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PHOTOCHEMICAL STABILITY OF PAPERS

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ABSTRACT

Papers were irradiated with a carbon arc through a filter that completely eliminated infrared, and ultraviolet shorter than approximately 330 millimicrons. Sheet temperature was kept near 30° C during irradiation, through contact with a thermostated metal backing, thereby eliminating heat effects, shown otherwise to overshadow light effects, using intense sources.

In consequence, the results differed from those of previous workers. Yellowing of papers (without lignin) commonly ascribed to light was found to result from heat or age, but not light; papers bleached when heat effects were eliminated during irradiation. Even lignified paper was bleached by light in nitrogen.

Paper scorched brown at high temperatures or yellowed at 100° C, and yellow papers 250 years old were bleached by light.

Lack of oxygen inhibits but does not altogether prevent photochemical deterioration. The role of water vapor differs fundamentally for cotton and wood-pulp paper.

Lignified paper is very unstable to light. Printers' ink extensively protects paper.

Irradiated papers are subsequently less stable in the dark than those not previously irradiated.

The order of photochemical stability of papers was as follows: new-rag, refined sulfite, old-rag, soda-sulfite, and newsprint. The light stability of new-rag papers was greatly affected by acid and rosin, whereas that of old-rag and soda-sulfite was only slightly affected, in contrast to heat stability, for which pH is important for all fibers. Newsprint, made neutral with $NaHCO_3$, showed a large increase in light stability. Rosin did not seriously affect the stability of any papers as long as their acidity was low.

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I. INTRODUCTION

The effect of light upon paper is one of the most important problems in the preservation of valuable records. Irreplaceable documents are being exhibited under conditions which may be unnecessarily adverse. This investigation was undertaken as a part of the general program of research at the National Bureau of Standards for the preservation of records, and deals with the factors influencing the light stability of white record papers, not only as regards atmospheric conditions but also with respect to paper components. A third phase of the subject, namely, the relative deterioration occurring at various wavelengths of the spectrum to which papers are ordinarily exposed, is still in the process of investigation.

The stability of papers toward various types of light has been the subject of previous investigations. Richter [1] [1] exposed a variety of papers, differing in kinds of fiber and sizing, to direct sunlight, and in a few experiments to a quartz-mercury arc, and measured the consequent changes in folding endurance, and to a lesser extent, changes in chemical characteristics. Edge and McKenzie [2] measured changes in the reflectance of wood-pulp papers exposed to direct sunlight, a quartz-mercury arc, and a carbon arc. Oguri [3] measured the changes in copper number of a tissue paper and a filter paper caused by a quartz-mercury arc. The effect of sunlight upon newsprint was studied by Bakker [4].

It is evident, however, that these types of light do not correspond to the light to which papers are normally subjected, namely, diffused indirect daylight transmitted by window glass or tungsten incandescent-lamp light. The exact duplication of sky light as transmitted by window glass is not necessary for a study of the effects of normal lighting upon papers, nevertheless, certain objectionable characteristics of direct sunlight or of the usual high-intensity sources can be eliminated. The ultraviolet region of sunlight extending from 290 to 330 millimicrons, shown by Richter [1] to account for almost half of the effect of sunlight upon paper, is normally excluded by window glass and, therefore, has no counterpart in interior daylight. Also, Oguri [3] has shown that over 90 percent of the radiant energy from a quartz-mercury arc harmful to paper is excluded by window glass. Intense sources, including direct sunlight, furthermore, give rise to temperature effects which have no counterpart in interior daylight. The high temperatures attained by sheets of paper during irradiation with powerful light sources was discussed by one of the writers elsewhere [5].

Köhler [6] exposed some papers covered with various colored glasses to north sky light, as well as to direct sunlight, and thus, in the former procedure, avoided the objection mentioned. The purpose of his investigation, however, was to select a protective window glass for the Archives at Stockholm from various commercial products rather than a study of factors affecting the stability of papers. The study was limited to three papers, for which changes in folding endurance were measured. Changes in copper number for one paper during the 128-day period of exposure were also measured. The changes during this period were quite large owing to the rather poor quality of papers used, since the best, a rag paper, had an initial copper number of 1.6.

[1] Figures in brackets indicate the literature references at the end of this paper.

In the present investigation a large number of experimental book and writing papers produced in the paper mill at the Bureau, as well as commercial newsprint paper, were irradiated under conditions that were rigidly controlled. The papers, which embodied large differences in kind and quality of fiber, content of lignin, rosin, and other sizing materials, acid, and filler, were maintained near 30° C (30° to 32°) during irradiation. All unusually short and long wavelengths were excluded by a special filter combination. The relative humidity was fixed at a definite value, except when moisture or oxygen content was intentionally varied.

In the present work, it is believed that the conditions under which light usually affects white record papers have been attained more nearly than heretofore, and that the results dealing with the factors influencing the light stability, the permanence of papers once exposed to light, and the color changes in papers caused by light, are representative of the behavior of record papers under the most prevalent conditions of use.

II. APPARATUS

A commercial arc lamp with ½-inch electrodes of solid carbon, enclosed in Pyrex, operating at 2,080 watts and 16.5 amperes, was used in all experiments. The flame of the arc was 15.8 cm from the center of the sheet during irradiation. In combination with this lamp, a liquid filter [5] consisting of a glass cell, made up of one sheet of Corex-*D* glass and one sheet of ordinary window glass, and through which was pumped a 0.117-*M* solution of cupric chloride to remove the infrared, was used. The radiant energy thus reaching the papers consisted essentially of the strong cyanogen band at 389 millimicrons [7] superposed on a black-body continuum arising from the incandescent positive electrode, and did not include any radiant energy having a wavelength shorter than approximately 330 nor longer than 750 millimicrons.

The spectral distribution of this light and that of the sky light [2] entering the laboratory through windows was studied by the method of transmission through glass filters having sharp cut-offs and known spectral-transmission curves. A two-photocell balanced circuit with potentiometer (for the arc light, an automatic-recording potentiometer) was used for measuring transmissions. It was found that 80 percent of the filtered arc light lay in the region between approximately 330 and 440 millimicrons. Of the sky light, 25 percent was found to lie in this region and less than 0.1 percent in the infrared region beyond 750 millimicrons.

Inasmuch as the light usually affecting papers is in the region [3] between approximately 330 and 440 millimicrons, and since the filtered arc light included neither the shorter ultraviolet nor infrared, it is probable that the light used in this work differed from normal lighting in its effect upon papers mainly in intensity.

The remainder of the apparatus and its effectiveness are described in detail in a paper by one of the writers [5]. Principal emphasis was placed on control of the temperature of the paper during irradiation. The temperature of the sheets was maintained near 30° C by intimate contact, through suction, with a thermostated aluminum backing,

[2] Eastern sky at 2:15 p. m. on a clear day (April 23, 1942).
[3] Unpublished findings by the present writers.

supplemented by the removal of most of the undesired infrared. The air which continually flowed through the sheets during irradiation was kept at constant moisture content corresponding to a relative humidity of 58 percent at 30° C. For experiments in which moisture was practically excluded, the air was dried to a relative humidity not higher than 0.015 percent by continuous circulation over anhydrous magnesium perchlorate. For experiments in which oxygen was practically excluded, dry nitrogen was continuously circulated over copper gauze at 500° C, giving a content of O_2 of less than 0.03 percent. For one experiment the content of O_2 was probably much lower than this figure, since a small glass irradiation chamber was substituted for the usual large one to reduce leakage of O_2 into the system by diffusion.

