1

OFFICE OF THE QUARTERMASTER GENERAL

MILITARY PLANNING DIVISION

RESEARCH AND DEVELOPMENT BRANCH

TEXTILE SERIES - REPORT NO. 33

ACTION OF ALKALI UPON CELLULOSE

BY DR. ALBERT SCHAEFFER

A research report prepared in the Textile Application Laboratory, I. G. Farben, Hoechst and translated at the request of the "Textile Team" of the Research and Development Branch, Office of The Quartermaster General.

Original document obtained during field investigation conducted under the direction of Headquarters, Theater Service Forces, European Theater (Main) Office of the Theater Chief Quartermaster (FWD), Technical Intelligence Branch.

apr. 1947

Released for Public Information
by
The Office of the Publication Board
U.S. Department of Commerce

FOREWORD

In view of the necessity for conservation of German textile materials, Dr. Albert Schaeffer of the Textile Application Laboratories, I. G. Farbenindustrie, Hoechst, recognized the importance of fundamental studies with the aim of increasing the durability of cellulosic fibers such as cotton and rayon. A lengthening of the wear life of such materials would be a boon to the war economy of his country both by easing the load on the synthetic fiber industry and by extending the availability of the depleted cotton supply.

Dr. Schaeffer's work included a systematic investigation of alkalies and their effect upon cellulose. Such chemicals are used in one form or another in various stages of textile processing and are also present in both home and commercial laundering compounds. A search of the literature indicated that alkalies act upon cellulose to widely varying degrees. Some studies showed them to be quite harmful and others gave evidence that their effect is negligible. Data have been collected at different steps of the washing and laundering processes under various conditions to determine the action of the single components of the cleansing agents on cottons and rayons.

The information compiled by Dr. Schaeffer and published in this report in its entirety should prove helpful to textile manufacturers, laundries, and manufacturers of wet processing and washing agents. The commercial fibers represented as Staple Fibers No. 1, No. 2, and No. 3 have been identified, respectively, as Vistra, Cuprama, and Lanusa. Staple fibers No. 4 and No. 6 have not been identified, but are believed to be viscose-process rayons.

It is believed that correct and reliable information has been obtained from the German scientists, but it should be understood that the United States Government is not responsible for any inaccuracies, nor can liability be assumed for any patent violations which may result from the use of the processes described herein.

STEPHEN J. KENNEDY
Chief, Textile and Leather Products
Section

April 1947

TABLE OF CONTENTS

ACTION OF ALKALI UPON CELLULOSE

Part I

Investigation of the Effects of Common Laundering Alkalies

INTRODUCTION

There are many references in the literature describing the action of alkalies on cellulosic fibers in concentrations and under conditions encountered in the washing process. However many different viewpoints are represented in this work. There were variations in the fibers used and the conditions under which they were treated as well as in the methods by which the effects were measured. Therefore it is clear that the results of these experiments are often different and sometimes even contradictory. It is impossible to determine clearly from the literature the conditions under which the alkalies deteriorate the cellulosic fibers to a greater or less extent. However, in all publications it is emphasized that a mild alkaline treatment of the fibers is necessary both in the processes of manufacture and in commercial or home laundries.

Therefore it appeared necessary to undertake a systematic examination of the entire subject of degradation of cellulosic fibers by alkali to determine the effect of each step in the process. Study was also made of various conditions of laundering and of the action of the individual components of washing agents.

PROCEDURE

In all our experiments the fibers were treated in a boiling bath. Since a small number of alkali treatments have only a slight influence on the chemical and physical properties of the cellulosic fibers, it was decided to subject them to 50 consecutive half-hour boils. After each boil the fibers were rinsed until neutral, centrifuged, dried for one hour at 65° C., exposed for some time in the open air to cool, and then placed in a fresh bath. In this manner the fibers could be boiled three to four times each day and the 50 treatments could be completed in 15 to 18 days.

Distilled water was used in all cases for preparing the baths and rinsing the fibers in order to eliminate the influence of hard water on the test results. Thus were secured unobjectionable and uniform data on the action of alkalies upon cellulosic fibers.

The treatments and examinations of the fibrous material were not confined to one kind of fiber, but were extended to different commercial brands of regenerated cellulose and in some cases to cotton. However, as it is not the aim of the present examination to evaluate the different commercial fibers, in this report they are designated by numbers, rather than by trade names.

The following chemical and physical methods of examination were used for the investigation of the fibers before and after treatment:

Chemical Methods of Examination

1. Decomposition of the Fiber. After the first ten and then after each tenth boil the bath was filled to its original volume and the decomposed and dissolved cellulose was quantitatively determined by oxidation with potassium bichromate and sulphuric acid. These products of decomposition were calculated as cellulose $(C_6H_{10}O_5)_x$.

2. Degree of Polymerization or Damage Factor (Schädigungszahl).* After the first and then after each tenth boil a sample of the fiber was withdrawn and its damage factor determined.

3. Absorption of Alkali by the Fiber. The quantity of alkali in the bath was determined by titration before and after the treatments. Thereby the quantity of alkali absorbed by the fiber during the treatment could be ascertained.

4. Ash Contents of the Fiber. Determinations were made before the first and after the 50th treatment.

Physical Methods of Examination

1. Tensile Strength of the Wet Fiber and Elongation at Break of the Wet Fiber. The determinations were made before and after the first and after each 10th treatment.

2. Microscopical Examinations. Photomicrographs were made before the first and after the 50th treatment.

Manner of Representing the Experimental Results

In some cases the experimental results were presented in tables, but mainly in the form of curves to ensure clarity.

---

* Further information regarding the damage factor appears in the following references:

Eisenhut, O. Mel. Tex. Ber. 22, 424-6 (1941)
Vetter, H. " " " 22, 426-8 (1941)
Chem. Abs., 38, 2212 (1944)

First Series of Experiments

Effect of the Ratio of Goods to Liquor. In both home and commercial laundries, the ratio of goods to liquor varies with the prevailing arrangements and conditions. Therefore, it was important to determine the influence this ratio has on the action of alkalies upon the cellulosic fibers. For example, using the same concentration of alkali in grams per liter, a 1 to 100 ratio of goods to liquor would give 20 times as much alkali for the same weight of fiber as a 1 to 5 ratio. In other words, it must be determined whether the change in the chemical and physical properties of the cellulosic fibers is dependent primarily on the concentration of the alkaline solution or on the ratio between the total alkali present and the weight of the fiber present.

To determine this, experiments were made with the following proportions of goods to liquor:

Series A	Series B
1:10	1:10
1:20	1:8
1:50	1:5
1:100	

Fibrous material: Staple fiber No. 1 (Viscose type)
Staple fiber No. 2 (Cuprammonia type)
Staple fiber No. 3
Staple fiber No. 4

Treatment: 50 boils each of 1/2 hour; 1 g per liter of analytically pure anhydrous sodium carbonate; 1,000 cc of bath in each case.

Determinations: Quantity of decomposed and dissolved cellulose, damage factor, tensile strength of the wet fiber, elongation at break of the wet fiber, and absorption of alkali by the fiber.

Results. The results of these tests on spun rayon made from staple fiber 2 are given graphically in Figures 1 to 8.

The absorption of alkali is given in the following table:

	Ratio	mg Na_2O per 100 g fiber after each boil
Series A	1:10	121
	1:8	117
	1:5	125

Fiber Degradation

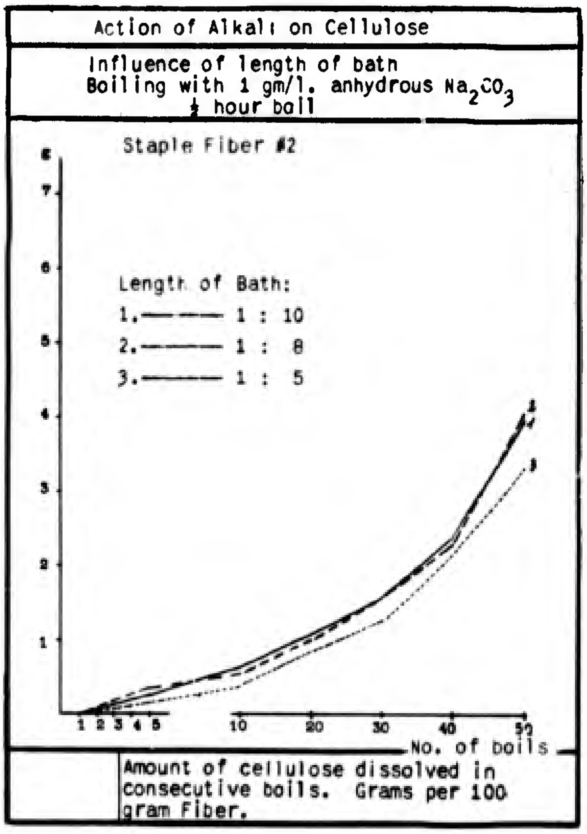


Figure 1

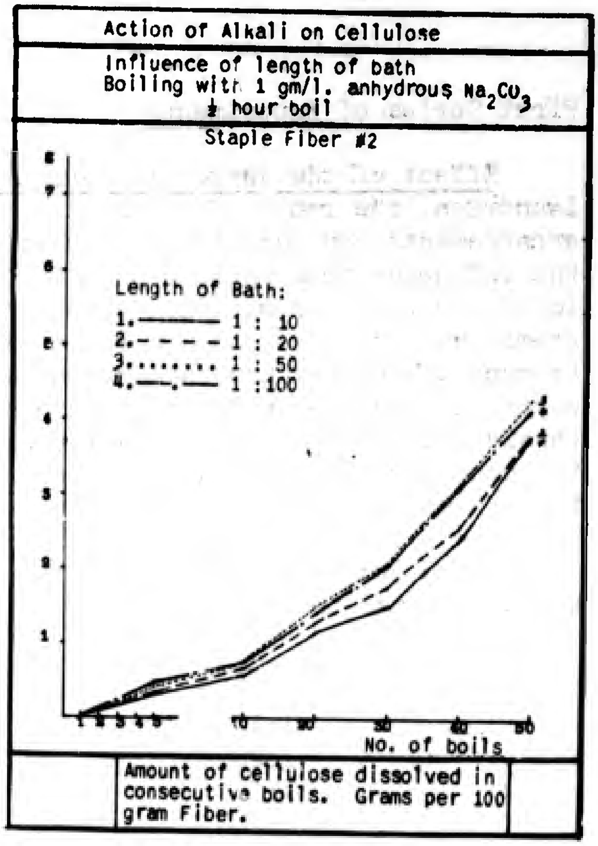


Figure 2

Damage Factor

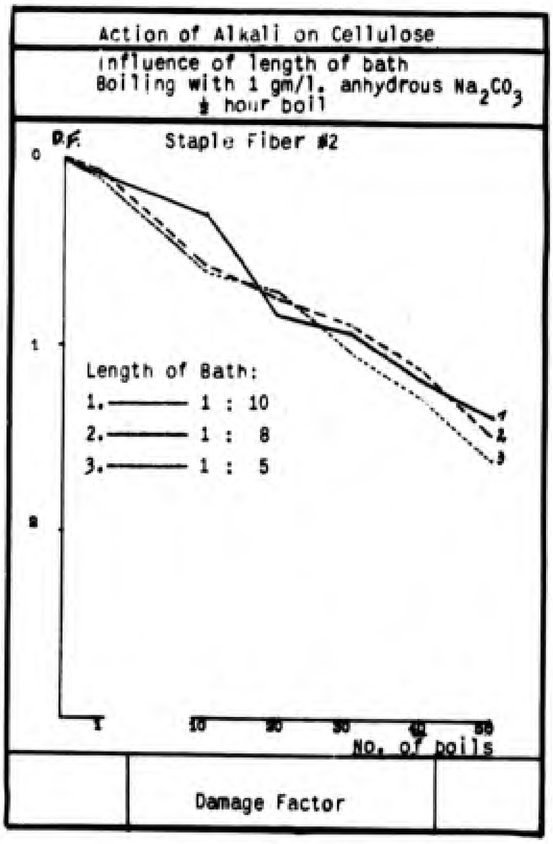


Figure 3

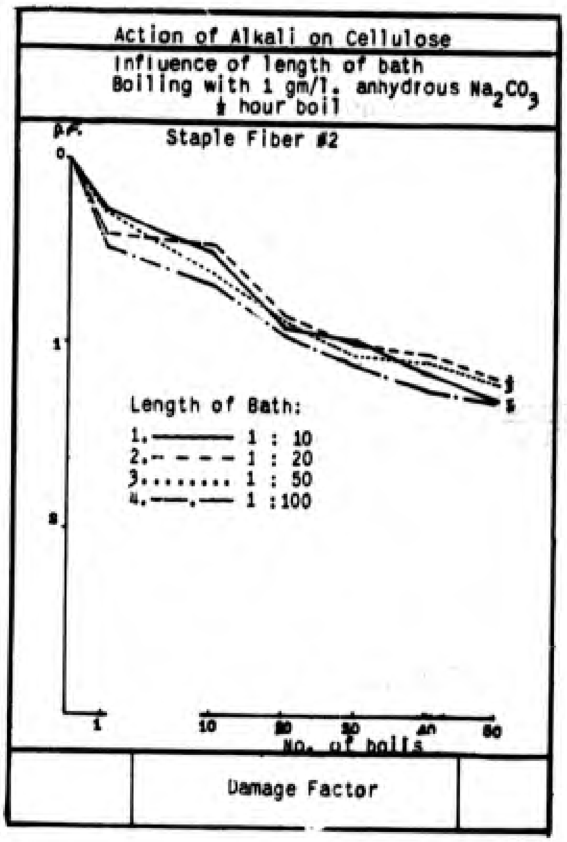


Figure 4

Tensile Strength of the Wet Fiber

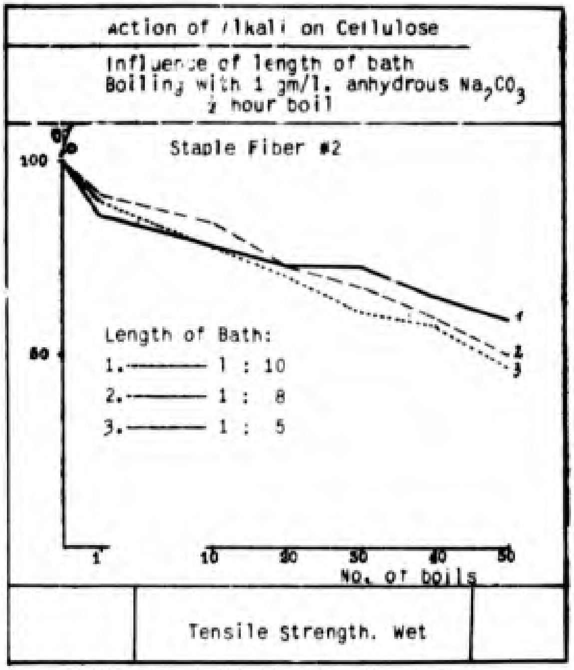


Figure 5

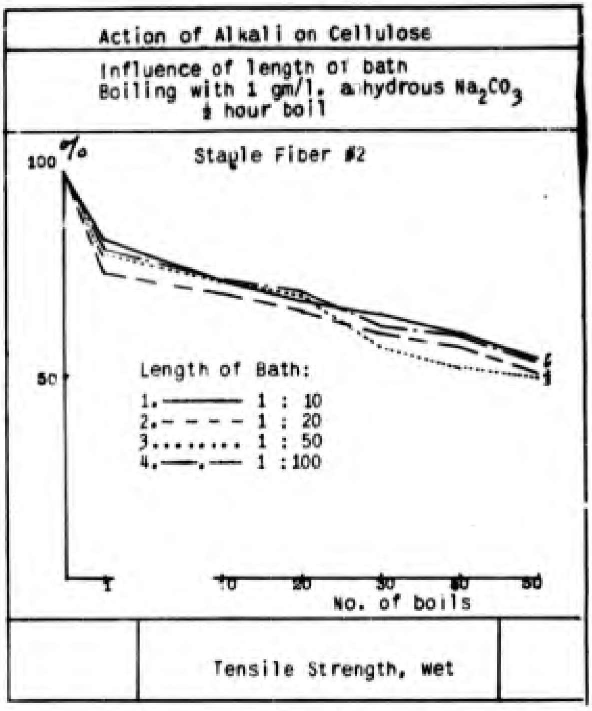


Figure 6

Elongation at the Break of the Wet Fiber

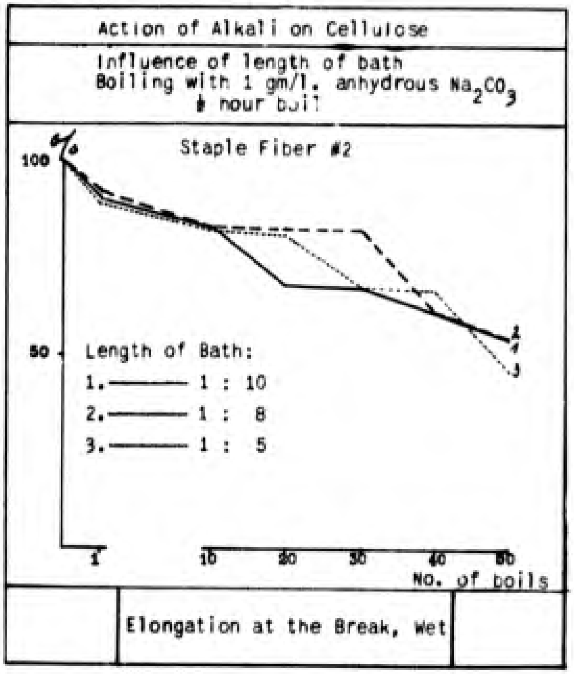


Figure 7

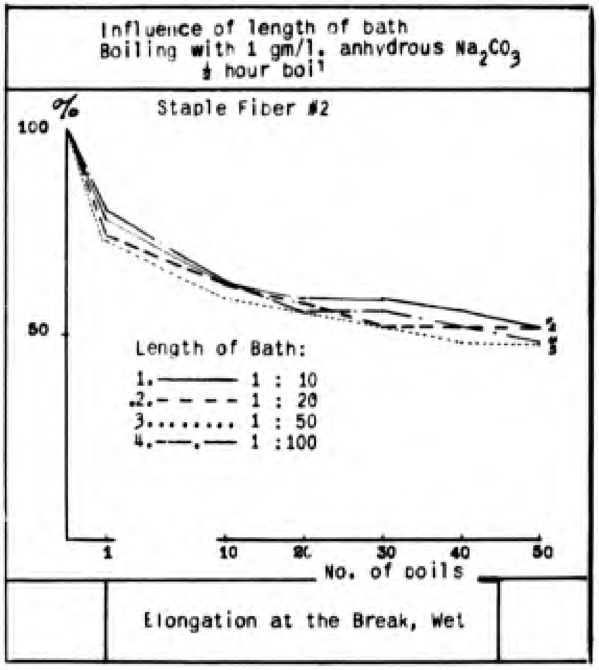


Figure 8

	Ratio	mg Na_2O per 100 g fiber after each boil
Series B	1:10	114
	1:20	106
	1:50	115
	1:100	106

These chemical and physical results show that the decomposition of a fiber is constant when different proportions of goods to liquor are used. Furthermore the absorption of alkali by the fiber in the separate boils does not depend on the bath ratio.

The variations of the values in some experiments lie within the limit of error. When criticizing the experimental results relating to the decomposition of fiber and the absorption of alkali by the fiber using different proportions of goods to liquor, it must be considered that the values were found by investigating the baths, and that the results were related to the quantities of fiber used. The limits of error relating to the volume of bath, are the same in each case.

For example, where a 1 to 100 bath is used only one tenth as much fiber is treated per unit of bath volume as compared to a 1 to 10 bath. Thus, the limit of error based on the fiber weight is ten times greater in the first case than in the second.

The experiments with staple fibers No. 1 and No. 3 confirm the experimental results obtained with staple fiber No. 2, so that it seems to be unnecessary to represent the corresponding curves and tables.

The result of this series of experiments may be summarized as follows:

When boiling cellulose fibers in a bath containing alkali, the changes of the fiber found by chemical and physical methods do not depend on the proportion of goods to liquor.

Second Series of Experiments

Action of Different Alkalies Upon Cellulose. In this series of experiments the cellulosic fibers were subjected to 50 boils in the presence of alkalies generally used in the washing process and in different concentrations. Before and after the treatments the fibers were exhaustively examined by chemical and physical methods.

The cellulose fibers were treated with the following alkalies:

1. Sodium hydroxide, analytically pure.
2. Anhydrous sodium carbonate, analytically pure.
3. Sodium monosilicate (sodium metasilicate), $Na_2O \cdot SiO_2 \cdot 4\ H_2O$.

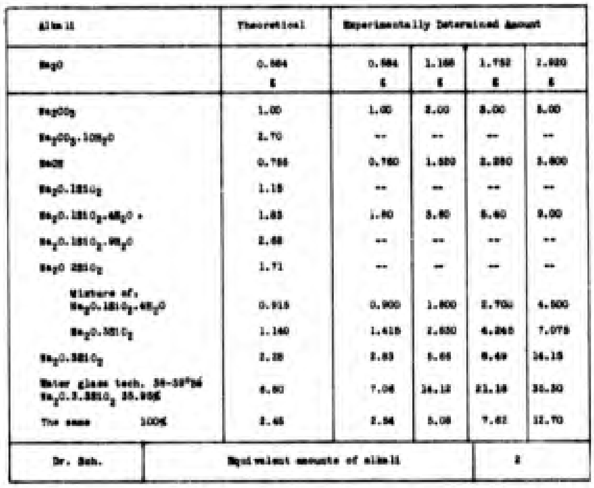
4. Sodium disilicate.
   As this preparation was not available, a mixture of equivalent parts of sodium monosilicate and sodium trisilicate was used.
5. Sodium trisilicate, $Na_2O \cdot 3\ SiO_2$.
6. Technical water glass, 38 - 39°Be, $Na_2O \cdot 3 \cdot 3\ SiO_2$; 35.95% solids.
7. Water (for comparison).

The fibers were treated in baths with 4 different alkali concentrations:

1. 0.584 g per 1 Na_2O cor. 1.0 g per 1 anhydrous Na_2CO_3.
2. 1.168 " " 1 " " 2.0 " " 1 " "
3. 1.732 " " 1 " " 3.0 " " 1 " "
4. 2.920 " " 1 " " 5.0 " " 1 " "

The corresponding equivalent quantities of the other alkalies are shown in Figure 9.

The pH value of these alkali solutions in the different concentrations may be taken from Figure 10 (potentiometrical values at 20° C.). Here it must be considered that the distilled water of the treating baths contains varying quantities of dissolved carbonic acid converting the alkalies to sodium carbonate or sodium bicarbonate and thus diminishing somewhat the pH value of the solutions, although the contents of Na_2O in the bath are not changed.



Alkali	Theoretical	Experimentally Determined Amount			
Na_2O	0.584 g	0.584 g	1.168 g	1.752 g	2.920 g
Na_2CO_3	1.00	1.00	2.00	3.00	5.00
$Na_2CO_3 \cdot 10H_2O$	2.70	--	--	--	--
NaOH	0.755	0.760	1.520	2.280	3.800
$Na_2O \cdot 1SiO_2$	1.15	--	--	--	--
$Na_2O \cdot 1SiO_2 \cdot 4H_2O$ +	1.83	1.90	3.80	5.60	9.00
$Na_2O \cdot 1SiO_2 \cdot 9H_2O$	2.68	--	--	--	--
$Na_2O\ 2SiO_2$	1.71	--	--	--	--
Mixture of, $Na_2O \cdot 1SiO_2 \cdot 4H_2O$	0.915	0.900	1.800	2.700	4.500
$Na_2O \cdot 3SiO_2$	1.140	1.415	2.830	4.245	7.075
$Na_2O \cdot 3SiO_2$	2.28	2.83	5.66	8.49	14.15
Water glass tech. 38-39°Bé $Na_2O \cdot 3.3SiO_2$ 35.95%	6.80	7.06	14.12	21.18	35.30
The same 100%	2.45	2.54	5.08	7.62	12.70

Dr. Sch.	Equivalent amounts of alkali	2

Figure 9

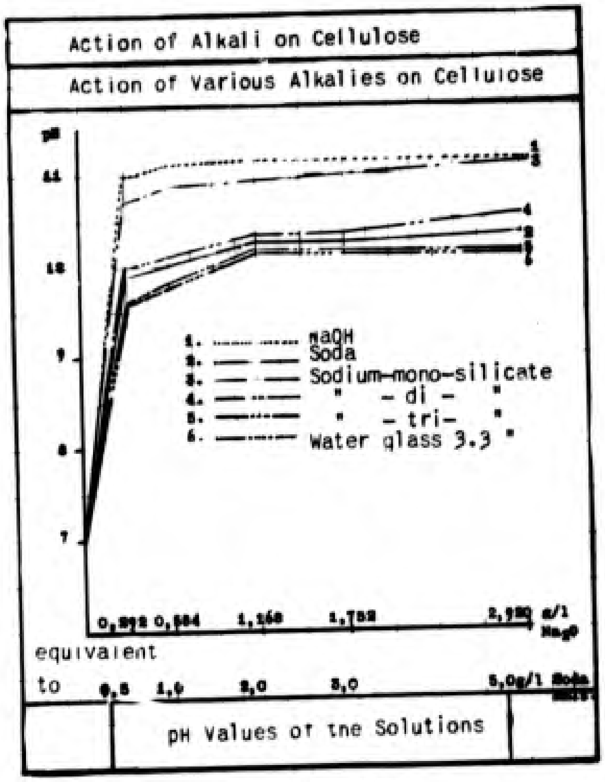


Figure 10

Action of Alkali on Cellulose

Action of Different Alkalies on Cellulose

Concentration: 0.584 g/l Na_2O
Equivalent to: 1.0 g/l Na_2CO_3

No. of Boils of Fiber	Water	NaOH	Na_2CO_3	$Na_2O.SiO_2$	$Na_2O.2SiO_2$	$Na_2O.3SiO_2$	Waterglass
Staple Fiber 1							
1	Yellow Brown	Yellow Brown	Yellow Brown	Yellow Brown	Yellow Brown	Yellow Brown	Yellow Brown
2	Pale Yellow	Yellowish	Pale Yellow	Yellowish	Pale Yellow	Pale Yellow	Pale Yellow
3	Colorless	Pale Yellow	Colorless	Colorless	Colorless	Colorless	Colorless
4	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Staple Fiber 2							
1	Pale Yellow	Yellow Brown	Yellow Brown	Yellow	Yellow	Yellow	Yellow
2	Colorless	Yellow Brown	Yellow Brown	Yellow	Yellow	Yellow	Yellow
3	Colorless	Yellow Brown	Yellow Brown	Yellow	Yellow	Yellow	Yellow
4	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Staple Fiber 4							
1	Pale Yellow	Yellow	Yellow	Yellow	Pale Yellow	Pale Yellow	Pale Yellow
2	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
3	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
4	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Raw Cotton							
1	Colorless	Yellow	Pale Yellow	Pale Yellow	Pale Yellow	Pale Yellow	Pale Yellow
2	Colorless	Pale Yellow	Colorless	Colorless	Colorless	Colorless	Colorless
3	Colorless	Pale Yellow	Colorless	Colorless	Colorless	Colorless	Colorless
4	Colorless	Pale Yellow	Colorless	Colorless	Colorless	Colorless	Colorless

Figure 11

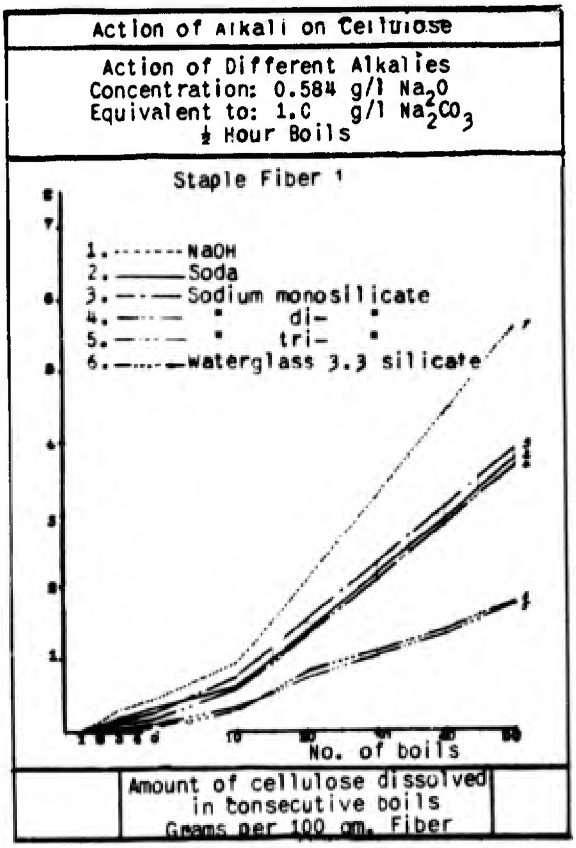


Figure 12

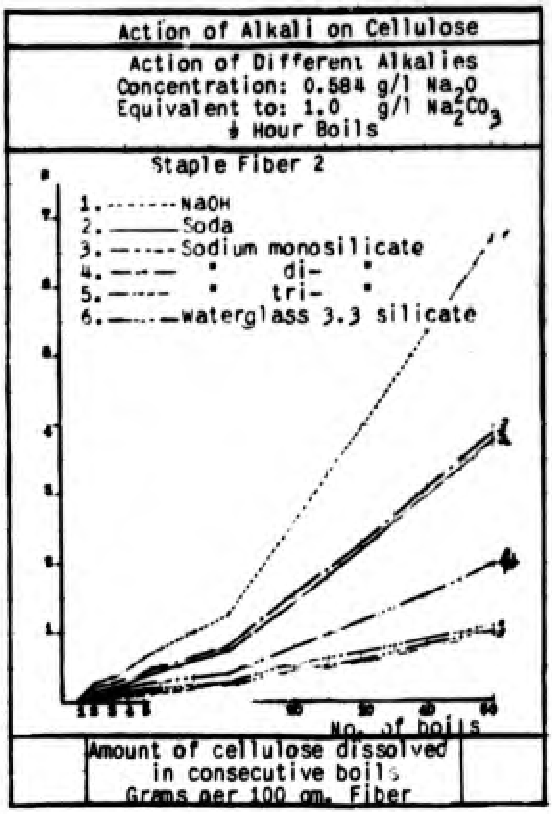


Figure 13

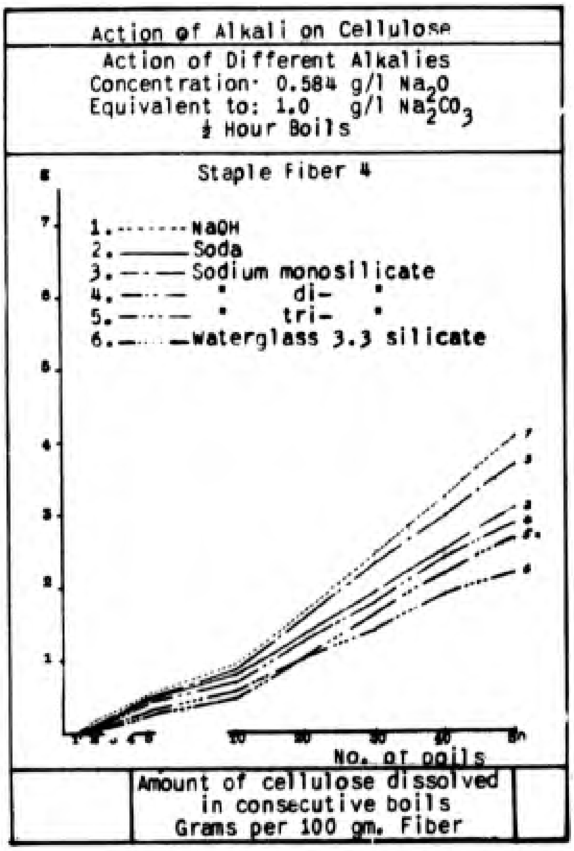


Figure 14

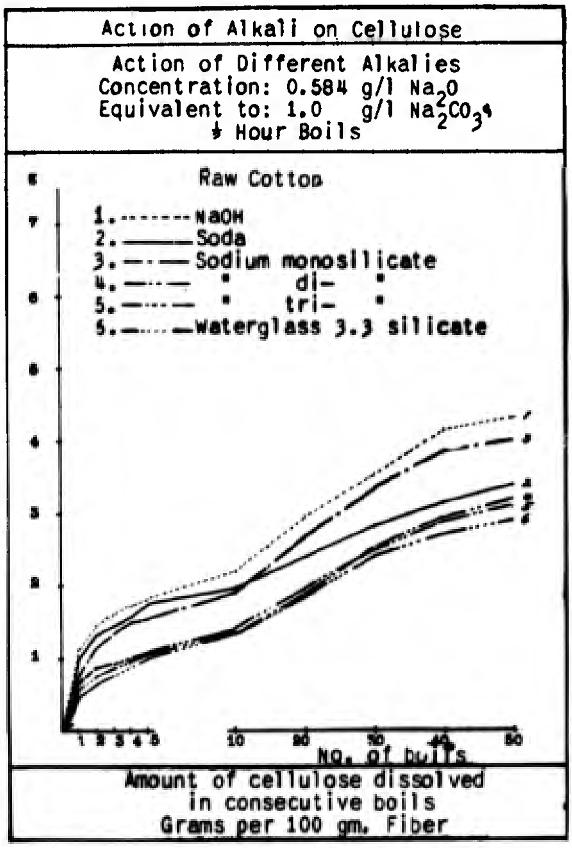


Figure 15

Fibrous material: Staple fiber No. 1
Staple fiber No. 2
Staple fiber No. 4
Raw cotton yarn

Treatment: 50 boils each of 1/2 hour.
Proportion of goods to liquor 1:20
Quantity of bath 1000 cc.

