A STUDY OF THE PROGRESSIVE OXIDATION OF CELLULOSE BY HYPOCHLORITE SOLUTIONS

Thesis for the Degree of M. S.

C. L. Elaine Alvord

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Submitted to the Faculty of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of Master of Science.

C. L. Elaine Alvord

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I wish to thank Professor Bruce E. Hartsuck for the suggestions and help he gave so graciously during the course of this study.

Table of Contents.

The work that has been done on the oxidation of cellulose, consists, for the most part, of studies on the properties of oxycellulose and the final products of the oxidation reaction. The work reported in this thesis shows a somewhat different mode of attack, in that the progress of the oxidation reaction was studied.

Preliminary experiments on this problem based on an article by Forster and Pearman*, were discussed in a senior report by the author.

The oxidation of cellulose and the resulting products involve so many complications that Emil Hauser** has said, "The further we penetrate into the field of cellulose chemistry, the less explored it becomes, the less clarity prevails about the course of the reactions and the nature of the derivatives. This is especially true of the oxidation of cellulose and its important oxidation products, the oxycelluloses, so named by their discoverer, Witt."

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* Forster and Pearman, "The Bleaching of Trade Sulfite Pulps and Cotton with Calcium Hypochlorite Solutions", Jr. of Soc. of Chem. Ind., 1925, Vol. 44, No. 20.

** Text-book of Cellulose Chemistry, Emil Hauser. Translated by West and Esselen. McGraw-Hill Book Company, Inc., New York, 1924.

Field Flower brand muslin, boiled and thoroughly washed several times with distilled water to remove the sizing, was used in this study.

The "lime water bleach" liquor was made by mixing 100 grams of bleaching powder (24% chlorine) in a mortar with lime water. This was poured into a liter graduate, made up to one liter with lime water, allowed to settle, and the supernatant liquid was filtered through filter paper. More lime water was added to the solid material and the supernatant liquid filtered. The two filtrates were mixed and diluted to one liter with lime water.

The "distilled water bleach" was made in the same way, except that distilled water was used in place of lime water.

These bleach solutions contained from 12 to 15 grams of chlorine per liter.

Conditioning of Samples

All the cellulose and modified cellulose samples and the Gooches containing filter paper were conditioned and weighed. This conditioning was accomplished by leaving them in a normal atmosphere jar until a constant weight was attained. The normal atmosphere jar was a dessicator in which a condition of 65% relative humidity was maintained by the 35.7% sulfuric acid which replaced the usual drying agent. *

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* Wilson, Journal of Industrial and Engineering Chemistry, Vol. 13, p. 328.

Method for Bleaching

Ninety cubic centimeters of bleach liquor was poured over a weighed sample of cellulose contained in a 125 cubic centimeter glass bottle provided with a rubber stopper carrying an open tube to allow the escape of gases formed during the oxidation process. The bottle was placed in a water bath where a constant temperature was maintained. After a time the bottle was removed from the water bath and (1) a 5 cubic centimeter portion of the bleach liquor was removed with a pipette, and the chlorine determined by adding KI and HCl and titrating with standard $Na_2S_2O_3$ solution using starch solution as an indicator; (2) the remaining bleach liquor was filtered through a conditioned and weighed Gooch crucible with quantitative filter paper on the bottom, and the filtrate saved; (3) The cellulose was washed with distilled water, reagent HCl, then washed free of acid (litmus paper indicator) with distilled water, dried in the air, conditioned and weighed in the Gooch.

In the two series run in 1926, the tube in the stopper carried a pinch clamp and the pressure was released every 15 or 30 minutes. The bottles were shaken about every half hour.

In the remainder of the work the tubes were left open and the bottles were shaken every 10 minutes.

Bleach solution kept at 50°C for four hours showed no decrease in oxygen content. Therefore, it can be assumed that the oxygen disappearing from the bleach has reacted with cellulose.

Determination of Solubility in 3% NaOH

A sample of cellulose was boiled in a reflux condenser for 1 hour with 100 parts by weight of 3% NaOH. The solution was filtered

through filter paper in a conditioned and weighed Gooch, the filtrate saved, and the residue washed with reagent HCl, then with distilled water until free of acid (litmus paper indicator), dried in the air, conditioned and weighed. The loss of weight of the sample was calculated. The original commercially bleached Field Flower muslin was 3.9% soluble in 3% NaOH.

Comparison of Lime Water and Distilled Water Bleaches

TIME - From a study of Tables I, II, III, and IV, and Figure I it is obvious that less time is required to use all of the oxygen from the distilled water bleach than from the lime water bleach, and that the critical period when oxygen is consumed at a greatly increased rate appears sooner in the distilled water bleach than in the lime water bleach. It has been mentioned before that the two series done in 1926 were under slightly different conditions than the later series. Therefore, the work shown in Table I can not be expected to check with that shown in Table III, or the work in Table II with that in Table IV.

Rate of Oxygen Consumption

It is also shown in the tables and in Figure I that the amount of oxygen used per gram of cellulose increases gradually for a time, then there is a sudden marked increase, followed by a gradual decrease in the rate of oxygen consumption.

In every case this critical period appeared later in the lime water bleach than in the distilled water bleach. The study of the alkalinity of the bleach liquors which is discussed later shows that the critical period begins just as the reaction of the bleach passes from alkaline to acid. The approach of the critical period is retarded

by the higher alkalinity of the lime water bleach.

Table I

Series 1 - (1926) Distilled water bleach on Field Flower muslin at 50°C.

5 c.c. original bleach used 15.9 c.c. of 0.1075N $Na_2S_2O_3$

No.	Weight of samples in grams	Hours in bleach	C.c. of $Na_2S_2O_3$ per 5 c.c. bleach	Grams loss in weight	Per cent loss of weight in bleach	Grams O_2 used per gram sample	Grams O_2 used per gram loss in weight	Per cent soluble in NaOH
1	2.5380	1	14.87	.0143	.5634	.00621	1.1020	3.524
2	2.5369	2	14.12	.0403	1.6950	.01074	.6758	
3	2.5055	3	13.07	.0820	3.2740	.01728	.5281	
4	2.4972	3½	12.14	.1120	4.4810	.02357	.5257	
5	2.5850	3½	10.54	.1420	5.4920	.03173	.5776	14.27
6	2.4906	4	7.01	.2146	8.6770	.05462	.6339	25.45
7	2.5492	4½	3.41	.2901	11.3800	.07498	.6588	30.62
8	2.5539	5	1.29	.3526	13.8000	.08753	.6357	38.98
9	2.5061	5½	.50	.3986	15.9100	.09403	.5912	41.66

Table II

Series 10 - (1926) Lime water bleach in Field Flower muslin at 50°C.

5 c.c. original bleach used 15.9 c.c. of 0.1075N $Na_2S_2O_3$

No.	Weight of samples in grams	Hours in bleach	C.c. of $Na_2S_2O_3$ per 5 c.c. bleach	Grams loss in weight	Per cent loss of weight in bleach	Grams O_2 used per gram sample	Grams O_2 used per gram loss in weight	Per cent soluble in NaOH
10	2.4855	1	14.83	.0150	.6034	.006587	1.0915	6.38
11	2.5288	2	13.90	.0520	2.0560	.01213	.5899	6.29
12	2.4808	3	12.90	.0912	3.5920	.018504	.5034	7.061
13	2.5135	3½	12.60	.1078	4.2900	.02006	.4678	
14	2.4907	4	12.07	.1113	4.4680	.0235	.52655	8.245
15	2.5265	4½	9.02	.1696	7.1990	.02956	.43025	17.700
16	2.5552	5	3.00	.2840	11.1100	.07725	.695	34.550
17	2.5357	5½	1.54	.3245	12.7800	.08665	.6929	38.000
18	2.4923	6	.80	.3531	14.1900	.09271	.6544	38.5[illegible]

Table III

Series 50 - Distilled water bleach on Field Flower muslin at 50°C.

5 c.c. of original bleach used 18.28 c.c. of 0.09541N $Na_2S_2O_3$

No.	Weight of samples in grams	Hours in bleach	C.c. of $Na_2S_2O_3$ per 5 c.c. bleach	Grams loss in weight	Per cent loss of weight in bleach	Grams O_2 used per gram sample	Grams O_2 used per gram loss in weight
50	2.5039	1	17.1	.0309	1.235	.006476	.659
51	2.5082	1' 30"	16.48	.0515	2.053	.009781	.4806
52	2.5089	2	15.94	.0784	3.125	.01281	.4451
53	2.4997	2' 30"	13.1	.1430	5.72	.01748	.3055
54	2.5103	2' 45"	9.14	.2415	9.62	.05002	.52
55	2.5030	3' 20"	2.7	.3677	14.68	.08553	.5821
56	2.5040	3' 34"	1.	.4225	16.87	.0941	.5619
57	2.4998	4	0.1	.4429	17.72	.09991	.5639

Table IV

Series 60 - Lime water bleach on Field Flower muslin at 50° C.

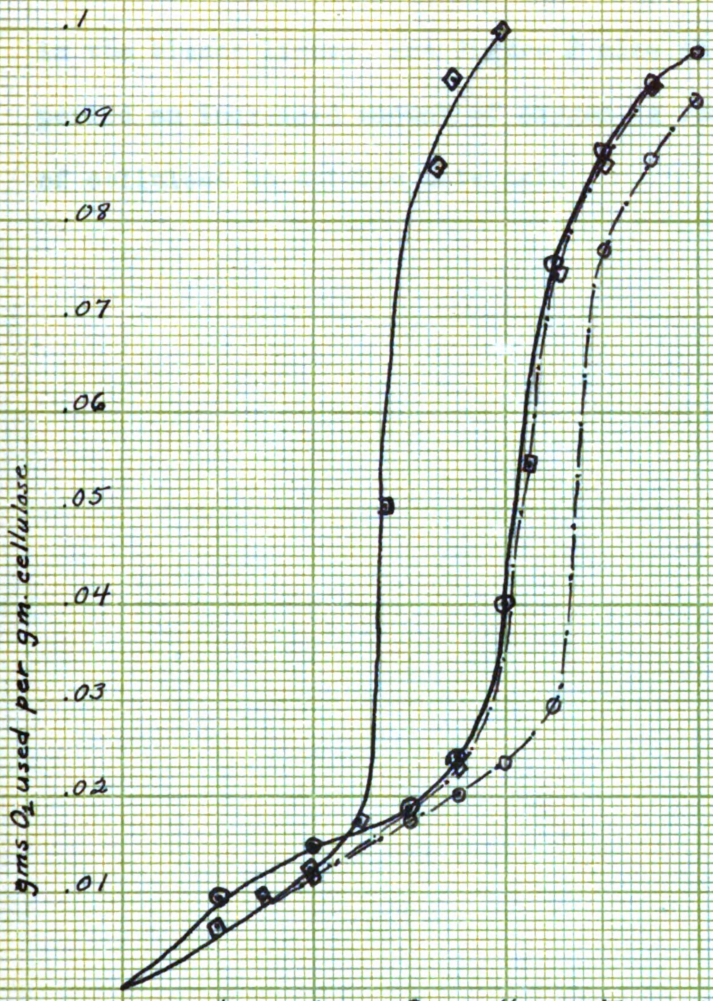
5 c.c. of original bleach used 17.95 c.c. of 0.09541N $Na_2S_2O_3$

No.	Weight of samples in grams	Hours in bleach	C.c. of $Na_2S_2O_3$ per 5 c.c. bleach	Grams loss in weight	Per cent loss of weight in bleach	Grams O_2 used per gram sample	Grams O_2 used per gram loss in weight
60	2.5027	1	16.2	.0335	1.338	.009607	.7177
61	2.5050	2	15.18	.0786	3.130	.01519	.4842
62	2.5015	3	14.46	.0984	3.934	.01918	.4873
63	2.5065	3½	13.52	.1125	4.489	.02428	.5410
64	2.5093	4	10.5	.1680	6.695	.04079	.6093
65	2.5040	4½	4.16	.2862	11.430	.07566	.6620
66	2.5033	5	1.96	.3363	13.430	.08776	.6532
67	2.5029	5½	.7	.3939	15.740	.09469	.6017
68	2.5092	6	.04	.4253	16.950	.09806	.5786

Series 20 - Distilled water bleach on Field Flower muslin at 40° C.