These were the usual conditions of irradiation. In a few comparison experiments the cupric chloride cell and paper thermostating arrangement were omitted. The distance from the arc to the sheet was changed in certain experiments. Papers were usually irradiated on one side of the sheet, although in many experiments both sides were irradiated. Departures from the usual conditions are stated in each instance.

III. SAMPLES STUDIED AND METHODS OF ANALYSIS

Thirty-one representative white, undyed book and writing papers produced in the semicommercial paper mill at the National Bureau of Standards from a variety of commercial materials were used for study. The pertinent characteristics of the papers are listed in the tables accompanying this publication. The papermaking details were given in other publications of the Paper Section [8]. One commercial newsprint paper was also included in the study. This paper may be considered as representative of highly lignified papers in general, and was very useful because of the large chemical changes caused in it by relatively mild exposures to light. Some very old commercial papers were used in a few experiments.

The names of the various types of papers used in the investigation are those current in the paper industry and probably require definition. "New rag" is obtained from unused cotton fabric and represents a type of cellulose with relatively large stable molecules. "Old rag" is used cotton fabric which has been bleached, often drastically, to remove colors, and represents a type of cellulose with smaller molecules arising from this treatment and from the wear and washing of the fabric as a garment. Soda and sulfite pulps are produced from wood by alkaline and acid treatments, respectively, to remove lignin. These represent the cheaper grades of pulps used for record papers and contain substances other than cellulose, which produce yellowing and deterioration of the paper with age. "Refined" sulfite, therefore, is sulfite pulp which has been subjected to treatments designed to remove the substances other than cellulose, and is thus a more stable material. Newsprint consists largely of ground wood containing the original lignin.

Various test methods to determine the extent of deterioration caused by light were employed. The volumetric alpha-cellulose method was found to be the most generally useful. pH (cold extract) and resin were also determined. These three methods are described elsewhere by one of the writers [9]. Fluidities of dispersions of cellulose in cuprammonium solution were measured [10] in a number of instances. Copper number and folding endurance [11] were also determined.

Since the values for copper number merely substantiated the alpha-cellulose results, they are omitted except in a few cases of particular interest. The values for folding endurance are also omitted, inasmuch as they also substantiated the alpha-cellulose results, but with far less precision, owing to the nature of the test. In general, after 17 hours of irradiation the rag papers had retentions of folding endurance upward of 75 percent, whereas the soda-sulfite papers ranged between 50 and 85 percent.

Although the alpha-cellulose results, as determined by the method employed, are practically independent of the presence of lignin in most analyses, this fact had to be confirmed for control analysis for the action of light. Therefore, a sample of irradiated newsprint was analyzed for alpha cellulose by both the volumetric and gravimetric method. Since in the gravimetric method the amount of lignin present must be corrected for, the lignin content was determined by the method of Ritter and Barbour [12]. Certain other lignin analyses were also carried out, using this method. Starch and glue [11] were also determined in a few instances.

The irradiated area of each sheet was 20 by 20 cm. pH, resin, and folding endurance were determined from strips; other tests were made on ground papers. Two, and often three, sheets of the same paper were irradiated, one at a time, to make possible all of the tests desired and to check and sometimes recheck experimental results.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

1. CHANGES IN PAPERS DURING IRRADIATION WITH AND WITHOUT TEMPERATURE CONTROL OF SHEETS

Inasmuch as stress in this investigation was laid upon the study of effects of light alone, as contrasted with the light-plus-heat effects usually obtained with intense sources, including direct sunlight, it is of interest to compare changes in papers during irradiation under these two conditions. It was previously shown [5] that various sheet materials, including paper, attain abnormally high temperatures when irradiated with a commercial carbon-arc lamp under conditions similar to those of the usual "light" stability tests.

(a) CHEMICAL DETERIORATION BY HEAT DURING IRRADIATION

Two series of experiments were conducted which differed essentially in that the temperatures of the sheets were maintained near 30° C in one series, thus precluding measurable thermal deterioration, whereas in the other series the temperatures were not controlled.

The sheets in both series were placed 25 cm from the flame of a Pyrex-enclosed carbon arc operating at 2,080 watts. No attempt was made to exclude the infrared in these experiments. The radiant intensity incident upon the sheets was 0.4 watt/cm^2, as measured with a calibrated thermopile-recorder system, described elsewhere by one of the writers [5, 13].

The results presented in table 1 show that extensive deterioration due to heat took place if the sheet temperatures were not controlled during irradiation with an arc lamp. The effect of heat may be several or many times greater than that of light.

TABLE 1.—*Predominance of heat effects over light effects during irradiation* [a] *with the carbon-arc lamp when sheet temperatures are not controlled*

Paper number [b]	Decrease in alpha-cellulose percentage	
	Sheets freely suspended. No temperature control [c]	Sheets in intimate contact with aluminum backing. Temperature near 30° C
1129 (soda-sulfite)	54.7	3.6
1134 (soda-sulfite)	31.2	3.8
1191 (old rag)	4.5	1.1
1215 (old rag)	3.7	1.3

[a] The papers were irradiated for 17 hours at a distance of 25 cm from the arc and with the same incident radiant intensity in each experiment. The moisture content of the sheets was not controlled. See text for further details.
[b] See table 3 for further details of these papers.
[c] From the results previously published by one of the writers [5], it is estimated that the temperature attained by the sheets under these conditions was between 160° and 200° C.

(b) COLOR CHANGES ARISING FROM HEAT AND FROM LIGHT

The yellowing of paper upon exposure to "light" is a familiar phenomenon. Richter [1] reported a yellowing of all the types of papers studied, including rag, purified and ordinary wood pulp, sized and unsized, during a 100-hour exposure to Miami, Fla. autumn sunlight. Sunlight, however, was used in the early days of papermaking to bleach papers.

These opposite effects, bleaching and yellowing, were observed by Edge and McKenzie [2] with papers made from wood pulp and irradiated with sunlight. For eight papers, sunlight in England caused much more bleaching and less yellowing than the sunlight in the warmer and more humid Cairo, Egypt. Portions of the papers exposed in Cairo had been covered with an opaque paper. These covered portions, which were thus subjected to approximately the same heating as the exposed portions, yellowed more than the exposed portions. Specimens of the same papers, when exposed to a quartz-mercury or carbon arc, yellowed extensively.

In the present investigation it was found that all of the papers, excepting one containing appreciable quantities of lignin, bleached when irradiated in air when the temperature was maintained near 30° C during irradiation, but all of them yellowed during irradiation when the temperature was not controlled.

A typical example of these two opposing effects is shown in figure 1 for paper 1129. Both sheets *A* and *B* were irradiated at 25 cm from the flame of the same Pyrex-enclosed arc. Sheet *A* was maintained near 30° C; sheet *B* was freely suspended without temperature control, as in the usual commercial "light" stability testing equipment. The extent of yellowing or bleaching was determined by measuring the reflectance of a particular area of each sheet for violet-blue light (the

405- and 436-millimicron Hg lines, together) in an apparatus previously described elsewhere [14].