At the beginning of the treatments the presence of the different alkalies causes the fibers and the baths to be stained more or less strongly yellow-brown to brown shades. These tints, however, disappeared after the third or fourth boil. Figure 11 illustrates the tints obtained by the treatment of different fibers in the first baths in the presence of the stated alkalies.

Determinations were made of the quantity of decomposed and dissolved cellulose, damage factor, tensile strength of the wet fiber, elongation at break of the wet fiber, consumption of alkali during the boiling operations, and ash content of the fiber after the 50th treatment. Microscopical observations were also made to supplement these studies.

Results. The results obtained in these investigations were likewise compiled in the form of curves and tables.

Decomposition of the fiber. Figures 12 to 15 illustrate the course of the decomposition of the different fibers during the boils in the presence of alkali in concentration No. 1 (1 gram per liter of anhydrous soda).

In the same manner the values were obtained with higher concentrations of alkali. However, the corresponding curves are not shown here lest the report become too extensive. In Figures 16 to 19 only the total quantities of cellulose decomposed and dissolved in the course of 50 boils are plotted against the different alkali concentrations. From these curves the relations of the quantity of decomposed fiber to the concentration of alkali can be clearly recognized.

From these curves it may be seen that, while decomposition by treatment with boiling water is approximately constant for all fibers, the various alkalies have different decomposing actions on the cellulosic fibers. With regard to the decomposing action on the fibers the following sequence was found:

Caustic soda	- Strongest decomposition of fiber.
Sodium-monosilicate	- Somewhat smaller decomposition of fiber.
Sodium-carbonate	- Considerably smaller decomposition of fiber.
Sodium-disilicate Sodium-trisilicate Water glass (3.3 silicate)	- Still smaller decomposition of fiber.
Water	- Smallest decomposition of fiber.

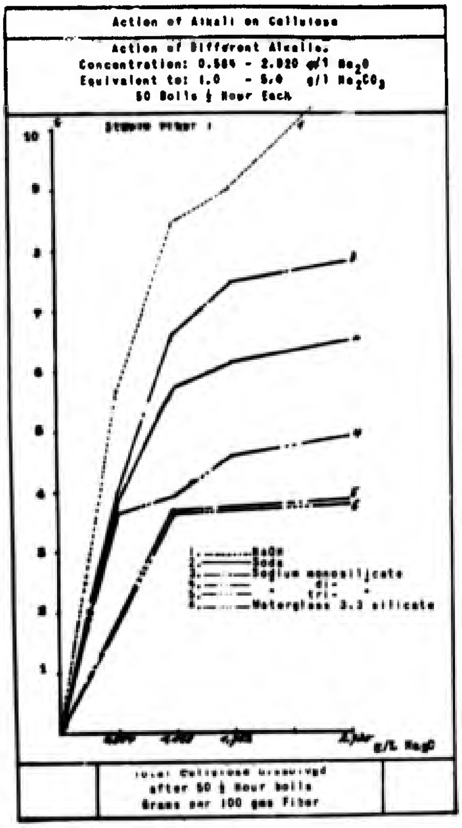


Figure 16

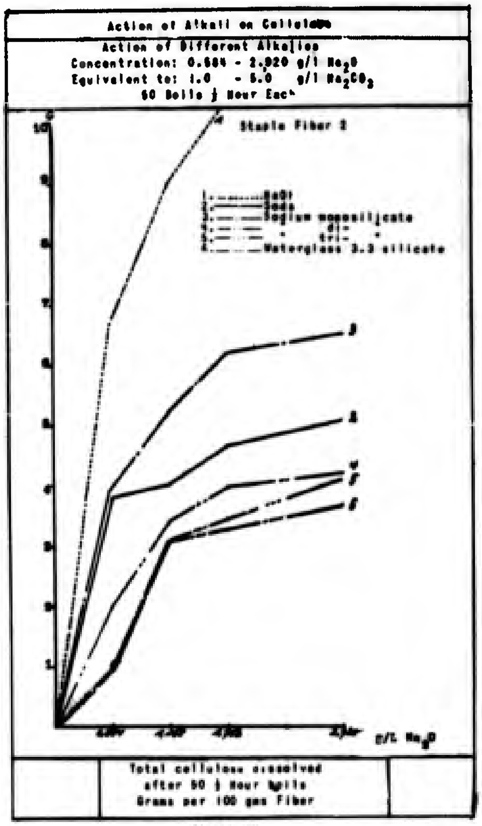


Figure 17

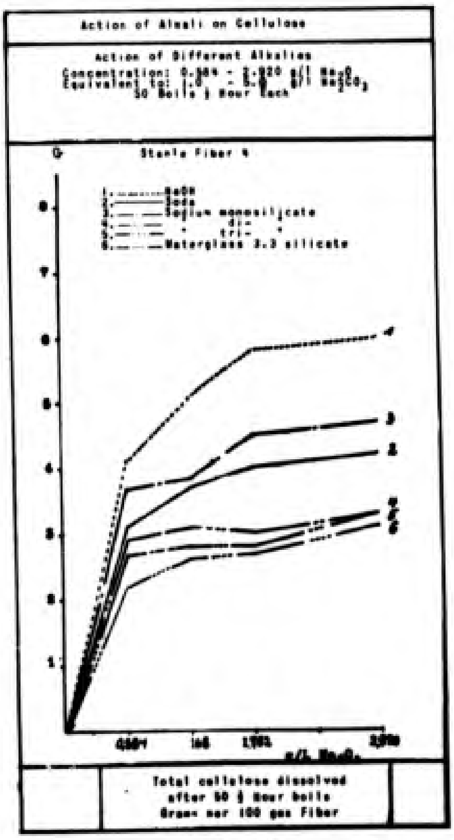


Figure 18

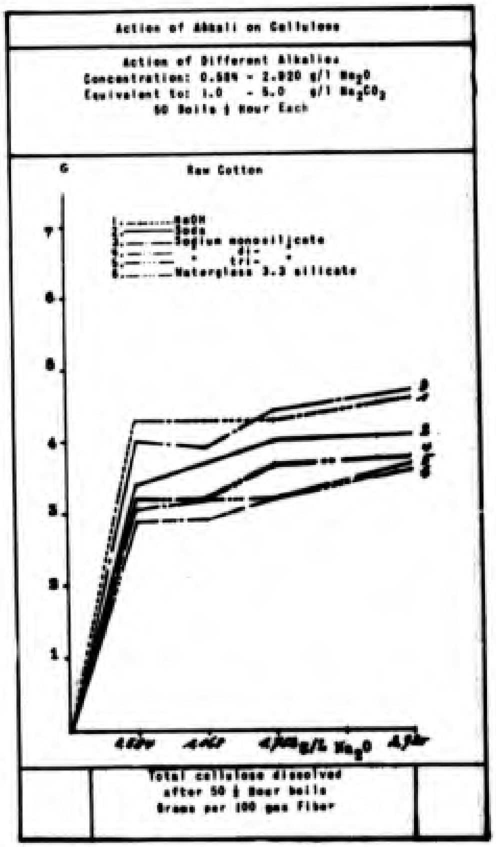


Figure 19

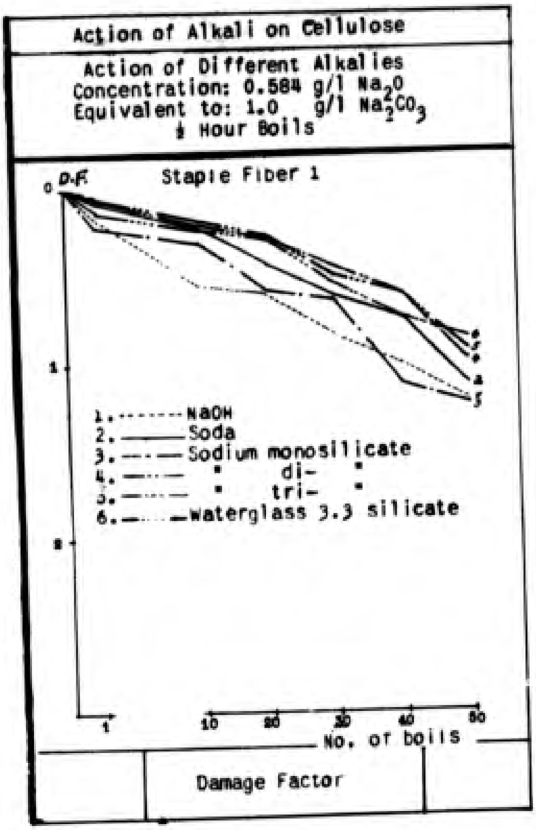


Figure 20

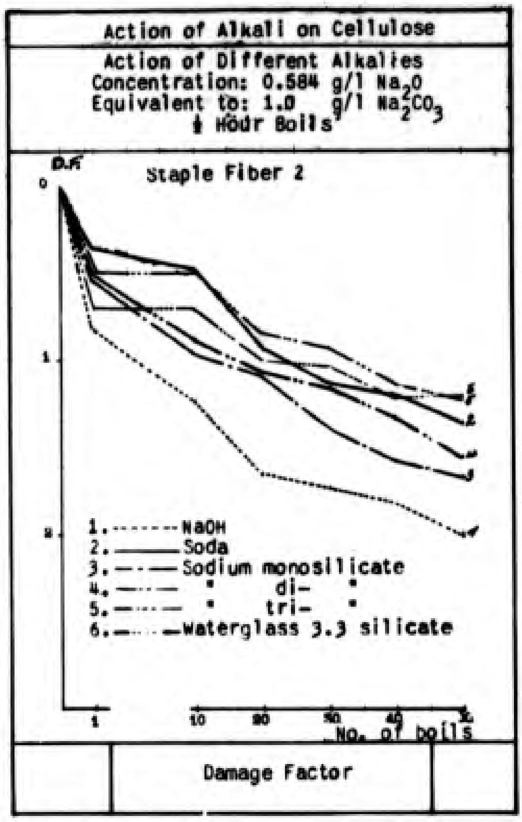


Figure 21

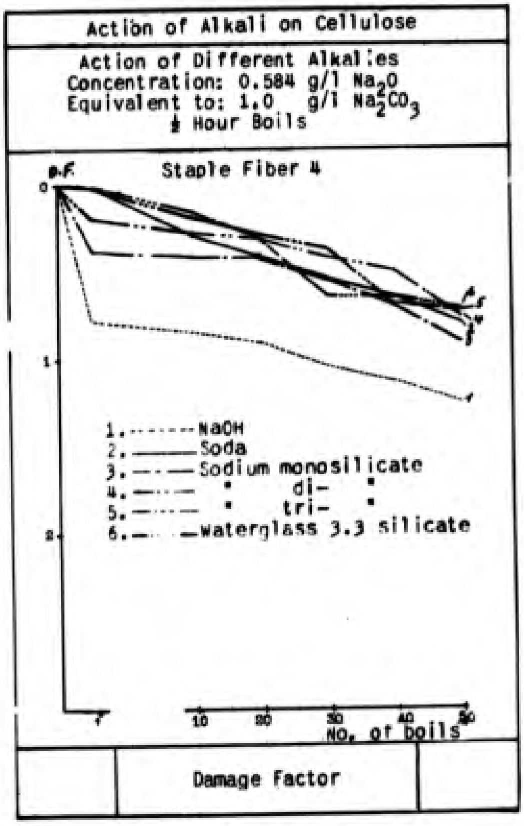


Figure 22

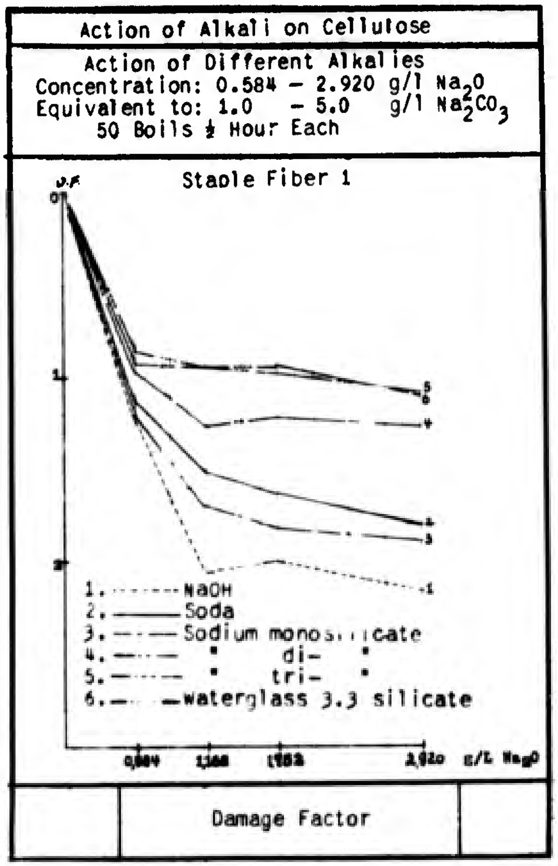


Figure 23

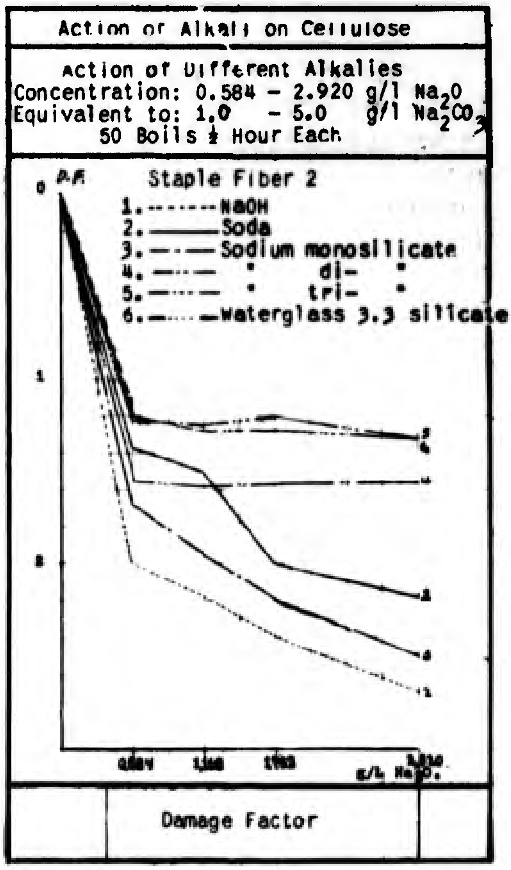


Figure 24

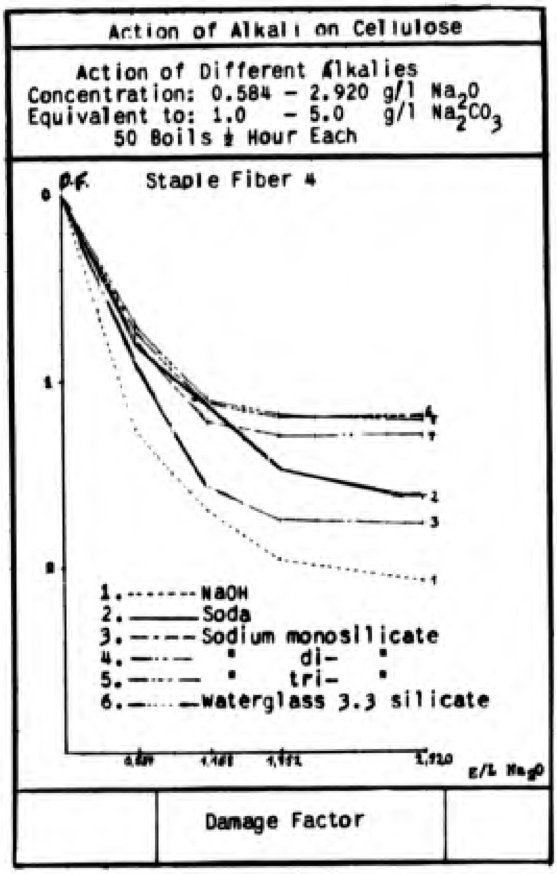


Figure 25

The differences in degree of decomposition of some fibers by the action of different alkalies are very considerable. For example, cotton shows appreciably smaller differences. When using a solution of caustic soda, sodium monosilicate or sodium carbonate, fiber decomposition increases as more concentrated alkalies are used. However, the rate of decomposition becomes slower with increasing alkali concentrations. When using sodium disilicate, sodium trisilicate or water glass the maximum deterioration is already attained in most cases when working in a low concentration.

No relation can be found between the pH value of the alkali solutions and fiber decomposition. It can only be said that comparing two solutions of different alkalies with the same alkali-concentration (based on Na_2O content), the solution with the higher pH value causes the stronger decomposition of the fiber.

Damage Factor (Schädigungszahl)

The damage factors are graphically shown in Figures 20 to 25. Figures 20, 21, and 22 show the increase in the damage factor when boiling with alkalies in concentration No. 1. Figures 23, 24, and 25 show the variation in damage factors after the 50 boils with different alkali concentrations. The damage factor of cotton was not determined.

An examination of the damage factor curves will lead to the same conclusions as have already been reached by a consideration of the results on fiber decomposition so that no further discussion of them is necessary.

Tensile Strength and Elongation at Break of the Wet Fiber. The results of the tensile-strength tests are graphically shown in the same manner as those of the chemical examinations of the fibers. In Figures 26, 27, 28, and 29 are shown the tensile-strength values of yarns before and after being treated with alkalies in concentration No. 1. Figures 30, 31, 32, and 33 show the tensile strength after the 50th treatment with the alkalies in different concentrations.

From these charts it may be seen that the results of tensile-strength tests correspond with the results of chemical examinations of the fibers.

In the case of elongation at the break the results are not shown because the action of different alkalies upon the elasticity of the fibers was not sufficiently uniform to permit the drawing of any conclusions. It is merely apparent from these experiments that caustic soda solution, sodium monosilicate and sodium carbonate cause an appreciably greater decrease in elongation of the fibers than sodium disilicate, sodium trisilicate and water glass.

Absorption of Alkali. The alkali content of each bath was determined by titration before and after the treatments. In this way the absorption of

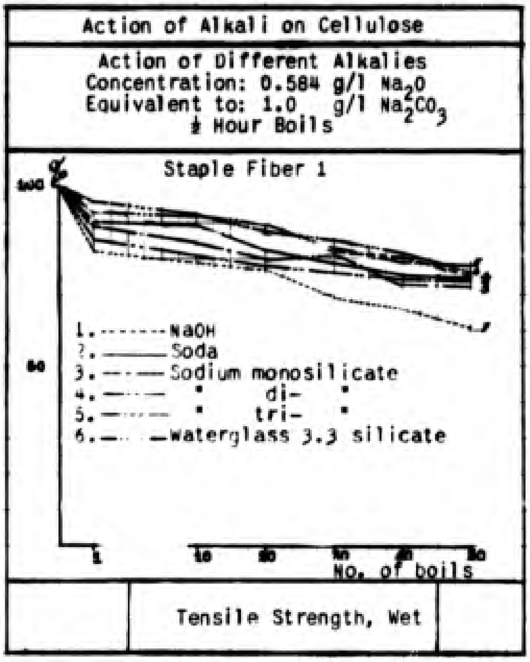


Figure 26

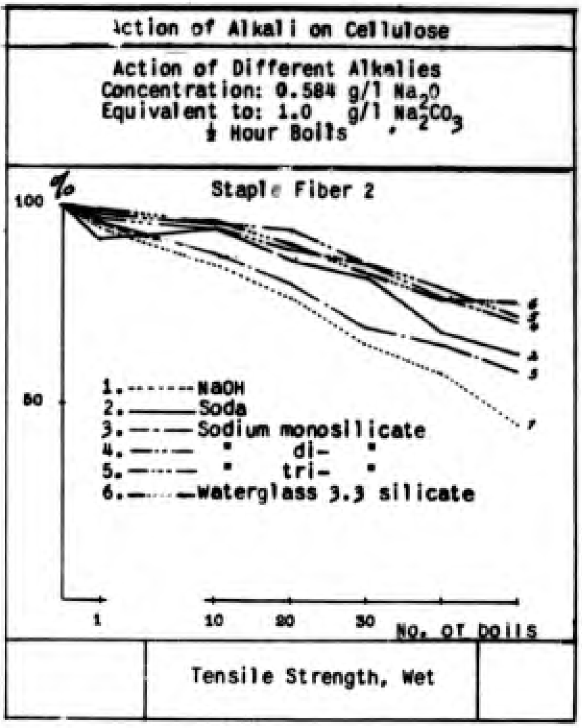


Figure 27

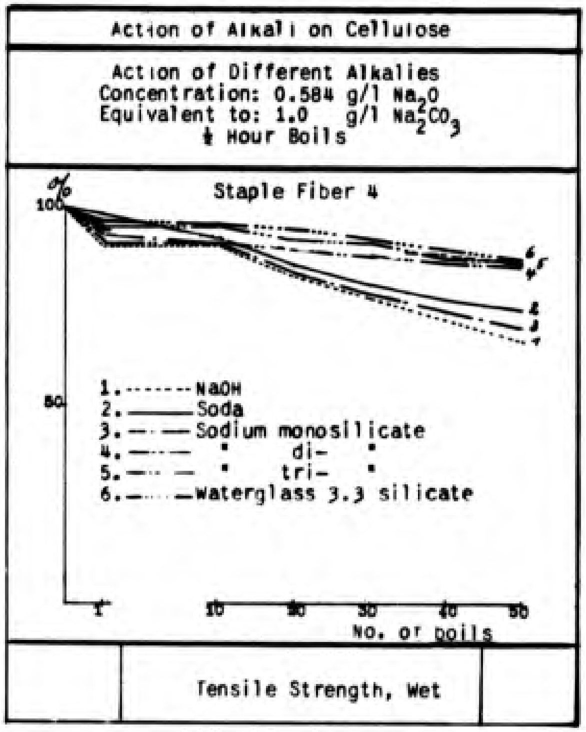


Figure 28

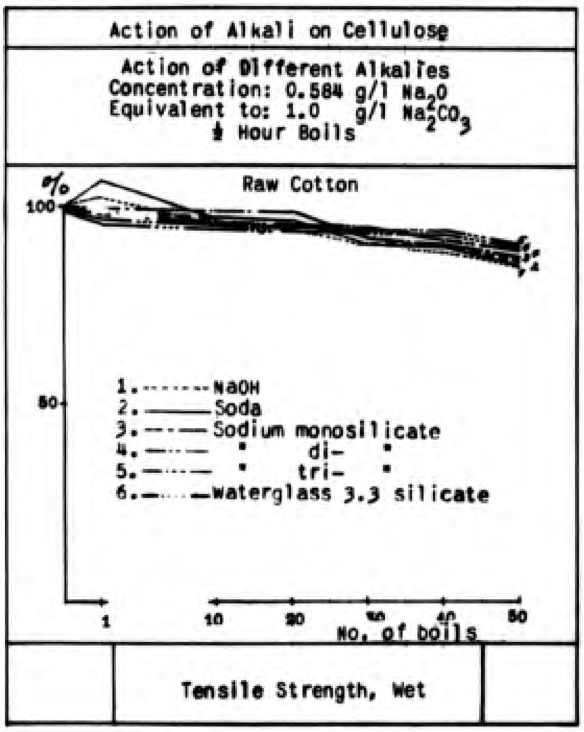


Figure 29

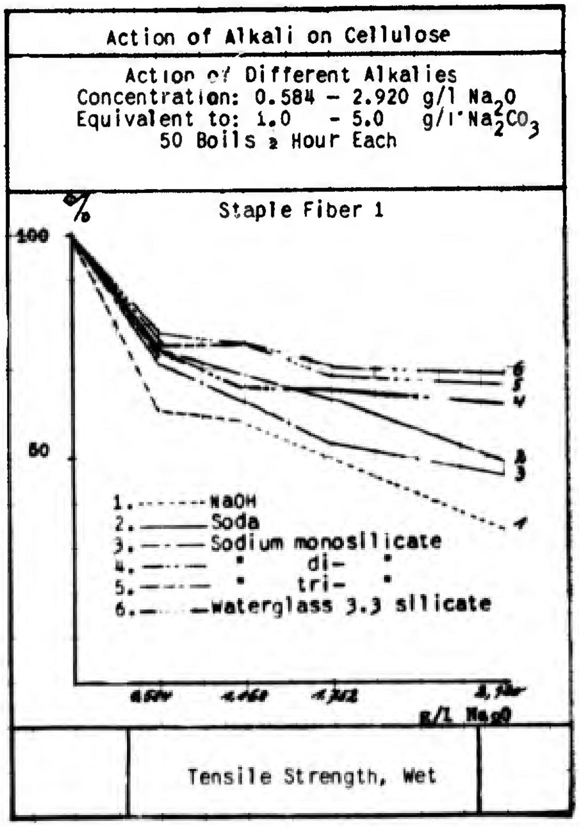


Figure 30

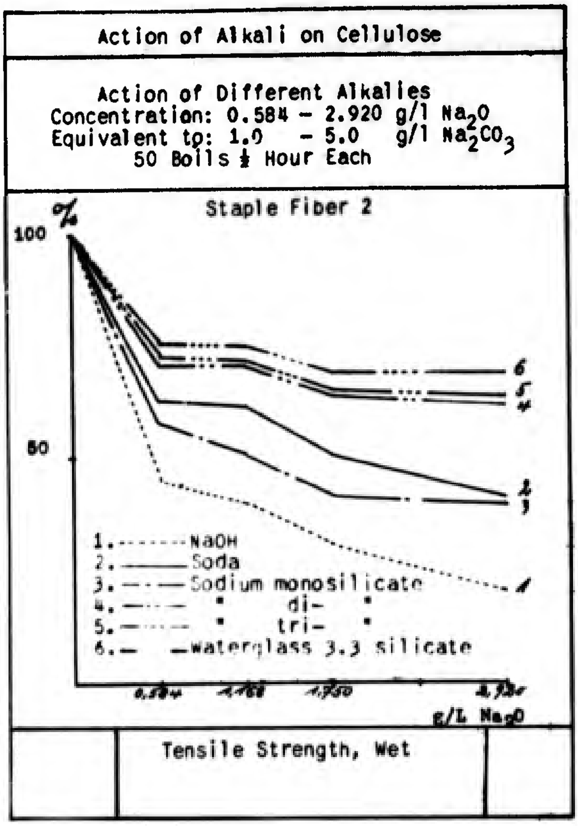


Figure 31

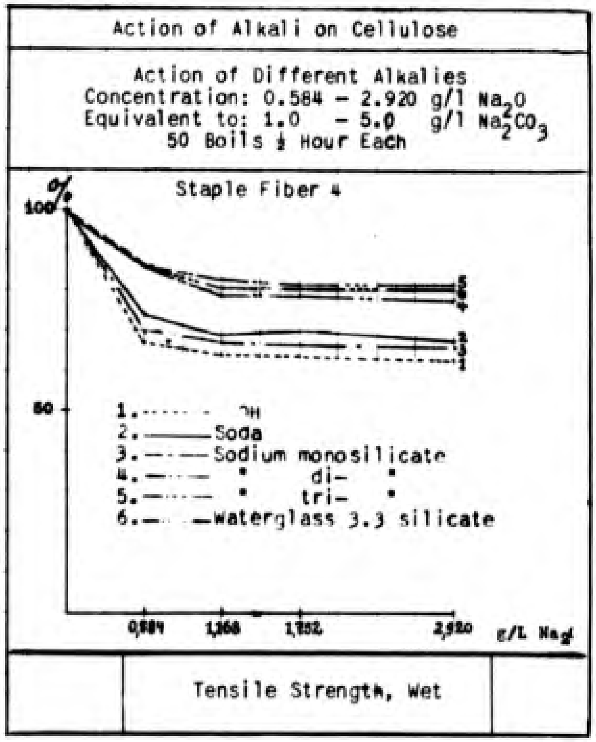


Figure 32

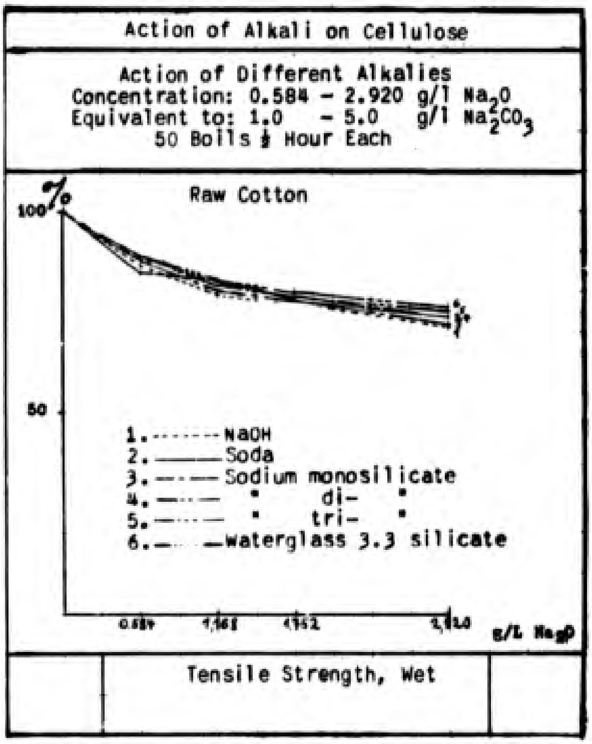


Figure 33

Action of Alkali on Cellulose

Action of Different Alkalies
Concentration: 0.584 - 2.920 g/l Na_2O
Equivalent to: 1.0 - 5.0 g/l Na_2CO_3
½ Hour Boil

Alkali	g/L Na_2O			
	0,584	1,168	1,752	2,920
NaOH	150	152	-	157
Soda	104	108	-	103
Sodium monosilicate	110	106	-	111
Sodium disilicate	106	104	-	107
Sodium trisilicate	108	105	-	106
Water glass 3.3 silicate	112	108	-	111