5 c.c. of original bleach used 18.51 c.c. N/10 $Na_2S_2O_3$

No.	Weight of samples in grams	Hours in bleach	C.c. of $Na_2S_2O_3$ per 5 c.c. bleach	Grams loss in weight	Per cent loss of weight in bleach	Grams O_2 used per gram sample	Grams O_2 used per gram loss in weight	Per cent soluble in NaOH
20	2.4985	2	17.59	.0242	.968	.005302	.5475	4.66
21	2.5299	3' 50"	16.40	.0626	2.475	.01201	.4855	9.58
21¼	2.5069	4' 30"	16.70	.0762	3.040	.0104	.3421	6.46
21½	2.5319	5	15.59	.0702	2.773	.01456	.5251	9.37
21¾	2.5195	5' 30"	15.46	.0888	3.524	.01744	.4958	12.25
22	2.5282	6	11.30	.1528	6.043	.04107	.6797	21.66
23	2.5109	6' 25"	8.94	.2379	9.475	.05488	.5793	30.22
23½	2.4938	6' 50"	6.66	.2849	11.420	.06843	.5991	32.44
24	2.5162	7' 16"	5.00	.4783		.07731	.4067	40.91
25	2.5092	7'36"	3.58	.3686	14.790	.08572	.5834	37.51
26	2.5182	7' 57"	2.42	.3609	14.33	.092	.642	39.25
27	2.5086	8' 17"	2.33	.3660	14.59	.09289	.6364	41.23
28	2.4979	8' 50"	1.62	.3704	14.83	.09813	.6567	41.73
29	2.5275	9' 18"	1.1	.3362	13.3	.09964	.7455	36.16



lime water bleach 2.5 gms. cellulose 50°C '27 Table IV
" " " 2.5 " " 50°C '26 " II
distilled " " 2.5 " " 50°C '27 " III
" " " 2.5 " " 50°C '26 " I

FIGURE 1

SOLUBILITY - The first part of the curve in Figure 2 shows that the cellulose is gradually being modified in such a way that it is soluble in the bleach liquor, and Figure 2 also shows that during the critical period an increased amount of oxygen is required to oxidize a unit weight of cellulose to soluble material.

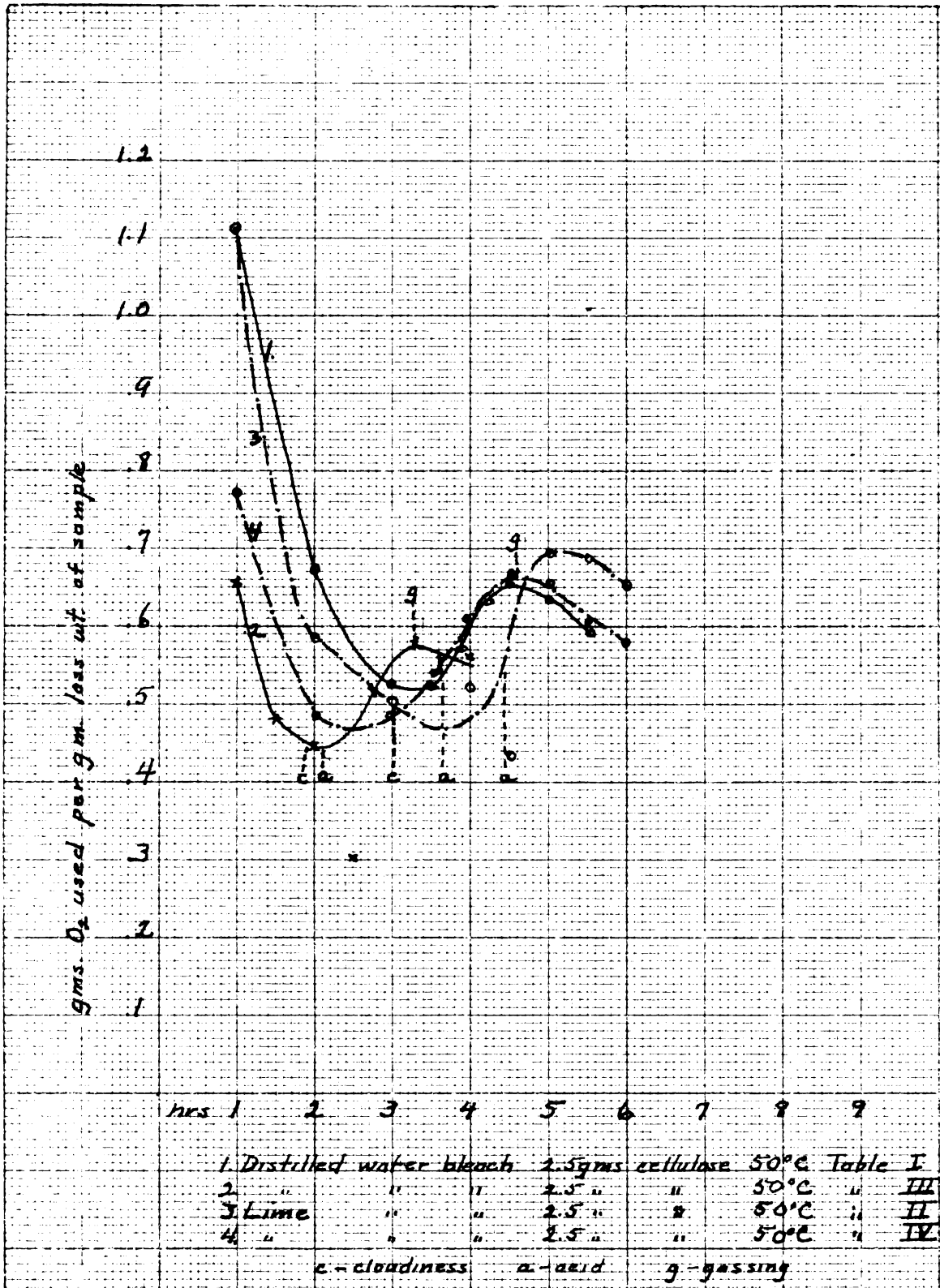

gms. O_2 used per gm. loss wt. of sample
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
hrs 1 2 3 4 5 6 7 8 9
1. Distilled water bleach 2.5gms cellulose 50°C. Table I.
2. " " " 2.5 " " 50°C. " III
3. Lime " " 2.5 " " 50°C. " II
4. " " " 2.5 " " 50°C. " IV
c - cloudiness a - acid g - gassing

FIGURE 2.

The acidity of the bleach liquor may account for the critical period. It is delayed by alkalinity. This was indicated by the following experiment. Three 2.5 gram samples of cellulose were placed in distilled water bleach at 40° C. After 3 hours 10 cubic centimeters of 10% KOH were added to Bottle, No. 1, 5 cubic centimeters of 10% KOH were added to Bottle, No.2, but nothing was added to Bottle, No.3.

Table VI

At 3 hours approximately 16.8 c.c.$Na_2S_2O_3$ would be used for 5 c.c. of bleach from Series 20 - 29.

No. 1		No. 2		No.3	
Hours in bleach	C.c. of $Na_2S_2O_3$ per 5 c.c. bleach	Hours in bleach	C.c. of $Na_2S_2O_3$ per 5 c.c. bleach	Hours in bleach	C.c. of $Na_2S_2O_3$ per 5 c.c. bleach
6' 20"	14.10	6' 5"	14.9	6' 25"	6.4
7' 15"	13.8	8' 5"	14.44	7' 20"	3.3

