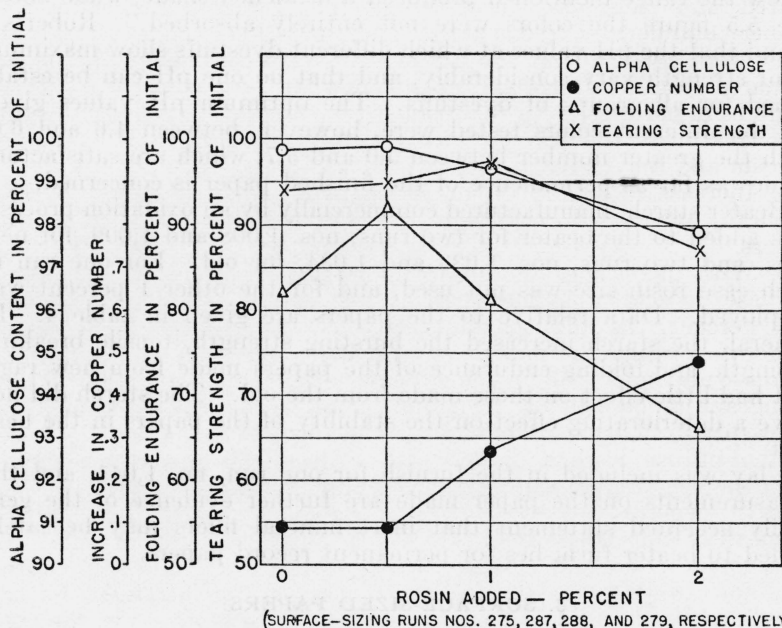


FIGURE 10.—Comparative stability of surface-sized new-rag papers of varying rosin content.

(See fig. 5 for base papers.)

tive agencies—light, temperature, humidity, acidic pollution of air—and recommendations as to storage conditions for prolonging the life of paper, the reader is referred to a previous Bureau publication.¹⁵

IX. SUMMARY

The relations of the cellulosic purity of the particular grades of rags used and of the processing treatments employed to make them into paper, on the stability, as indicated by the heat test, and on the strength of the rag-fiber writing papers made, were found to be as follows:

1. The new rags had a higher degree of cellulosic purity and were stronger than the old rags. These differences were reflected in the papers made from the rags. The new-rag papers were very stable and very strong when properly made, while the old-rag papers were less stable and were weak.

2. In the preparation of the half-stuff the cellulosic purity of the rags was not changed much, but in general was improved somewhat.

3. The beaten fibers from the new rags were long, clean, and well fibrillated; those from the old rags were shorter, more broken, and less fibrillated.

4. In general, rosin sizing decreased the folding endurance somewhat, but had little effect on bursting, tearing, or tensile breaking strength.

¹⁵ Summary Report of Bureau of Standards Research on Preservation of Records, Misc. Pub. BS M144 (1934).

5. With increasing amounts of rosin at pH 5, the folding endurance and tearing strength decreased somewhat when the papers were heated, and there was a decrease in alpha cellulose and increase in copper number. These changes are evidences of deterioration. They were noticeable at about 1-percent rosin content for the papers prepared from new rags and at a somewhat lower content for those made from old rags. All the rosin-sized papers were yellowed by the heat treatment, the degree of discoloration depending on the amount of rosin and the degree of acidity.

6. Increase in acidity of unsized papers had little effect on their strength, but caused decrease in the folding endurance of rosin-sized papers.

7. With increasing amounts of alum and resultant corresponding increases in acidity, as measured by pH, with constant rosin content of 2 percent, the folding endurance and tearing strength decreased moderately when the papers were heated, and there was a decided decrease in alpha cellulose and increase in copper number. These changes in alpha cellulose and copper number accelerated at acidities below pH 5. Of papers of the same acidity, those having the lower content of rosin were the more stable. The effects of acidity resulting from the use of alum were similar for the two kinds of rags.

8. In general the starch beater sizing increased the bursting strength of the papers made from new rags but had little effect on those made from old. Other investigators have found that starch does not always increase the strength of papers. The starch did not have a deteriorating effect on the stability of the papers in the heat test.

9. The increased strength imparted to the paper by surface sizing (with glue or starch) was largely lost in the heat test. In general, surface sizing did not materially affect the papers of high stability, although it seems to have served as a protective surface which retarded chemical deterioration of the less stable papers.

10. Clay filler, used in one paper only, had no effect on the stability of the paper.

It is believed that these results were secured with representative raw materials and processes obtaining at the time the work was done, which was during the years 1933-34.

It should be emphasized that the purpose of the work was to correlate the properties of the rags with the properties of the paper, when the paper was made by the methods and with the equipment described herein. If a better grade of old rags had been used, or if the process of manufacture had been modified, the qualities of the papers might, of course, have been different from those found.

The authors are indebted to John O. Burton and E. E. Creitz, of this Bureau, and to Royal H. Rasch, formerly research associate at this Bureau, for the Brown Co., Berlin, N. H., for chemical tests of the rags, half-stuffs, and finished papers, and to Miss M. L. Rollins, of this Bureau, for the photomicrographs.,

WASHINGTON, February 4, 1935.