Staple Fiber 1
Absorption of alkali by cellulose after each individual boil.
mg per 100 gms. Fiber

Figure 34

Action of Different Alkalies
Concentration: 0.584 - 2.920 g/l Na_2O
Equivalent to: 1.0 - 5.0 g/l Na_2CO_3
½ Hour Boil

Alkali	g/L Na_2O			
	0,584	1,168	1,752	2,920
NaOH	186	192	-	194
Soda	124	121	-	127
Sodium monosilicate	128	130	-	123
Sodium disilicate	136	127	-	121
Sodium trisilicate	127	121	-	132
Water glass 3.3 silicate	126	124	-	129

Staple Fiber 2
Absorption of Alkali by cellulose after each individual boil.
mg per 100 gms. Fiber

Figure 35

Action of Different Alkalies
Concentration: 0.584 - 2.920 g/l Na_2O
Equivalent to: 1.0 - 5.0 g/l Na_2CO_3
½ Hour Boil

Alkali	g/L Na_2O			
	0,584	1,168	1,752	2,920
NaOH	146	153	-	152
Soda	80	76	-	81
Sodium monosilicate	80	80	-	83
Sodium disilicate	92	83	-	79
Sodium trisilicate	80	79	-	82
Water glass 3.3 silicate	78	84	-	80

Staple Fiber 4
Absorption of alkali by cellulose after each individual boil.
mg per 100 gms. Fiber

Figure 36

Action of Alkali on Cellulose

Action of Different Alkalies
Concentration: 0.584 - 2.920 g/l Na_2O
Equivalent to: 1.0 - 5.0 g/l Na_2CO_3
½ Hour Boil

Alkali	g/L Na_2O			
	0,584	1,168	1,752	2,920
NaOH	186	192	-	189
Soda	124	121	-	120
Sodium monosilicate	120	117	-	127
Sodium disilicate	123	119	-	126
Sodium trisilicate	126	123	-	119
Water glass 3.3 silicate	134	121	-	126

Raw Cotton
Absorption of alkali by cellulose after each individual boil.
mg per 100 gms. Fiber

Figure 37

Action of Different Alkalies
Concentration: 0.584 - 2.920 g/l Na_2O
Equivalent to: 1.0 - 5.0 g/l Na_2CO_3
50 Boils ½ Hour Each

Alkali	Un-treated	g/L Na_2O			
		0,584	1,168	1,752	2,920
—	0,25	—	—	—	—
NaOH	-	0,14	0,22	0,24	0,26
Soda	-	0,12	0,17	0,23	0,21
Sodium monosilicate	-	0,56	0,83	0,89	0,97
Sodium disilicate	-	0,35	0,60	0,78	1,23
Sodium trisilicate	-	18,92	23,73	24,63	27,10
Water glass 3,3 silicate	-	20,53	24,72	26,73	28,98
Water	-	0,13	-	-	-

Staple Fiber 1
Mineral Content of the Fiber
After 50 Boils
Grams per 100 gms of Fiber

Figure 38

Action of Alkali on Cellulose

Action of Different Alkalies
Concentration: 0.584 - 2.920 g/l Na_2O
Equivalent to: 1.0 - 5.0 g/l Na_2CO_3
50 Boils ½ Hour Each

Alkali	Un-treated	g/L Na_2O			
		0,584	1,168	1,752	2,920
—	0,86	--	—	—	—
NaOH	-	0,74	0,72	0,73	0,76
Soda	-	0,72	0,70	0,75	0,78
Sodium monosilicate	-	0,05	1,10	0,98	1,02
Sodium disilicate	-	0,80	0,83	0,91	0,93
Sodium trisilicate	-	9,63	9,98	21,41	28,03
Water glass 3.3 silicate	-	8,37	11,13	20,63	26,77
Water	-	0,74	-	-	-

Staple Fiber 2
Mineral Content of the Fiber
After 50 Boils
Grams per 100 gms of Fiber

Figure 39

Action of Alkali on Cellulose

Action of Different Alkalies
Concentration: 0.584 - 2.920 g/l Na_2O
Equivalent to: 1.0 - 5.0 g/l Na_2CO_3
50 Boils ½ Hour Each

Alkali	Un-treated	g/l Na_2O			
		0,584	1,168	1,752	2,920
-	0,62	-	-	-	-
NaOH	-	0,52	0,50	0,53	0,51
Soda	-	0,38	0,37	0,42	0,41
Sodium monosilicate	-	0,90	1,18	1,22	1,13
Sodium disilicate	-	0,62	1,07	1,11	1,10
Sodium trisilicate	-	13,31	17,21	22,53	32,50
Water glass 3.3 silicate		12,32	18,73	20,17	24,23
Water	-	0,38	-	-	-

Staple Fiber 4
Mineral Content of the Fiber
After 50 Boils
Grams per 100 gms of Fiber

Figure 40

Action of Alkali on Cellulose

Action of Different Alkalies
Concentration: 0.584 - 2.920 g/l Na_2O
Equivalent to: 1.0 - 5.0 g/l Na_2CO_3
50 Boils ½ Hour Each

Alkali	Un-treated	g/l Na_2O			
		0,584	1,168	1,752	2,920
—	0,28	-	-	-	-
NaOH	-	0,10	0,14	0,11	0,16
Soda	-	0,10	0,08	0,12	0,10
Sodium monosilicate	-	0,47	0,72	0,69	0,63
Sodium disilicate	-	0,32	1,02	1,03	1,32
Sodium trisilicate	-	8,65	9,80	16,21	25,28
Water glass 3.3 silicate		8,21	13,18	18,47	23,18
Water	-	0,17	-	-	-

Raw Cotton
Mineral Content of the Fiber
After 50 Boils
Grams per 100 gms of Fiber

Figure 41

alkali by the fiber in the course of each treatment was determined. The results are presented in Figures 34 to 37.

From these figures it follows that the maximum alkali absorption of the fiber is attained in each case with concentration No. 1. Higher concentrations do not cause a stronger absorption of alkali. It must be emphasized here that use of caustic soda solution results consistently in a greater absorption of alkali (based on Na_2O) than the other alkalies. From this it may be concluded that the action of caustic soda solution causes the formation of sodium cellulose, and that the action of the other alkalies merely cause an absorption of alkali by the fiber. The amount of absorbed alkali is different for each fibrous material.

When determining the mineral components in the fibers before and after 50 treatments, it was discovered that the alkali content of the fibers is not increased by a multiplicity of treatments. It was therefore concluded that the alkali absorbed by the fiber during the treatment is washed out again in the rinsing process.

Ash Content of the Fibers. The mineral components of the fibers were determined before and after 50 treatments with the different alkalies in different concentrations, by ashing the fibers at 600° C.

The results of these analyses are shown in Figures 38 to 41.

From these results it may be seen that the small mineral ingredients of the untreated fiber either remain unchanged or are diminished by the treatment with caustic soda or sodium carbonate solution.

Sodium monosilicate and sodium disilicate in any concentrations cause a slight increase in the mineral ingredients of any fiber to which they may be applied.

However, sodium trisilicate and water glass cause a strong deposit of mineral ingredients in the fiber. The inorganic compounds absorbed depends upon the alkali concentration in the bath and on the kind of fiber. As the treatment of the fiber with the alkali, as well as the rinsing in all cases, was performed with distilled water, these ingredients can be only silicic acid, since the free alkali content if the fibers as determined by titration had not increased but even diminished.

In these results it is remarkable that sodium trisilicate and water glass in all cases cause a significant amount of minerals to be absorbed by the fiber, whereas, when using sodium disilicate, only a small quantity could be found. However, as stated before, the sodium disilicate used is not a uniform product but a mixture of equivalent parts of sodium monosilicate and sodium trisilicate. Therefore, from these experiments it may be supposed that sodium monosilicate prevents the deposit of silicates in the fibers.

Action of Alkali on Cellulose

Action of Different Alkalies
Use of Alkali Mixtures
Total Concentration: 0.584 g/l Na_2O
Equivalent to: 1.0 g/l Na_2CO_3
50 Boils ½ Hour Each

Alkali	Mineral Content Untreated
Untreated	0,14
100% Water glass 3.3 silicate	22,93
90% Water glass 3.3 silicate 10% Sodium monosilicate	14,28
80% Water glass 3.3 silicate 20% Sodium monosilicate	13,32
50% Water glass 3.3 silicate 50% Sodium monosilicate	0,93
100% Sodium monosilicate	0,47

Staple Fiber 1

Mineral Content of the Fiber
After 50 Boils
Grams per 100 gms Fiber

Figure 42

Action of Alkali on Cellulose

Action of Different Alkalies
Use of Alkali Mixtures
Total Concentration: 0.584 g/l Na_2O
Equivalent to: 1.0 g/l Na_2CO_3
50 Boils ½ hour Each

Alkali	Mineral Content Untreated
Untreated	0,14
100% Water glass 3.3 silicate	22,93
90% Water glass 3.3 silicate 10% Soda	18,80
80% Water glass 3.3 silicate 20% Soda	10,52
50% Water glass 3.3 silicate 50% Soda	4,23
100% Soda	0,11

Staple Fiber 1

Mineral Content of the Fiber
After 50 Boils
Grams per 100 gms Fiber

Figure 43

This supposition was confirmed by a further series of experiments. Staple fiber No. 1 was subjected to 50 boils with a mixture of water glass (3.3 silicate) and sodium monosilicate, and a mixture of water glass (3.3 silicate) and sodium carbonate.

These alkalies were used in such quantities that together they corresponded to concentration No. 1 (0.584 g/l of Na_2O).

The results of these examinations are shown in Figures 42 and 43.

These examinations confirm former experimental results and prove that sodium monosilicate and sodium carbonate effectively impede the precipitation of silicic acid on the fiber. This is demonstrated by the fact that the quantity of the precipitate decreases with increasing amounts of either sodium monosilicate or sodium carbonate.

This action of sodium monosilicate and sodium carbonate may be explained as follows:

In an aqueous solution of sodium trisilicate a state of equilibrium is reached between molecularly and colloidally dissolved silicate, which depends upon the concentration, the temperature and the other electrolytes present in the solution.

$$\begin{array}{ccc} Na_2O \cdot 3\ SiO_2 & \longleftrightarrow & Na_2O \cdot 3\ SiO_2 \\ \text{Molecular} & \longleftrightarrow & \text{Colloidal} \end{array}$$

It is probable that the only parts of the silicate which are deposited on the fiber are those which are colloidally dissolved and that those which are molecularly dissolved do not become so absorbed. By adding sodium carbonate, sodium monosilicate, and probably also caustic soda solution or other alkalies forming molecular solutions, the equilibrium is displaced from right to left, i.e., the colloidal part of the solution is diminished and, accordingly, the precipitate of silicate on the fiber also becomes less.

<u>Microscopical Observations.</u> Photomicrographs were taken of the fibers before and after 50 treatments by Dr. Reumuth's phase-contrast method. These photographs do not represent isolated findings, but were selected from a large number of such microscopical observations which confirmed each other and give a clear conception of the changes of fiber structures after 50 boils in the presence of alkali.

The photomicrographs of staple fiber No. 1 are shown in Figure 44.

The following observations are made:

The untreated fiber already shows a large number of cross cracks. By the boiling operations either in water or in alkaline solutions, these

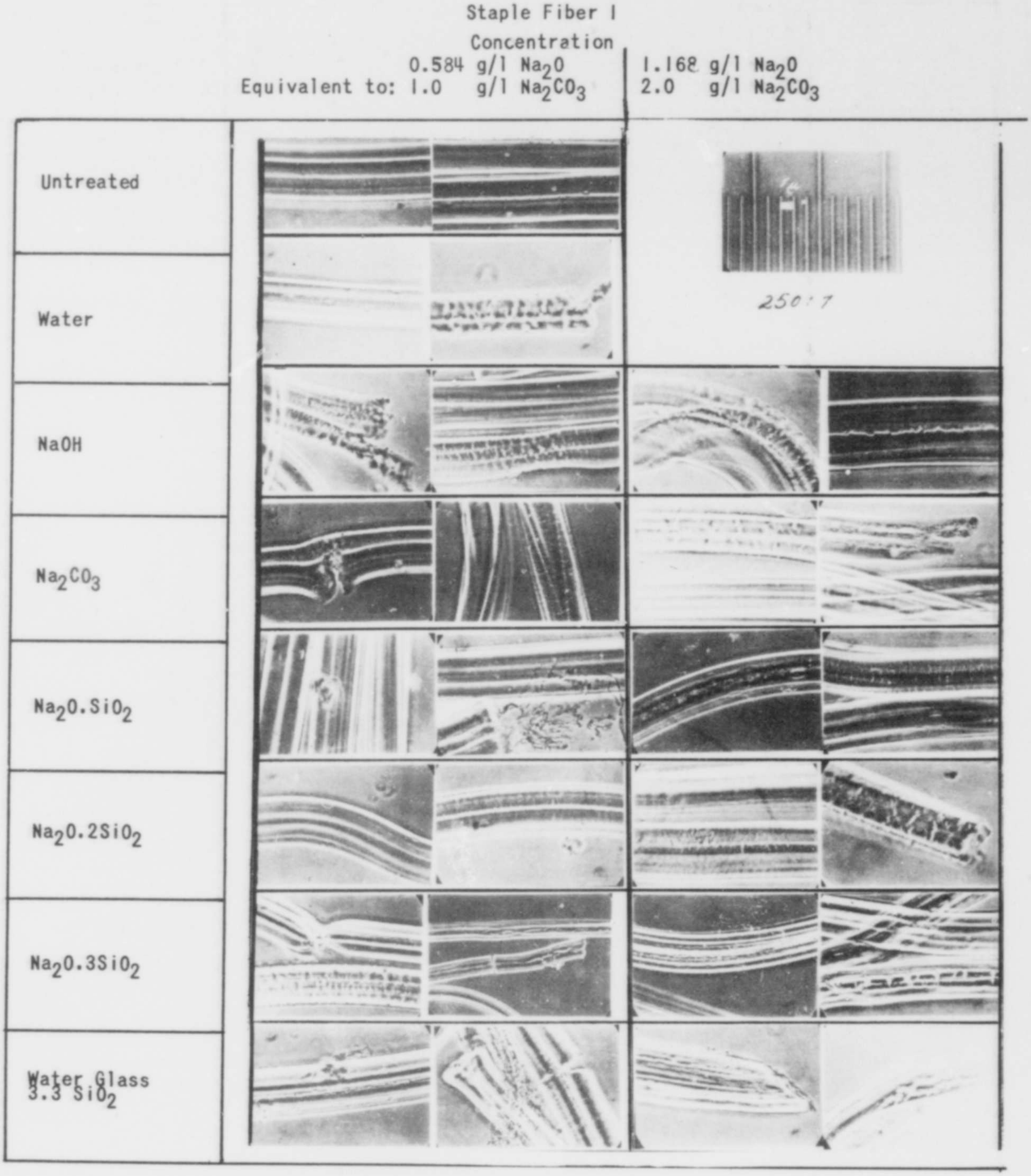

Staple Fiber I
Concentration
0.584 g/l Na2O
Equivalent to: 1.0 g/l Na2CO3
1.168 g/l Na2O
2.0 g/l Na2CO3
Untreated
Water
NaOH
Na2CO3
Na2O.SiO2
Na2O.2SiO2
Na2O.3SiO2
Water Glass 3.3 SiO2
250:7

Figure 44

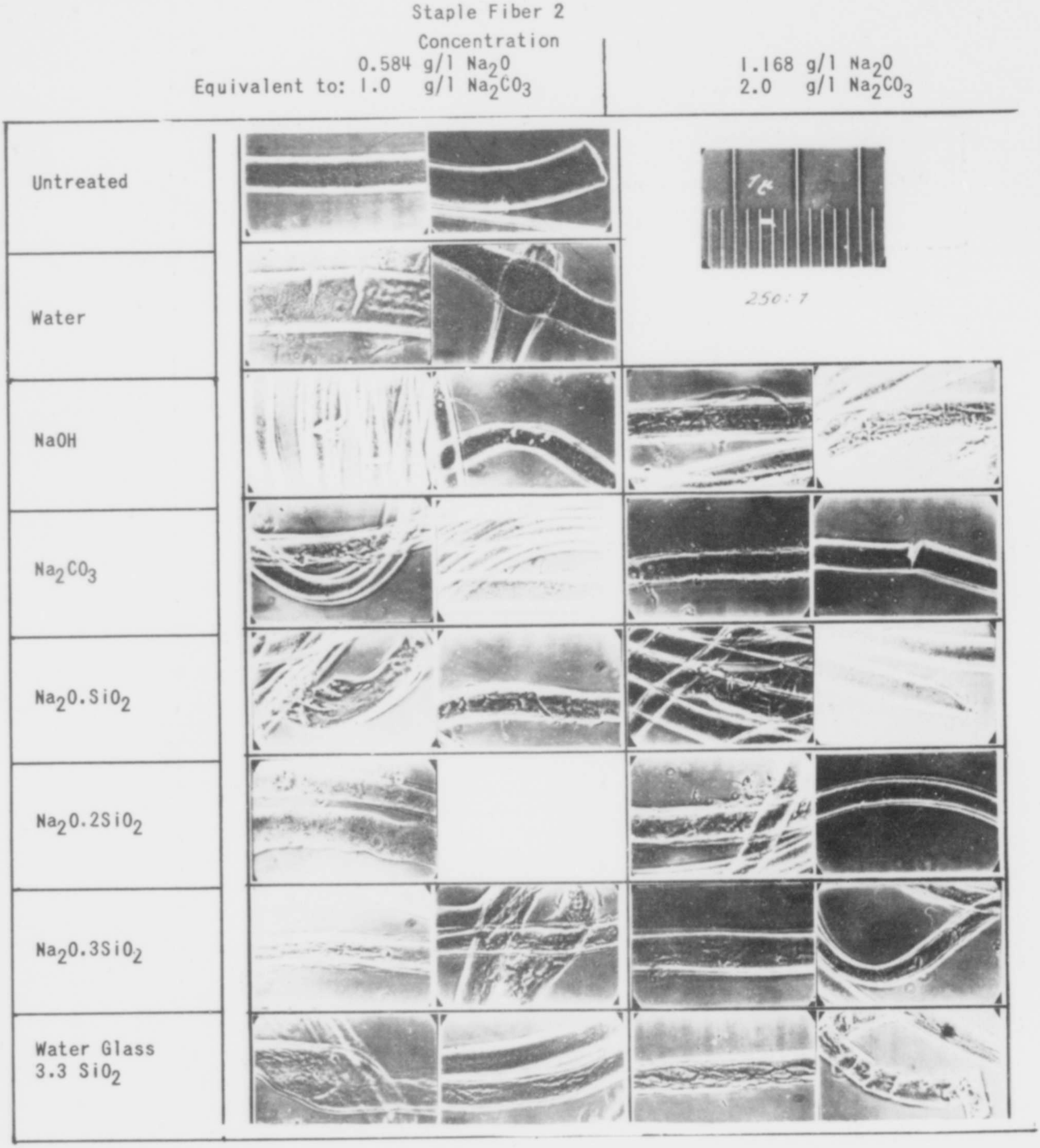

Staple Fiber 2
Concentration
0.584 g/l Na_2O
Equivalent to: 1.0 g/l Na_2CO_3
1.168 g/l Na_2O
2.0 g/l Na_2CO_3
Untreated
Water
NaOH
Na_2CO_3
$Na_2O.SiO_2$
$Na_2O.2SiO_2$
$Na_2O.3SiO_2$
Water Glass
3.3 SiO_2
1μ
250:1

Figure 45

Staple Fiber 4

Concentration

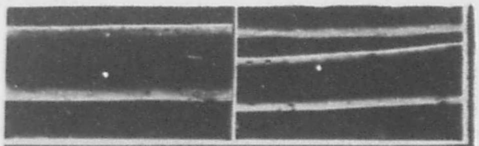
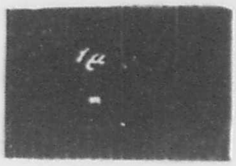
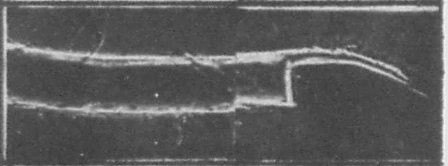
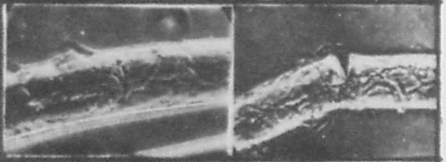
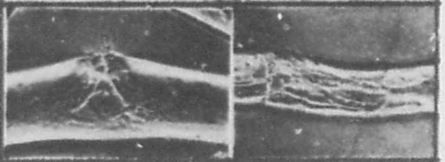
	0.584 g/l Na_2O Equivalent to: 1.0 g/l Na_2CO_3	1.168 g/l Na_2O 2.0 g/l Na_2CO_3
Untreated		 180:1
Water		
NaOH		
Na_2CO_3		
$Na_2O.SiO_2$		
$Na_2O.2SiO_2$		
$Na_2O.3SiO_2$		
Water Glass 3.3 SiO_2		

Figure 46

cross cracks are increased and parts of them are appreciably broadened. They are especially distinct after treatment with caustic soda solution or sodium carbonate. Sodium monosilicate has a somewhat more favorable effect, whereas sodium disilicate produces cross cracks to a greater extent or broadens them. Especially unfavorable is the action of sodium trisilicate and water glass which, moreover, cause a strong mineral deposition on the fiber. In addition to the cross cracks which in some cases cause a complete separation of the fiber, there can be seen that a more or less strong cleavage has taken place on the end of the fiber after all treatments, including that with water.

The photomicrographs of staple fiber No. 2 are shown in Figure 45.

The following observations are made:

The cross cracks and cleavages of fibers of staple fiber No. 1 could also be found in staple fiber No. 2. However, in the latter the cross cracks are more numerous and stronger. The mineral deposition on the fiber, when using trisilicate or water glass, is smaller than in the case of staple fiber No. 1 which also corresponds with the analytical results.

The photomicrographs of staple fiber No. 4, are shown in Figure 46.

The following observations are made:

When treating staple fiber No. 4, cross cracks similar to those of the previous fibers are to be observed. However, these cross cracks apparently do not go deeply into the interior in all cases, but most frequently cause a superficial splintering of small parts of the fiber. The mineral deposition on the fiber, when using sodium trisilicate or water glass is greater than in the case of staple fiber No. 2 and smaller than in the case of staple fiber No. 1.

The photomicrographs of raw cotton are shown in Figure 47.

The following observations are made:

When treating cotton, cross cracks in the fibers may likewise be observed after 50 treatments. By boiling in water numerous cross cracks are formed, but these extend to cleavages only in some cases. When using caustic soda or sodium carbonate, appreciably broader cross cracks appear which, especially in the case of sodium carbonate, often cause a complete cleavage of the fiber. Caustic soda solution behaves somewhat more favorable than sodium carbonate. Sodium monosilicate and sodium disilicate likewise cause numerous cross cracks in the fiber, although these do not extend to cleavages as in the case of sodium carbonate. Water glass and sodium trisilicate cause cleavages of the fiber in a higher degree than sodium monosilicate and sodium disilicate and furthermore give considerable mineral deposition.

Raw Cotton

Concentration

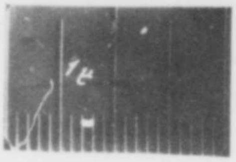
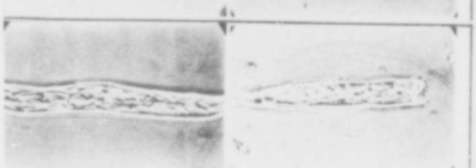
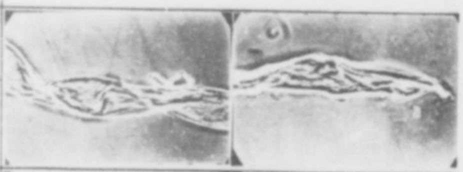
	0.584 g/l Na_2O Equivalent to: 1.0 g/l Na_2CO_3	1.168 g/l Na_2O 2.0 g/l Na_2CO_3
Untreated		 180:1
Water		
NaOH		
Na_2CO_3		
$Na_2O.SiO_2$		
$Na_2O.2SiO_2$		
$Na_2O.3SiO_2$		
Water Glass 3.3 SiO_2		

Figure 47

Inconsistent Experimental Results. In the course of the experiments results were obtained which sometimes disagreed with the general findings and indicated an extraordinarily strong fiber decomposition during the boiling operations. At first these values were considered as mistakes and were disregarded. However, further experiments continued to give such unusual results and the values obtained broadly agreed with the values formerly considered as erroneous. Therefore, these results could not be dismissed as defective experiments, but it had to be assumed that extraordinary reactions had taken place during the boiling operations in the presence of alkali causing an especially strong fiber decomposition.

By further experiments to discover the reactions causing this remarkable decomposition, it was found that oxygen dissolved in the baths was an important factor. The report on these experiments and on the conclusions drawn therefrom is presented in Part II of this paper.

Analytical Methods Used

1. Determination of Decomposed and Dissolved Cellulose. Determination of the fiber lost in the boiling process is somewhat difficult. Weighing the fibrous material before and after the treatments does not indicate this loss satisfactorily because it reveals the quantity of mechanically lost fibers in addition to the quantity of dissolved cellulose. Furthermore, the contents of water and ash in the fiber are changed by the treatment.

However, the determination of the quantity of dissolved cellulose-decomposition products by means of oxidation with potassium bichromate and sulfuric acid is useful. The decomposition products were calculated as cellulose $(C_6H_{10}O_5)x$.

Before beginning the boiling treatment, the level of the liquor with the submerged fibers is marked on the beaker. After the boiling treatment this is brought to its former height and a sample is taken out of the bath in order to determine the contents of cellulose. In determining the total volume after the treatment, the temperature of treatment and the expansion of the volume caused thereby must be considered. One liter of an aqueous solution of 95-98° C. corresponds after the cooling to 20° C. theoretically with 960 ml. However, since some water evaporates during the cooling, the volume of the solution diminishes to a greater extent. In the present experiments the volume diminished from 1,000 cc to 930 ml. Therefore, the analytical values are to be multiplied by a correction factor (f = 0.93).

The following procedure was used:

25 ml. of the bath at 20° C. are mixed in a 500 cc flask with
6 " of 0.5 normal solution of potassium bichromate,
65 " of water and
35 " of sulfuric acid of 76-77%.

The mixture is boiled for 3 minutes and after cooling 160-170 ml. of water is added to bring the volume up to 300 ml. The potassium bichromate oxidizes the cellulose according to the following equation:

$$C_6H_{10}O_5 + 12\,O = 6CO_2 + 5H_2O$$

The excess bichromate is determined by titration with 0.1 normal solution of ferrous ammonium sulphate using o-phenantrolin as indicator.

In order to adjust the unstable solution of ferrous ammonium sulphate to the stable solution of potassium bichromate and to determine the quantity of organic substances present in the baths before the boiling treatment, two blank treatments (one with boiling, the other without boiling) are performed in each series of the experiment.

If the amount of 0.1 normal ferrous ammonium sulfate is:

in the main experiment	a cc,
in the blank experiment without boiling	b cc,
in the blank experiment with boiling	c cc,

then the cellulose contents (x) in 1,000 cc of bath is:

$$x = \frac{c-a}{b} \times 810 \times f \text{ mgm.}$$

The correction factor f must be found in each case by experiment. Staple fiber and artificial silk generally contain sizes and other materials. They are mostly water-soluble organic substances which dissolve during the first treatment and then likewise are oxidized by potassium bichromate and sulfuric acid. Therefore, the values obtained, especially after the first treatment, are too high. In order to avoid this, these initial values were always reduced by those obtained after the first treatment in water. However, as this procedure often results in inconsistent values obtained after the first boiling treatment, the curves were plotted using the values obtained after the second treatment. The inaccuracy caused thereby is very small and generally is less than 1% of the total quantity of decomposed and dissolved cellulose.

In the experiments with cotton, this correction is omitted, since this fiber does not contain any such size. However, in this case all noncellulosic materials contained in the raw cotton, so far as they are decomposed and dissolved, are determined as cellulose.

2. Determination of the Consumption of Alkali in the Boiling Treatment. The determination of the alkali content of the baths before the treatment is carried out by direct titration with hydrochloric acid, with the use of methyl orange or bromthymol blue as indicator.

After the boiling treatment the bath is filled up with water to the original volume, then an aliquot part is taken off and used for titration. A titration immediately after the boiling treatment is impossible because of the fact that the decomposed and dissolved cellulose have a reducing action on the indicator which makes the final titration point difficult to observe. Therefore, the bath is mixed at first with an excess of sulfuric acid, boiled for 5 minutes and after cooling the sulfuric acid is determined by titration with caustic soda solution.

As some authors have maintained that the titration of sodium silicates gives no exact end point, this process was thoroughly examined. It was found that the accuracy is 98.9% when titrating with normal solution of acid and methyl orange as indicator. When using methyl red as indicator, the accuracy is 98.0%

3. Ash Content of the Fibers. The incineration of the fibers was carried out in a muffle furnace at 600° C. The stated values relate to absolutely dry fibers.

Summary

On the base of comprehensive experiments the following could be established:

1. When treating cellulosic fibers in boiling baths with alkali, the physical and chemical changes of the cellulosic fibers do not depend on the proportion of goods to liquor in the bath.

2. The degree to which the cellulosic fiber is damaged by the action of different alkalies in boiling baths depends upon the kind of fiber and the nature and concentration of the alkali. The extent of fiber impairment was found by determining the quantity of decomposed and dissolved cellulose, the damage factor, the tensile strength and the elongation at break, and by microscopical observations.

3. As to the specific chemical and physical action of the different alkalies upon the cellulose the following order could be established:

Caustic soda solution	- Strongest decomposition of fiber
Sodium monosilicate	- Somewhat smaller decomposition of fiber
Sodium carbonate	- Considerably smaller decomposition of fiber
Sodium disilicate	- Still smaller decomposition of fiber
Sodium trisilicate	
Water glass 3.3 silicate	
Water	- Smallest decomposition of fiber

4. When using caustic soda, sodium monosilicate or sodium carbonate, the degree of fiber damage increases with growing alkali concentrations. However, the rate at which the fiber is impaired is diminished as the alkali concentrations become greater. When using sodium disilicate, sodium trisilicate or water glass (3.3 silicate) the maximum fiber damage in most cases is attained with small alkali concentrations.

5. There is no relationship between the pH value of the alkali solutions and the degree of fiber damage. It could only be observed that, comparing two solutions of different alkalies but equal alkali concentrations (based on Na_2O), the solution with the higher pH value has the most deleterious effect on the fiber.

6. The quantities of alkali absorbed by the cellulosic fibers during the boiling treatment depend essentially on the kind of fiber, but not on the concentration of the baths. When using caustic soda in the boiling bath, the fibers in all cases absorb appreciably more alkali (based on Na_2O) than when other alkalies are used.

7. Mineral deposits were observed only when using sodium trisilicate in which case the silicate deposited depends on the concentration of the baths. By using other alkalies, especially sodium monosilicate or sodium carbonate, the deposition on the fiber is largely prevented.

A method of determining the quantity of cellulose decomposed and dissolved during the boiling treatment is given.

Part II

The Effect of Drying or Oxygen on the Alkali Boil

In Part I of this paper, two experiments were reported, in one of which the ratio of goods to liquor was varied, and in the other, six different alkalies at four concentrations were used under general laundry conditions. Some of the results indicated excessive fiber decomposition, the cause of which was investigated in the experiments described in this section.

Since the experimental conditions were such that thermal decomposition of the fiber was improbable, the effect of repeated dryings after each of the boils was investigated. In addition, an exhaustive study was made of the effect of oxygen dissolved in the bath.