The sodium thiosulfate used in these titrations was 0.0988N

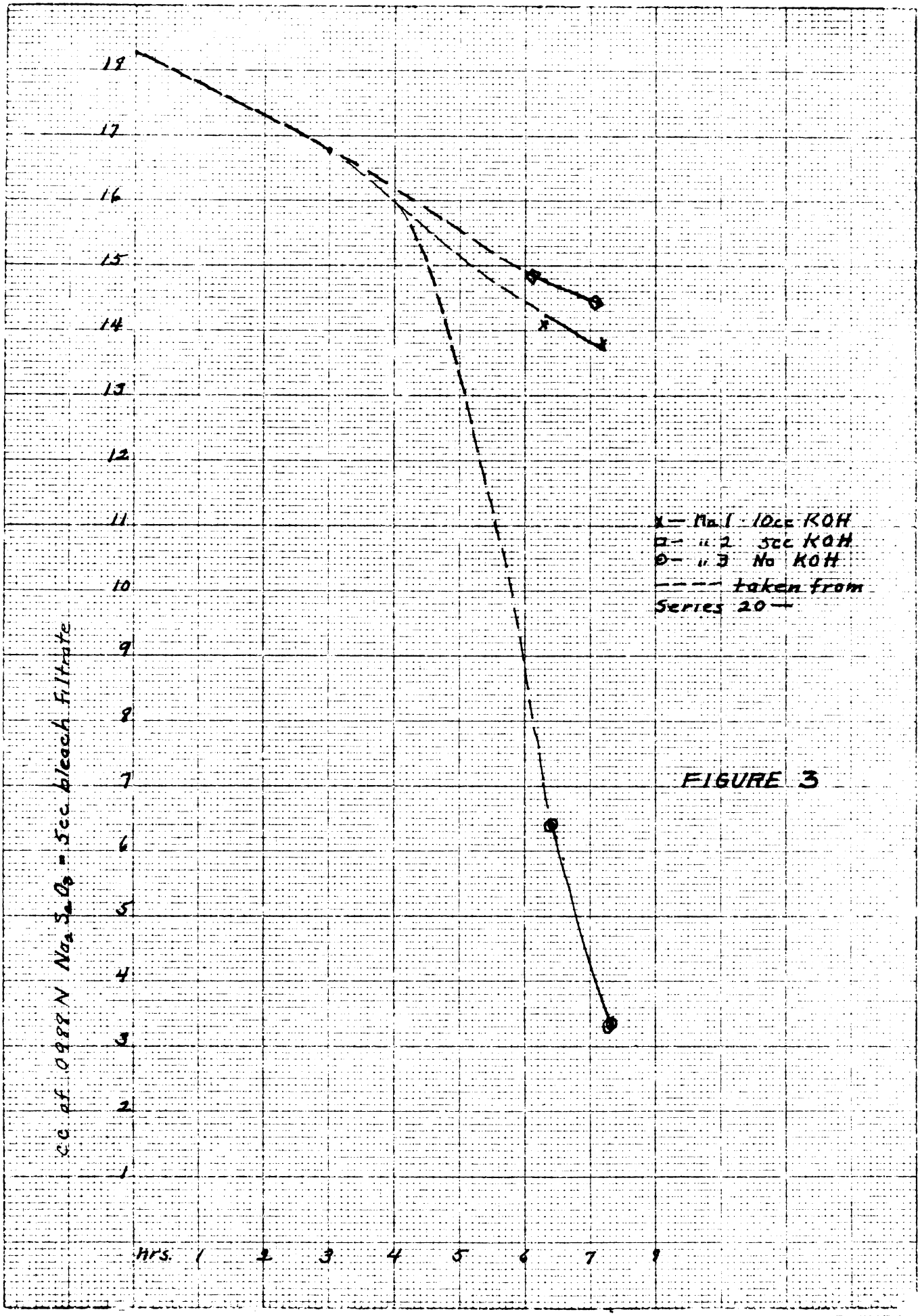

cc of .0988 N $Na_2S_2O_3$ = 5cc bleach Filtrate
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
Hrs. 1 2 3 4 5 6 7 8
x— No 1 10cc KOH
□— " 2 5cc KOH
○— " 3 No KOH
---- taken from Series 20—

FIGURE 3

That some of the oxygen disappearing from the bleach was used to further oxidize products soluble in the bleach was shown by the following experiment.

One 2.5 gram sample of cellulose was bleached with distilled water bleach at 50°C for 1½ hours and another sample for 2½ hours. The partially exhausted bleach was filtered, cooked, a sample titrated with $Na_2S_2O_3$ solution, 50 c.c. added to 40 c.c. new bleach and this mixture kept at 50° C.

The chlorine in the mixture was determined at certain intervals. The amount of oxygen in the mixtures decreased which showed that oxidation products of cellulose soluble in the bleach could be further oxidized. That there is an accumulation of these soluble products is shown by the fact that the oxygen disappears more rapidly in the second mixture than in the first.

Table VII

5 c.c. of original bleach used 17.82 c.c. of 0.09541N $Na_2S_2O_3$

1½ hour filtrate Mixture : 16.02 c.c. $Na_2S_2O_3$		2½ hour filtrate Mixture : 53 c.c. $Na_2S_2O_3$	
Hours	C.c. $Na_2S_2O_3$	Hours	C.c. $Na_2S_2O_3$
0	16.92	0	10.86
1½	16.70	1	5.26
2½	16.44	1½	3.66
3½	16.42		
4	16.38		

When the solid residues from the bleach were boiled for 1 hour with 100 parts by weight of 3% NaOH, the solubility increased with the degree of modification. During the critical period the per cent solubility in NaOH increased much more rapidly than the per cent solubility in the bleach liquor, as shown in Figure 4.

It is stated by Hibbert and Parsons* that oxycellulose is not as resistant as cellulose to aqueous alkaline solutions. It appears that during the critical period oxycellulose is being formed very rapidly. (Figure 4)

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* Hibbert and Parsons, Journal of the Society of Chemical Industry, Vol. XLIV, No. 41, Oct. 9, 1925.

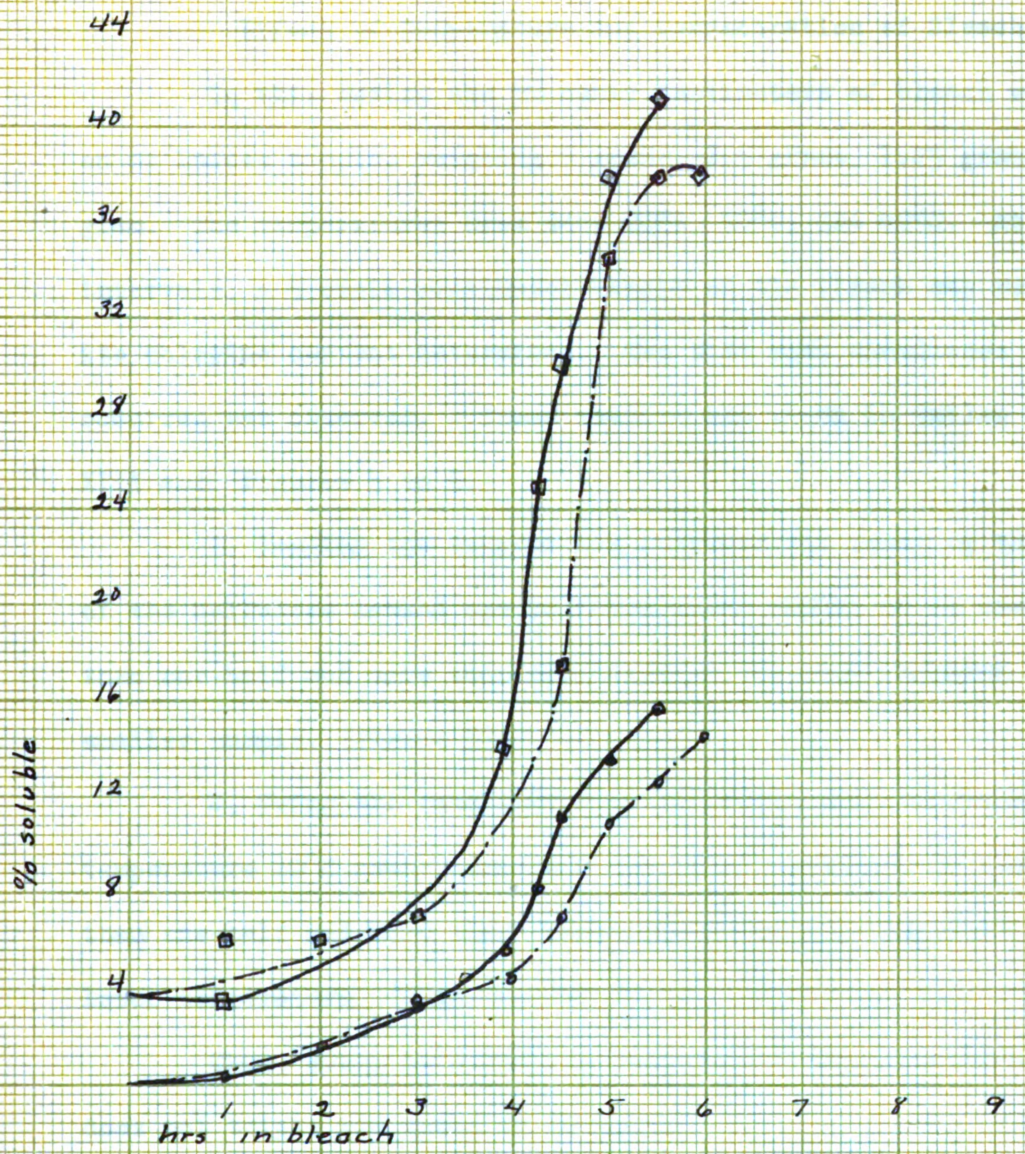


Table I
□— % soluble in NaOH
○— % " " bleach

Table II
□—·— % soluble in NaOH
○—·— % " " bleach

FIGURE 4

Effect of Temperature and Concentration of Bleach.

In this series the 90 cubic centimeters of bleach were placed on cellulose samples weighing 5 grams, 2.5 grams, 1.25 grams, and 0.62 gram. The temperatures used were 40°C, 50°C, and 60°C. At suitable intervals, a 5 cubic centimeter sample of the bleach was removed and its chlorine content determined. The time when cloudiness and gassing occurred was observed. These results are shown in Tables VIII to XIII and Figures 5 to 9.

1. Keeping the temperature constant but doubling the weight of the cellulose caused one half the total oxygen to be used in less than one-half and more than one-third of the time required by the smaller sample. (Figure 5)

2. Using the same weight of cellulose and increasing the temperature 10°C caused one-half the total oxygen to be used in less than one-half and more than one-third of the time required at the lower temperature. (Figures 6 to 9)

Thus, every 10°C rise in temperature more than doubles but does not triple the speed of reaction.

Table VIII

Distilled Water Bleach at 40°C.

Wt. of samples - 5.0145 grams			2.508 grams			1.251 grams			0.621 gram		
Cloudiness - 3' 20"			5 hours								
Gassing - 4' 20"			7' 20"			6' 20"					
C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours
16.84		0	16.84		0	16.84		0	16.84		0
15.05	.005838	2' 6"	16.2	.003747	2' 12"	16.55	.003394	2' 16"	16.77	.001654	2' 22"
12.98	.011295	2' 51"	15.3	.00901	4	15.85	.01161	5'16"	16.25	.01395	6' 17"
8.98	.023	3' 31"	13.08	.022	5	15	.02158	7' 52"	16.1	.01749	9
4.6	.03582	3' 50"	9.4	.04353	6	13.4	.0508	9			
1.48	.04495	5' 7"	5.08	.0688	6' 37"						
.54	.0477	6' 7"	1.55	.08946	7' 22"						
			.9	.09326	9						

Table IX

Lime Water Bleach at 40°C

Wt. of samples - 5.0195			2.56 grams			1.2565 grams		
Cloudiness - 3½ hours			6½ hours					
Gassing - 6½ hours								
C.c. $Na_2S_2O_3$ per 5 c.c. bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c. bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c. bleach	Grams O_2 used per gram sample	Hours
16.8		0	16.8		0	16.8		0
15.62	.003391	2	16.	.004471	2' 30"	15.56	.014246	6' 30"
14.8	.005788	3	14.98	.01032	5' 15"	14.9	.02194	10' 5"
14.42	.006782	3' 30"	14.45	.01335	6' 38"			
12.46	.01263	5	14.13	.01519	7' 30"			
5.47	.03306	16	13.	.02167	8			
1.2	.04555	7' 17"	10.4	.03667	9			
.4	.04788	8' 37"						

Table X

Distilled Water Bleach at 50°C.