The two competing processes, bleaching and yellowing, are thus shown to have occurred simultaneously, the net observable effect indicating whether light or heat changes predominated. Thus, if a white paper turns yellow when irradiated, it may be inferred that

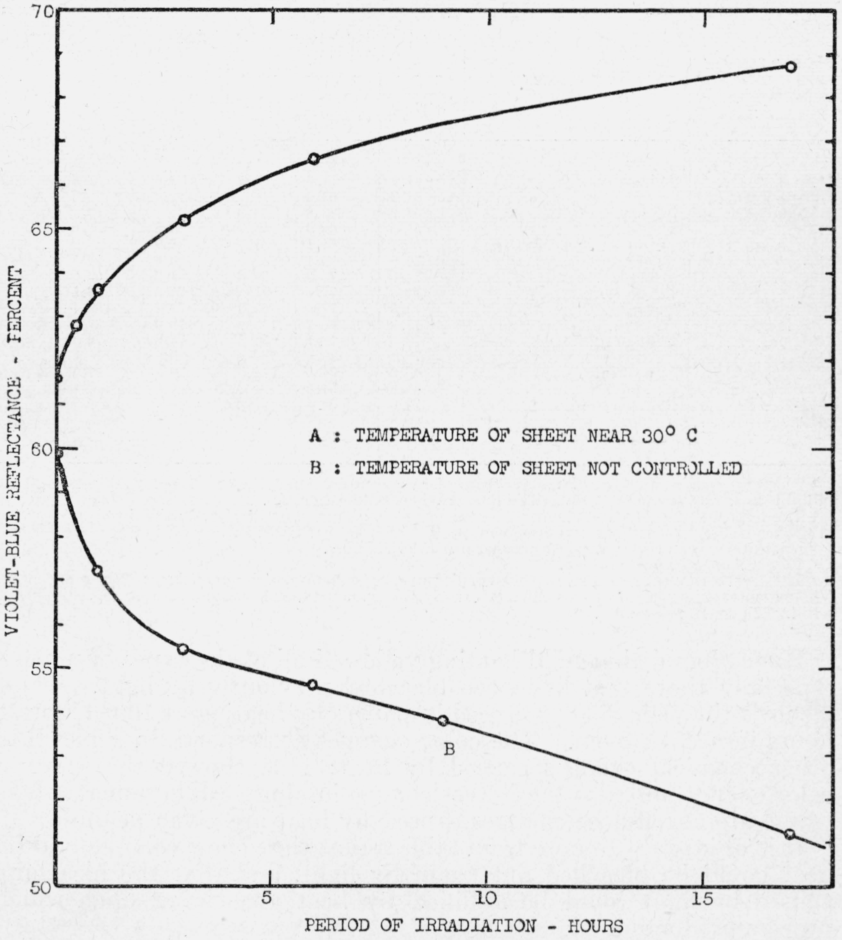

FIGURE 1.—*Color changes in paper irradiated with and without temperature control, using the carbon arc.*

reactions other than photochemical ones have played the dominant role.

These remarks do not apply to papers containing appreciable quantities of lignin, for this material caused yellowing of paper even in the absence of heat effects. Extensive yellowing occurred in newsprint when irradiated under the usual conditions at 30° C in air. This yellowing resulted from the lignin and was obviously different from the yellowing of cotton fibers containing no lignin, or the yellowing of delignified wood fibers, such as in paper 1129 and the other soda-sulfite papers which contained less than 0.5 percent of lignin. However, when the yellowing due to lignin was prevented by lack of oxygen the cellulose fibers in newsprint were bleached by light. This yellowing and bleaching of newsprint by light is shown in table 2, experiments *N* and *N*-no O_2.[4]

TABLE 2.—*Effect of light and heat upon the violet-blue reflectance*[a] *of papers*

Paper number and experimental condition	Kind of paper	Effect of light,[b] then heat,[c] on reflectance			Effect of heat, then light, on reflectance		
		Original	Light 40 hours[d]	Heat	Original	Heat	Light 17 hours
		%	%	%	%	%	%
1138	Soda-sulfite	[e] 61.2	71.3	58.1	[e] 63.6	56.8	66.6
1138-no H_2O	do	[e] 61.2	63.2	49.7			
1138-no O_2	do	[e] 59.2	62.8	54.2			
1133	do	55.5	66.6	59.2	55.5	52.6	
1143	do	56.7	66.1		57.0	53.2	62.0
1173	do	70.6	79.1		69.6	65.7	
1182	New rag	74.2	77.2	68.8	74.2	69.2	75.1
1183	do	75.8	77.6	71.3	75.8	72.5	
1203	Old rag	73.3	77.4	69.3	73.4	69.1	75.8
1215	do	77.9	80.8		78.0	77.0	
1164	Refined sulfite	73.6	76.1	70.5	73.8	70.4	70.8
1166	do	73.2	75.6	69.8			
N	Newsprint	46.0	34.0				
N-no O_2	do	45.8	51.0				
p-1700	Rag, very old	32.0	53.4				
p-1791	do	46.8	65.7				
p-280°	Sulfite, scorched	36.0	53.7				

[a] The reflectance at 45° from normal incidence, for the combination of the two mercury lines, 405 and 436 millimicrons, was measured as described in a previous publication [14].
[b] The light was that of the arc lamp under the usual conditions of irradiation, for the time periods given at the head of the two columns, excepting newsprint, which was irradiated for 10 hours in these experiments.
[c] All heating took place in air in the dark at 100° C for 72 hours.
[d] 20 hours on each side of sheet.
[e] These values are the reflectances of a particular area, 30 by 58 mm, of different sheets of the same paper. The measurements were always confined to exactly the same area, and the values were reproducible to within 0.2 percent reflectance.

It was found that mild heating yellowed all of the types of papers, especially those that had been bleached previously by light. Table 2 shows the yellowing produced in papers by heating at 100° C for 72 hours in a dark oven. The color changes correspond, in general, to other chemical changes caused by heat: 1133 showed the smallest color change and also the lowest change in alpha-cellulose percentage (some alpha-cellulose changes caused by heat are given in table 12).

It is of interest to note from table 2 that the yellow color caused by heat could be bleached out again by light, and that the bleaching caused by light could be nullified by heat, depending upon which process predominated.

The yellowing effect of heat was found to be large if the paper was previously (or concurrently) irradiated, especially if the irradiation took place in the absence of water vapor, as in experiment 1138-no H_2O. In this instance, the area of the sheet which had been exposed to light turned much yellower during heating than the borders of the sheet which had not been exposed to light, since they were covered by the clamping mechanism during irradiation.

Thus papers which are irradiated with strong light sources, including sunlight, without effective temperature control of the sheet, yellow

[4] An extremely low concentration of oxygen was probably attained in the latter experiment, since the irradiation took place in a small, all-glass chamber which was substituted for the large chamber usually used [5]. The former experiment, with air, was also performed in this apparatus for purposes of comparison. In both cases, the usual stream of conditioned circulating gas served to cool the rather limited area of paper.

owing to heat, assisted by the desiccation caused by the heat prevailing in the sheet during irradiation.