Third Series of Experiments

Effect of the Drying Process on the Fiber. In the 50 boils with water or alkaline solutions the action on the fiber constantly varies, the boiling causing the swelling of the fiber and subsequent drying causing its contraction. Therefore, it was the aim of the present series of experiments to determine the effect of this alternate swelling and contraction of the fiber on its strength and other properties.

Procedure. For the purposes of simplification, the experiments were divided into two groups:

Group A: Treatment of one fiber with different alkalies in different concentrations.

Group B: Treatment of four different fibers with sodium carbonate in one concentration.

The following experiments were performed:

Group A

1) A continuous 25-hour boil.
2) 50 boils, each of half an hour, followed by rinsing, centrifuging and drying the fiber after each treatment, using a fresh bath each time.

Alkalies used:

1) Anhydrous sodium carbonate, analytically pure.
2) Sodium monosilicate (sodium metasilicate) $Na_2O \cdot SiO_2 . 4H_2O$.

3) Technical Water Glass 38-39° Be ($Na_2O \cdot 3 \cdot 3\ SiO_2$), 35.95%.

4) Water (for comparison).

Concentrations used:

The treatment of the fiber was carried out in three different concentrations of alkali, based on Na_2O.

Concentration No. 1: 0.584 g/l Na_2O equivalent to 1.0 g/l anhydrous sodium carbonate
No. 2: 1.168 g/l Na_2O equivalent to 2.0 g/l anhydrous sodium carbonate
No. 3: 1.752 g/l Na_2O equivalent to 3.0 g/l anhydrous sodium carbonate
Proportions of goods to liquor 1:20
Quantity of bath: 1000 cc
Kind of fiber: Spun rayon No. 5.

Group B

Boils: As in Group A.

Alkali: 1 g/l analytically pure anhydrous sodium carbonate.

Proportion of goods to liquor: 1:20
Quantity of bath: 1000 cc
Kind of fiber: Spun rayon No. 1
" " " 2
" " " 4
Raw cotton yarn.

Determinations: Quantity of decomposed and dissolved cellulose.
Damage factor (Schädigungszahl).
Tensile strength of the wet fiber.
Elongation at break of the wet fiber.
Ash contents of the fiber.
Photomicrographs.

Experimental Results. The results of this series of experiments are presented in the form of tables and curves.

Decomposition of fiber:

Figures 48 to 50 show that considerably less cellulose is decomposed and dissolved by a single continuous boiling treatment of 25 hours with water or with alkalies in the different concentrations than by 50 boils, each of half an hour, followed by rinsing and drying the fiber after each boil. Furthermore, the quantities of cellulose decomposed by the 25-hour boil, using different concentrations are always nearly the same, whereas considerable difference in the quantities was found, when using the 50 boils with subsequent dryings using different alkali concentrations.

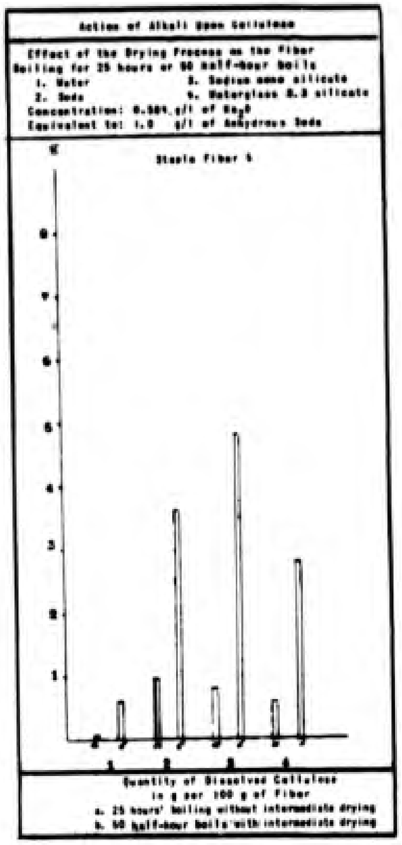


Figure 48

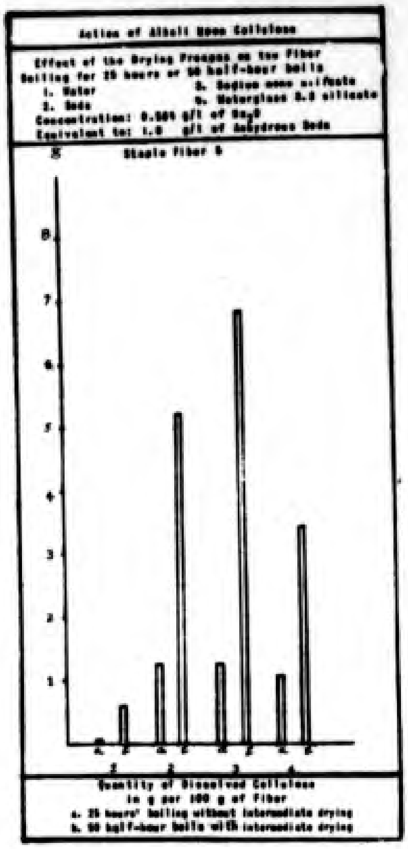


Figure 49

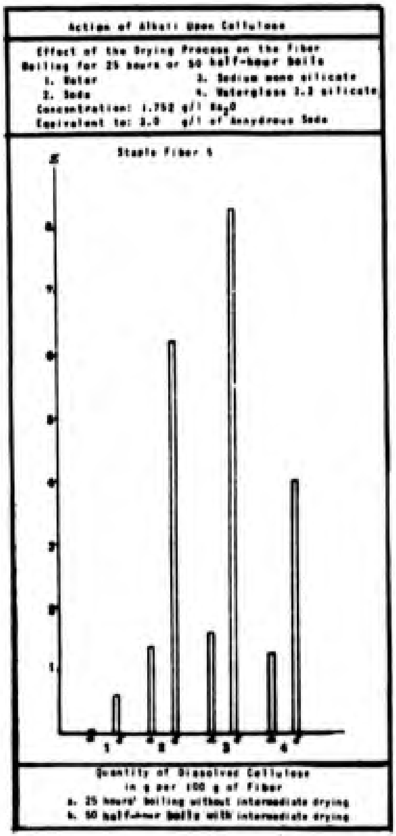


Figure 50

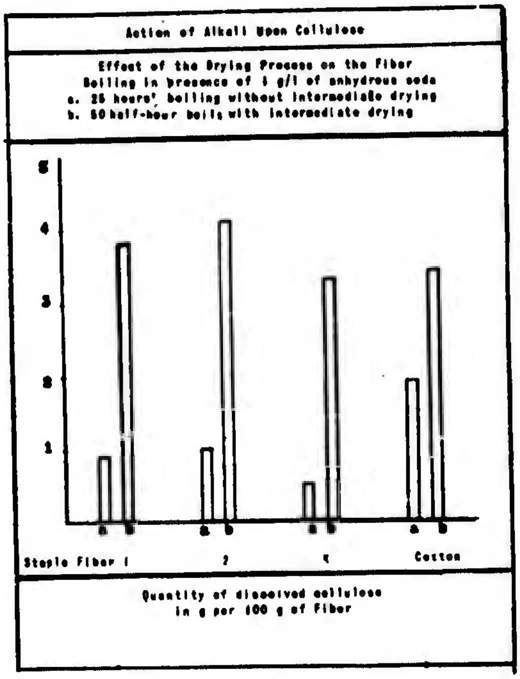


Figure 51

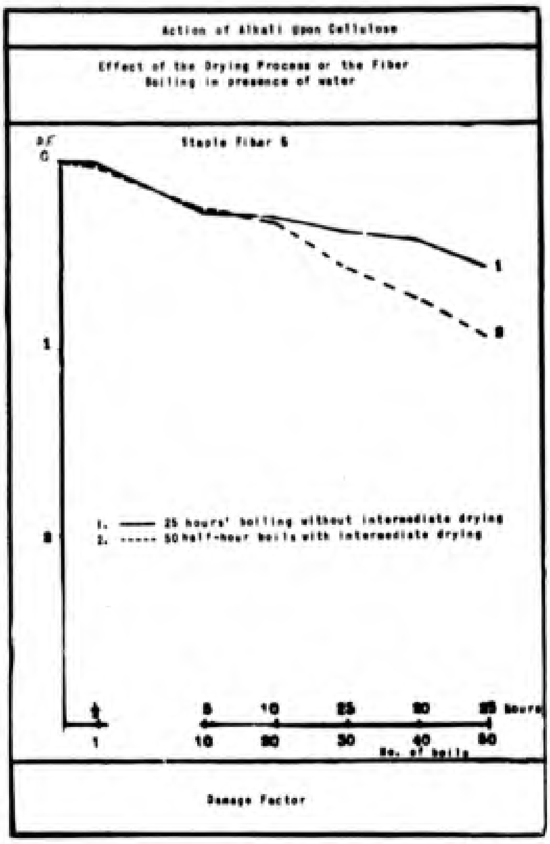


Figure 52

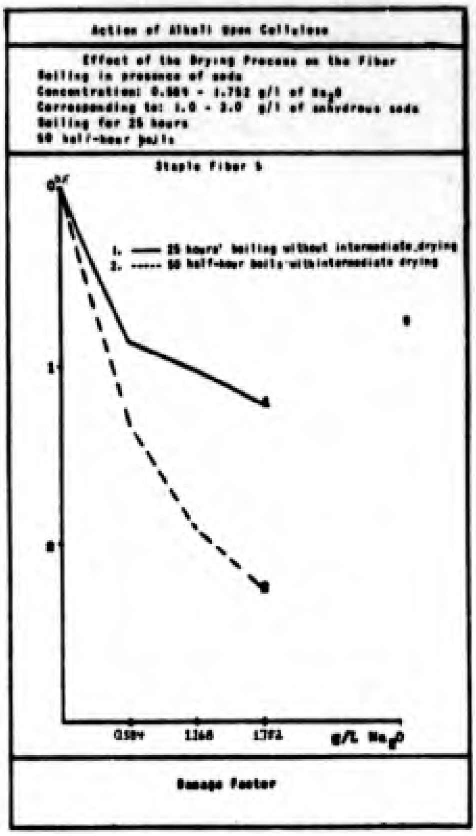


Figure 53

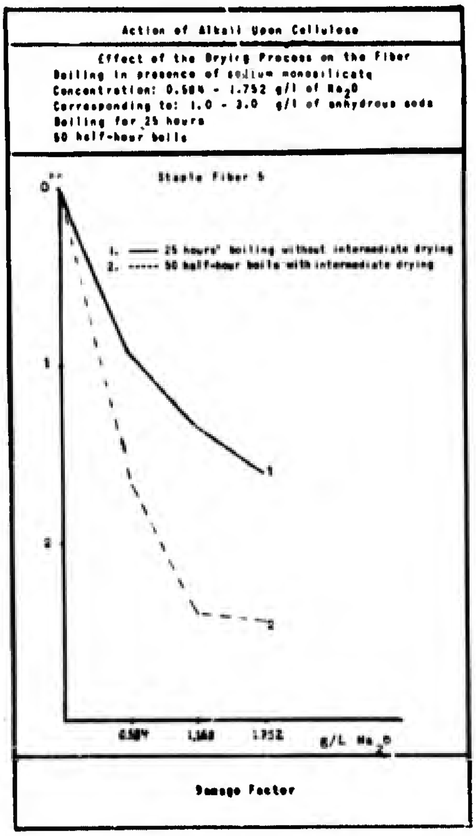


Figure 54

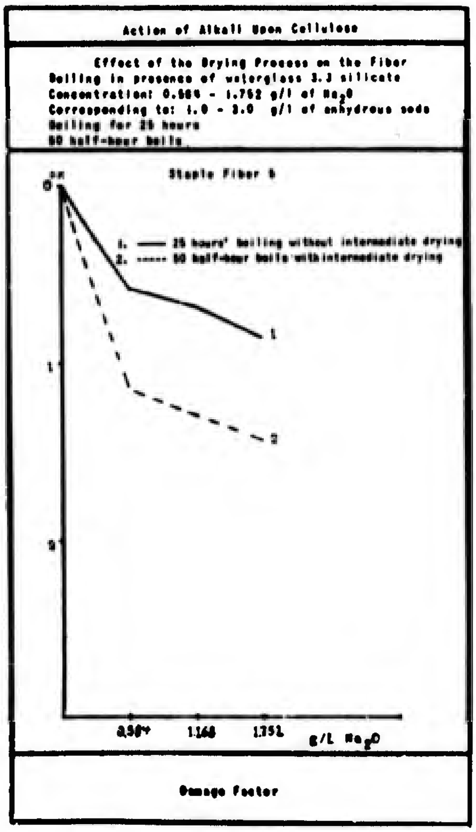


Figure 55

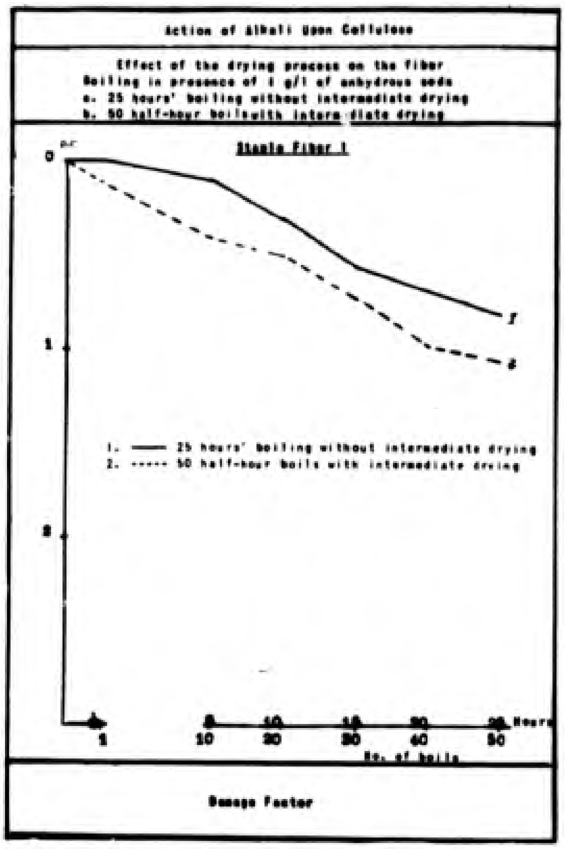


Figure 56

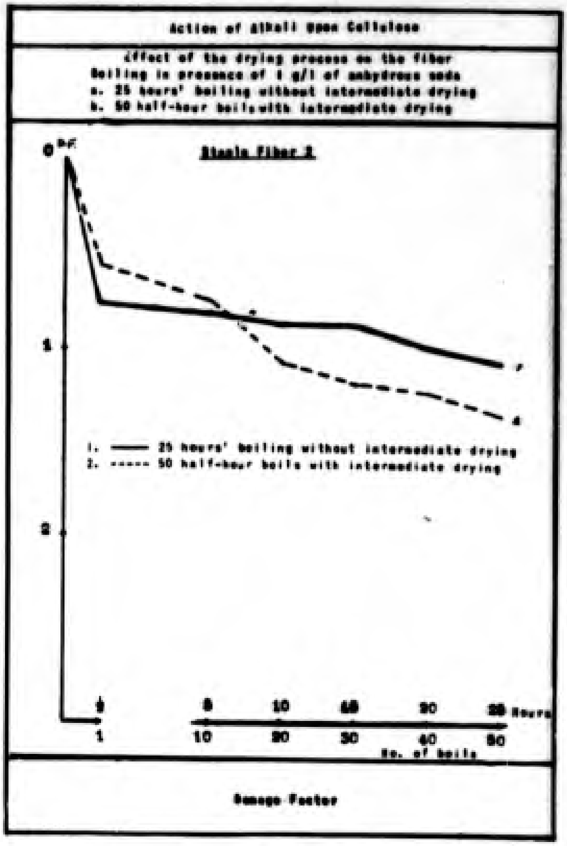


Figure 57

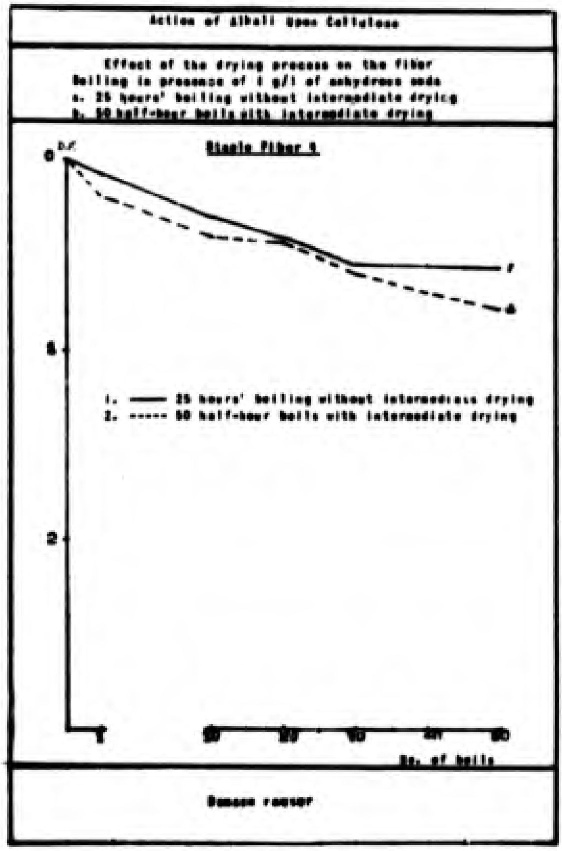


Figure 58

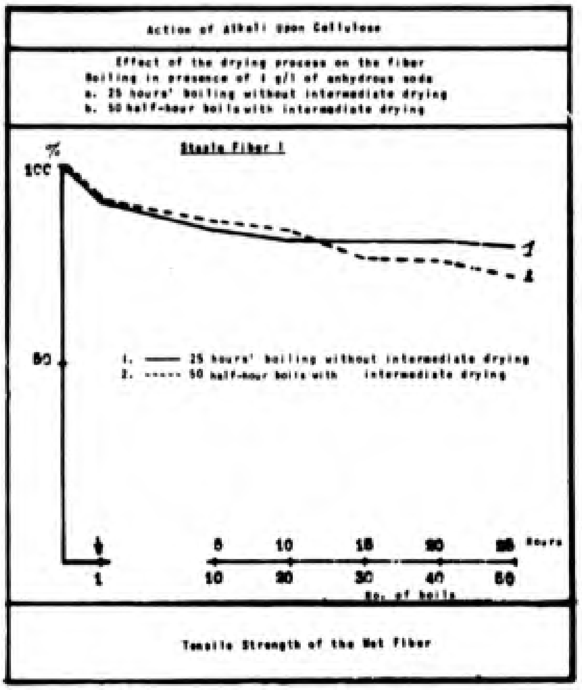


Figure 59

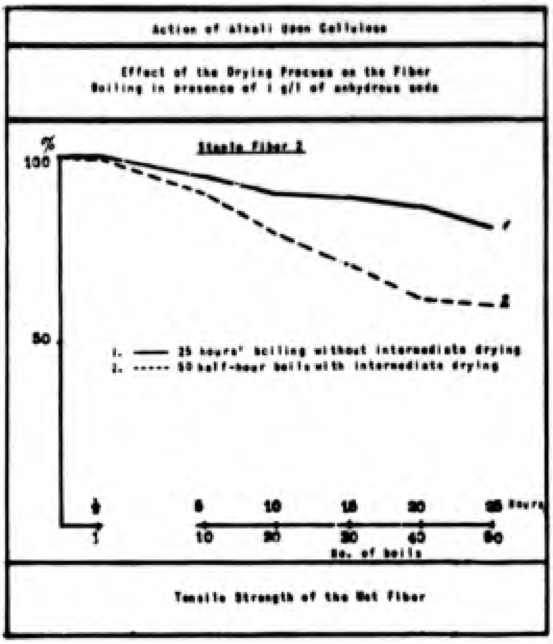


Figure 60

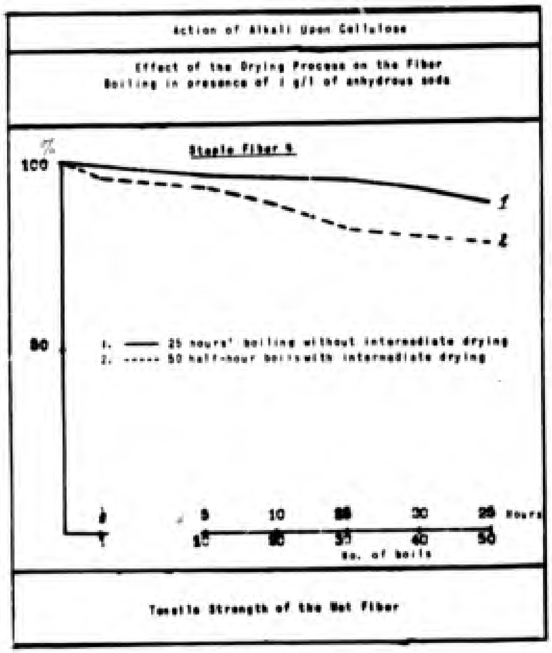


Figure 61

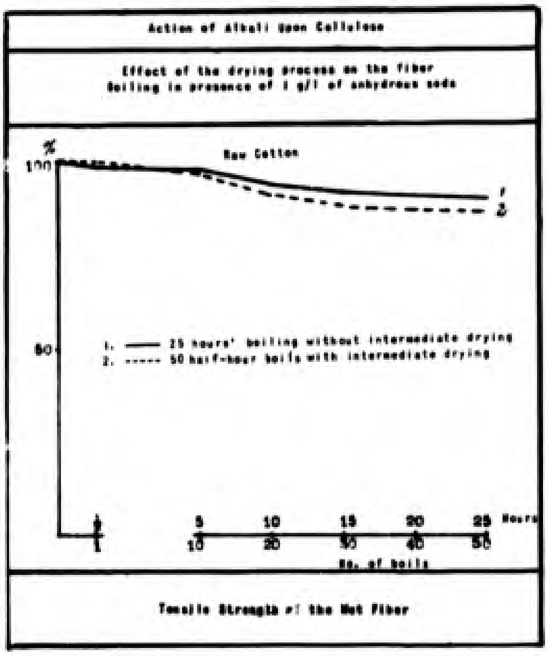
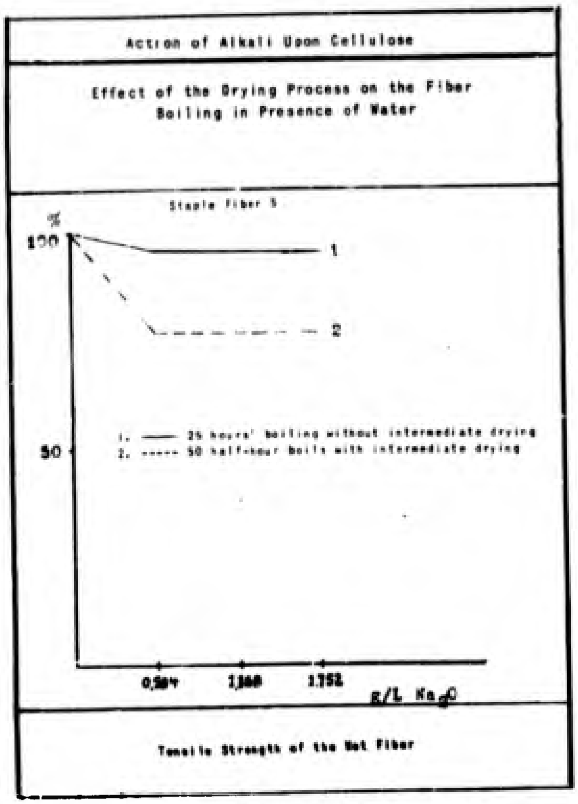


Figure 62



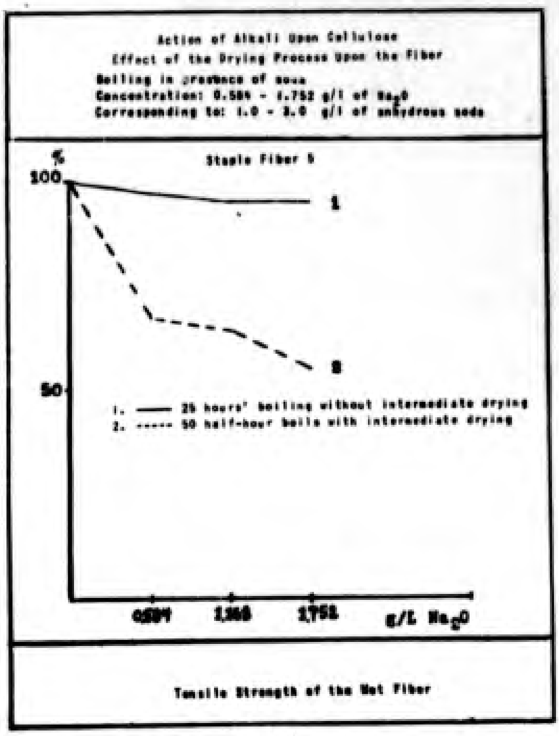
Action of Alkali Upon Cellulose

Effect of the Drying Process on the Fiber
Boiling in Presence of Water

Staple Fiber 5

Tensile Strength of the Wet Fiber

Figure 63

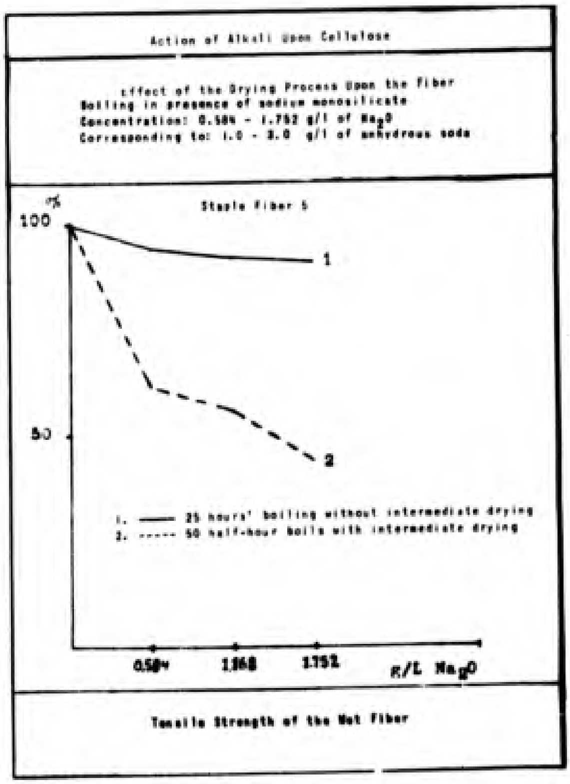


Action of Alkali Upon Cellulose
Effect of the Drying Process Upon the Fiber
Boiling in presence of soda
Concentration: 0.584 - 1.752 g/l of Na_2O
Corresponding to: 1.0 - 3.0 g/l of anhydrous soda

Staple Fiber 5

Tensile Strength of the Wet Fiber

Figure 64



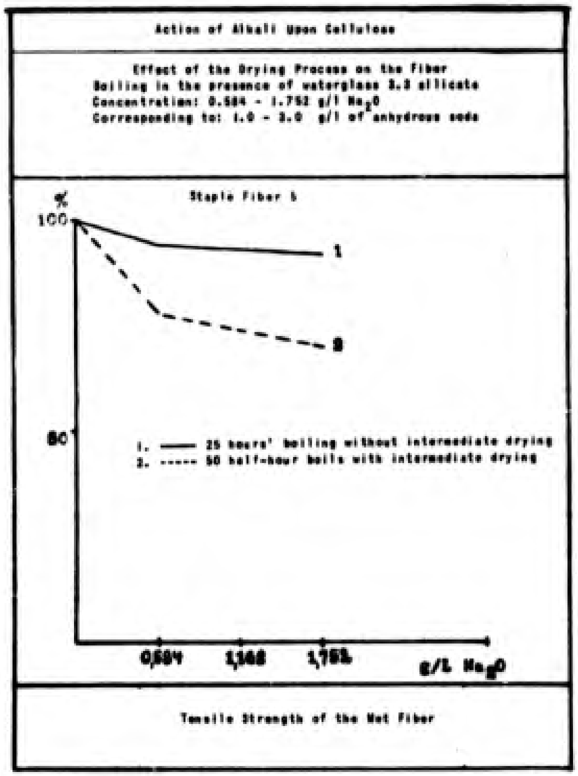
Action of Alkali Upon Cellulose

Effect of the Drying Process Upon the Fiber
Boiling in presence of sodium monosilicate
Concentration: 0.584 - 1.752 g/l of Na_2O
Corresponding to: 1.0 - 3.0 g/l of anhydrous soda

Staple Fiber 5

Tensile Strength of the Wet Fiber

Figure 65



Action of Alkali Upon Cellulose

Effect of the Drying Process on the Fiber
Boiling in the presence of waterglass 3.3 silicate
Concentration: 0.584 - 1.752 g/l Na_2O
Corresponding to: 1.0 - 3.0 g/l of anhydrous soda

Staple Fiber 5

Tensile Strength of the Wet Fiber

Figure 66

Figure 51 shows that similar results were obtained with spun rayons made for staple fibers 1, 2, and 4, and with raw cotton yarn. With raw cotton the difference between the 25-hour boil and the 50 one-half hour boils was not as great as with the staple fiber materials. In this case, consideration must be given to the fact that pectin compounds, waxes, fats, and other organic impurities are inherent in the raw cotton and are dissolved and determined as cellulose.

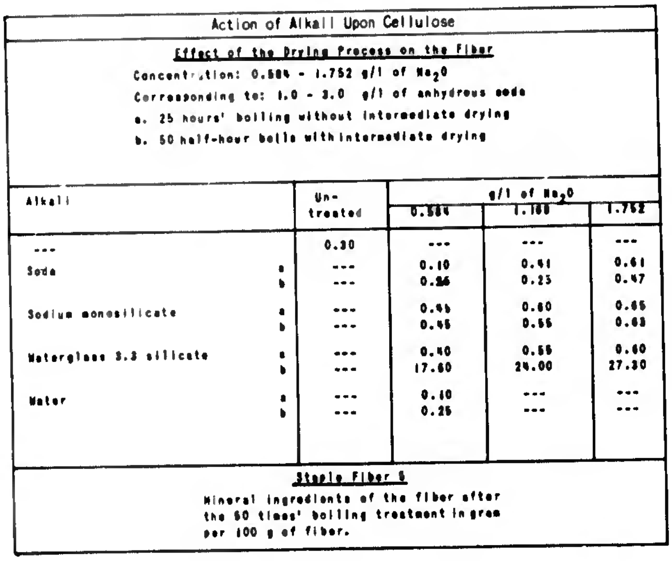
Damage Factor (Schädigungszahl). According to the experimental results, repeated boils with subsequent dryings have the effect of increasing the damage factor to an appreciably greater degree than does one long boil without dryings. (See Figures 52 to 58.)

The differences vary according to the fibers used. Among the alkalies used in the treatments with or without dryings sodium monosilicate causes especially high differences in the damage factor, whereas water glass (3.3 silicate) causes only small differences and the value of sodium carbonate lies between those of the two other alkalies.

The results of these determinations essentially confirm the observations made in the investigation of fiber decomposition.

Tensile Strength and Elongation at Break of the Wet Fiber. Mechanical tests on the various fibers confirmed the results of chemical tests and showed that the effect of 50 one-half hour boils with subsequent rinsings and dryings was greater than one continuous 25-hour boil. The loss in wet tensile strength as shown in Figures 59 to 66 was always greater with 50 one-half hour boils, sometimes as much as 50%. Results differed with the various fibers. Data on the wet elongation of the fibers confirmed the results of the tensile-strength tests, but are not presented here.