Wt. samples - 5 grams			2.507 grams			1.2516 grams			0.621 gram		
Cloudiness			1½ hours			2½ hours			4 hours		
Gassing - 1½ hours			2½ hours			5 hours					
C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours
16.84		0	16.84		0	16.84		0	16.84		0
16.44	.001174	15"	15.8	.006087	1	16.18	.007389	1	16.08	.01796	2
15.9	.002759	30"	15.06	.01042	1' 30"	15.58	.01477	2	15.32	.03591	4
15.18	.004872	45"	12.54	.02517	2	15.18	.01946	2' 30"	15.08	.04159	4' 30"
13.7	.009215	1'	8.84	.04683	2' 15"	14.44	.02814	3	14.08	.06522	5' 30"
3.7	.03856	1' 30"	1.16	.09178	2' 30"	11.16	.06659	4	8.62	.1942	6'30"
2.24	.04285	1' 40"	.64	.09482	3	5.2	.1365	4' 30"	3.66	.3114	7' 5"
.75	.04712	2	.12	.09786	3' 15"	2.6	.1669	5	2.56	.3374	7' 35"
.32	.04848	2' 15"	.			1.46	.1803	5' 45"	1.84	.3544	8' 5"
.1	.04913	2' 30"				.64	.1899	6' 15"	.3731	.3731	8' 50"

Table XI

Lime Water Bleach at 50° C.

Wt. samples - 5.0213 grams			2.0506 grams			1.2545 grams			0.616 gram		
Cloudiness - ¾ hour			3 hours			5 hours			4 hours		
Gassing - 2' 10"			4¼ hours								
C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours
16.8		0	16.8		0	16.8		0	16.8		0
16.28	.001461	15"	15.84	.005504	1	15.54	.0145	2	15.8	.02334	3
15.8	.002864	30"	14.82	.01148	2	15.	.02082	3	14.6	.05193	6' 45"
15.32	.004266	45"	13.6	.01862	3	14.36	.02883	4' 15"	14.3	.05907	7' 30"
14.18	.007598	1'	8.28	.04977	3' 45"	13.9	.03369	5	14.16	.06241	8
13.38	.009935	1'30"	2.46	.08385	4' 15"	10.72	.07088	6	14.	.06776	8' 45"
11.38	.01578	1'45"	1.34	.09041	4' 30"	3.84	.1514	6' 30"			
4.85	.03486	2	.55	.09503	4' 45"	1.76	.1753	6' 55"			
.42	.04781	2' 30"	.			1.04	.1841	7' 30"			
						.54	.19	8			

Table XII

Distilled Water Bleach at 60°C.

Wt. samples - 5.01 grams		2.506 grams		1.2575 grams		0.622 gram	
Cloudiness - 30"		45"		1' 10"		1' 30"	
Gassing - 40"		1'		2'			
c.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	c.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	c.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	c.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours
16.8		0	16.8		0	16.8		0	16.8		0
15.9	.002753	15"	15.14	.009954	15"	15.74	.01284	40"	15.38	.034444	1' 30"
11.78	.01482	30"	12.86	.0232	45"	14.62	.0259	1' 15"	14.6	.05284	2' 5"
.1	.04903	45"	2.74	.08256	1'	5.18	.1361	1' 45"	5.3	.2722	2' 50"
			.1	.09802	1' 15"	1.8	.1755	2'	3.1	.3241	3' 5"
						.1	.1999	2' 15"	2.	.3501	3' 30"
									1.	.3749	3' 50"
									.54	.3845	4' 8"
									.22	.393	4' 30"

Table XIII

Lime Water Bleach at 60°C.

Wt. samples - 5.04 grams			2.509 grams			1.254 grams			0.623 gram		
Cloudiness - 40"			1 hour			2¼ hours			3 hours		
Gassing - 1 hour			1½ hours			3' 10"			4 hours		
C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours	C.c. $Na_2S_2O_3$ per 5 c.c bleach	Grams O_2 used per gram sample	Hours
16.8		0	16.8		0	16.8		0	16.8		0
16.02	.002213	15"	15.36	.008305	30"	15.26	.01779	1'	14.64	.0504	2' 50"
13.64	.00623	30"	14.64	.01252	45"	13.96	.033	2'	7.9	.2092	4' 30"
12.08	.01368	45"	13.9	.01692	1'	9.52	.08495	2' 30"	4.08	.2991	4' 45"
2.44	.04175	1'	11.62	.03018	1' 15"	2.76	.1641	2' 55"	3.02	.3241	5'
.38	.04666	1' 10"	3.04	.08036	1' 30"	.66	.1886	3' 15"	2.66	.342	5' 15"
..05	.04871	1' 20"	.78	.08357	1' 40"	.02	.1961	3' 35"	1.64	.3566	5' 30"
			.06	.09778	1' 50"				1.14	.3684	5' 45"
									.52	.3742	6' 15"
									.06	.3938	6' 45"

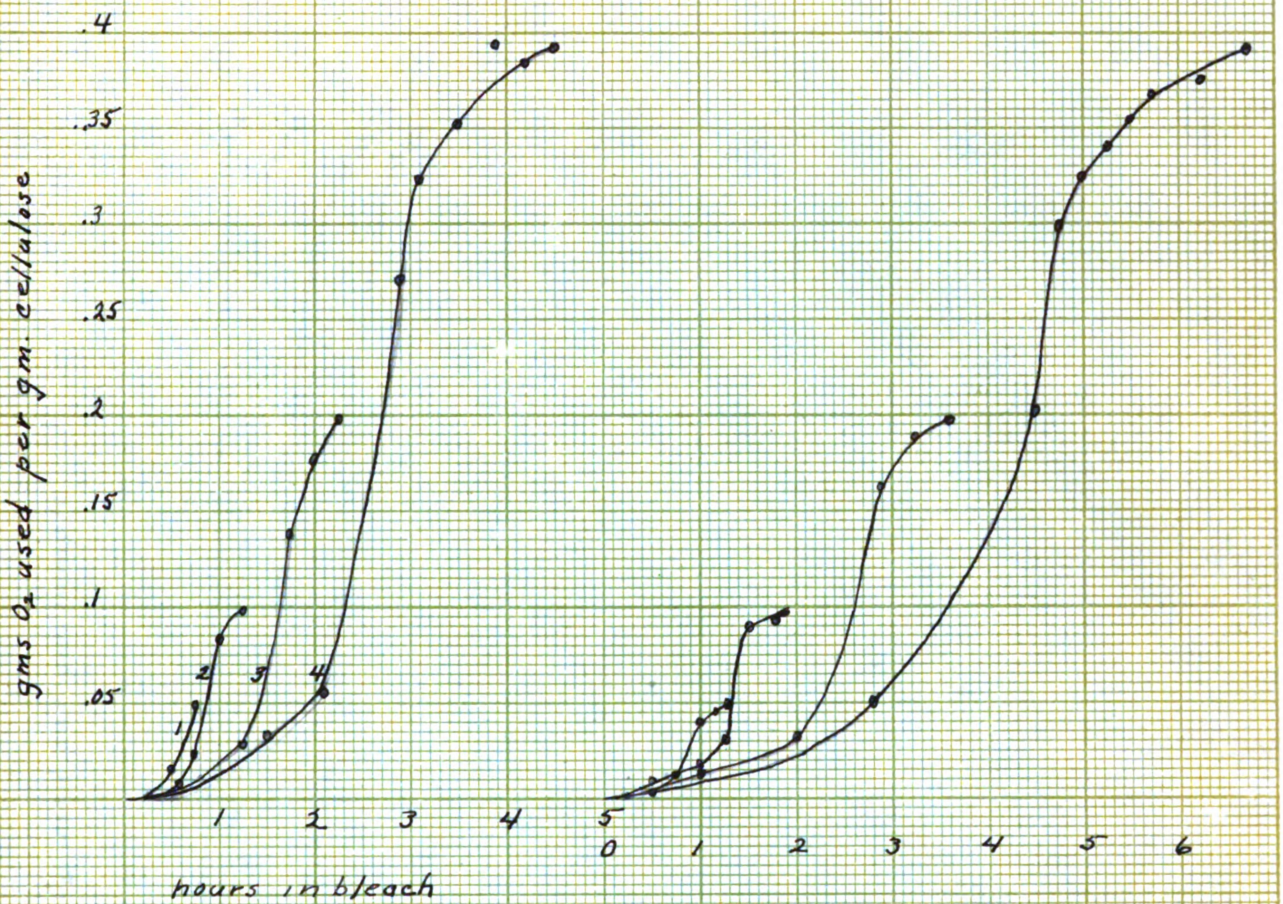


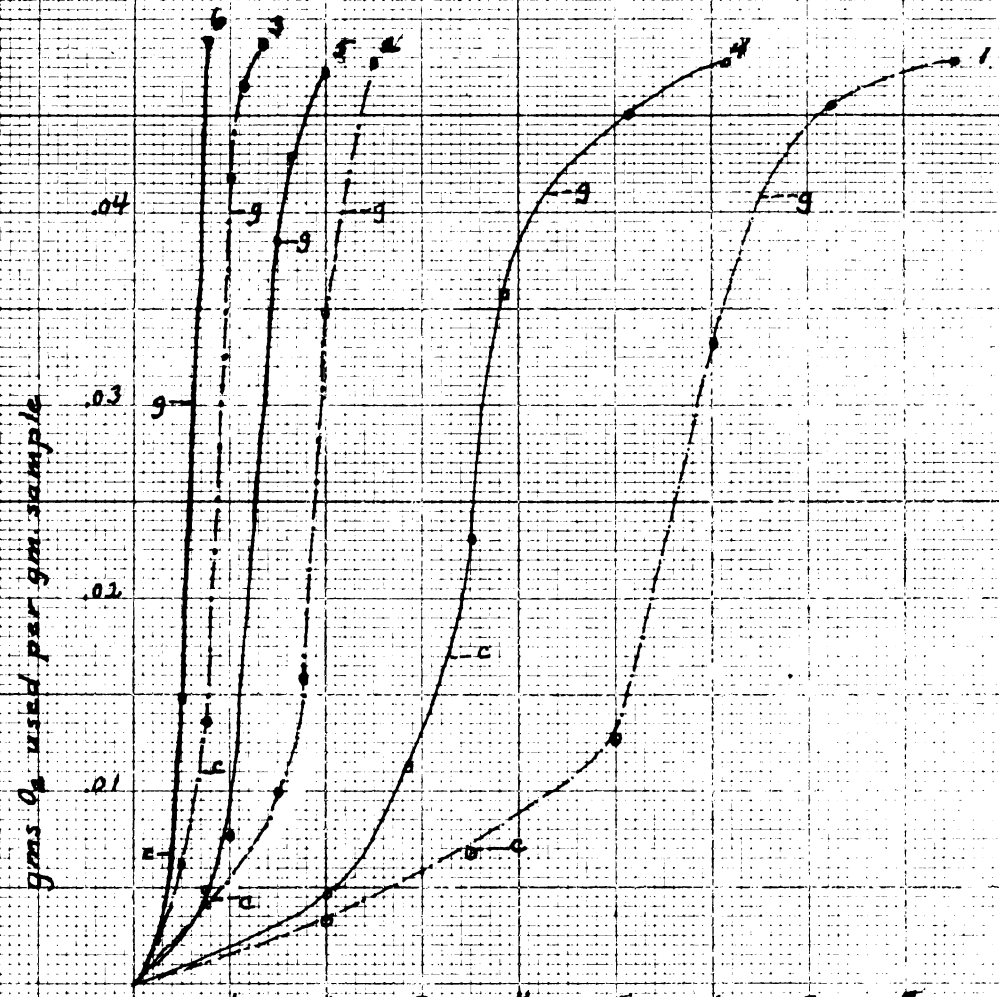
Table
Distilled water bleach 60° C

1. 5 gms cellulose
2. 2.5 " "
3. 1.25 " "
4. .62 " "