Another sheet of 1138 which had been irradiated in the absence of water vapor and then not used for further experimentation was stored in a cool, dark place. After 15 months it was found to have yellowed markedly in the areas that had been irradiated, but not in those covered by the clamping mechanism during irradiation. In this instance, age instead of heat had caused the irradiated paper to yellow. This probably explains the yellowing observed by Köhler [6] in papers exposed for 128 days to north sky light, under which conditions heat effects were probably negligible. Thus light did not cause papers (containing no lignin) to yellow, but the irradiated fibers underwent relatively rapid changes with age—more rapidly at higher temperatures—which were not photochemical and which confuse the study of the direct effect of light upon paper. This stresses the fact that direct-light effects must be studied not only in the absence of heat effects, but also in the absence of age effects, i. e., the light must be of sufficient intensity to cause a change rapidly enough to render concurrent age effects negligible.

Water vapor and oxygen were found to play an important part in the bleaching of paper by light, inasmuch as the lack of these gases greatly decreased the extent of bleaching in experiments 1138-no H_2O and 1138-no O_2, although other reactions were not inhibited by the lack of water vapor, as seen from the subsequent extensive yellowing by heating. Paper 1138-no O_2 yellowed much the same upon subsequent heating as if it had not been previously irradiated (see 1138, column 6 of table 2).

The bleaching effect of light was observed also in the case of papers yellowed with relatively great age or scorched at high temperatures. One paper, manufactured before the year 1700, was of a blotched brown; another, made before 1791, was of an even, deep-yellow color; and a third was an experimental hand sheet made from refined sulfite pulp, containing a thermojunction to permit measurement of the sheet temperature on exposure to a carbon-arc lamp. This third paper had attained a temperature of 280° C, as shown in a previous publication [5], and had been scorched to a brown color in a few minutes. These three papers, when exposed to the light at 30° C, bleached extensively. The scorched paper nearly regained its original whiteness, whereas the second paper became as white as a bleached new-rag paper. The three papers with color changes are listed in table 2 as *p*-1700, *p*-1791, and *p*-280°, respectively.

This effect may have practical significance for documents discolored by age or heat; bleaching may greatly heighten the contrast and permit more legible photographs to be made. This method of bleaching, of course, has the drawback that the light concurrently causes deterioration of the cellulose.

2. EFFECT OF VARIOUS FACTORS UPON THE LIGHT STABILITY OF PAPERS

(a) AMOUNT OF LIGHT ABSORBED AND METHOD OF ITS MEASUREMENT

Only the light absorbed by a sheet of paper can cause deterioration, the extent of which is a function of the amount of light absorbed, all other factors being equal. Values for the percentage of light absorp-

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tion and decreases in alpha-cellulose percentage for the papers are listed in table 3.

TABLE 3.—*Influence of various factors upon the light stability of papers* [a]

Paper no.[b]	Filler, etc.	Rosin[c]	pH[d]	Light absorption	Decrease in alpha-cellulose[e] percentage during irradiation for— 17 hr	Decrease in alpha-cellulose[e] percentage during irradiation for— 40 hr[f]	Lowering of pH[g]
	PAPERS MADE FROM NEW RAGS						
		%		%			
1177	10 to 13% clay	0	5.6	12	1.0	2.0	0.0
1178	do	0	5.1	12	1.6	4.0	.0
1179	do	1.4	6.0	21	1.0	2.6	.2
1182	do	1.5	4.8	20	4.2	5.5	.3
1183	do	0.6	5.8	15	1.7	3.4	.5
1186	do	.7	4.8	21	3.0	3.7	.1
991	None	0	6.9	10	0.8		.4
991	None; 2.1% glue	0	6.1	13	1.1		.4
1013	None	1.0	6.2	16	1.2		.8
1013	None; 1.9% glue	1.0	5.6	17	1.4		.6
1013	None; 1.8% starch	1.0	5.8	13	1.0		.5
	PAPERS MADE FROM OLD RAGS						
1191	12% clay	0	6.8	16	3.2	5.3	0.4
1193	do	0	5.0	16	2.9	6.2	
1200	do	1.2	6.1	18	3.5	6.2	.8
1203	do	1.3	5.2	23	4.0	7.1	.3
1214	None	0.3	5.8	21	3.4		
1215	14% $CaCO_3$	0	9.4	12	3.3	4.6	
1209	{4.2% TiO_2 {8.4% $BaSO_4$	.6	5.0	25	2.2		
1211	{7.2% ZnS {5.8% $BaSO_4$	.7	6.0	26	4.7		
	PAPERS MADE FROM SODA AND SULFITE (1:1) PULPS						
1133	None	0	6.4	34	5.6	6.8	0.0
1134	8 to 10% clay	0	6.1	32	5.3	9.5	.3
1129	do	0	4.8	32	5.1	9.5	.2
1143	None	.6	5.6	35	5.8	9.5	.6
1136	8 to 10% clay	.9	5.8	30	7.0	10.9	.4
1138	do	1.6	4.9	30	6.2	10.4	.4
1173	21% $CaCO_3$	1.3	8.8	28	5.1	7.8	
1144	7% TiO_2	0.6	5.4	29	5.8		
1153	{6.2% ZnS {5.1% $BaSO_4$	.9	5.2	34	5.7		
	PAPERS MADE FROM REFINED SULFITE PULP						
1160	8 to 11% clay	0	6.6	16	1.3	2.7	0.3
1164	do	.9	5.6	21	2.4	5.2	
1166	do	.8	4.8	22	2.9	4.7	.3
	PAPERS MADE FROM HIGHLY LIGNIFIED FIBERS (NEWSPRINT)						
N-a	None		5.0	60	31.3		1.7
N-b	$NaHCO_3$ added		7.2	65	9.3		

[a] Sheets maintained at 30° C in air at 58% relative humidity.
[b] For other characteristics of the papers, see reference [8].
[c] Analytical resin values corrected for natural resins, fats, waxes, etc.
[d] pH of the cold-water extract of unirradiated sheets.
[e] To permit comparison with the results of other workers, increases in copper numbers for representative papers during 40 hours of irradiation are included as follows: No. 1136, 3.2; No. 1164, 1.6; No. 1182, 2.1; No. 1193, 1.2; No. 1203, 2.3. These changes are similar to those found by Richter [1].
[f] 20-hr irradiation on each side of sheet.
[g] Change in pH during 17-hr period of irradiation.

It was found that papers having high absorption values, the newsprint and the soda-sulfite papers, deteriorated more than those having lower absorptions, such as new rag, old-rag, and refined sulfite papers. It is probable, however, that the fiber components were responsible for the differences in light stability, and that the absorption was only incidentally greater, although the two factors may have operated simultaneously. The condition of the fiber is obviously important, since the old rag papers were, in general, less stable than the new rag papers.

Other factors, such as content of lignin, rosin, and acid, are more important than the extent of absorption in determining paper deterioration, as shown strikingly by the extreme example, *N*-b, which, although having a somewhat higher absorption than *N*-a, was much more stable than the latter because of the presence of $NaHCO_3$, which apparently increased the light stability of the lignin.