Ash Content. As can be seen from the table below, the boiling treatment of the fiber without dryings, even when high alkali-silicate concentrations were used, caused only a small quantity of mineral compounds to be deposited on the fiber.



Action of Alkali Upon Cellulose

Effect of the Drying Process on the Fiber

Concentration: 0.584 - 1.752 g/l of Na_2O

Corresponding to: 1.0 - 3.0 g/l of anhydrous soda

a. 25 hours' boiling without intermediate drying

b. 50 half-hour boils with intermediate drying

Alkali		Un-treated	g/l of Na_2O		
			0.584	1.168	1.752
---		0.30	---	---	---
Soda	a	---	0.10	0.41	0.61
	b	---	0.26	0.23	0.47
Sodium monosilicate	a	---	0.44	0.60	0.65
	b	---	0.45	0.55	0.63
Waterglass 3.3 silicate	a	---	0.40	0.55	0.60
	b	---	17.60	24.00	27.30
Water	a	---	0.10	---	---
	b	---	0.25	---	---

Staple Fiber 5

Mineral ingredients of the fiber after the 50 times' boiling treatment in gram per 100 g of fiber.

Figure 67

The successive swelling and contraction of the fibers due to boiling and drying results in an absorption of inorganic materials which is especially large in the case of water glass. A single boil, even if continued for a very long period, is not sufficient to deposit appreciable quantities of silicate on the fiber.

Microscopic Observations. A series of photomicrographs of spun rayon No. 5 were taken by Dr. Remuth's phase contrast-process both before and after treatment. Some of these are reproduced in Figure 68. They are typical of the results obtained and illustrate the changes in fiber structure. Isolated results, which may have been obtained accidentally, have not been used.

These photomicrographs show that in the boiling treatment, without dryings, only a few fiber cracks were formed. Furthermore, splintering in the middle and at the end of the fiber can be observed only occasionally. However, after 50 boils with dryings, cross cracks which often cause cleavages of the fiber are to be seen in all cases. Thus, microscopic observations give evidence of the effect of the alternate swelling and contraction of the fibers.

Summary of the Results of the Third Series of Experiments. These examinations show that the fiber is considerably damaged by the alternate swelling and contraction caused by the boiling and drying operations.

The results however, do not explain the causes of the extraordinary fiber decomposition reported in Part I of this paper.

Fourth Series of Experiments

Influence of the Atmospheric Oxygen Contained in the Bath on the Cellulose. When comparing the examinations of the fibers after a 25-hour continuous boil and 50 one-half hour boils, the influence of the oxygen dissolved in the bath on the cellulose must be considered. The maximum content of oxygen in one liter of water at different temperatures is as follows:

20° C.:	0.0434 g of oxygen
50° C.:	0.0265 g " "
80° C.:	0.0138 g " "
100° C.:	0.0000 g " "

Assuming that the alkaline solutions contain the same maximum quantity of dissolved oxygen as water, then the maximum quantity of 0.0434 g of oxygen dissolved in the bath, in the 25-hour continuous boil acts only once on the fiber. However, in the 50 boils, wherein each boil is performed in a fresh bath, the maximum quantity of oxygen acts during each boil, i.e., 50 times on the fiber. In the following series of experiments the influence of the oxygen dissolved in the baths on the cellulose fiber was examined.

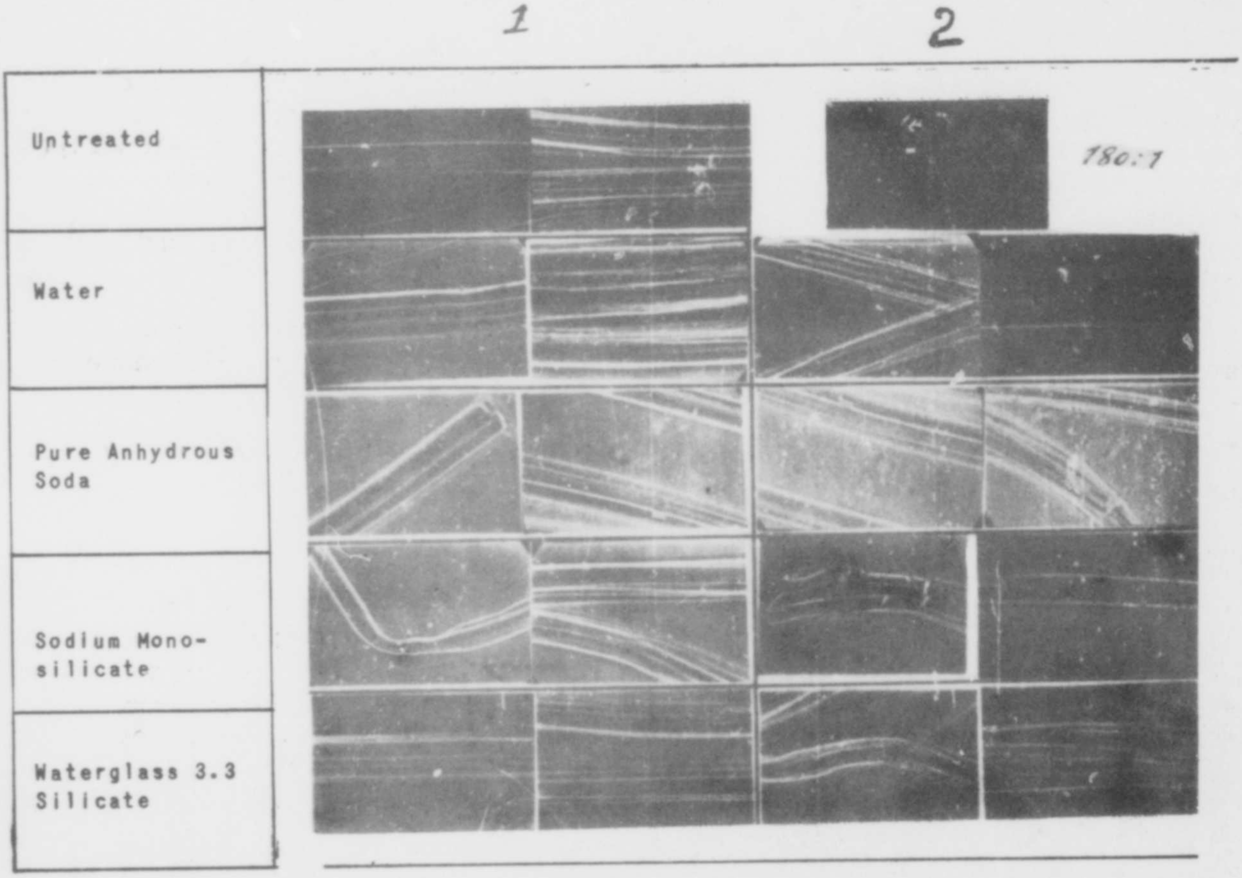
Procedure. The following experiments were carried out:

Effect of the Drying Process on the Fiber

Staple Fiber 5

1. 25 hours' boiling without intermediate drying
2. 50 half-hour boilswith intermediate drying

Concentration: 1.752 g/l of Na_2O
Corresponding to: 3.0 g/l of anhydrous soda



Photographs taken by
Textile Micro Laboratory of Dr. Reumuth of I.G. Farben, Hoechst.

Figure 68

1) 50 boils each of one-half hour, in which air was continually introduced from ten minutes before the start of each boil until the treatment was completed.

2) 50 boils each of one-half hour, using water which was first well boiled out. Ten minutes before the start and during the whole treatment nitrogen was continuously introduced into the baths.

In both cases a reflux condenser was used to control the gases present. The ratio of goods to liquor was 1:20, and the volume of the bath 1,000 ml.

Alkalies:

1) Sodium carbonate
2) Sodium monosilicate

Alkali Concentrations:

No. 1: 0.584 g/l Na_2O cor. to 1.0 g/l soda
No. 2: 1.168 g/l Na_2O " " 2.0 g/l "

Fibrous Material used:

Spun rayon No. 1
" " No. 2
" " No. 4
Raw cotton yarn

Determinations:

Damage factor
Tensile strength of the wet fiber

Experimental Results. These experiments indicate that in the case of cotton and spun rayons No. 1 and No. 4, there was no significant difference in the damage factor or tensile strength when either air or nitrogen was bubbled through the boiling bath. However, when spun rayon No. 2, which is made by the cuprammonium process, is used greater differences were found. Generally, the boils made with the introduction of air caused only slightly more damage than the usual process. When atmospheric oxygen was completely excluded by bubbling nitrogen through the solution there was, in all cases, less damage and in some instances the difference was considerable. Where there was a considerable difference in the amount of damage, traces of copper could be detected by microanalysis. Therefore, it is inferred that these small amounts of copper in the fiber act as oxygen carriers and accelerate the decomposition of the fiber by oxidation.

Figures 69 to 78 show the differences of the damage factors and the tensile strengths of spun rayon No. 2, determined after treatment with admission of air and that with introduction of nitrogen.

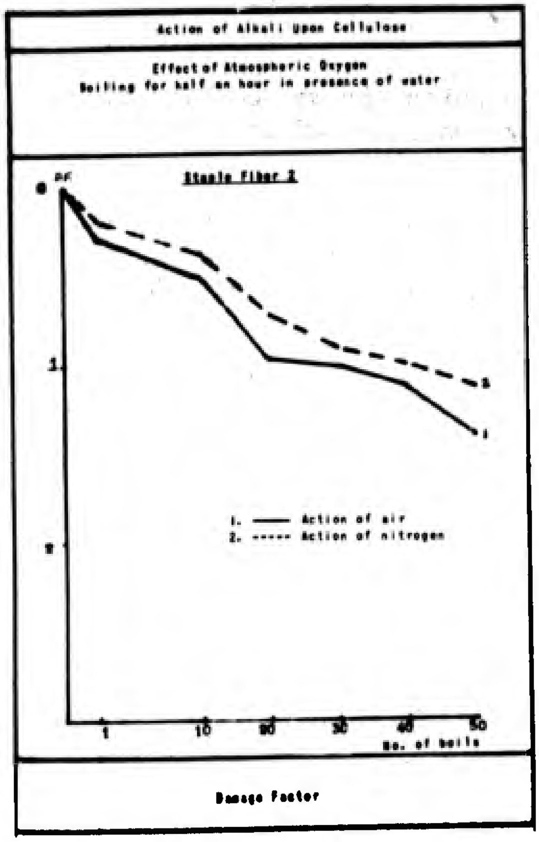


Figure 69

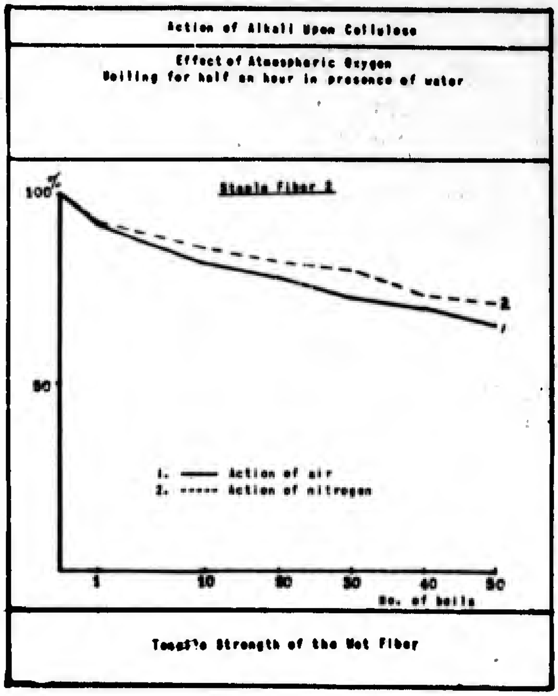


Figure 70

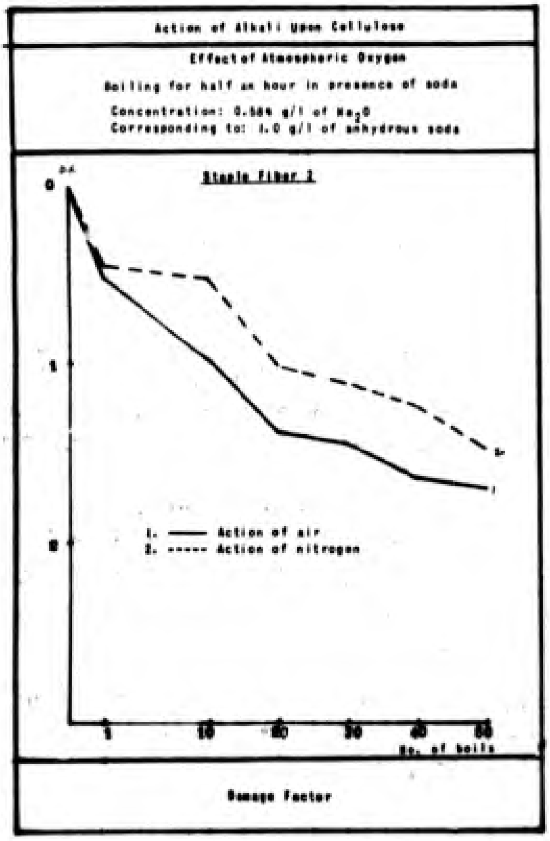


Figure 71

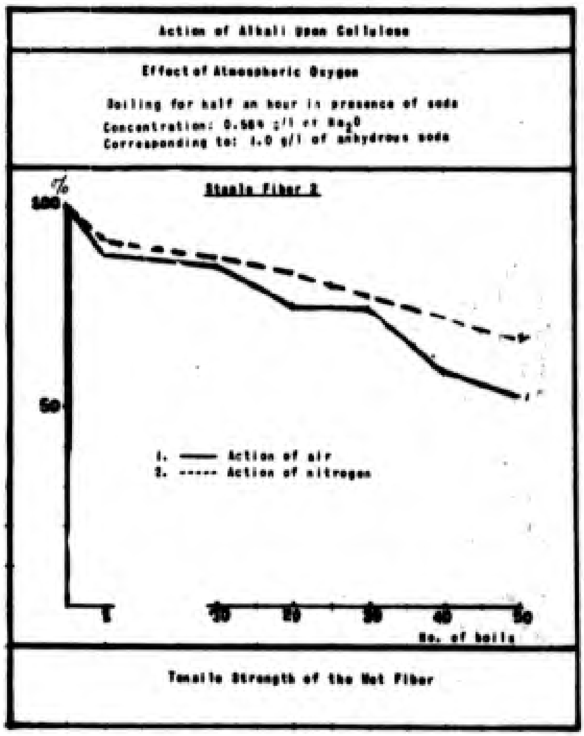


Figure 72

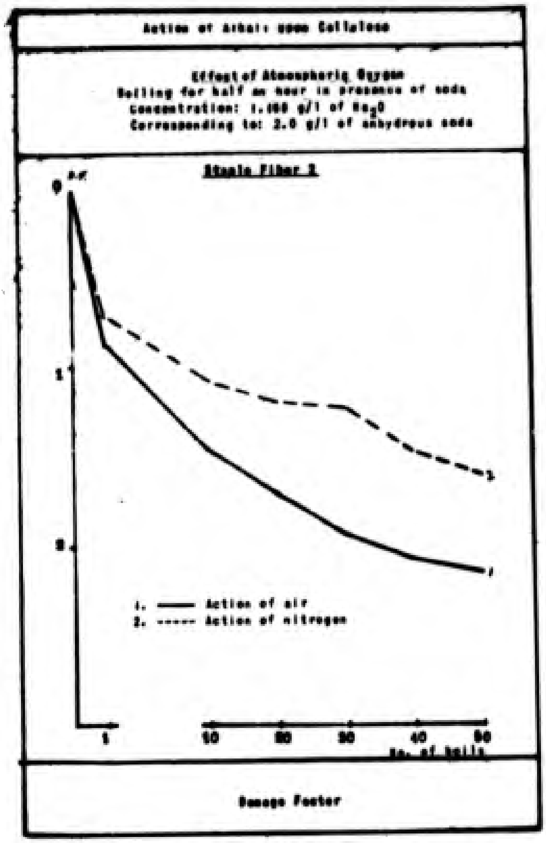


Figure 73

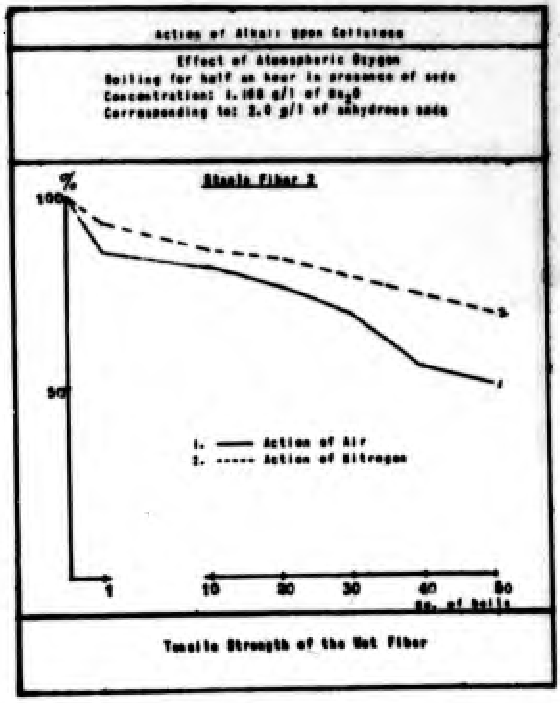


Figure 74

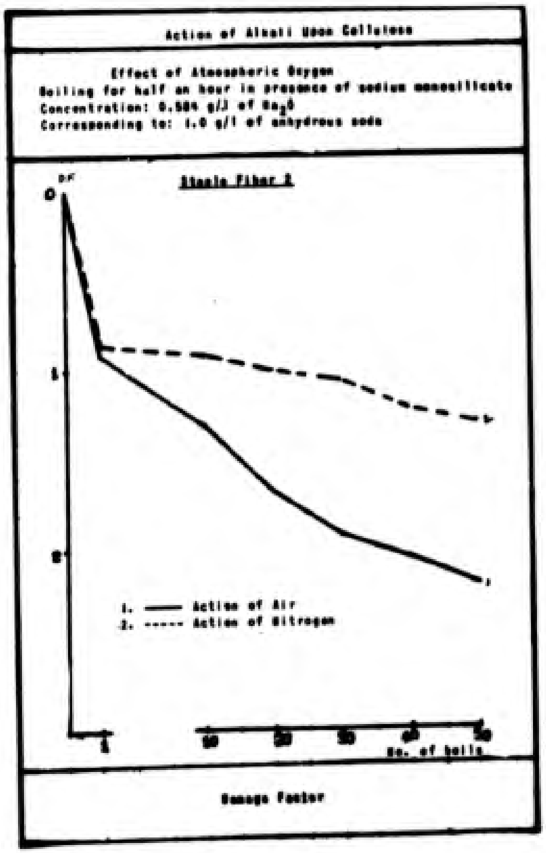


Figure 75

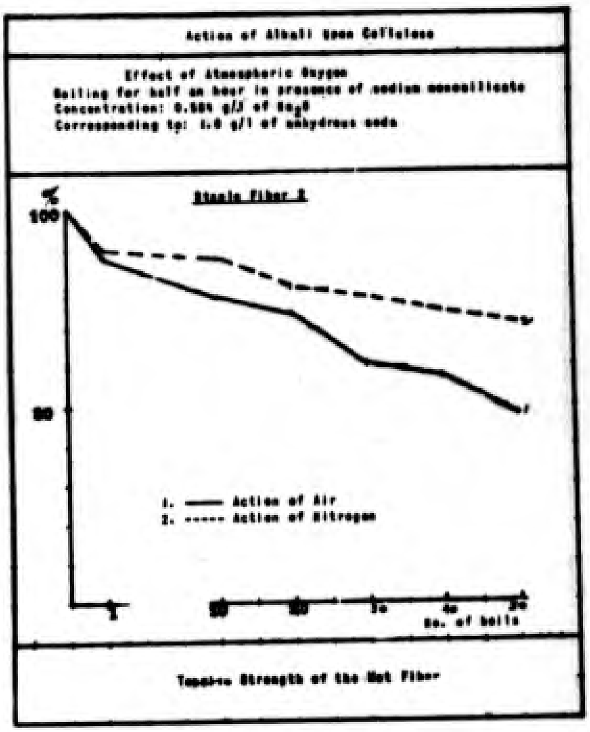


Figure 76

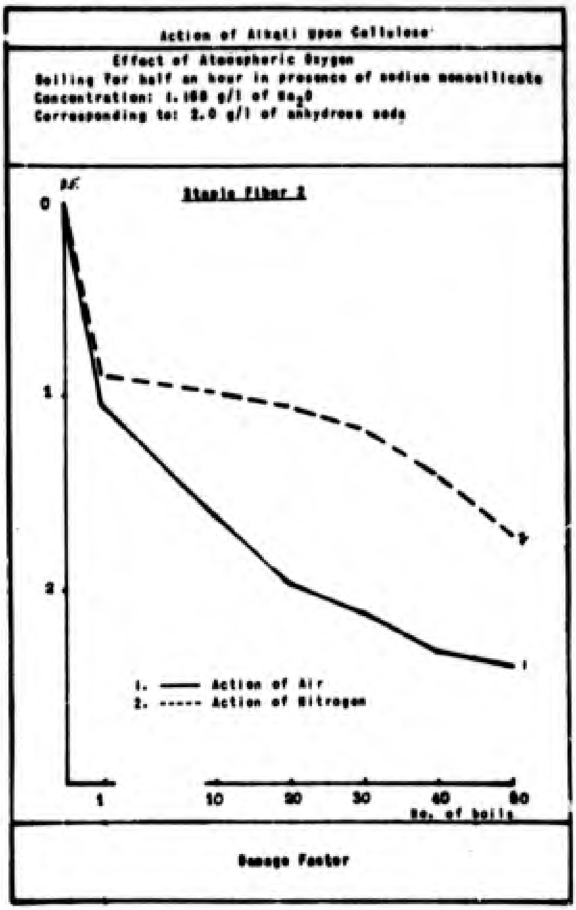


Figure 77

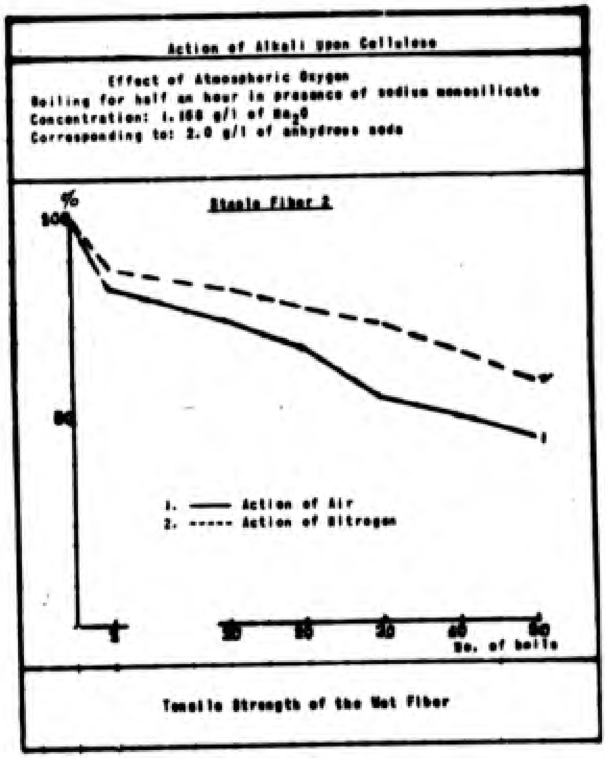


Figure 78

Summary of the Results of the Fourth Series of Experiments. It has been found that to a large extent the oxygen dissolved in the baths is the cause of the increase in damage factor and of the decrease in tensile strength of the cellulosic fibers during treatment in presence of alkali.

However, the oxygen dissolved in the baths is only active if the fibers or the baths contain an active oxygen carrier. Therefore, an especially strong decomposition of fiber by the action of oxygen could be observed when using staple fiber No. 2, since this fiber contains clearly detectable quantities of copper. Schwarz* has confirmed these observations. He treated fibers in baths with alkalies in the presence of oxygen and small quantities of copper salts. He observed an appreciably greater fiber decomposition when treating in a bath with addition of copper salts than in a bath without addition of these salts.

The unusually strong fiber decomposition in some experiments can be explained as being the result of salts which act as oxygen carriers. They may occur as impurities in the fibers or the alkalies.

Fifth Series of Experiments.

Boiling Treatment in the Presence of a Reducing Agent. The results of the investigations of the action of atmospheric oxygen in the baths on the cellulosic fibers led to a further series of experiments wherein the boiling treatments were carried out in the presence of a reducing agent.

Method of Procedure:

Treatment:	50 one-half hour boils Proportions of goods to liquor: 1:20 Quantity of bath: 1000 ml.
Fibrous Material:	Spun rayon No. 1 " " No. 2
Alkali:	1 g/l of analytically pure anhydrous sodium carbonate
Reducing Agent:	Hydrosulfite, conc. Rongalite C (sulfoxylate formaldehyde) Hydroxylamine Pyrocatechol Hydroquinone 4-methylamine-phenol 4-hydroxyphenylglycine

In each case 1 g/l of the sodium salt was used.

Determinations:	Tensile strength of the wet fiber Damage factor

---

* Unpublished communication by Dr. Schwarz at Oppau.