Table
Lime water bleach 60° C

1. 5 gms cellulose
2. 2.5 " "
3. 1.25 " "
4. .62 " "

FIGURE 5

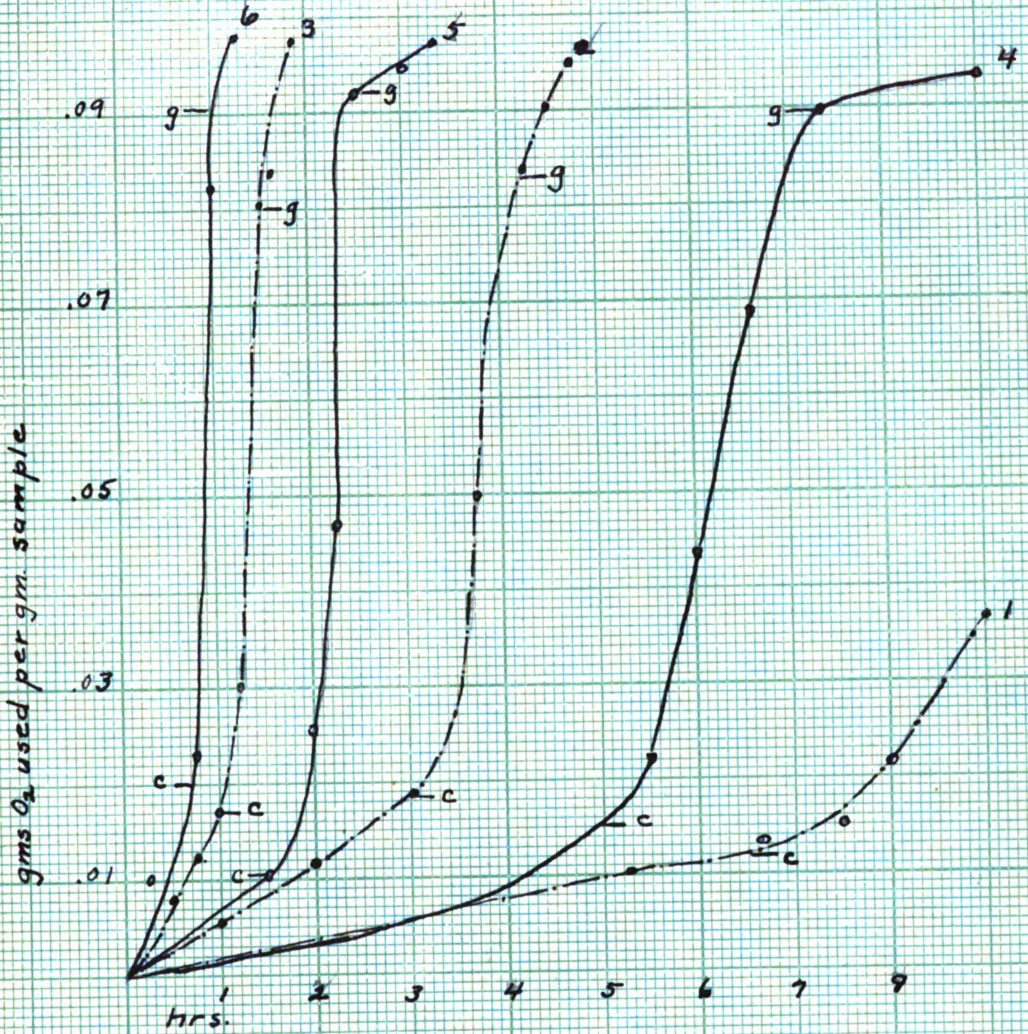


Tables

1. 5 gms. cellulose at 40°C Lime water bleach
2. 5 gms. " " 50°C " " "
3. 5 gms. " " 60°C " " "
4. 5 gms. cellulose at 40°C Distilled water bleach
5. 5 gms. " " 50°C " " "
6. 5 gms. " " 60°C " " "

c - cloudiness g - gassing

FIGURE 6

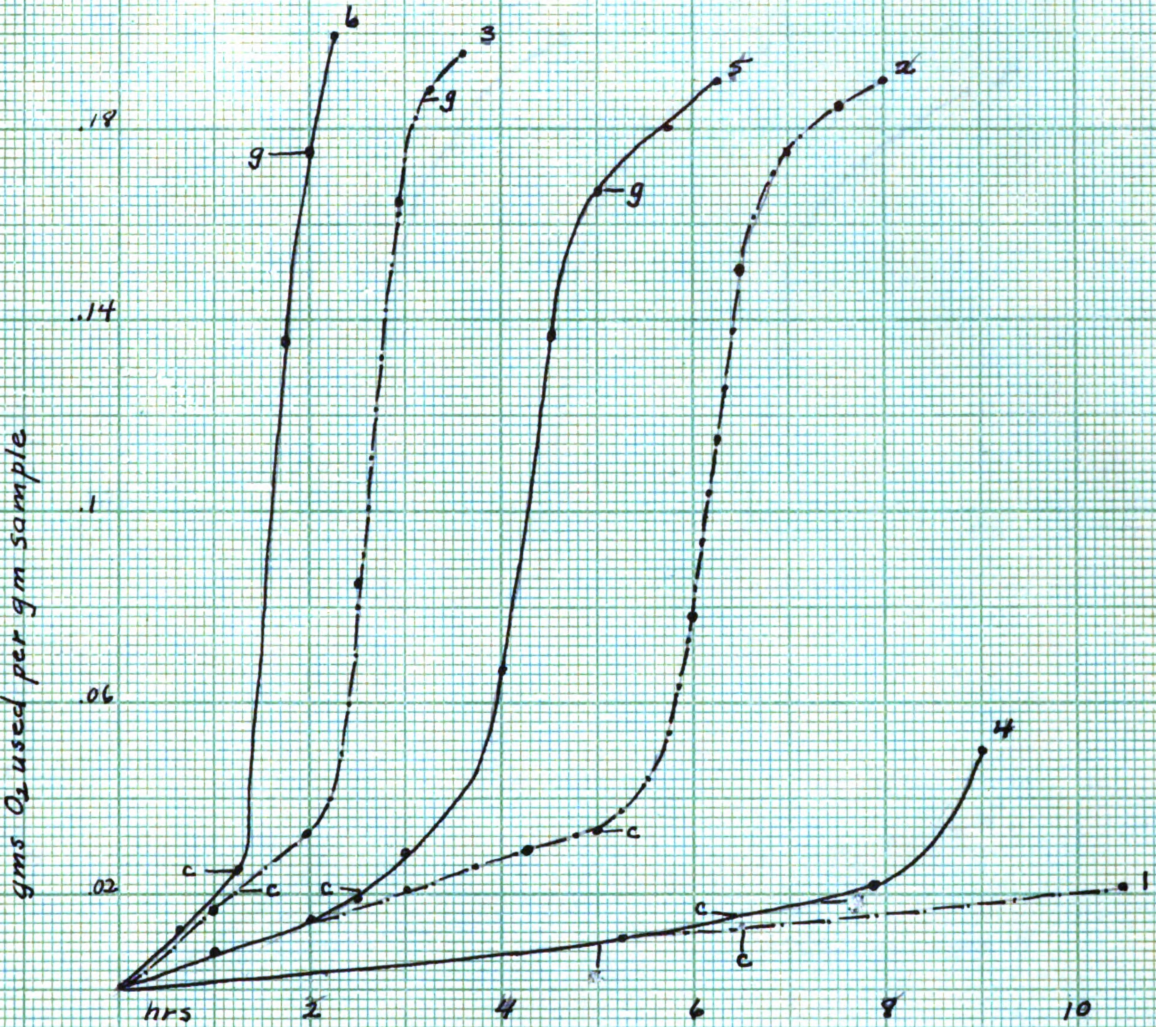


Tables

1. 2.5 gms. cellulose in Lime water bleach at 40°C
2. 2.5 gms. " " " " " " 50°C
3. 2.5 gms. " " " " " " 60°C
4. 2.5 gms. cellulose in Distilled water bleach at 40°C
5. 2.5 gms. " " " " " " 50°C
6. 2.5 gms. " " " " " " 60°C