Substances other than cellulose influenced the light absorption by the sheet, with varying consequences. The rosin in 1179 almost doubled the light absorption but caused little or no increase in deterioration. Certain fillers changed the absorptions of the rag papers with but slight effects on light stability. The darkening of newsprint by the addition of $NaHCO_3$ increased the absorption. These effects on light absorption arose from the presence of relatively large amounts of material. It was, therefore, of interest to change the absorption of paper by adding only minute amounts of absorbing materials. Accordingly, some experiments were conducted with papers dyed by dipping in 1-percent acetone solutions of various dyes. Aqueous solutions were avoided to preserve flatness in the sheets for adequate temperature control during irradiation.

The results in table 4 show that the dyeing doubled and trebled the light absorption but that the light stabilities of the papers were not lowered in every instance. The data indicate that certain dyes present in very small amounts are capable of transferring the absorbed radiant energy to some types of fibers in such manner as to cause deterioration. The data also show that deterioration is not proportional to the extent of absorption, other things being equal. It should be mentioned that the dyes were usually completely faded during the first half of the period of irradiation. Similar sensitization appears to have been found by others working with textile materials [15].

TABLE 4.—*Effect of various dyes*[a] *upon the light*[b] *stability of papers*

Paper number and dye	Decrease in alpha cellulose percentage	Light absorption
		Percent
1160	1.3	16
1160+eosin	4.9	32
1160+aniline yellow	1.1	47
1160+alizarin cyanine yellow	1.8	47
1160+nigrosine	2.3	----------
1160+sudan II	2.5	41
1214	3.4	21
1214+eosin	4.3	45
1214+cyanine green	2.4	48
1203	4.0	23
1203+eosin	3.0	47

[a] Dyed by dipping in 1-percent solutions of the dyes in acetone.
[b] 17 hours of irradiation under the usual conditions.

The absorption values given in tables 3 and 4 were calculated from reflectance and transmission values, inasmuch as the fraction of the incident light absorbed by the sheet corresponds to the light *not* lost by reflection and transmission.

The absolute total reflectance and transmission of each sheet were measured by methods described elsewhere in detail by one of the writers [14]. The reflectance at 45° from normal incidence was used. Since the carbon arc used varied greatly in color and intensity from one instant to another, average values for ½-hour periods were obtained by substituting a recording potentiometer, including a 100-ohm galvanometer, for the usual manually operated potentiometer. The light intensities necessary for the direct operation of this instrument by the photocells had to be higher than is compatible with greatest precision in the circuit used, but tests with rotating sectored disks, transmitting 25 and 50 percent, showed that transmissions could be measured to an accuracy of ±0.5-percent transmission with this arrangement.

The fractional absorption, A_p, of a sheet of paper, p, is defined in terms of its reflectance, R_p, and its transmission, T_p, as follows:

$$A_p = 1 - R_p - T_p. \tag{1}$$

In the case of a sheet mounted on an aluminum backing, as in the usual experimental arrangement, some of the radiant energy transmitted by the sheet is returned by reflection to the sheet. By summing up the infinite series of reflections undergone by this radiant energy between the sheet and the aluminum, it can be shown that the fraction of the total radiant energy available to the sheet by reflection from the backing of reflectance R_{Al} is $T_pR_{\mathrm{Al}}/(1-R_pR_{\mathrm{Al}})$, of which quantity the sheet absorbs the fraction A_p.

Combining the fractions of the incident and reflected light absorbed, it is seen that the paper mounted on the aluminum backing absorbs the fraction A'_p of the total incident light:

$$A'_p = A_p\left(1 + \frac{T_pR_{\mathrm{Al}}}{1-R_pR_{\mathrm{Al}}}\right). \tag{2}$$

The value of R_{Al} was determined experimentally as follows: The reflectance of a paper mounted on the aluminum backing may be designated as $R_{p+\mathrm{Al}}$, and can be shown by the method of summation of an infinite series to be

$$R_{p+\mathrm{Al}} = R_p + \frac{T_p^2R_{\mathrm{Al}}}{1-R_pR_{\mathrm{Al}}}. \tag{3}$$

The quantities $R_{p+\mathrm{Al}}$, R_p, and T_p, for the light used in the usual experimental arrangement, were measured for three thin papers, and when substituted into eq 3 gave a value of $R_{\mathrm{Al}}=0.73$ [5] as an average of three closely agreeing results.

All the values for light absorption listed in tables 3 and 4 were calculated by using eq. 1 and 2. Since the optical values changed because of bleaching, or, in the case of newsprint, yellowing, measure-

[5] This value for the reflectance of the etched aluminum backing may be compared with 0.734, the average reflectance for the region of 400 to 740 millimicrons, obtained from a rather flat curve, using the General Electric Recording Spectrophotometer. This curve was obtained by H. J. Keegan, of the Bureau. The data were then converted to absolute values of reflectance.

ments were made before and after irradiation and the average values used for calculation.

(b) OXYGEN AND MOISTURE IN SURROUNDING ATMOSPHERE

The light stability of paper was found to be very materially increased by a lack of oxygen in the surrounding atmosphere. The data showing this for widely differing papers are given in table 5. All chemical changes during irradiation were found to be smaller in purified nitrogen than in air.

TABLE 5.—*Effect of oxygen and moisture upon the light[a] stability of papers*

Paper number	Decrease in alpha-cellulose percentage			Increase in copper-ammonia fluidity			Lowering of pH		
	Air [b]	Nitrogen [c]	Dry air [d]	Air [b]	Nitrogen [c]	Dry air [d]	Air [b]	Nitrogen [c]	Dry air [d]
WOOD-PULP PAPERS									
				Rhes	*Rhes*	*Rhes*			
1133 (soda-sulfite)	5.6	1.4	2.7	2.9	0.0	1.2	------	------	------
1136 (soda-sulfite)	7.0	2.6	4.8	4.0	.1	1.2	0.4	0.2	0.55
1138 (soda-sulfite)	6.2	2.6	6.2	2.8	.3	1.4	.45	.4	.55
1166 (refined sulfite)	2.9	------	2.5	------	------	------	------	------	------
N (newsprint)	31.3	6.5	20.0	9.7	5.1	------	1.7	.75	1.6
RAG PAPERS									
1182 (new rag)	4.2	1.2	5.2	1.3	0.0	0.9	0.3	0.0	0.45
1186 (new rag)	3.0	1.4	5.3	1.7	.3	1.7	.1	.0	.35
1191 (old rag)	3.2	.3	------	1.0	.0	------	.4	.05	------
1200 (old rag)	3.5	.9	5.2	1.4	.0	1.0	.85	.0	1.15
1203 (old rag)	4.0	1.0	6.8	1.4	.1	1.3	.3	.25	.8

a 17 hours of irradiation under the usual conditions, except as indicated.
b 58-percent relative humidity at 30° C.
c Contained less than 0.03 percent of O_2 after purification. See reference [5] for all details.
d Less than 0.02-percent relative humidity at 30° C.