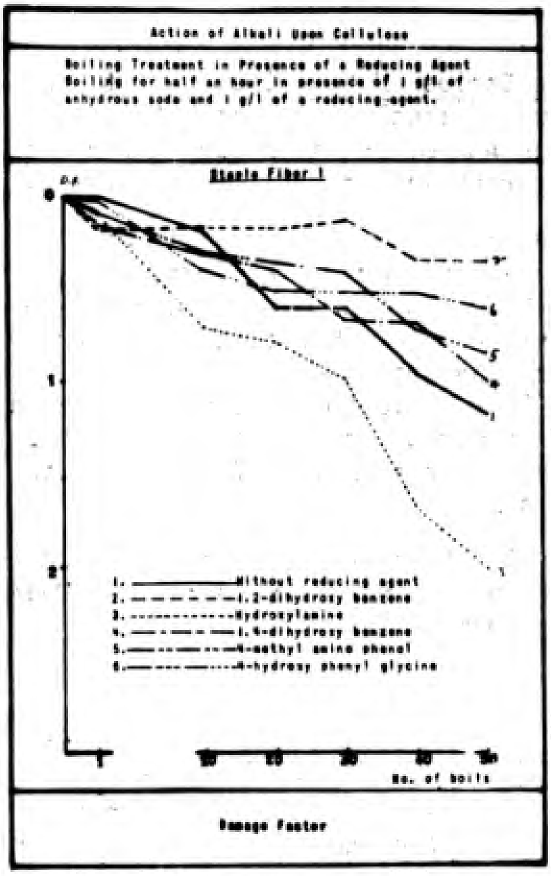


Figure 79

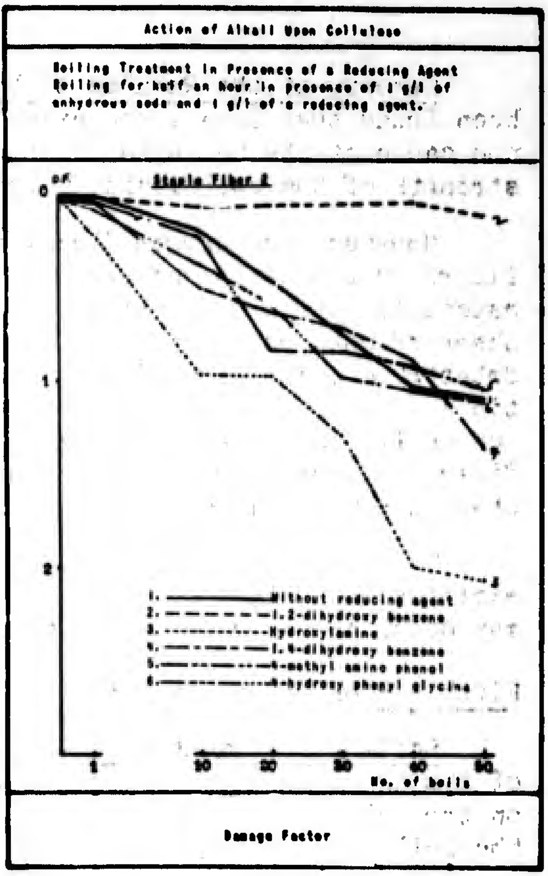


Figure 80

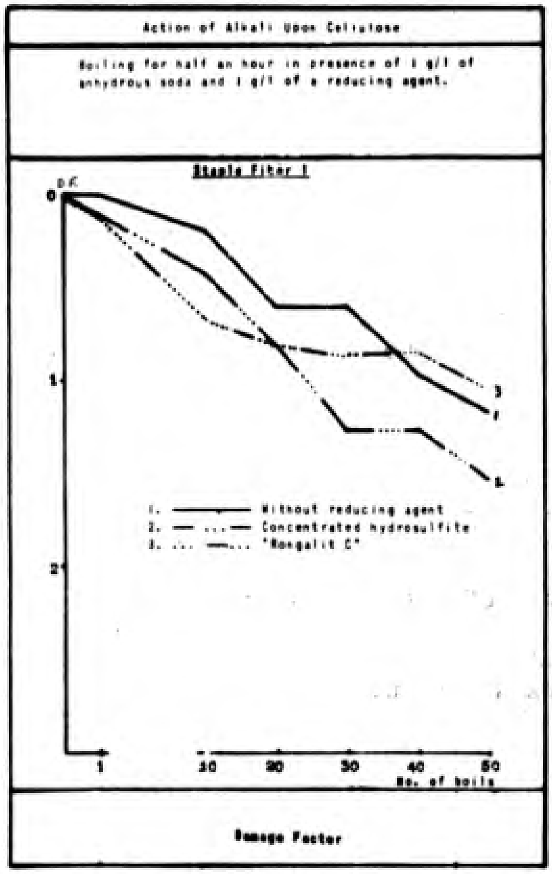


Figure 81

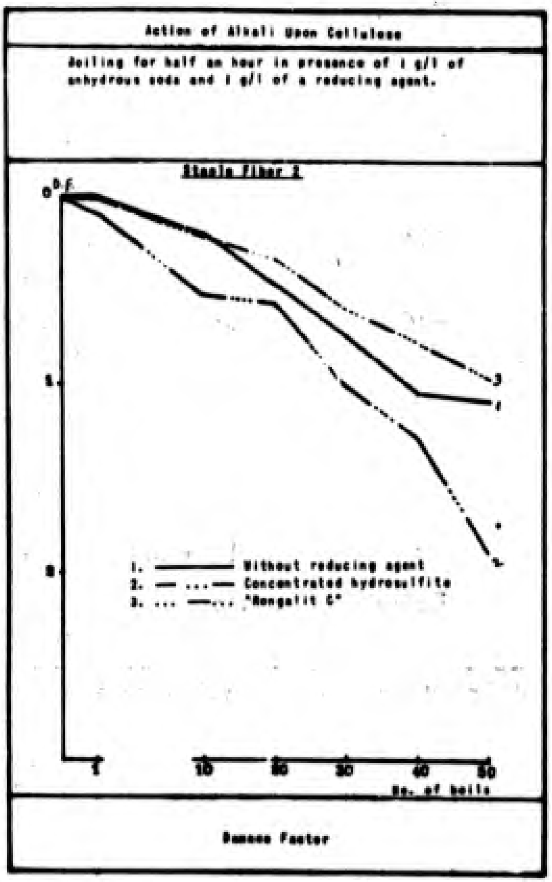


Figure 82

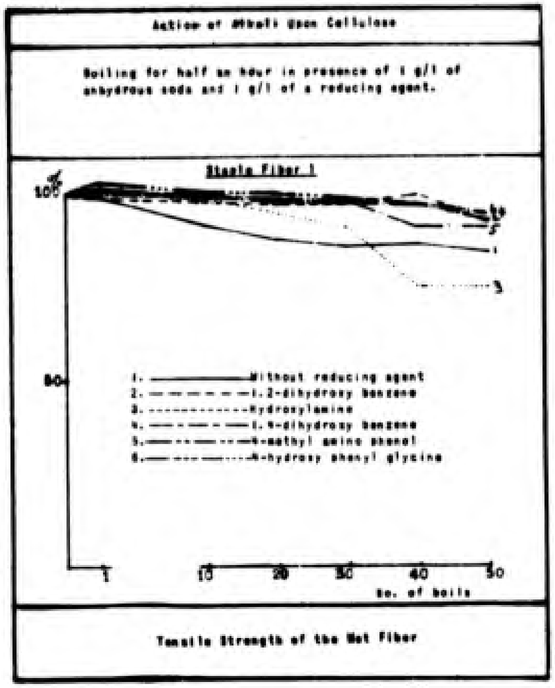


Figure 83

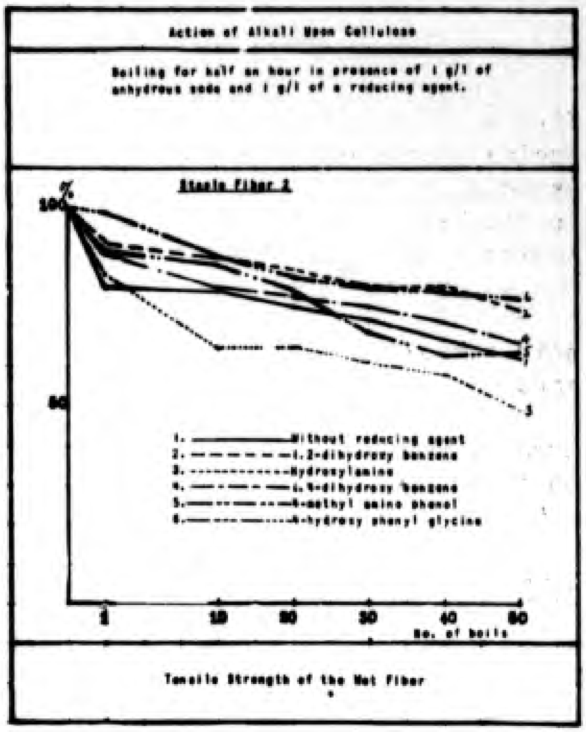


Figure 84

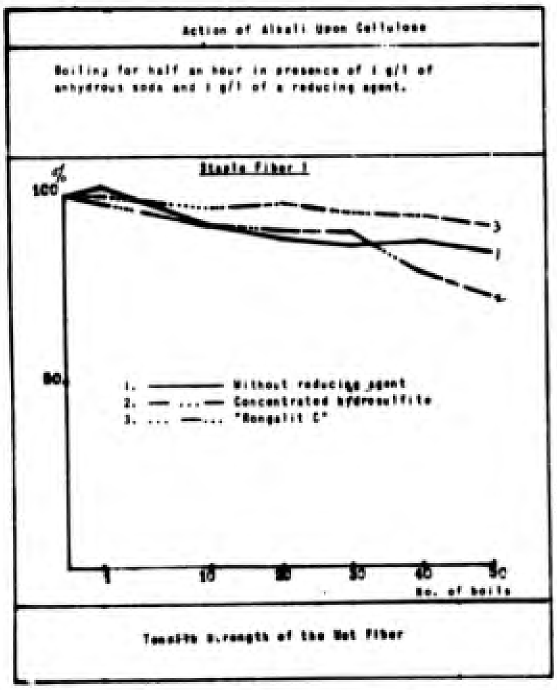


Figure 85

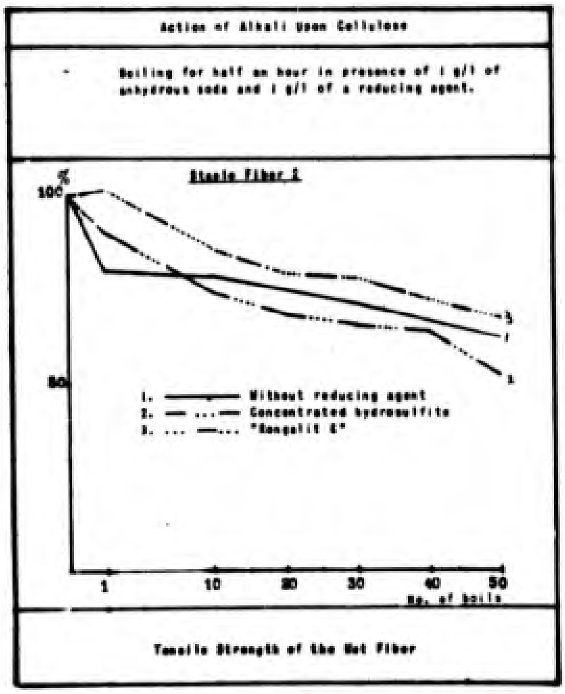


Figure 86

Part III

Chemical Reactions Possible During Treatment of Cellulose with Alkali in Presence of Oxygen

After extensive investigations it has been shown that the decomposition of fibers, the increase in damage factors, the decrease of tensile strength and elongation, etc., in the course of the alkaline treatment of cellulosic fibers are caused by the oxygen dissolved in the baths. (See Parts I and II.) In this section the relationship between experimental results and possible chemical changes in the cellulose structure is discussed.

The formula of cellulose, as generally acknowledged today, is as follows:

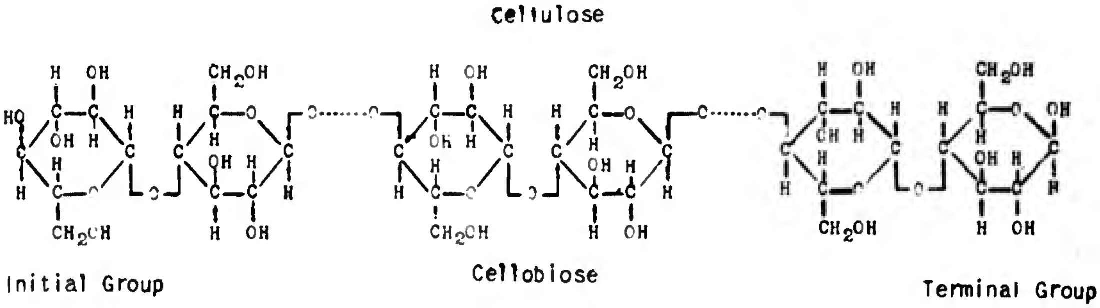


FIGURE 87

The following atoms or atomic groups of cellulose are capable of reacting:

A. One primary and two secondary hydroxyl groups of each glucopyranose unit. The one additional secondary hydroxyl group of the initial member of each cellulose molecule may be disregarded, considering the numerous other hydroxyl groups in the molecule.

These hydroxyl groups are capable of forming alkali salts, ethers or esters. By the action of an oxidizing agent the hydroxyl groups may be oxidized, primary hydroxyl groups being transformed into aldehyde or carboxyl groups, and the secondary hydroxyl groups being transformed into ketonic groups. However, the aldehyde group seems to be unstable as its presence could not be clearly established. When oxidizing the two secondary hydroxyl groups of a glucopyranose ring, the diketone thus obtained is transformed into the corresponding dienediol (Figure 88) since the diketone is unstable to alkali. In the following formulae the spatial arrangement of the groups is disregarded:

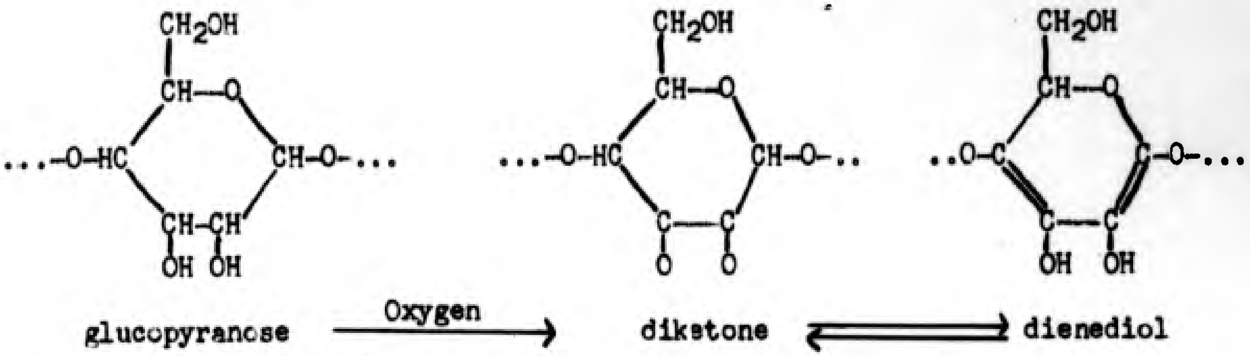


Figure 88

As to the manner of decomposition of the dienediol compound no observations were made; cleavage products likewise were not found. It may be supposed that the cleavage of the diketone in its dienediol form causes also the cleavage of the cellulose chain into two parts.

B. The "terminal group" of each cellulose chain, i.e., the hydroxyl group standing in the terminal member of each cellulose molecule, is of especial importance. As the glucopyranose is to be regarded as having the constitution of a cyclic semi-acetal, the hydroxyl group of the terminal member of the chain may act in its tautomeric form as aldehyde group which has a reducing action, forms aldoximes, hydrazones, etc., and is capable of being oxidized to the carboxyl group.

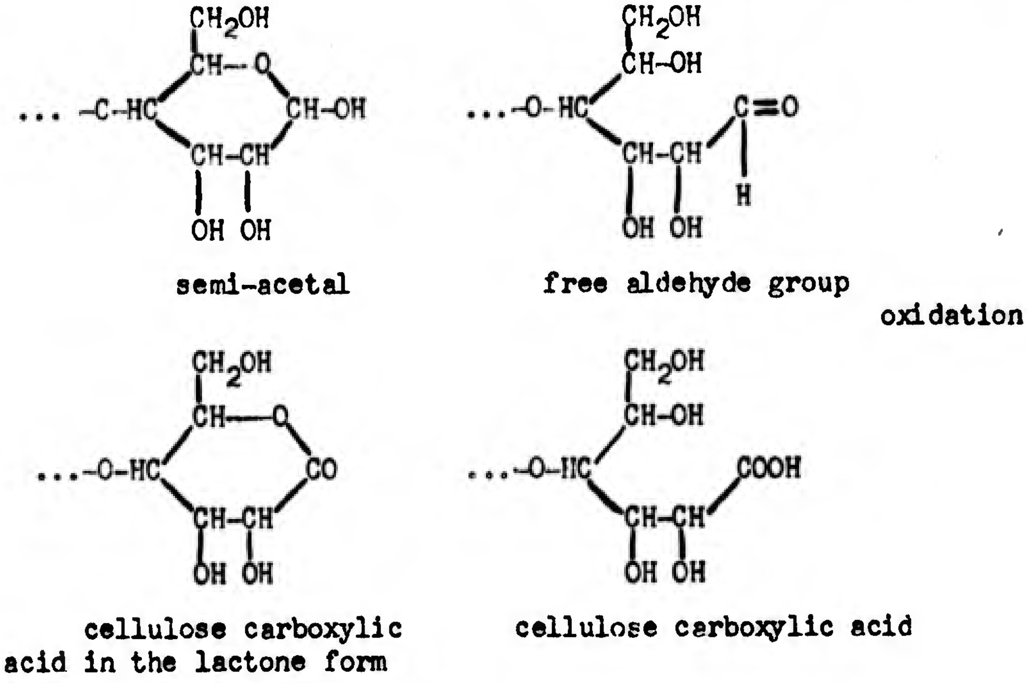
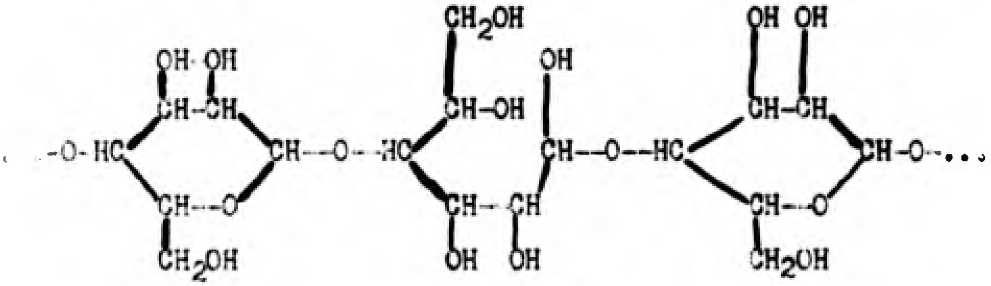


Figure 89

C. The oxygen bridges connecting the glucopyranose rings are split by hydrolysis when subjected to an acid treatment. The degree of splitting and the number and the molecular magnitude of the products thus obtained depend on the particular acid used, the hydrogen ion concentration, the temperature and time of reaction, and other experimental conditions. Apparently the oxygen bridges are not split by hydrolysis when applying an alkaline treatment. In any case, such splitting has not heretofore been clearly proved. It may be mentioned here that disaccharides such as cane sugar, are not split by hydrolysis into glucose and fructose, when subjected to an alkaline treatment and that their oxygen bridges remain intact. As to the other actions of the alkalies on disaccharides, no exact information is available.

D. The glucopyranose rings, like all six-membered heterocyclic compounds containing oxygen, are not completely stable to alkali. The splitting of the pyran ring as it occurs in such substances as tetrahydropyran (pentamethylene oxide) and the pyrones has been investigated* and the decomposition products determined. Since cellulose contains the glucopyranose ring it would seem likely that it would split in a similar manner upon treatment with alkalies without the rupture of the oxygen bridge between the pyranose units. Staudinger** assumes and fully discusses such a splitting in the bleaching process. In the following formula such a splitting is illustrated:



Cellulose with split glycopyranose-ring

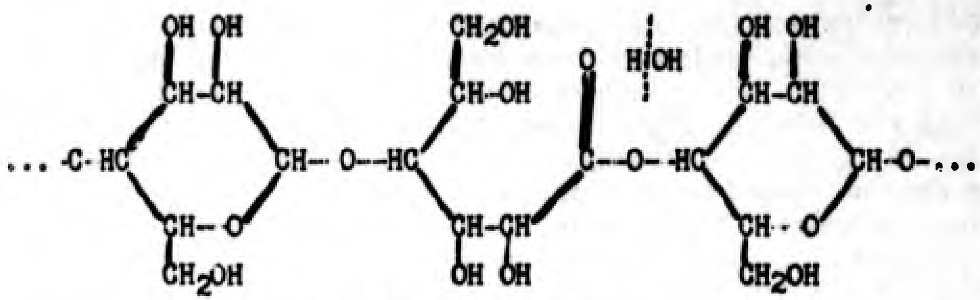
Figure 90

The two hydroxyl groups formed by the splitting of the ring may be oxidized to ketonic groups. When oxidizing the hydroxyl group in position one (i.e. that attached to the carbon of the oxygen bridge), the ether-like linkage of the glucose groups changes to an ester-like one:

---

* Hochstetter, Armin - Monatschefter fur Chemie - <u>23</u>, 1071-1074 (1902)
Demjanow, N. - Chemiches Zentral Blatt - <u>84</u>, 2037 (1913)
Clarke, Hans T. - Journal of Chem. Soc. of London - <u>101</u>, 1788-1809 (1912)

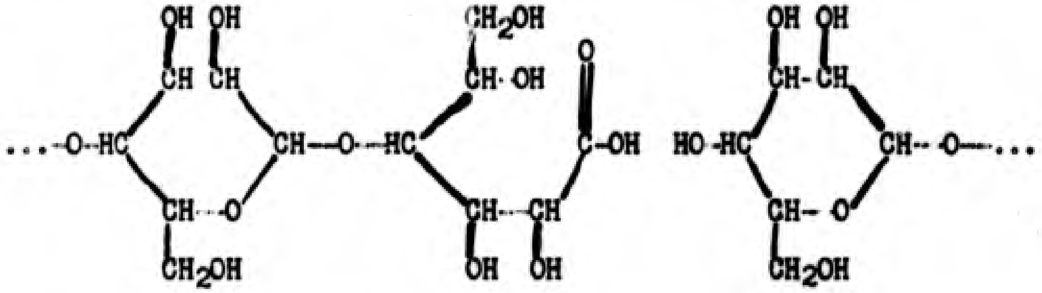
** Staudinger, H. - Mel. Tex. Ber. - <u>22</u>, 369 (1941)



Cellulose with ester group

Figure 91

This ester group is easily saponified by the action of alkali, thus causing the splitting of the cellulose chain:



Cellulose after saponification of the ester-group

Figure 92

In this series of reactions a cellulose chain was split into two parts, one of which contains a carboxylic group in the terminal unit, by the following steps: (a) splitting a glucopyranose ring, (b) oxidizing the hydroxyl group formed in the first step to a ketonic group, and (c) saponifying the ester compound obtained.

These possible reactions when oxygen and alkalies act on cellulose will be considered in more detail in the later papers dealing with the experimental results.

Oxidation of the Terminal Group and of Primary Hydroxyl Groups to Form Carboxyl Groups. The carboxyl groups in cellulose may be determined quantitatively by different analytical methods. Although these methods are still not entirely satisfactory, yet it could be shown that the number of carboxyl groups in cellulose increases when it is subjected to repeated treatments with alkalies in the presence of oxygen.

Whether hydroxyl groups other than the "terminal groups" are oxidized has not been shown. The presence of these carboxyl groups modifies to a certain extent the physical and chemical properties of the cellulosic fiber. One of the most notable changes is an increase in alkali solubility of the fibers. Small changes in tensile strength and elongation might be expected. However, the oxidation of the terminal group or of the primary hydroxyl groups to form carboxyl groups does not in itself cause splitting of the main chains of cellulose and thus give large decreases in tensile strength and increase in damage factors. Yet, the cellulose fibers treated with alkali in presence of oxygen always suffer a considerable increase in damage factor. This proves that, besides the formation of carboxyl groups, other reactions are occurring which cause fiber decomposition.

Oxidation of Secondary Hydroxyl Groups to Form Ketonic Groups. When treating the cellulosic fibers with alkali in presence of oxygen, secondary hydroxyl groups of the cellulose may be oxidized to ketonic groups. These groups react like all ketones with hydrazines to form hydrazones. As phenyl hydrazine, generally used for this purpose, yields only weak yellow shades in the reaction with oxidized cellulose, it was replaced by a coupling hydrazine of the naphthalene series, i.e., 2-hydrazino-8-hydroxy-naphthalene-6 sulfonic acid (Figure 93) which causes the formation of a hydrazone capable of being more easily recognized.

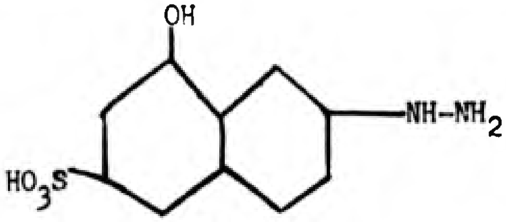


Figure 93

If some secondary hydroxyl groups of the cellulose have been oxidized to ketonic groups by the alkaline treatment in presence of oxygen, these ketonic groups will react with the said hydrazine to form a hydrazone of the cellulose. When treating this hydrazone with a diazonium solution, the coupling takes place in 7-position of the naphthalene compound with formation of an azo dye on the fiber. However, as the terminal aldehyde group of the cellulose and the corresponding cellulose carboxylic acid in its lactone form also react with hydrazines with formation of hydrazones, the untreated fiber will also be dyed although only very weakly.

The cellulosic fibers were treated with a hydrazine and a diazonium compound before and after the repeated alkaline treatments. Thus, it was found that the treated fibers were dyed somewhat more deeply than the untreated fibers, but that the differences were very small. Therefore, it must be supposed that only very small quantities of hydroxyl groups are oxidized to ketonic groups by the alkaline treatment of the fibers. The somewhat deeper tints may be explained by the assumption that the carboxyl groups formed by the alkaline treatment reacted in their lactone form with the hydrazine. These results do not support the hypothesis that a diketone is formed and then changed into a dienediol by the alkali when cellulosic fibers are given repeated alkali boils in the presence of oxygen.

Splitting of a Glucopyranose Ring of the Cellulose-Main-Chain, Oxidation of the Product Obtained to the Ester Cellulose, and Saponification of the Ester-Group. The decomposition of the fiber in the course of the alkaline treatment in presence of oxygen may proceed in the manner illustrated in Figures 90, 91, and 92 as follows: By the action of alkali the glucopyranose rings are split without the cellulose chain being interrupted. One of the hydroxyl groups formed in this step is oxidized by atmospheric oxygen to a ketonic group with the formation of an ester group which is saponified by the alkali. By this reaction the cellulose chain is split into two or more parts, each of which contains a new terminal group in the form of a carboxyl group which may be present as a free carboxyl group or as a lactone compound with the formation of a ring. When assuming this series of reactions in the alkaline treatment of the cellulose fiber in the presence of oxygen, it follows that the degree of polymerization of the fiber must decrease and the number of carboxyl groups must increase. Both these effects were established by experiments. Although the above series of reaction have not been fully established it is believed that they form a good working hypothesis for further investigations.

Detection of Hydrogen Peroxide Formed in the Boiling Treatment of Cellulosic Fibers with Alkali in the Presence of Oxygen. If the oxygen dissolved in the baths acts upon the cellulose during the alkaline treatment, it is reduced to water with the formation of hydrogen peroxide as an intermediate step.

$$O_2 \xrightarrow{\text{reduction}} H_2O_2 \xrightarrow{\text{reduction}} 2H_2O$$

The formation of hydrogen peroxide in the course of the alkaline treatments of the fibers may be determined in the following way:

"Luminol" (Figure 94) i.e. 3-amino-phthalic acid-hydrazide,*

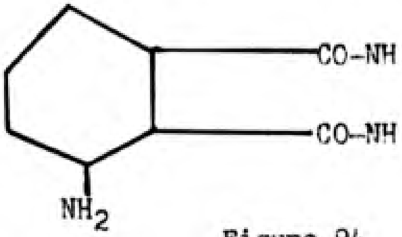


Figure 94

when oxidized in alkaline solution with hydrogen peroxide, shows luminescence. The exact nature of the reaction is not known. However, if haemine (hexanitrocobaltiate) is added, the sensitivity is increased so that a content of 3 x 10^{-5}% hydrogen peroxide may be detected.

---

* Weber, Karl - Ber. 75B, 565-73 (1942)

When boiling cellulosic fibers such as cotton and the commercial fibers used in this investigation for a prolonged time in the presence of sodium carbonate, then rapidly cooling the solution and adding "Luminol", luminescence effects were observed. In case of staple fibers No. 1 and No. 2 the luminescence is just perceptible, whereas in case of No. 3 and of cotton it is strongly marked.

A solution of sodium carbonate, when boiled and cooled in the same manner but without any fiber, does not show this reaction.

When cellobiose is boiled with a solution of sodium carbonate, the luminescence effect is likewise observed, its intensity increasing when the solution is allowed to stand for a longer time.

According to these experiments, hydrogen peroxide is formed as an intermediate product when cellulosic fibers are boiled in presence of sodium carbonate. However, it must be emphasized that this luminescence effect does not necessarily indicate the presence of hydrogen peroxide, as it has been observed that some alkalies in aqueous solution such as caustic soda, sodium monosilicate, water glass, etc., cause the same effect without boiling and without adding any cellulosic fiber to the solution. Furthermore, in the literature some organic compounds are reported to yield similar luminescence effects when treated with "Luminol". Thus it follows that the proof of the intermediate formation of hydrogen peroxide in the boiling of cellulose fibers with sodium carbonate solution is not completely established.

Part IV

The Effect of Magnesium Silicate

Three different staple fibers were subjected to 50 successive alkaline boils with and without the addition of magnesium silicate. The fibers were examined by various physical and chemical methods both before and after the treatments.

Procedure

The cellulosic fibers were subjected to 50 half-hour boils. After each boil they were rinsed with distilled water, dried at 65° C., exposed to the open air for a prolonged time and then subjected to the next treatment in a fresh bath.

Alkalies Used

The fibers were treated with the following alkalies:

1) Anhydrous sodium carbonate, analytically pure.
2) Sodium monosilicate (sodium metasilicate) $Na_2O \cdot SiO_2 \cdot 4H_2O$.
3) Technical water glass of 38-39° Be, $Na_2O \cdot 3 \cdot 3\ SiO_2$ 35.95% solids.

Concentration of Alkali

The baths for treating the fibers were used in two different concentrations:

No. 1: 0.584 g/l of Na_2O corresponding to 1.0 g/l of Na_2CO_3.
No. 2: 1.752 g/l of Na_2O corresponding to 3.0 g/l of Na_2CO_3.

Addition of a Magnesium Silicate to the Bath

The fibers were boiled in baths with and without the addition of magnesium monosilicate or magnesium trisilicate according to the following plan:

1) Without addition.
2) With addition of 0.1 g/l of magnesium monosilicate $MgO \cdot SiO_2$.
3) With addition of 0.5 g/l of magnesium monosilicate $MgO \cdot SiO_2$.
4) With addition of 0.1 g/l of magnesium trisilicate $MgO \cdot 3SiO_2$.
5) With addition of 0.5 g/l of magnesium trisilicate $MgO \cdot 3SiO_2$.

Fibrous Material

Staple fiber No. 1
Staple fiber No. 2
Staple fiber No. 3

Methods of Examination:

1) Fiber Decomposition. After each of the first five boils and then after each 10th boil, the bath was filled up to the original volume and the quantity of dissolved and decomposed cellulose was quantitatively measured by oxidizing it with potassium bichromate in presence of sulfuric acid. When calculating the analytical results, the decomposition products were assumed to be cellulose of the formula $(C_6H_{10}O_5)x$.

2) Damage Factor (Schädigungszahl). Determinations were made after the first and then after each 10th boil.

3) Tensile Strength of the Wet Fiber. Determinations were made after the first and then after each 10th boil.

4) Method of Representing the Experimental Results. The results were represented, for the sake of simplicity, in the form of curves, which are reproduced at the end of this section. The results of corresponding determinations are represented on the same sheet in order to make it possible to compare the different methods.

Index of the Curves

Boiling in Presence of	Concentration No.	Staple Fiber No.	Fig.	Page
Sodium carbonate	1	1	95-97	69
" "	1	2	98-100	70
" "	1	4	101-103	71
" "	3	1	104-106	72
" "	3	2	107-109	73
" "	3	4	110-112	74
Sodium monosilicate	1	1	113-115	75
" "	1	2	116-118	76
" "	1	4	119-121	77
" "	3	1	122-124	78
" "	3	2	125-127	79
" "	3	4	128-130	80
Water glass 3.3 silicate	1	1	131-133	81
" " " "	1	2	134-136	82
" " " "	1	4	137-139	83
" " " "	3	1	140-142	84
" " " "	3	2	143-145	85
" " " "	3	4	146-148	86

Results of Examination

From these curves it follows that when the fiber is treated with alkali, magnesium silicates have a considerable fiber-preserving action, magnesium trisilicate being more active than magnesium monosilicate.

As only 0.1 and 0.5 g/l of the magnesium silicates were used, the concentration necessary for attaining the best protective effect cannot be ascertained from these experiments. However, they show that 0.1 g/l of magnesium silicate does not give satisfactory protection of fiber, whereas, 0.5 g/l gives maximum protection, but may be more than necessary.

The following table indicates the number of boils without the addition of a magnesium silicate which cause the same damage to the fibers as obtained by 50 boils in presence of 0.5 g/l of magnesium monosilicate or magnesium trisilicate. For example, in the case of staple fiber No. 1, 50 boils with 0.5 g/l magnesium monosilicate and 1 g/l sodium carbonate dissolves the same amount of cellulose as 28 boils with 1 g/l sodium carbonate alone.

From this table it may be seen that, according to the kind of fiber, the alkali, the concentration, and the method of examination, 20 to 30 boils without addition of a magnesium silicate causes the same fiber damage as 50 boils with the addition of a magnesium silicate.