c - cloudiness g - gassing

FIGURE 7

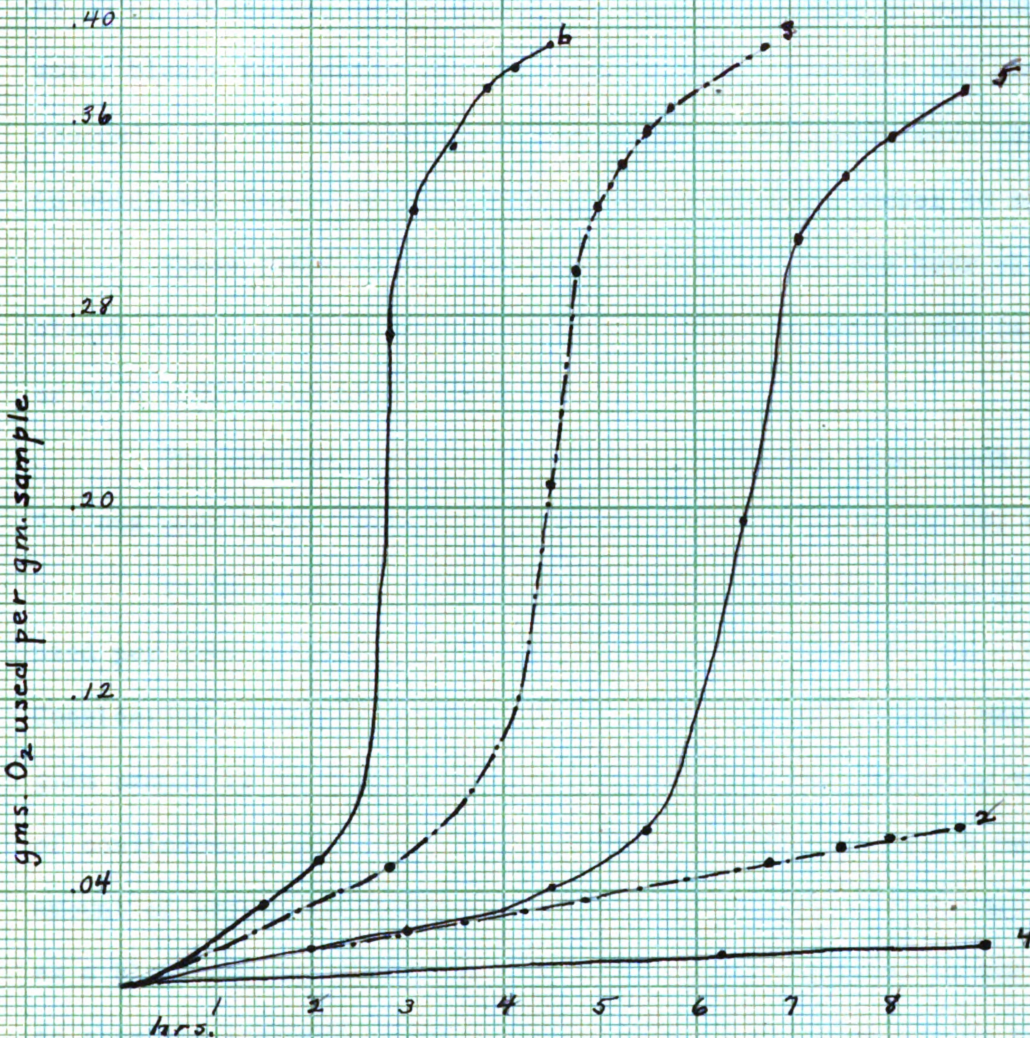


Tables

1. 1.25 gms. cellulose in Lime water bleach at 40°C
2. 1.25 gms. " " " " " " 50°C
3. 1.25 gms. " " " " " " 60°C
4. 1.25 gms. cellulose in Distilled water bleach at 40°C
5. 1.25 gms. " " " " " " 50°C
6. 1.25 gms. " " " " " " 60°C

c – cloudiness g – gassing.

FIGURE 8



Tables

1. ———
2. .62 gms. cellulose in Lime water bleach at 50°C
3. .62 gms. " " " " " " 60°C
4. .62 gms. cellulose in Distilled water bleach at 40°C
5. .62 gms. " " " " " " 50°C
6. .62 gms. " " " " " " 60°C

FIGURE 9

Effect of Previous Modification of Cellulose

The modified cellulose was prepared by oxidizing 2.5 gram samples at 50°C. Distilled water bleach was used for series 50 - 57 and lime water bleach for series 60 - 68. At suitable intervals the reaction was stopped. In this way two series of modified cellulose were obtained in which the degree of modification increased from member to member.

These modified celluloses were treated for one hour with fresh bleach (90 c.c. on a sample) at 50° C. This is called the (a) series or 50 a - 57 a and 60 a - 68 a.

The residues from 50 a - 57 a were treated with fresh bleach. for one more hour. This is called the 50 b - 57 b or the (b) series.

In Table XIV a comparison is made between the grams of oxygen used per gram of cellulose in the 50 -57 series and the 50a - 57a series. Considering number 52 and 52a, it is seen that more oxygen was used per gram sample in the additional one hour than in the preceding two hours of continuous bleaching. Since unmodified cellulose used a certain amount of oxygen per gram in one hour, this figure (.0065) was regarded as a blank and was subtracted from the figures obtained in the (a) series to show the increase in the amount of oxygen consumed due to previous modification of the cellulose. The same calculations were made on the (b) series with similar results. From these figures it was concluded that the partially oxidized cellulose was more easily attacked by oxygen and that this susceptibility to further oxidation increased with the degree of previous oxidation. The table shows that this increased amount of oxygen consumed caused a great increase in the per cent loss in weight of the sample.

Table XV shows a similar comparison of results obtained from lime water bleach. The effect of previous oxidation of the cellulose is the same in this series as in the 50 - 57 series. The most notable difference is shown in the time factor. It has been mentioned before that the action of lime water bleach is slower than the action of distilled water bleach.

In Tables XVI and XVII the following data was calculated on the basis of the weight of the original sample :

(1) total grams of oxygen used in all the bleaches,

(2) total loss in weight in all the bleaches,

(3) total grams of oxygen used per gram loss in weight,

(4) total per cent loss in weight.

In Figure 10 it is shown that, more oxygen is required to cause 1 gram loss in weight in 2 hours intermittent bleaching (50a) than is required to produce this loss in weight in 2 hours continuous bleaching. This is true also of (50) and (50b). The first part of these curves is explained by two facts. (1) Bleach liquor that has been used one hour is more alkaline than bleach that has been used 2 hours. It has been shown that alkalinity inhibits the oxidation process. (2) The first few minutes of the bleaching period are required for the temperature of the liquor to change from room temperature to 50°C. It has been shown that the rate of reaction is greatly influenced by changes in temperature.

As the curve of 50 - 57 turns upward at the critical period, oxygen is being used to further oxidize soluble products. When these soluble products are removed, more of the oxygen from the bleach liquor acts on the insoluble but modified cellulose. Since the amount of soluble products that could accumulate in one hour would be comparatively

small, the decrease in the amount of oxygen required to produce a definite loss of weight indicates that the modified cellulose is more easily oxidized to soluble material, and that this effect increases with the degree of modification.

This conclusion is not in accordance with the results of Clibbens and Ridge *. However, they used lower temperatures and a weaker bleach.

The same reasoning applies to the curves shown in Figure 11.

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* Clibbens and Ridge, Journal of Textile Institute, Vol. XVIII, No.4, April 1927.

Table XIV

Distilled Water Bleach at 50° C.

No.	Hours in bleach	Grams O_2 used per gram cellulose	O_2 used per gram cellulose in (a)	O_2 per gram cellulose in (a) less .0065	O_2 per gram cellulose in (b)	O_2 per gram cellulose in (b) less.0065	Grams O_2 used grams loss	Grams O_2 used grams loss (a)	Grams O_2 used grams loss (b)	% loss weight	% loss weight (a) series	% loss weight in (a) series less1.235
50	1	.0065	.0076	.0011	.0156	.0091	.659	3.736	.452	1.235	.203	
51	1½	.0098	.0108	.0043	.0312	.0347	.481	.7755	.3597	2.053	1.396	.161
52	2	.0128	.0222	.0157	.0583	.0518	.445	.5615	.4938	3.125	3.958	2.723
53	2¾	.0175	.0674	.0609	.0990	.0925	.3055	.5486	.4627	5.72	12.29	11.055
54	2¾	.0500	.0854	.0789	.1073	.1008	.52	.4628	.5701	9.62	18.45	17.225
55	3	.0855	.0970	.0905	.		.58	.		14.68		
56	3½	.0948	.1095	.1030	.1271	.1216	.562	.5375	.567	16.87	20.37	
57	4	.0999	.111	.1045	.1251	.1196	.564	.5176	.5848	17.72	21.4	20.165

	% loss weight in (b) series	% loss weight in (b) series minus 1.235
50	3.44	2.205
51	8.68	7.445
52	11.81	10.675
53	21.4	20.165
54	18.83	17.595
55		
56	22.42	21.185
57	21.41	20.175

Table XV

Lime Water Bleach at 50° C.

No.	Hours in bleach	O_2 used per gm. cellulose	O_2 used per gm. cellulose in (a) series	O_2 per gm. cellulose (a) less .00961	O_2 used per gm. loss weight	O_2 used per gm. loss weight in (a)	% loss weight	% loss weight in (a)	% loss weight in (a) less 1.34
60	1	.00961			.7177		1.34		
61	2	.01519	.0141	.00449	.4842	.8618	3.13	1.63	.29
62	3	.01918	.0141	.00449	.4873	.7884	3.93	1.79	.45
63	3½	.02428	.0172	.00759	.541	.6323	4.49	2.72	1.38
64	4	.04079	.0265	.01689	.6093	.5066	6.69	15.22	3.88
65	4½	.07566	.0843	.07369	.662	.5116	11.43	16.48	15.14
66	5	.08776	.0405	.03089	.6532	.3229	13.43	12.54	11.24
67	5½	.09469	.0756	.06599	.6017	.4367	15.74	17.30	15.96
68	6	.09806	.0915	.08189	.5786	.4635	16.95	19.73	18.39

Table XVI

Distilled Water Bleach at 50°C.

No.	X: Weight of cellulose at start grams	X: Grams of O_2 used	X: Time in hours	X: Weight of cellulose left	X: Weight of cellulose used in (a) series	X: Grams O_2 used by cellulose (a) series experimental	Y: Weight O_2 which column X would use in 1 hr. calculated	Y: Weight of sample in X after 2nd bleaching	Y: Total O_2 used	Y: Total loss in weight	Y: Total O_2 used ÷ gms. loss weight
50	2.5039	.0162	1	2.4730	2.4628	.0187	0.0188	2.4578	.0349	.0461	.7570
51	2.5082	.0247	1½	2.4567	2.4578	.0266	.0266	2.4235	.0513	.0847	.6057
52	2.5089	.0308	2	2.4305	2.4357	.0541	.0541	2.3393	.0849	.1696	.5006
53	2.4997	.0712	2½	2.3567	2.3503	.1585	.1586	2.0613	.2297	.4384	.5240
54	2.5103	.125	2¾	2.2688	2.2487	.1921	.1938	1.8502	.3171	.6601	.4804
55	2.503	.214	3	2.1353	2.1140	.2146	.2168		.4286		
56	2.504	.2374	3½	2.0815	2.0505	.2245	.2279	1.6575	.4619	.8465	.5457
57	2.4998	.2498	4	2.0569	2.0007	.2220	.2282	1.6167	.4718	.8831	.5343

No.	O_2 per gm. loss weight in 50 series	Weight of cellulose used for (b) series grams	O_2 used by this weight in 1 hour	O_2 used if weight were Y	Total O_2 used in 3 bleaches	Weight after 3 bleaches	Total loss: weight in 3 bleaches	Total figures gms. O_2 used ÷ gms. loss weight
50	.659	2.453	.0382	.0382	.0731	2.3932	.1107	.6603
51	.481	2.412	.0753	.0756	.1269	2.2132	.2950	.4302
52	.445	2.3287	.1357	.1363	.2212	1.9917	.5172	.4277
53	.3055	2.0233	.2003	.2041	.4338	1.6202	.8795	.4932
54	.52	1.7178	.1844	.1986	.5157	1.5018	1.0085	.5114
55	.58							
56	.562	1.5631	.1986	.2106	.6725	1.2859	1.2181	.5521
57	.564	1.4557	.1882	.2024	.6742	1.1096	1.3902	.4850

Table XVII

Lime Water Bleach at 50° C.