All photochemical changes did not cease at the low concentration of oxygen, less than 0.03 percent by volume in the nitrogen used, as shown particularly by the changes in alpha cellulose. The chemical changes indicated by fluidity data, however, occurred only slightly or not at all, except in newsprint, at this concentration of oxygen. In a special experiment (described in footnote 4, page 62) with a probably much lower concentration of oxygen, the changes in newsprint were found to be practically the same as those shown in table 5. This would indicate, but, of course, not prove conclusively, that slight photochemical changes in paper occur even in the complete absence of gaseous oxygen.

The light stability of papers irradiated in extremely dry air (containing less than 0.0007 percent of gaseous water by volume) showed a fundamental difference between papers derived from wood and those derived from cotton. As seen from table 5, lack of water vapor caused smaller changes in alpha cellulose for the wood pulp papers, but larger changes for the papers derived from cotton, than resulted from light under normal conditions of moisture. The fluidity data are again inconclusive for the rag papers, as in the case of the experiments in nitrogen. It is of interest to note that the acidity of all types of papers was increased by irradiation in dry air. Control experiments in the dark showed no changes.

(c) TIME AND INTENSITY OF IRRADIATION.

The data of tables 3, 6, and 7 show that the alpha cellulose changes were proportional to less than the first power of the lengths of time of irradiation and light intensity, except, perhaps, in the early stages of irradiation. Exposure, of relatively unchanged fibers, by turning the sheet over, increased the rate of deterioration, as shown by the experiment with newsprint, *N*, table 6.

TABLE 6.—*Effect of varying the time of irradiation* [a]

Paper number	Decrease in alpha-cellulose percentage for various periods (hours) of irradiation						
	1 1/16	2 1/8	4 1/4	8 1/2	17	34	51
N (newsprint)	5.3	9.9	16.1	25.4	[b] 35.9 / [a] (42.8)	------	------
1136 (soda-sulfite)	------	------	------	3.9	7.0	10.4	12.5
1166 (refined sulfite)	------	------	------	1.6	2.9	3.8	4.7
1182 (new rag)	------	------	------	2.7	4.2	5.4	7.0
1203 (old rag)	------	------	------	2.2	4.0	------	8.2

[a] The usual conditions of irradiation prevailed for all the papers with the exception of one experiment with newsprint, in which case the sheet was irradiated for 8½ hours on each side. The corresponding value is given in parentheses.
[b] This value for newsprint, and that in tables 7 and 11, differ from that in tables 3, 5, and 8 because of a change of arc-lamp globes necessitated by breakage. Except for this instance, the globes were changed with sufficient frequence to avoid important differences arising from solarization of the glass.

TABLE 7.—*Effect of varying the light intensity*

Paper number	Decrease in alpha-cellulose percentage at various relative light intensities [a]					
	1.0 [b]	1/2	1/4	1/8	1/16	1/32
N (newsprint)	35.9	29.6	23.6	15.8	8.8	4.7
1136 (soda-sulfite)	12.5	10.8	--------	--------	--------	--------
1203 (old rag)	8.2	6.7	--------	--------	--------	--------

[a] The other conditions of irradiation were as usual. The newsprint paper was irradiated for 17 hours at each intensity, and the other 2 papers were irradiated for 51 hours at each intensity.
[b] Unity represents an absolute incident intensity of 0.17 watt/cm^2. Variation in intensity was secured by increasing the distance between the arc and the sheet according to the inverse-square law, taking the average intensity over the sheet into account.

The departure from proportionality of alpha-cellulose change with respect to time and intensity is seen to be rather small within the first 17-hour period for the various types of papers, with the exception of newsprint. Even in the latter case the departures do not affect the conclusions based upon the various data for newsprint.

(d) LIGNIN CONTENT

The extensive deterioration by light of newsprint paper probably arises from the photochemical reactivity of lignin. Along with the large change in alpha cellulose in this paper, *N*-a of table 3, the lignin content decreased from 19.1 to 13.7 percent during irradiation.[6] The other papers contained little or no lignin; paper 1133, for example, was found to have a lignin content of less than 0.5 percent.

[6] Similar changes in lignin contents of certain types of wood during irradiation with sunlight have been observed by Richter [1].

TABLE 8.—*Effect of gaseous oxygen upon the light*[a] *stability of newsprint*

Composition of atmosphere[b]	Decrease in alpha-cellulose percentage	Increase[e] in copper number	Lowering of pH
Air (21% O_2)	31.3	15.7	1.7
N_2[c] + 1.1% O_2[d]	17.1	----------	1.3
N_2 + 0.21% O_2	13.7	----------	1.1
N_2 + 0.11% O_2	12.2	4.6	1.0
N_2 + 0.03% O_2	6.5	2.2	0.75

[a] 17 hours of irradiation under the usual conditions, excepting oxygen content.
[b] All experiments were conducted at barometric pressure.
[c] Contained argon and any other inert gases usually present in commercial "water pump" nitrogen, after purification to remove oxygen.
[d] The various oxygen pressures were obtained by evacuating the system to the desired air pressure and refilling it with purified N_2, except in the experiment with the lowest concentration of O_2, which was obtained as described in refrence [5].
[e] Copper number for the unirradiated control was 5.4.

The chemical changes in newsprint irradiated at various concentrations of oxygen are shown in table 8. The sheets yellowed according to the oxygen content; only slight yellowing occurred at the lowest oxygen content listed, and none at all in the special experiment described in footnote 4.

The light stability of newsprint is very materially increased by buffering the sheet at pH 7.2, as shown by the data for paper *N*-b, table 3. In this experiment the sheet was dipped in a solution of $NaHCO_3$, and after air-drying, it was found to have retained 0.12 g of $NaHCO_3$, which gave the sheet a pH of 7.2. During subsequent irradiation, the lignin content decreased only 2.1 percent, indicating a relationship between lignin change and cellulose deterioration.

Whatever the steps between the initial absorption of radiant energy by lignin and the change in the cellulose may be, the rate of one or more of these reactions was greatly dependent upon the acidity of the paper. Relatively large quantities of acidic substances were produced during the irradiation, as shown by the change in pH from 5.0 to 3.3 for paper *N*-a. The first cold-water extract of 1 g of sample *N*-a, after and before irradiation, was found to require 10 ml and 1 ml, respectively, of 0.01 *N* NaOH for titration to an end point of pH=7.5, using the glass electrode in the absence of CO_2. The titration curve thus obtained was characteristic of an acid much weaker than acetic, in that the voltage changes were very gradual. The pH, 3.3, at the beginning of the titration, however, corresponded to an acid stronger than acetic. These two facts together indicate that a series of acids of various degrees of ionization were formed during the irradiation. The amount of material extractable with hot water increased from 1.0 to 9.6 percent during the irradiation.

It does not seem likely, however, that the hydrogen ions which these acidic reaction products yielded were responsible for the large effect of light upon newsprint paper, inasmuch as the data of table 9 show that sulfuric acid at a pH of 3.3 had only a small effect upon the light stability of this paper.

The resinous material in newsprint apparently did not affect the light stability appeciably. It was found that a sheet which had been extracted with ethyl alcohol, benzene, and ether before irradiation showed no improvement in light stability.