Number of Boils Without Magnesium Silicates Equivalent to 50 Boils With Magnesium Silicates

	Alkali Concentration No. 1			Alkali Concentration No. 3		
	Decomposition of Fiber	Average Degree of Polymerization	Tensile Strength	Decomposition of Fiber	Average Degree of Polymerization	Tensile Strength
Staple Fiber No. 1 Boiled with Soda Plus:						
0.5 g/l Mg-mono-SiO_3	28	32	22	36	14	15
0.5 g/l Mg-tri-SiO_3	26	21	5	27	8	(1?)
Staple Fiber No. 1 Boiled with Sodium Monosilicate Plus:						
0.5 g/l Mg-mono-SiO_3	34	27	20	35	33	26
0.5 g/l Mg-tri-SiO_3	30	19	(1?)	32	18	(1?)
Staple Fiber No. 1 Boiled with Water Glass 3.3-Silicate Plus:						
0.5 g/l Mg-mono-SiO_3	40	37	41	26	27	14
0.5 g/l Mg-tri-SiO_3	28	31	18	18	25	(1?)
Staple Fiber No. 2 Boiled with Soda Plus:						
0.5 g/l Mg-mono-SiO_3	33	18	34	38	14	40
0.5 g/l Mg-tri-SiO_3	28	(1?)	32	28	8	19

Number of Boils Without Magnesium Silicates (contd)
Equivalent to 50 Boils With Magnesium Silicates

	Alkali Concentration No. 1			Alkali Concentration No. 3		
	Decomposition of Fiber	Average Degree of Polymerization	Tensile Strength	Decomposition of Fiber	Average Degree of Polymerization	Tensile Strength
Staple Fiber No. 2 Boiled with Sodium Monosilicate Plus:						
0.5 g/l Mg-mono-SiO_3	45	15	37	28	30	24
0.5 g/l Mg-tri-SiO_3	33	12	33	27	22	17
Staple Fiber No. 2 Boiled with Water Glass 3.3-Silicate Plus:						
0.5 g/l Mg-mono-SiO_3	30	35	43	32	30	26
0.5 g/l Mg-tri-SiO_3	23	23	43	20	11	20
Staple Fiber No. 4 Boiled with Soda Plus:						
0.5 g/l Mg-mono-SiO_3	36	21	26	38	25	5
0.5 g/l Mg-tri-SiO_3	34	16	22	32	14	5
Staple Fiber No. 4 Boiled with Sodium Monosilicate Plus:						
0.5 g/l Mg-mono-SiO_3	33	31	39	32	15	30
0.5 g/l Mg-tri-SiO_3	30	17	8	30	8	22
Staple Fiber No. 4 Boiled with Water Glass 3.3-Silicate Plus:						
0.5 g/l Mg-mono-SiO_3	32	33	40	32	30	20
0.5 g/l Mg-tri-SiO_3	32	27	34	20	26	15

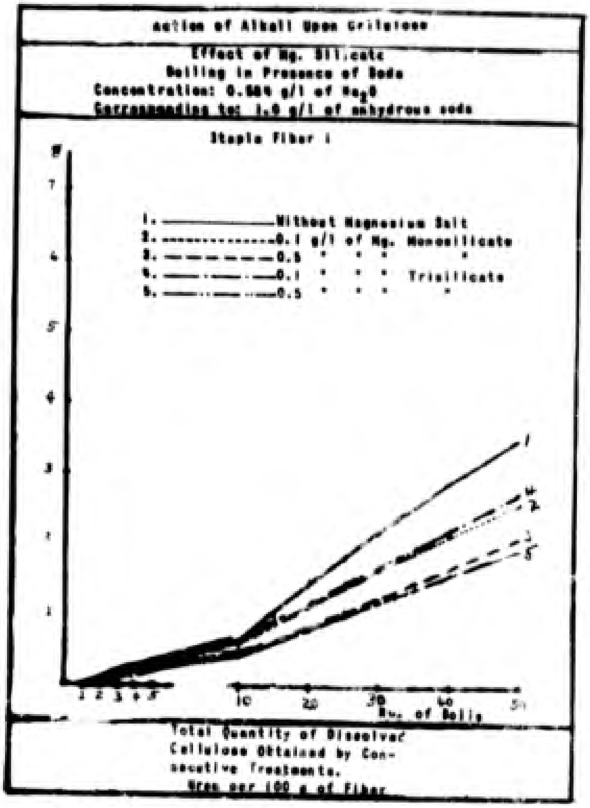


Figure 95

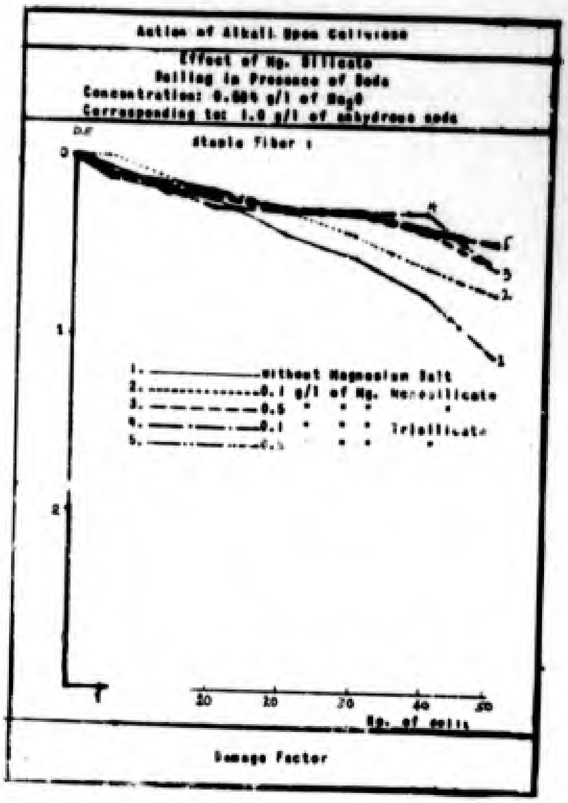


Figure 96

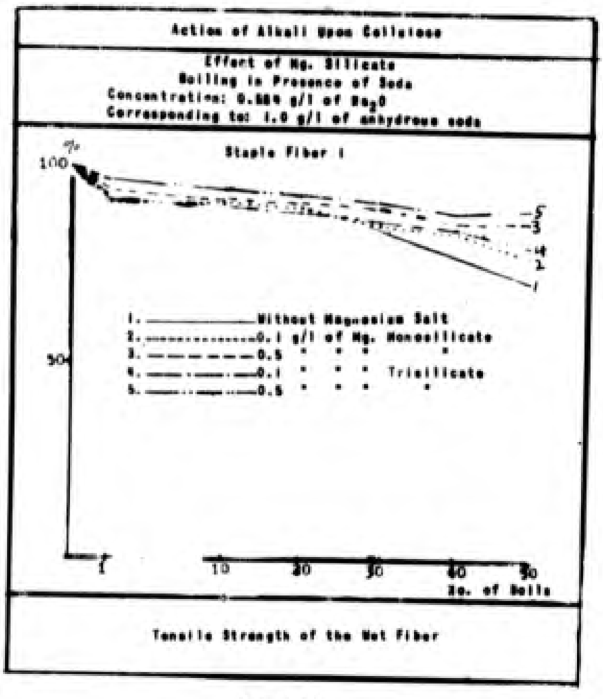


Figure 97

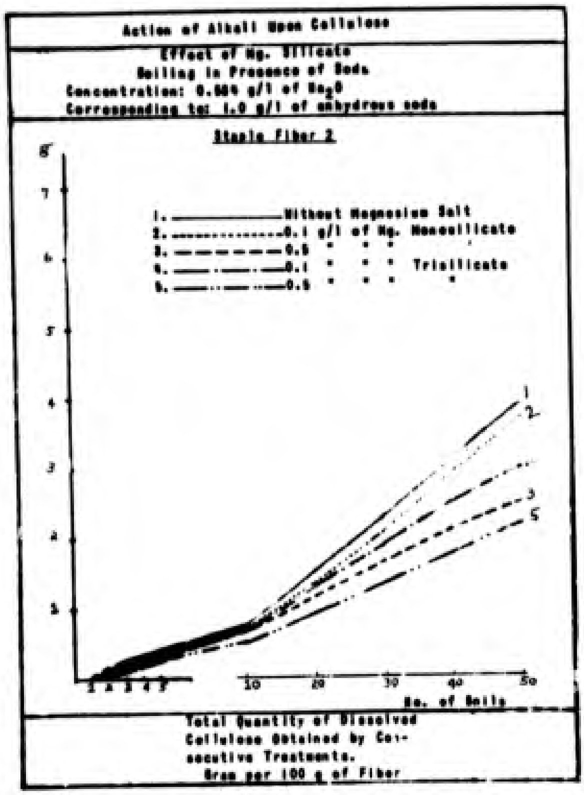


Figure 98

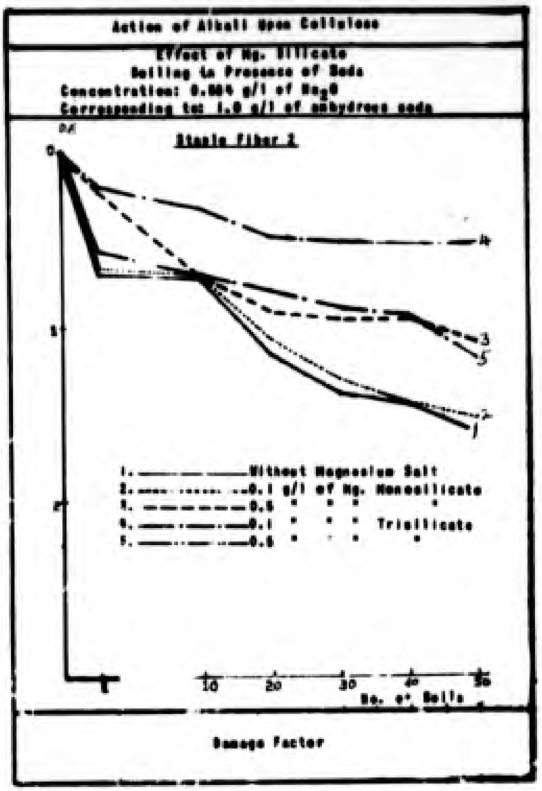


Figure 99

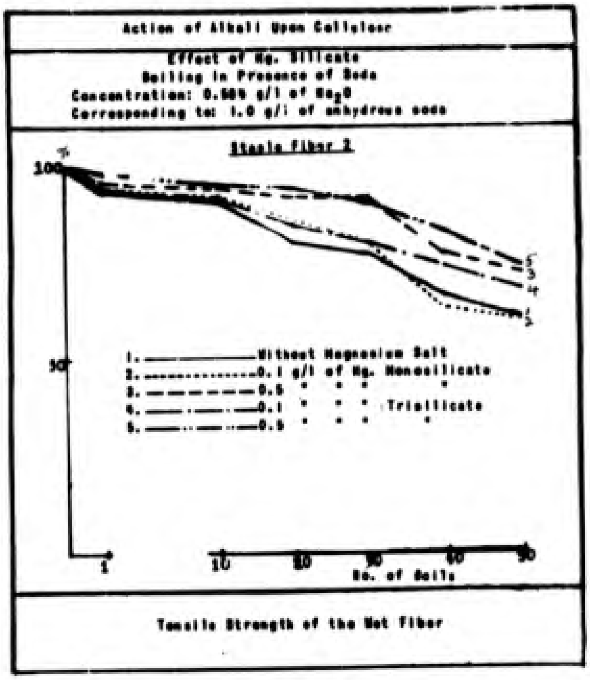


Figure 100

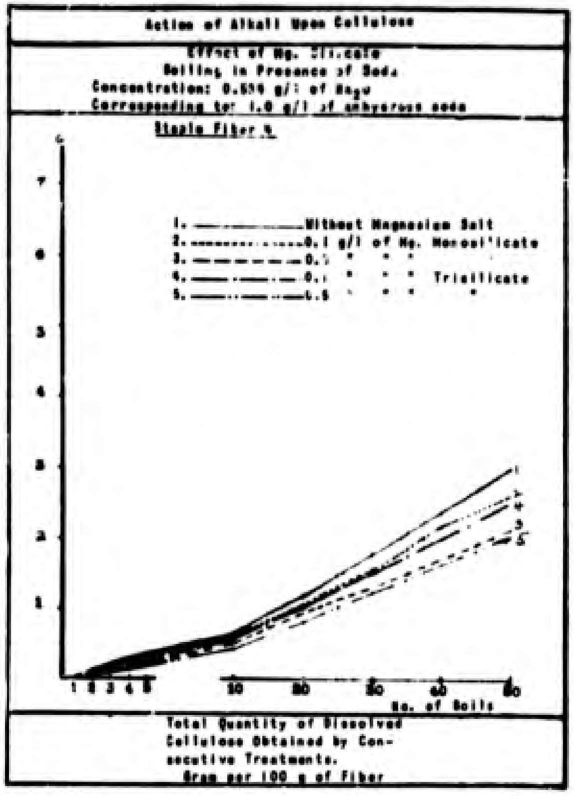


Figure 101

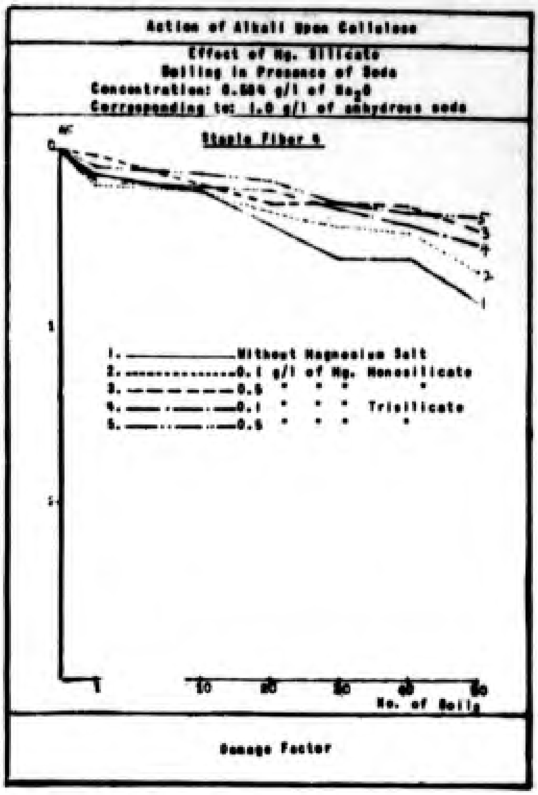


Figure 102

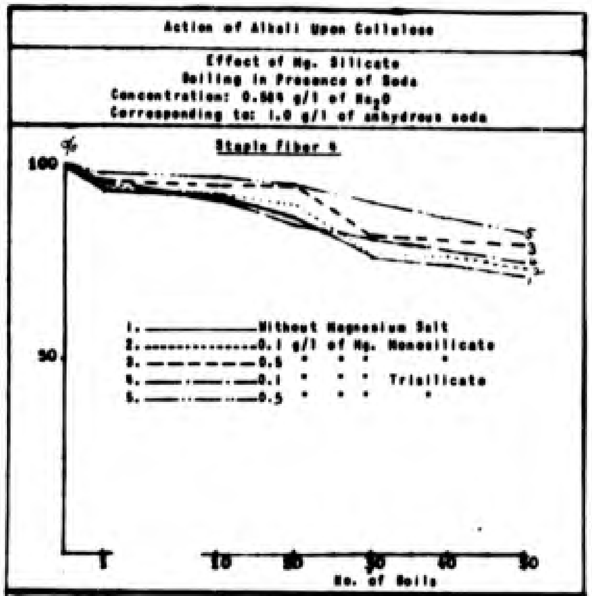


Figure 103

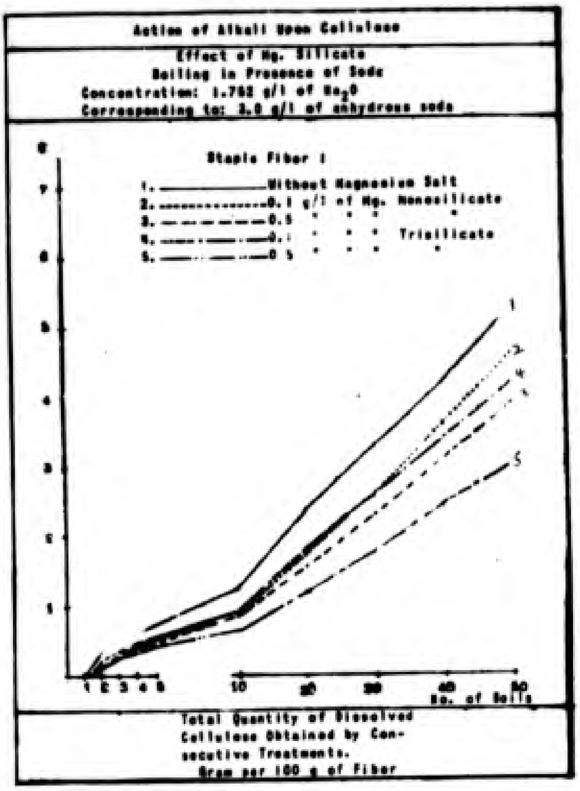


Figure 104

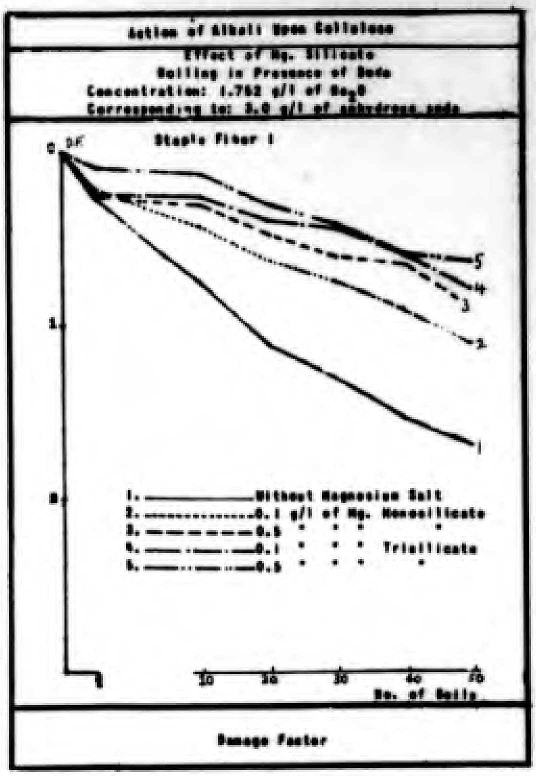


Figure 105

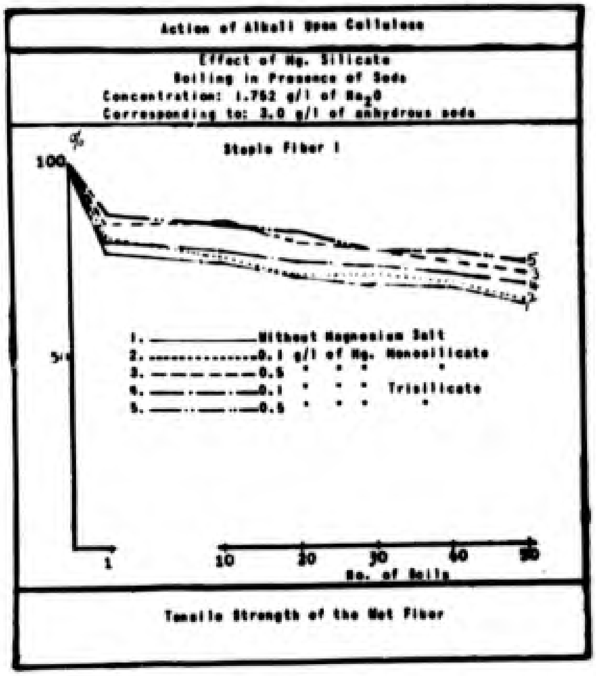


Figure 106

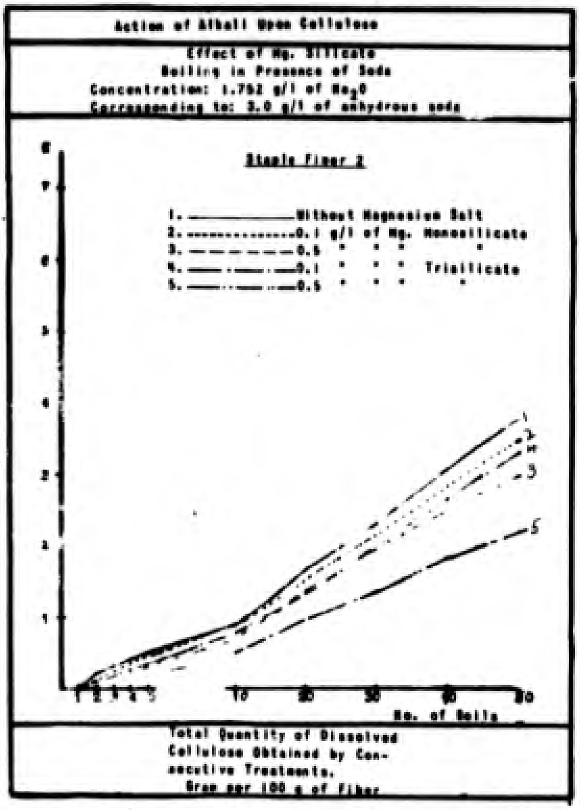


Figure 107

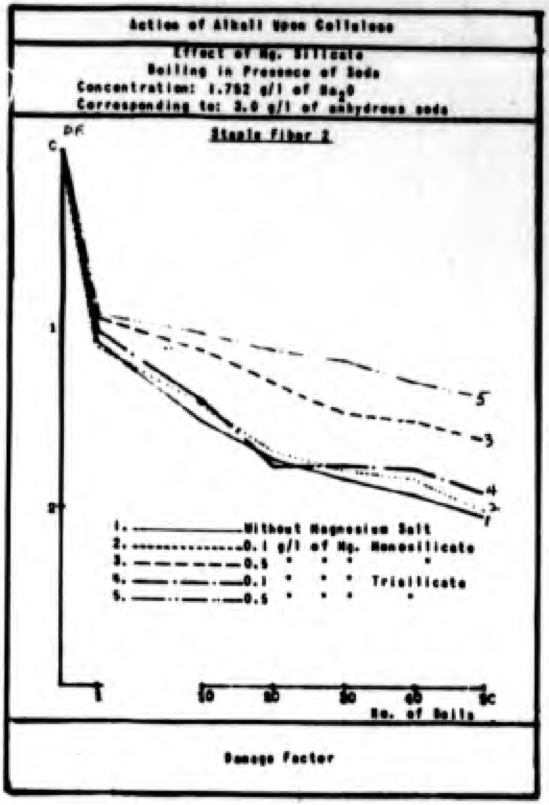


Figure 108

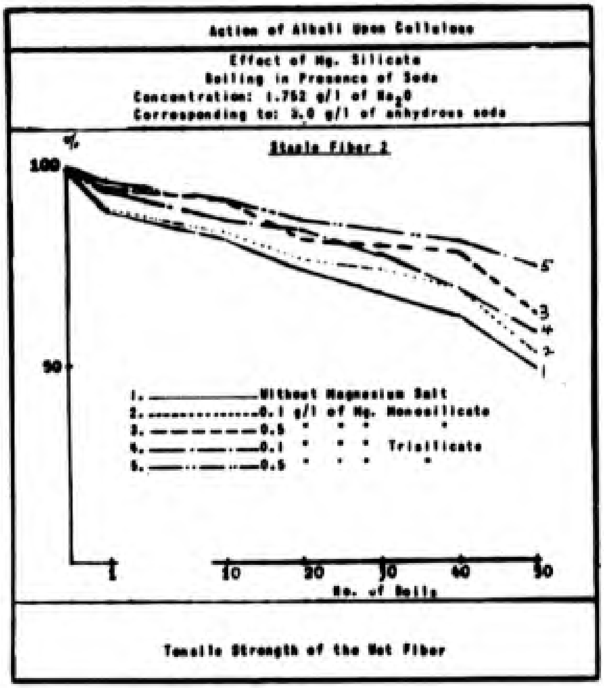


Figure 109

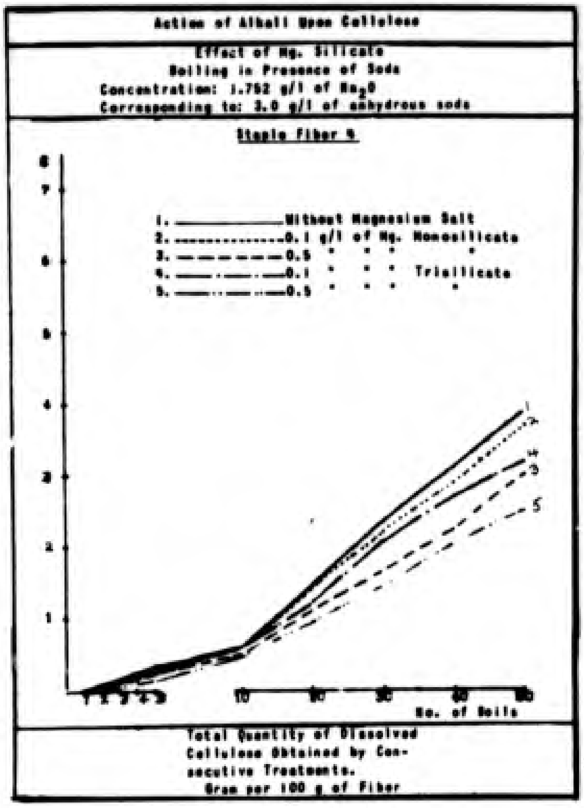


Figure 110

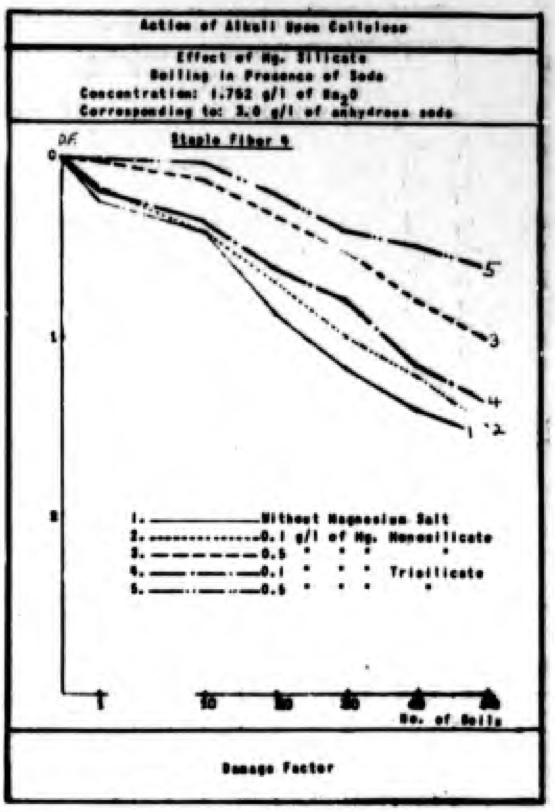


Figure 111

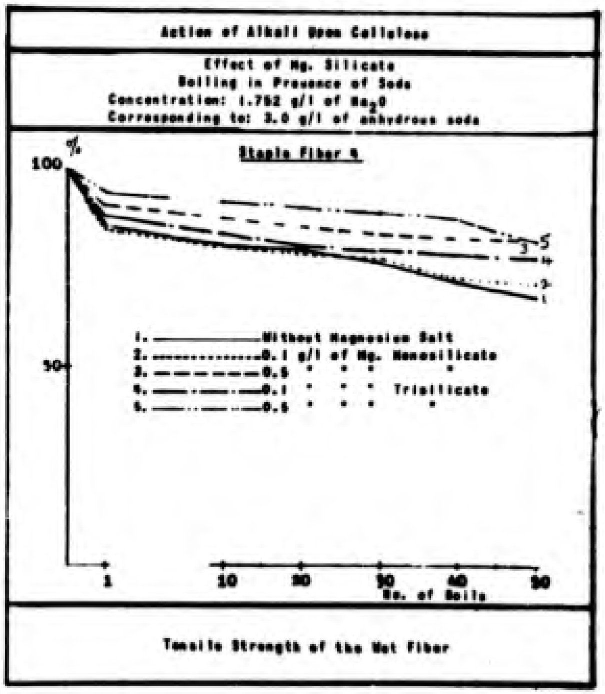
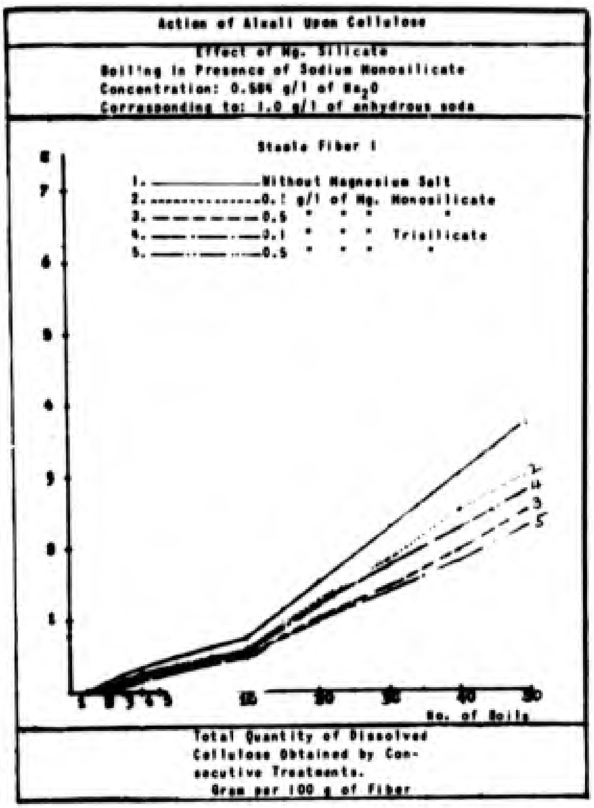


Figure 112



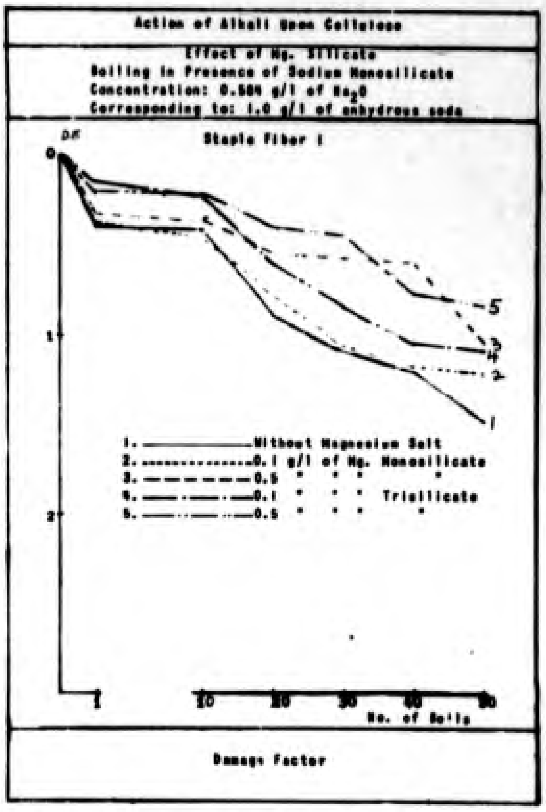
Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Sodium Monosilicate
Concentration: 0.584 g/l of Na_2O
Corresponding to: 1.0 g/l of anhydrous soda

Staple Fiber I

Total Quantity of Dissolved Cellulose Obtained by Consecutive Treatments. Gram per 100 g of Fiber

Figure 113



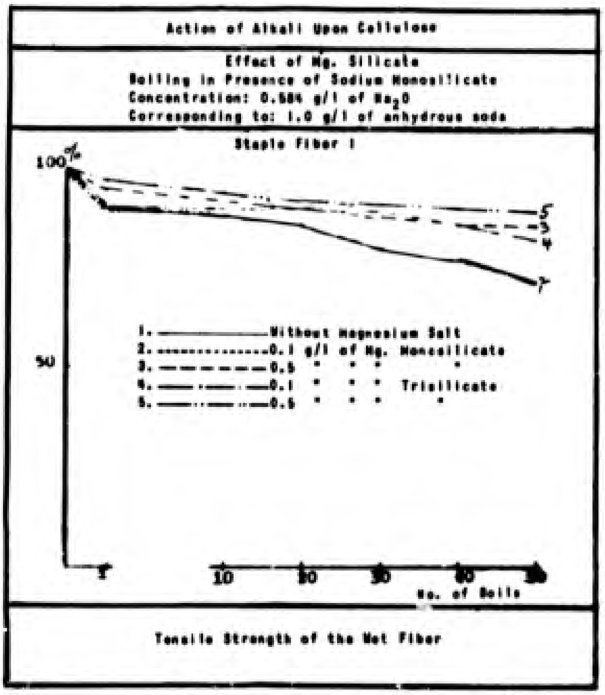
Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Sodium Monosilicate
Concentration: 0.584 g/l of Na_2O
Corresponding to: 1.0 g/l of anhydrous soda

Staple Fiber I

Damage Factor

Figure 114



Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Sodium Monosilicate
Concentration: 0.584 g/l of Na_2O
Corresponding to: 1.0 g/l of anhydrous soda