No.	X: Weight of cellulose at start	X: Gms. of O_2 used	Time	X: Weight of cellulose left	X: Weight of cellulose used in (a) series	X: Gms. O_2 used in (a) series	Y: Weight of O_2 which column X would use in 1 hr.	Y: Weight of sample in X after 2 nd bleaching	Y: Total O_2 used	Total loss in weight	Total O_2 used Gms. Loss weight	% loss total
60	2.5027	.0243	1	2.4692	2.47			2.4348		.0687		2.75
61	2.5050	.0383	2	2.4262	2.432	.0343	.0343	2.3922	.0726	.1184	.6132	4.73
62	2.5015	.0482	3	2.4031	2.4018	.0339	.0339	2.3588	.0821	.1414	.5806	5.65
63	2.5065	.0611	3½	2.3940	2.3815	.0411	.0411	2.3265	.1022	.1775	.5758	7.08
64	2.5093	.1026	4	2.3413	2.3218	.0619	.0619	2.2190	.1645	.2892	.5688	11.53
65	2.5040	.1897	4½	2.2178	2.1955	.1851	.1870	1.8523	.3767	.6480	.5813	25.88
66	2.5033	.2200	5	2.1670	2.1446	.0868	.0877	1.8952	.3077	.6052	.5084	24.18
67	2.5029	.2373	5½	2.1090	2.0946	.1583	.1594	1.7442	.3967	.7563	.5245	30.22
68	2.5092	.2464	6	2.0839	2.0491	.1874	.1906	1.6727	.4370	.8296	.5267	33.07

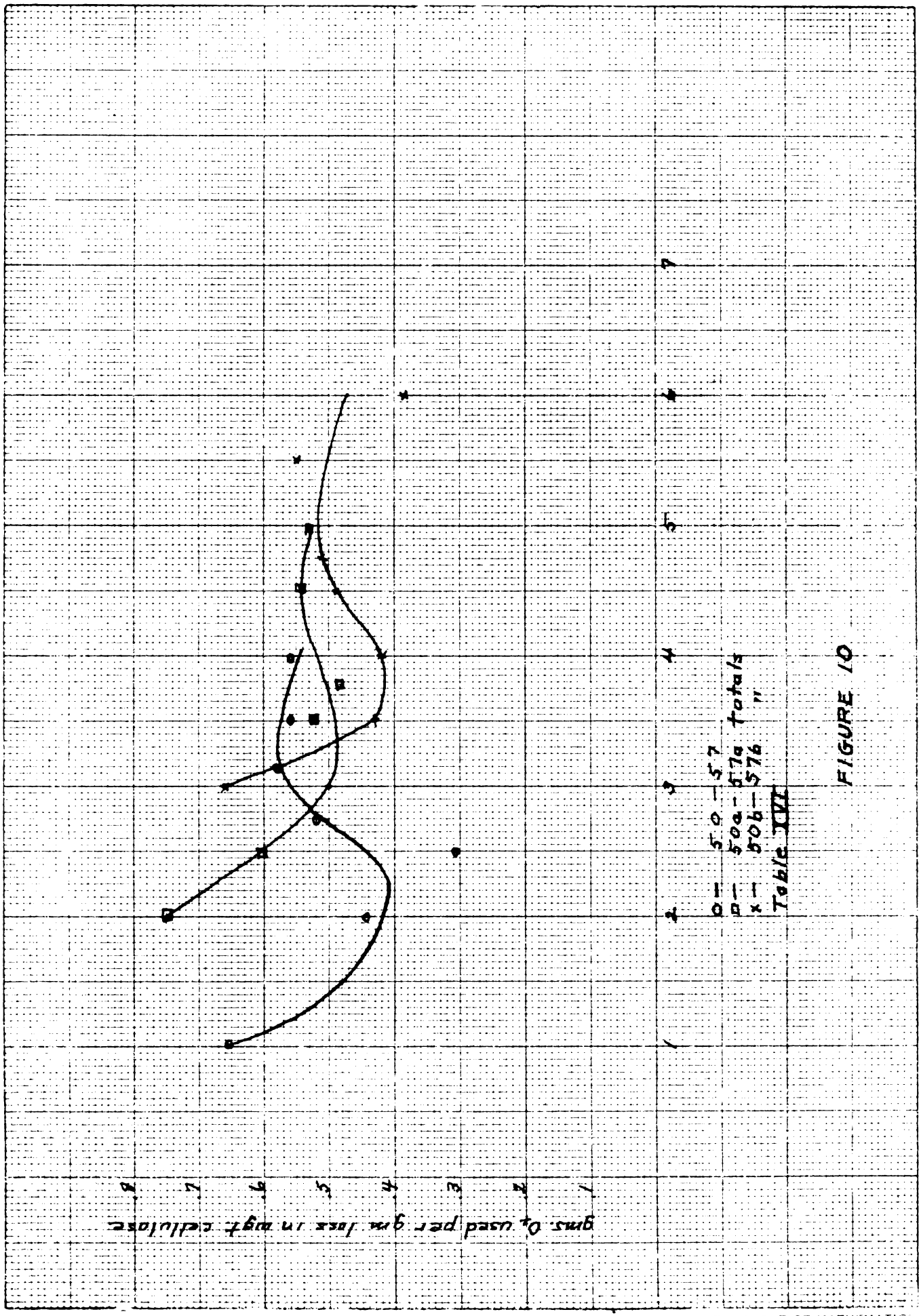


Table XVII

FIGURE 10

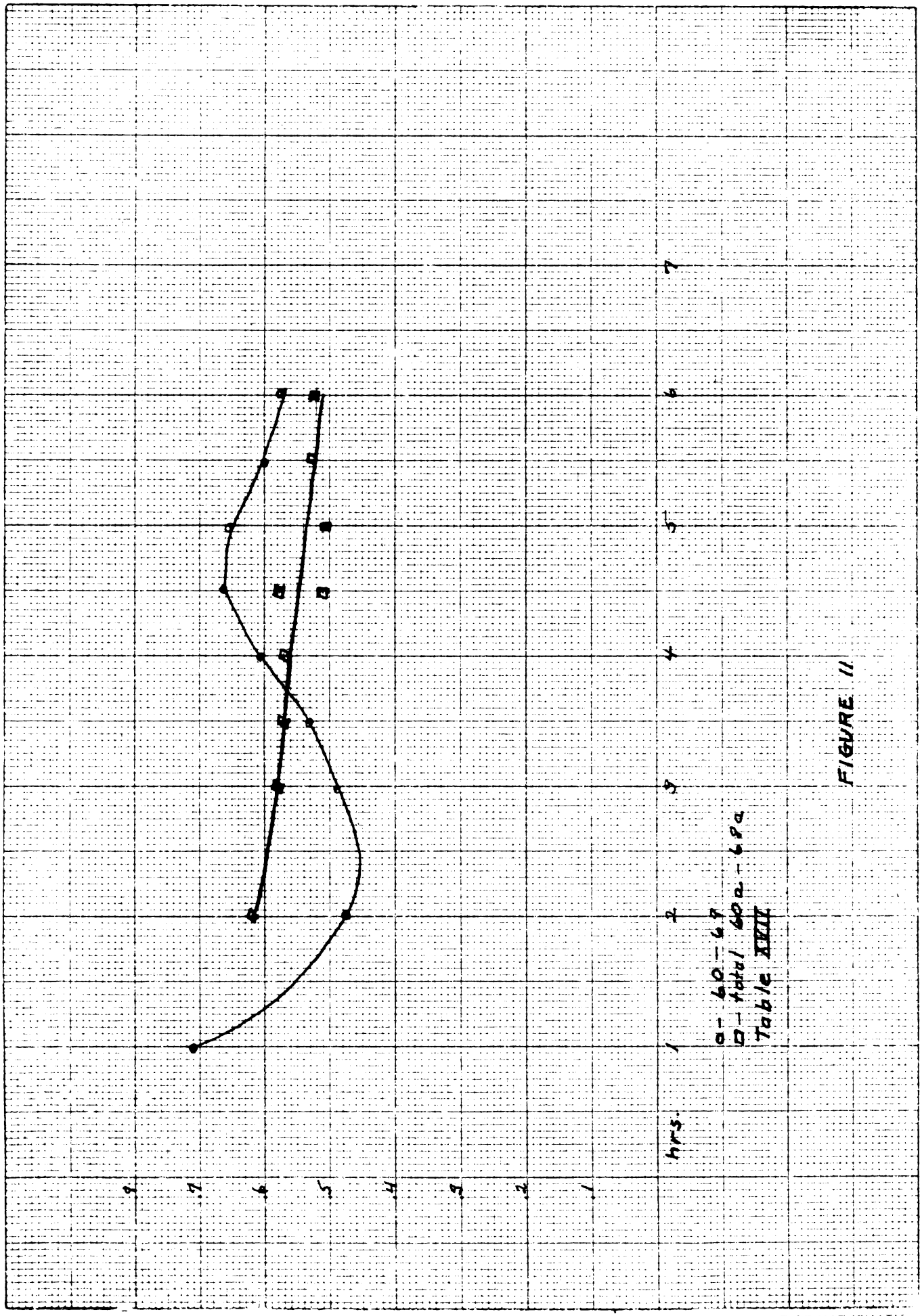


Table XXIII

FIGURE 11

Study on Acidity of Bleach

Twenty cubic centimeters of the bleach filtrate was decomposed by boiling with 10 cubic centimeters commercial hydrogen peroxide solution. It was then cooled and titrated with sulfuric acid and sodium hydroxide using methyl orange as an indicator. The normality of the acidity or alkalinity of the bleach was calculated.

In every series studied the alkalinity of the bleach decreased gradually for a time, but at the beginning of the critical period the bleach liquor became acid and the acidity increased rapidly for a time. Toward the end of the critical period the acidity decreased. These results given in Tables XVIII to XXI are shown graphically in Figure 12.

Table XVIII

Series 50 - 59. 2.5 grams cellulose in distilled water bleach at 50°C.