The effect of moisture upon the light deterioration of highly lignified papers is seen from table 5 to be moderate from the fact that extreme desiccation had only a minor effect. At an intermediate value of relative humidity, 35 percent at 30° C, the decrease in alpha-cellulose percentage was found to be 27.9 instead of 31.3. The increase in copper number corresponding to the 17-hour period of irradiation in very dry air was 11.4.

(e) ACIDITY

The results given in table 3 show that the sulfuric acid, present in papers because of the hydrolysis of aluminum sulfate used in their manufacture, had varying effects upon light stability, depending greatly, however, upon the type of fiber. This is in contrast to the thermal stability of papers, for which the pH, irrespective of fiber content, is a most important index of stability [8a].

The decrease by acid of the light stability of papers made from new rags can be seen from the pairs 1177, 1178; 1179, 1182; 1183, 1186. On the other hand, the light stability of papers made from old rags or wood pulps was much less affected by acid, as seen from the pairs 1191, 1193; 1200, 1203; 1133, 1134; 1129, 1173; 1164, 1166. The greatly increased stability of newsprint after the addition of $NaHCO_3$ to the sheet was apparently due to an increase in the light stability of lignin in the neutral medium rather than an increase in the light stability of cellulose.

Experiments with papers containing unusually large amounts of acid gave similar results. Sheets were dipped in solutions of sulfuric acid in absolute alcohol of concentrations necessary to give a pH near 3.6 in the treated sheets, and dried before irradiation. The results given in table 9 show that acid has a much larger effect upon the light stability of the paper made from new rags, 991, than upon the others. Control sheets containing like amounts of acid showed no alpha-cellulose changes when kept in the dark for the same period used for irradiation.

TABLE 9.—*Effect of sulfuric acid* [a] *upon the light stability of papers*

Paper number	Before addition of acid		After addition of acid	
	pH	Decrease [b] in alpha-cellulose percentage	pH	Decrease [b] in alpha-cellulose percentage
WOOD-PULP PAPERS				
1133 (soda-sulfite)	6.4	5.6	3.6	6.9
N (newsprint)	5.0	[b] 9.9	3.3	12.2
1160 (refined sulfite)	6.6	1.3	3.7	3.3
RAG PAPER				
991 (new rag)	6.9	0.8	3.6	5.3

[a] Acid was added to the sheets by dipping them in solutions of sulfuric acid in absolute alcohol of the concentrations necessary to give a pH near 3.6 of the treated sheet, as determined by trial.

[b] Change during irradiation under the usual conditions for 17 hours, with the exception of the newsprint, which was irradiated for 2⅛ hours to secure a comparable decrease in alpha cellulose.

(f) CONTENT OF ROSIN AND OTHER SIZING MATERIALS

Rosin, in the amount and manner in which it is usually introduced into paper by flocculation with aluminum sulfate, was found to be an unimportant factor in the deterioration of paper by light, unless the acidity is injuriously high. The effect of the latter condition is exemplified by the pair 1182, 1186, table 3. The effect, furthermore, was most pronounced for new-rag papers, since the soda-sulfite paper 1138, containing much rosin, was only slightly less stable than 1129, containing no rosin. At low acidities, even for new-rag papers, relatively large amounts of rosin had little or no effect, as shown by paper 1179. Paper 1173, in spite of the rosin, was one of the more stable papers of its group.

Rosin, when added to sheets of paper by brushing with solutions of rosin in absolute alcohol, increased the deteriorating effect of light as much as or, in some instances, even more than sulfuric acid. This is shown by the results listed in table 10 for sheets thus treated with rosin before irradiation. The original light stabilities of papers made from new cotton fibers or refined wood fibers were greatly lessened by rosin thus added, whereas the stability of the ordinary wood fibers was not greatly affected.

TABLE 10.—*Effect of rosin* [a] *and "hydrogenated rosin"* [b] *upon the light stability of papers*

Paper number	Rosin	Decrease in alpha-cellulose percentage [c]	Lowering of pH [d] [e]
	Percent		
1134 (soda-sulfite)	0	5.3	
1134 (soda-sulfite)	3.9	7.7	
1134 (soda-sulfite)	5.9	7.5	
1160 (refined sulfite)	0	1.3	0.3
1160 (refined sulfite)	2.3	5.7	.95
1160 (refined sulfite)	4.9	6.9	1.20
1160 (refined sulfite)	10.6	7.3	1.45
991 (new rag)	0	0.8	
991 (new rag)	1.4	3.9	
991 (new rag)	3.2	4.0	
991 (new rag)	5.6	4.7	
	Hydrogenated rosin		
	Percent		
1160 (refined sulfite)	2.2	6.0	1.25
1160 (refined sulfite)	4.8	7.2	1.45
1160 (refined sulfite)	9.7	8.5	1.60

[a] Papermakers' rosin grade "F" applied to sheets from solutions in absolute alcohol.
[b] Applied to sheets from solutions in absolute alcohol. See reference [16] for information about this material.
[c] Both types of rosin were removed from sheets before alpha-cellulose determination by extraction with absolute alcohol in a Soxhlet apparatus. Control tests showed no change in the paper during extraction, and the qualitative rosin test showed practically complete extraction.
[d] pH measurements made with rosins present in the sheets.
[e] Before irradiation, the papers containing rosin had a pH near 5.4, those containing "hydrogenated rosin" had a pH near 5.6.

The pH of papers containing rosin introduced in this manner was found to be near 5.4 before irradiation. The acidity of the rosin was, therefore, not great enough to account for the deteriorative effect of light, inasmuch as the much higher acidities of sulfuric acid in the papers listed in table 9 had, in general, smaller effects.

It appeared possible that the effect of rosin might be ascribed to the presence of double bonds in the rosin acid molecules. The experiments were, therefore, repeated with a rosin the double bonds of which had presumably been eliminated by hydrogenation [16].

The results with hydrogenated rosin are also given in table 10 and show that this material decreased the light stability of the papers somewhat more, if anything, than the unsaturated rosin. The pH changes during irradiation for both types of rosin were also quite similar and resembled those of lignin in magnitude.

It appears, therefore, that properties other than the presence of double bonds or the behavior as an acid were responsible for the deteriorative effect of rosin. The remaining apparent reason, that of increased light absorption, was considered. The light absorption was measured for the sheets of paper 1160 containing 0, 2.3, 4.9, and 10.6 percent of rosin, and were found to be 16, 19, 20, and 24 percent, respectively, which values obviously do not represent sufficient increases in absorption to explain the greater deterioration, not even when the 5- to 6-percent increase in absorption due to darkening caused by irradiation of these large quantities of rosin is taken into account.

The effect of glue upon the light stability of paper appears to be small, if it existed at all, since the slight increases in deterioration of papers 991 and 1013, table 3, could easily be accounted for by the increased acidity caused by the acid in the glue sizing solution. No effect of starch was found.

The sizing materials themselves were physically and chemically affected by light. The water resistance of sized papers was found to decrease during irradiation, as was also found by Zhereboff [17] and Richter [1] for sunlight. A rosin, a glue, and a starch-sized paper were each found to have lost over half their sizing values (in terms of time of penetration of water, using the dry indicator method) during the 17-hour period of irradiation.

During irradiation the rosin in the papers of table 3 became almost completely insoluble in anhydrous ether, although its solubility in ethyl alcohol apparently remained unchanged. Its acidimetric equivalent weight, as determined by titration with alcoholic KOH decreased from 340 to 213 g per equivalent, which, together with the lowering of the pH shown in table 10, shows that the rosin is decomposed into molecules having carboxyl groups. The rosin was also found to undergo oxidation as shown by the fact that its oxidimetric equivalent weight [9c] decreased from 3.63 to 3.13 g per equivalent.

Analyses for glue and starch before and after irradiation showed decreases of 5 to 10 percent of the amount of sizing material originally present.

(g) PROTECTION BY PRINTERS' INK

The data in table 11 show that paper is extensively protected by ink against the action of light. The papers were printed at the Government Printing Office, using the regular "job black" ink. The sheets were printed on one side only, either solid black or with lowercase, 5-point-face roman type. Experiments with the latter, however, were conducted only with newsprint, inasmuch as the protection afforded by letters extends normally to but 10 to 15 percent of the area of the sheet, and was, therefore, difficult to measure accurately except for unstable papers.

TABLE 11.—*Effect of printers' ink,*[a] *solid black, in protecting papers against light*[b]

Paper number	Decrease in alpha-cellulose percentage [c]	
	Plain	Printed solid black
N	35.9	[d] 8.1 (32.5)
1129	5.1	1.4
1134	5.3	1.5
1136	7.0	0.0
1191	3.2	1.1
1216	2.5	1.8

[a] The papers were printed at the Government Printing Office, using the regular "job black" ink, through the kind cooperation of Robert H. Simmons.
[b] 17 hours of irradiation under the usual conditions.
[c] The alpha-cellulose percentage of a printed paper is appreciably lower than that of the plain paper, owing to the presence of certain alkali-soluble materials in the ink. To obtain the decrease brought about by light, therefore, the unirradiated solid-black paper was analyzed for control purposes.
[d] The value in parentheses corresponds to a paper printed in the normal way with letters. Therefore, only a small part was protected by ink.

The behavior of ink, which is principally on the surface of a sheet, is thus seen to be quite different from the behavior of a sensitizing dye. Although the ink absorbed almost all of the incident light, little or no transfer of photochemically active energy to the fibers occurred.

3. EFFECT OF LIGHT UPON SUBSEQUENT THERMAL STABILITY OF PAPERS

The increase in acidity occurring in paper during exposure to light, as shown by the fall in pH, table 3, suggests that a paper, once exposed to light, will no longer be as stable, even if stored in the dark, as the same paper had it not been so exposed. This was found to be the case.

A variety of papers were first irradiated, and then one half of each sheet was heated in an "accelerated aging" oven in the dark in air at 100° C for 72 hours, along with sheets of the same papers not previously irradiated. The irradiated papers, the irradiated and heated papers, and the heated papers were then analyzed. The alpha-cellulose changes in the third series correspond to the thermal or ordinary stabil-

TABLE 12.—*Effect of light* [a] *upon subsequent stability of papers*

Paper number	Decrease in alpha-cellulose percentage during heating [b]	
	Paper not previously irradiated	Paper previously irradiated [c]
1129	14.9	29.7
1138	5.2	13.6
1143	5.8	9.5
1166	2.8	6.1
1191	3.1	5.5
1133	0.0	2.4
1182	4.0	5.0
1200	2.0	2.3
1203	5.4	4.4

[a] 40 hours of irradiation (20 hours on each side of sheet) under the usual conditions.
[b] Heating for 72 hours at 100° C in the dark in air.
[c] These values are the result of subtracting the values for alpha-cellulose change due to light from those due to light plus heat.

ity of the papers, and are listed in column 2 of table 12. The values for alpha-cellulose decrease in the irradiated and heated papers, diminished by the values for alpha-cellulose decrease during irradiation alone, yielded the values corresponding to the thermal or ordinary stability of papers exposed to light at some time and then stored in the dark. These results are listed in column 3 of table 12, and show that most papers once irradiated may be expected to be considerably less permanent than if they had not been exposed to light.

V. REFERENCES

[1] George A. Richter, *Relative permanence of papers exposed to sunlight*, Ind. Eng. Chem. **27**, 177, 432 (1935).

[2] S. R. H. Edge and Helen M. McKenzie, *Discolouration of wood pulp by light and heat*, Paper Makers Assn. Gt. Britain & Ireland, Tech. Sec. Proc. **17**, 437 (March 1937).

[3] Sutezo Oguri, J. Soc. Chem. Ind. Japan **37**, 201, 620 (1934); **39**, 35, 286 (1936); **40**, 300, 356 (1937); **41**, 3 (1938).

[4] H. Bakker (Yellowing of newsprint by sunlight) Chem. Weekblad **34**, 543 (1937).

[5] Herbert F. Launer, *Apparatus for the study of the photochemistry of sheet materials*, J. Research NBS **24**, 567 (1940) RP1300.

[6] Sigurd Köhler (Protection of paper against sunlight by colored glass windows) Tek. Tid. **7**, 49 (1935).

[7] W. W. Coblentz, M. J. Dorcas, and C. W. Hughes, *Radiometric measurements of the carbon arc and other light sources used in phototherapy*, BS Sci. Pap. **21**, 549 (1926) S539.

[8] (a) Merle B. Shaw and Martin J. O'Leary, J. Research NBS **21**, 671 (1938) RP1149; (b) Merle B. Shaw, George W. Bicking, and Martin J. O'Leary, J. Research NBS **14**, 649 (1935) RP794.

[9] Herbert F. Launer (a) alpha cellulose: J. Research NBS **18**, 333 (1937) RP979; **20**, 87 (1938) RP1068; (b) pH: J. Research NBS **22**, 553 (1939) RP1205; (c) resin: J. Research NBS **18**, 227 (1937) RP973. These three methods are available as TAPPI standards Nos. T 429m-39, T 435m-42 and T 408m-39, respectively.

[10] Ralph T. Mease, *Measurement of the apparent fluidity of dispersions of cellulose in cuprammonium solution*, J. Research NBS **22**, 271 (1939) RP1179.

[11] See corresponding TAPPI methods. Technical Assn. Pulp and Paper Industry, 122 East 42d Street, New York, N. Y.

[12] Geo. J. Ritter and James H. Barbour, *Effect of pretreatment of wood on the lignin determination*, Ind. Eng. Chem., Anal. Ed. **7**, 238 (1935).

[13] Herbert F. Launer, *An easily constructed, rugged, sensitive thermopile*, Rev. Sci. Inst. **11**, 98 (1940).

[14] Herbert F. Launer, *Reflection-transmission relationships in sheet materials*, J. Research NBS **27**, 429 (1941). RP1430; J. Opt. Soc. Am. **32**, 84 (1942).

[15] F. Scholefield and H. A. Turner, J. Textile Inst. **24**, 130P (1933).

[16] A. C. Dreshfield and J. H. Long, *Stabelite, a hydrogenated rosin for size*, Paper Trade J. **113**, 40 (July 17, 1941).

[17] L. P. Zhereboff, *Effect of sunlight on vegetable paper sizes*, Paper Trade J. **76**, 112 (March 15, 1923).

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