No.	Hours in bleach	Alkalinity	Acidity
50	1	.006815N	
51	1½	.006580N	
52	2	.	.001789N
53	2½		.01531 N
54	2¾		.02798 N
55	3		.01692 N
56	3' 34"		.009125N
57	4		.008045N

Table XIX

Series 50a -58a. Modified cellulose treated for 1 hour with fresh distilled water bleach

No.	Hours in bleach	Alkalinity	Acidity
50a		.004864N	
51a			.00481N
52a			.0175 N
53a			.02141N
54a			
55a			.01177N
56a			.01162N

Table XX

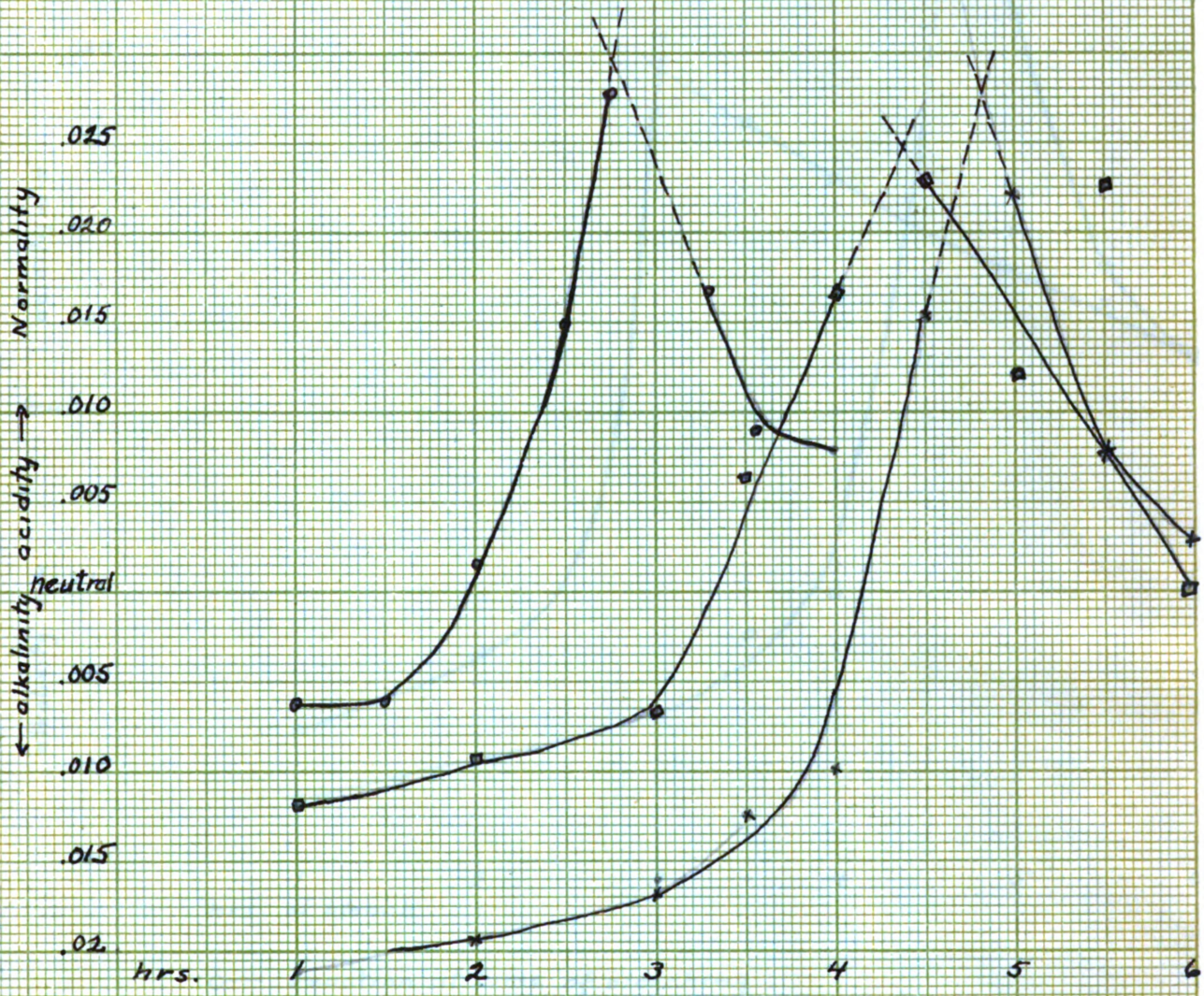
Series 60 - 2.5 grams of cellulose in lime water bleach at 50°C.

No.	Hours in bleach	Alkalinity	Acidity
60	1	.01200 N	
61	2	.009595N	
62	3	.00661 N	
63	3½		.000609N
64	4		.01658 N
65	4½		.02336 N
66	5		.01201 N
67	5½		.00228 N
68	6		.0005 N

Table XXI

Time - Water bleach filtrates from 1926 series at 50°C

	At time of bleaching			Three days later	
No.	Time in bleach	Alkalinity	Acidity	Alkalinity	Acidity
1	1	0.02144N		.01768N	
2	2	.01954N		.01386N	
3	3	.01699N			.01679N
4	3½	.01234N			.01601N
5	4	.01009N			.01312N
6	4½		.01562N		.0070 N
7	5		.02233N		.01038N
8	5½		.0081 N		.0061 N
9	6		.0031 N		.0029 N



o - series 50 - 57 Table XVIII
□ - " 60 - 68 " XX
× - " 1 - 9 " XXI

FIGURE 12

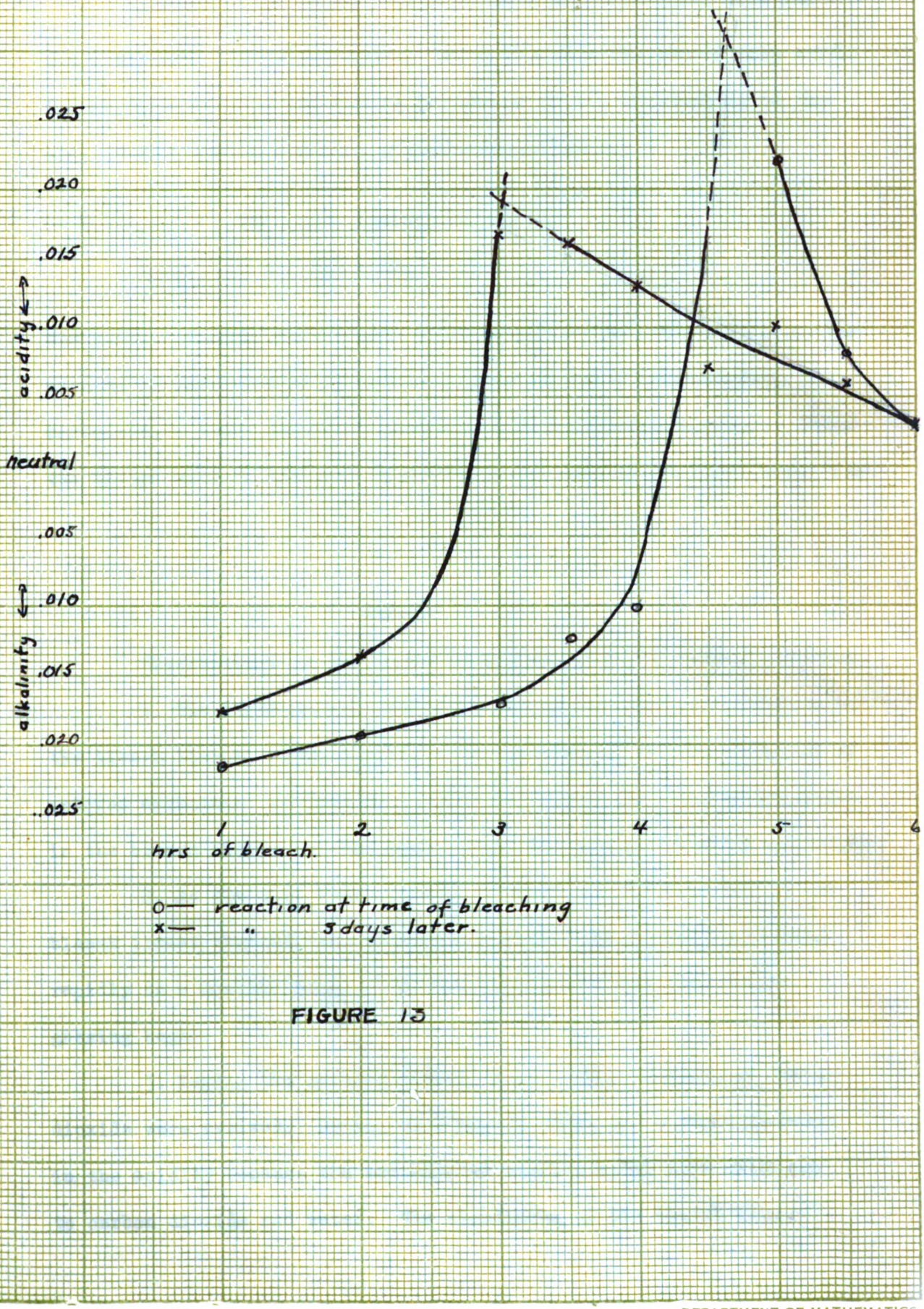

.025
.020
.015
.010
.005
acidity ←→
neutral
.005
.010
.015
.020
.025
alkalinity ←→
1
2
3
4
5
6
hrs of bleach.
o— reaction at time of bleaching
x— " 3 days later.

FIGURE 13

One series of bleach filtrates were kept for three days and the alkalinity determined again. Every filtrate had become more acid. The first members of the series had become cloudy on standing in the air. The following reaction explains these facts.

$$Ca\,H_2(CO_3)_2 + CO_2 \rightleftharpoons CaCO_3 + H_2CO_3$$

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

The soluble calcium bicarbonate gives and alkaline reaction. When the calcium is precipitated by carbon dioxide in the air as calcium carbonate, a small amount of carbonic acid is left in solution. These two things work in the same direction to produce an increase in acidity.

Summary

Observations on the general progress of the bleaching reaction.

1. The first marked change was the appearance of cloudiness in the bleach liquor. This cloudiness was due mainly to the formation of calcium carbonate, indicating a reaction between the calcium hydroxide in the bleach liquor and the carbon dioxide from the oxidized cellulose.

2. At the time when cloudiness appeared, the reaction of the bleach liquor changed from alkaline to acid. The acidity increased rapidly to a maximum point which was reached a short time before gassing began.

3. During the gassing period, considerable amounts of carbon dioxide were evolved. During this period there was a rapid decrease in the acidity because the accumulated organic acids were oxidized to carbon dioxide and water. The cloudiness of the bleach liquor

also decreases during this period, because the large amount of carbon dioxide converts the calcium carbonate to the more soluble bicarbonate.

The critical period shows the following characteristics:

1. A marked increase in the rate of oxygen consumption per gram of cellulose in a unit time.

2. A marked increase in the amount of oxygen required to cause a given loss of weight of the cellulose. This was because much of the oxygen was being used in the further oxidation of soluble products.

3. A marked increase in the per cent solubility of the cellulose in the bleach solution.

4. A greater increase in the per cent solubility of the residue from the bleach in 3% NaOH solution, which indicates the rapid formation of oxycellulose during this period.

5. The amount of oxygen disappearing from the bleach per hour increased greatly, i.e., the rate of oxygen consumption increased.

The rate of the oxidation of cellulose is greatly influenced by changes in temperature. A 10°C rise in temperature more than doubles but does not triple the speed of the reaction.

Cellulose that has suffered attack by oxidizing agents is more susceptible to further attack, and this susceptibility increases with the degree of previous oxidation.

A study of the progressive

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