Staple Fiber I

Tensile Strength of the Wet Fiber

Figure 115

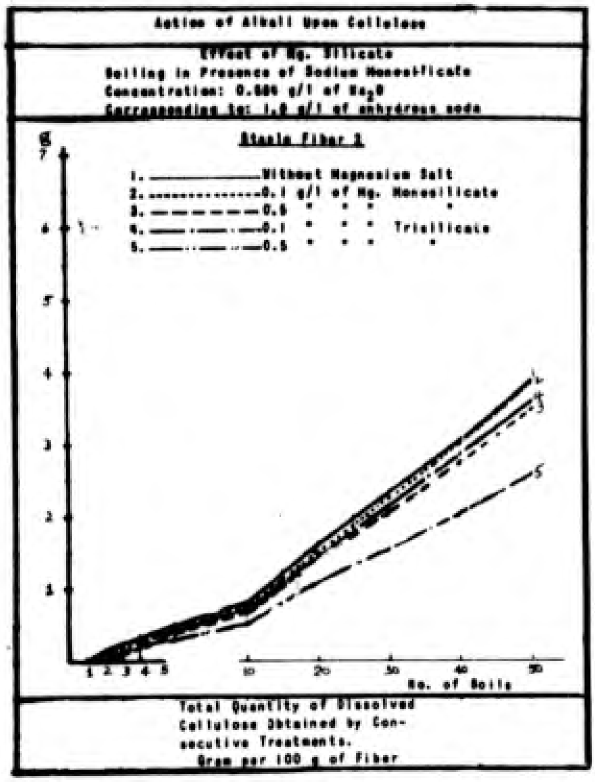


Figure 116

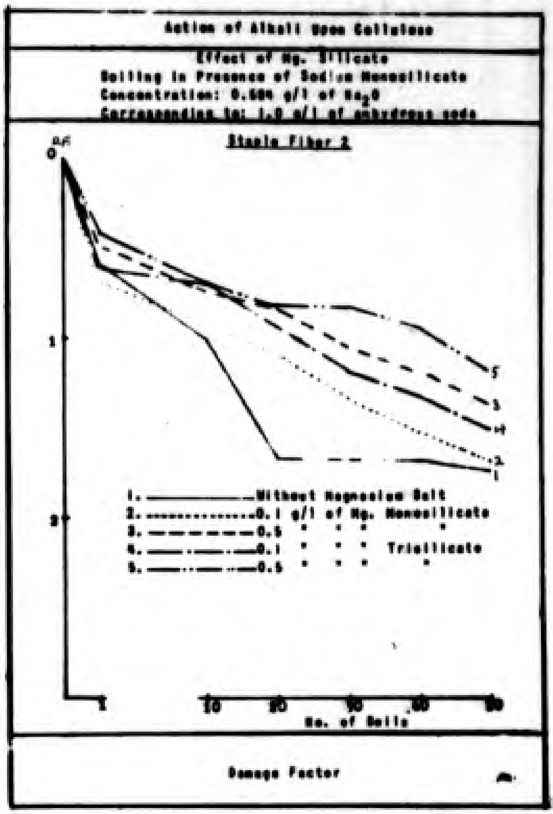


Figure 117

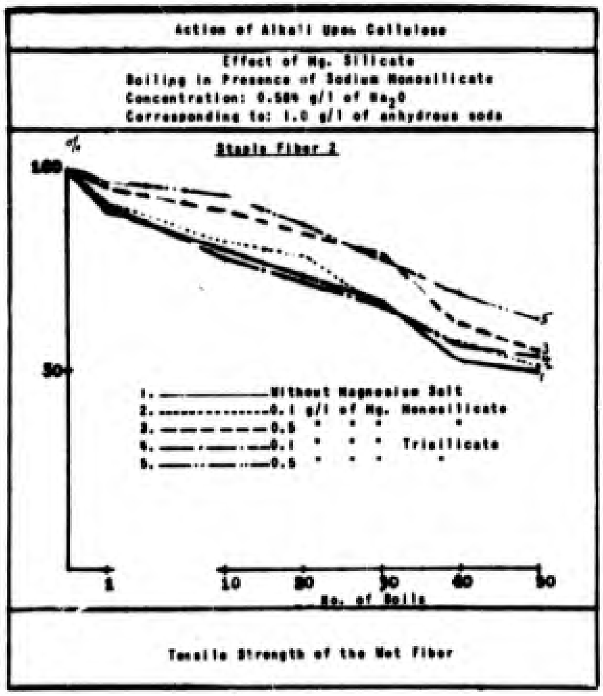


Figure 118

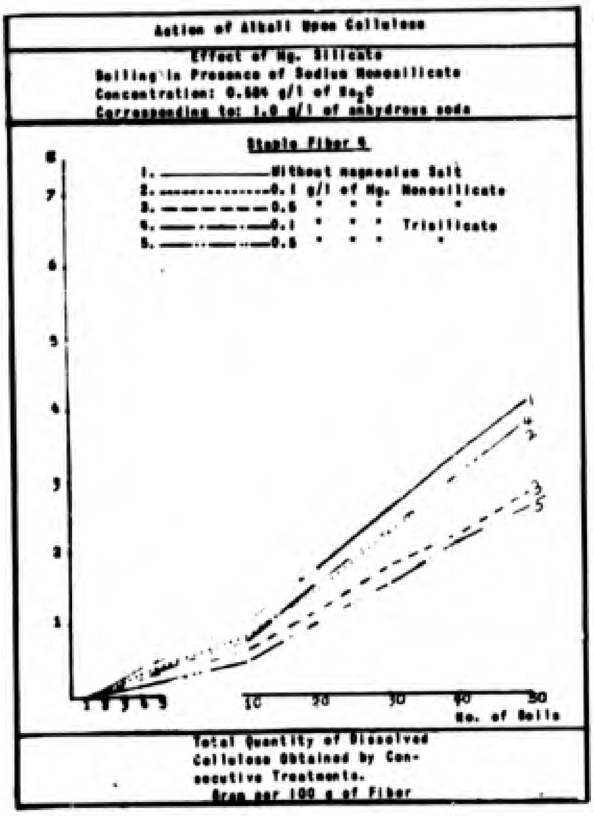


Figure 119

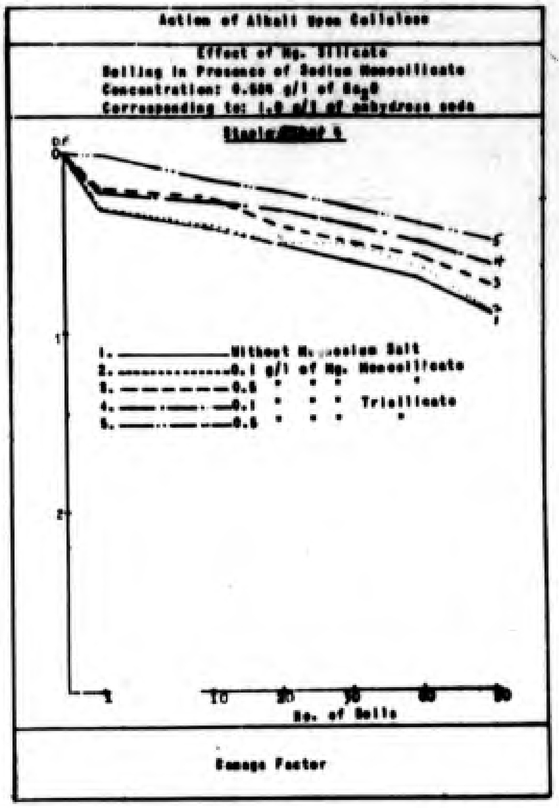


Figure 120

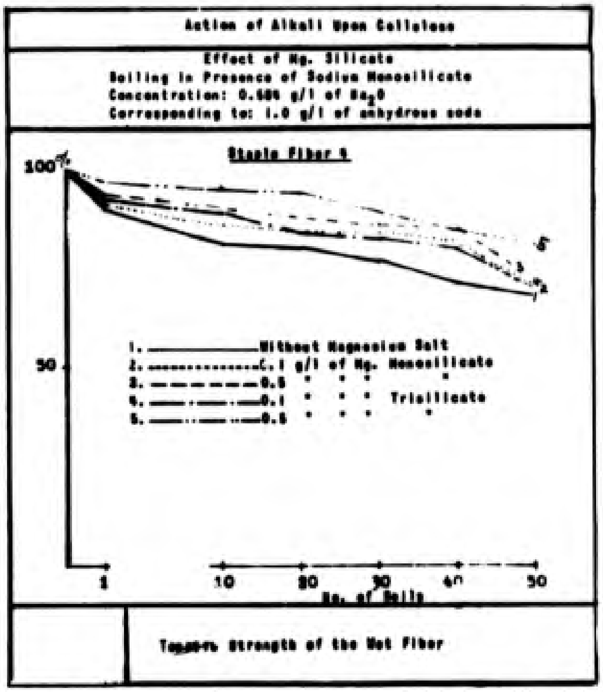
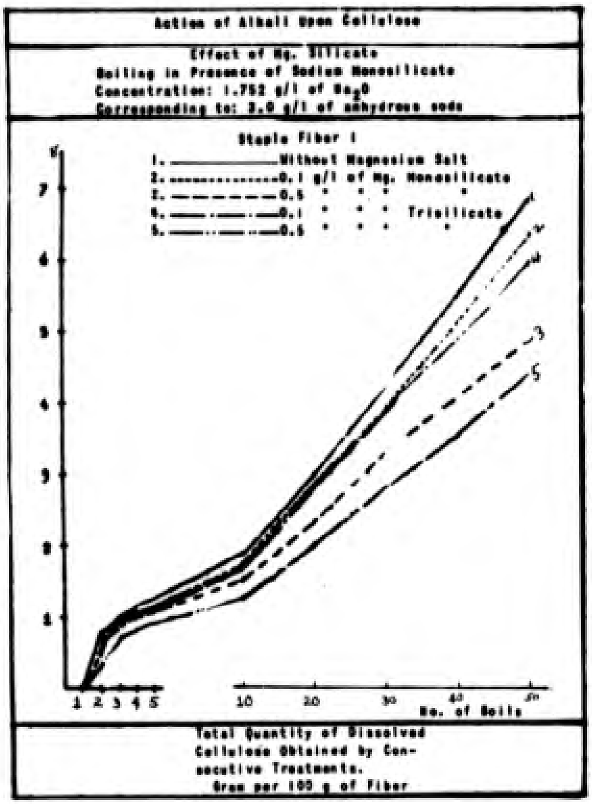


Figure 121



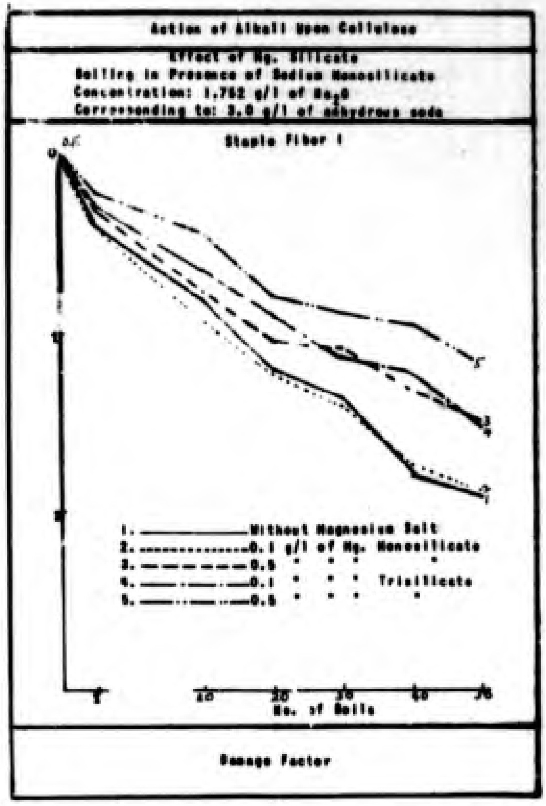
Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Sodium Monosilicate
Concentration: 1.752 g/l of Na_2O
Corresponding to: 3.0 g/l of anhydrous soda

Staple Fiber I

Total Quantity of Dissolved Cellulose Obtained by Consecutive Treatments.
Gram per 100 g of Fiber

Figure 122



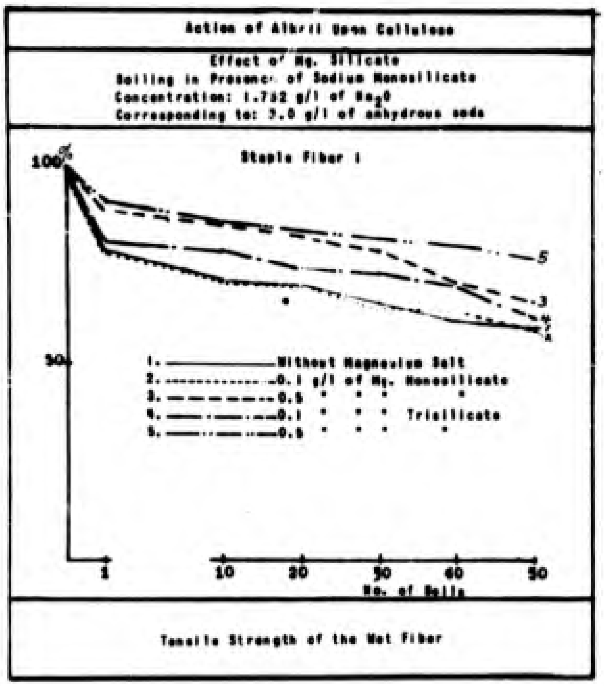
Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Sodium Monosilicate
Concentration: 1.752 g/l of Na_2O
Corresponding to: 3.0 g/l of anhydrous soda

Staple Fiber I

Damage Factor

Figure 123



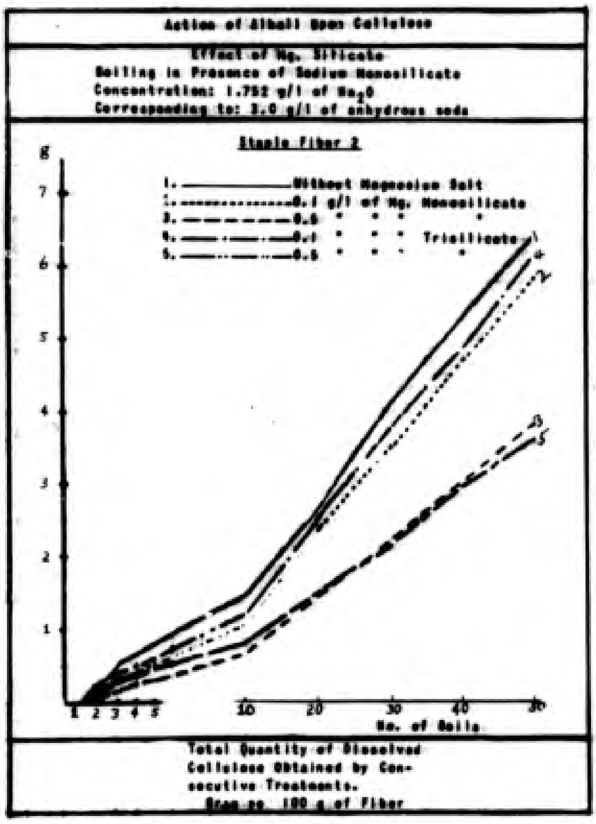
Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Sodium Monosilicate
Concentration: 1.752 g/l of Na_2O
Corresponding to: 3.0 g/l of anhydrous soda

Staple Fiber I

Tensile Strength of the Wet Fiber

Figure 124

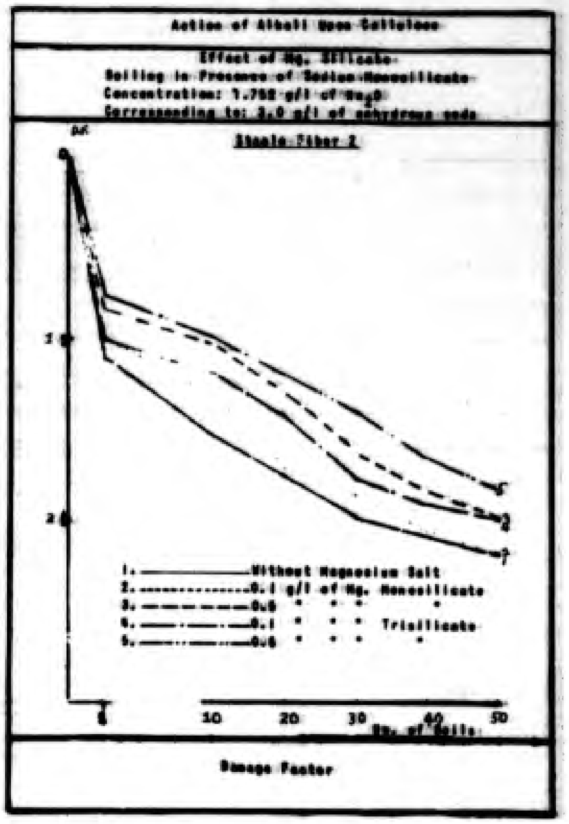

Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Sodium Monosilicate
Concentration: 1.752 g/l of Na_2O
Corresponding to: 3.0 g/l of anhydrous soda

Staple Fiber 2

Total Quantity of Dissolved Cellulose Obtained by Consecutive Treatments.
Gram pe. 100 g of Fiber

Figure 125

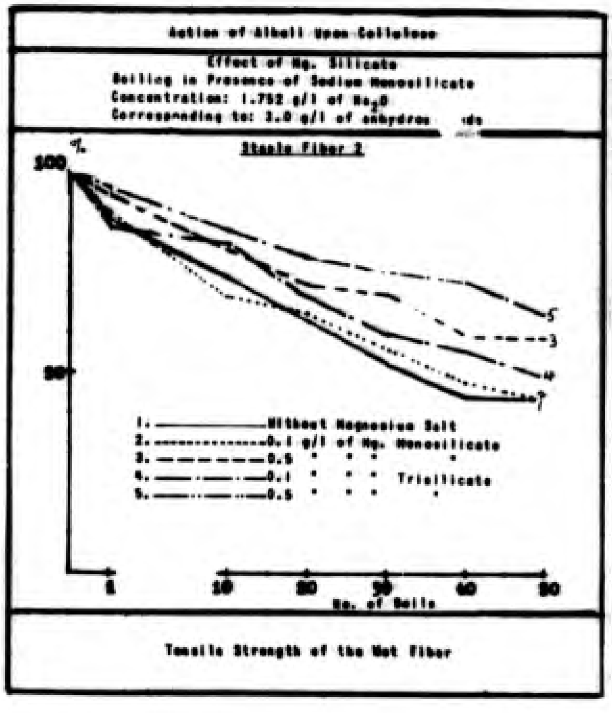

Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Sodium Monosilicate
Concentration: 1.752 g/l of Na_2O
Corresponding to: 3.0 g/l of anhydrous soda

Staple Fiber 2

Damage Factor

Figure 126


Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Sodium Monosilicate
Concentration: 1.752 g/l of Na_2O
Corresponding to: 3.0 g/l of anhydrous soda

Staple Fiber 2

Tensile Strength of the Wet Fiber

Figure 127

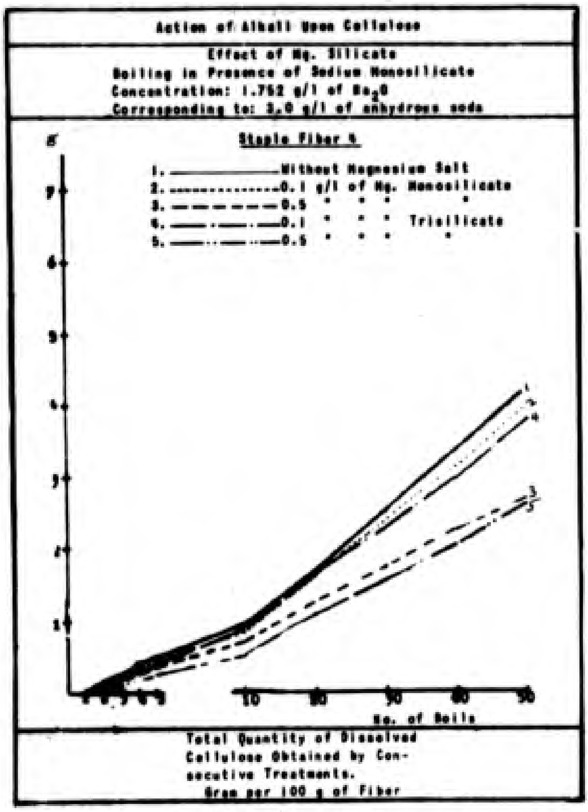


Figure 128

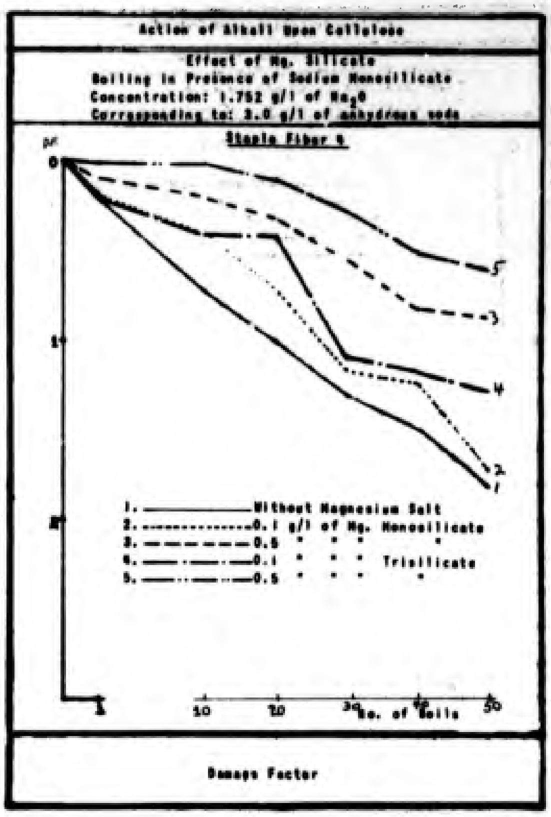


Figure 129

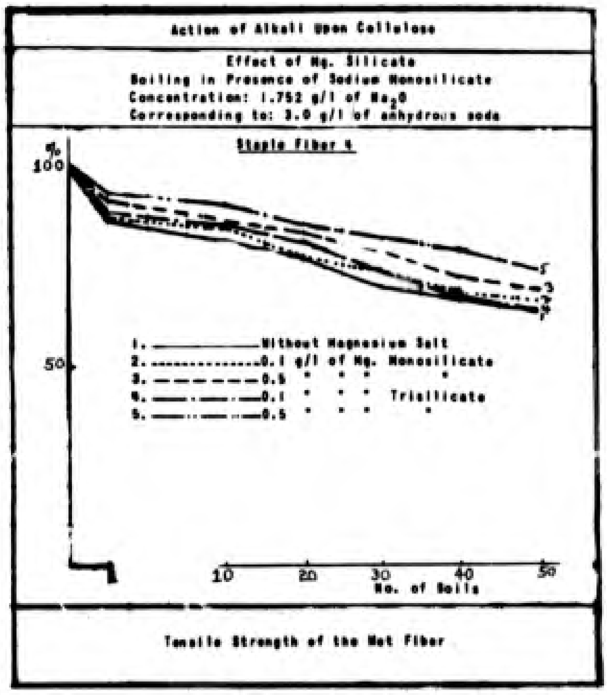


Figure 130

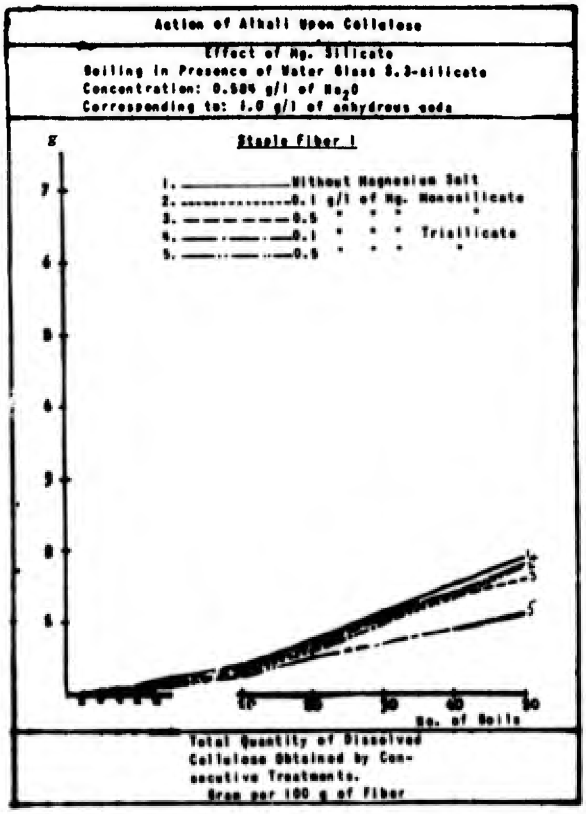


Figure 131

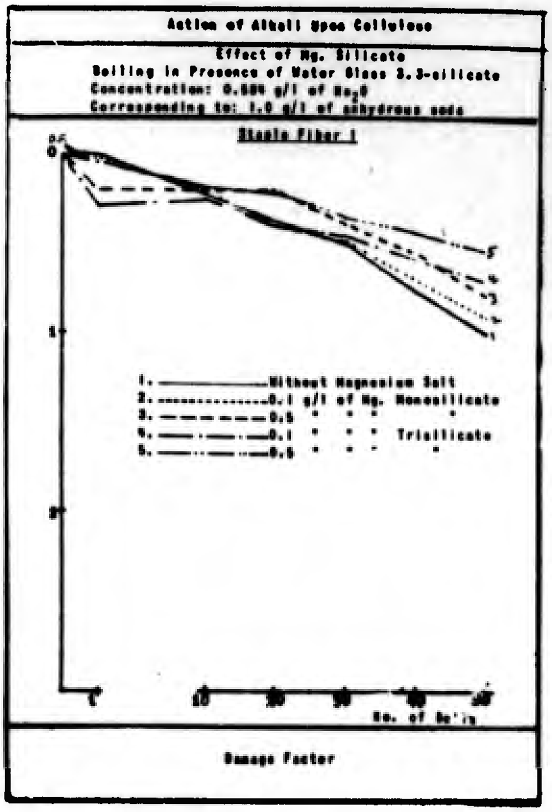


Figure 132

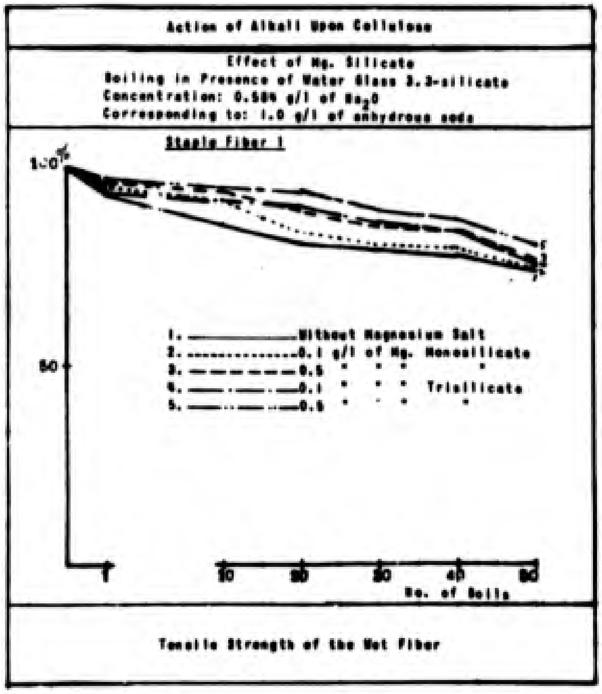


Figure 133

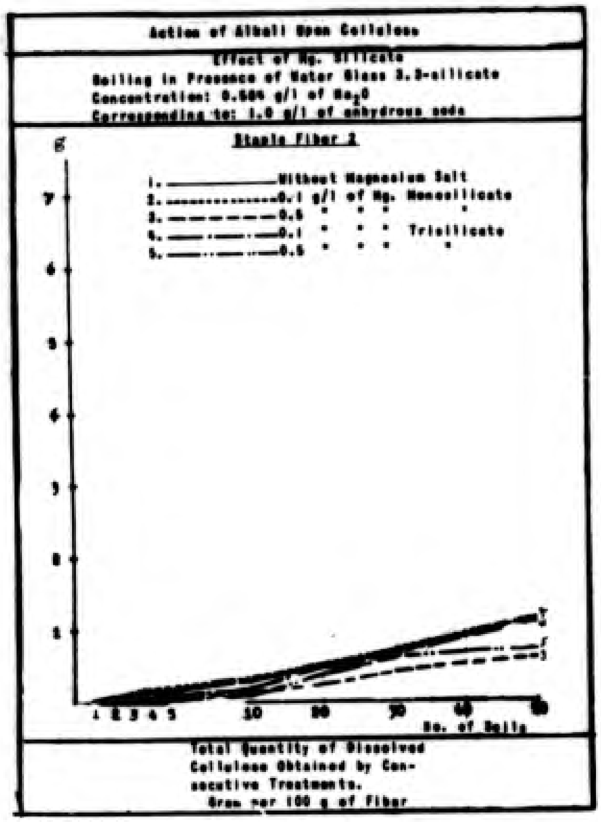


Figure 134

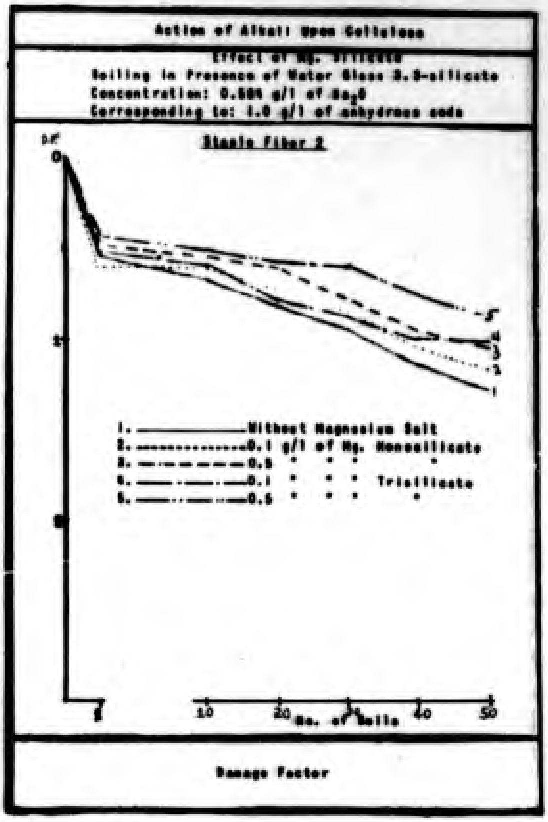


Figure 135

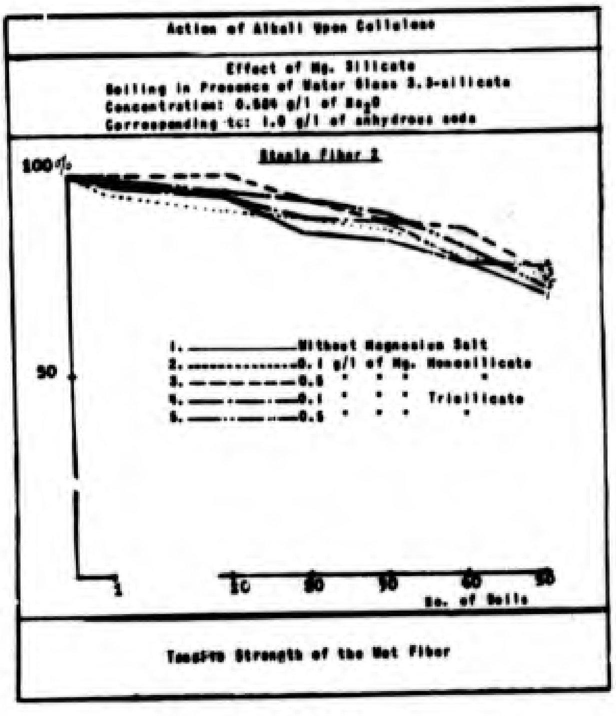
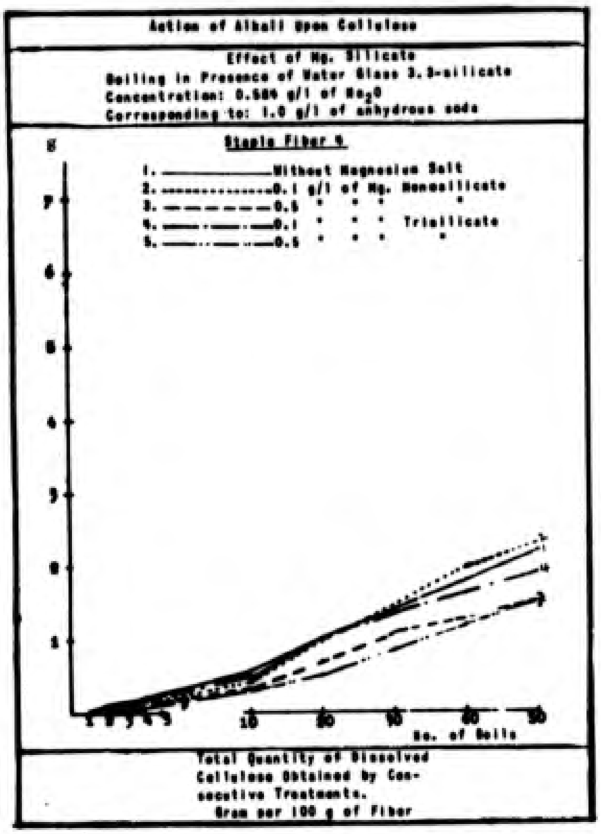


Figure 136



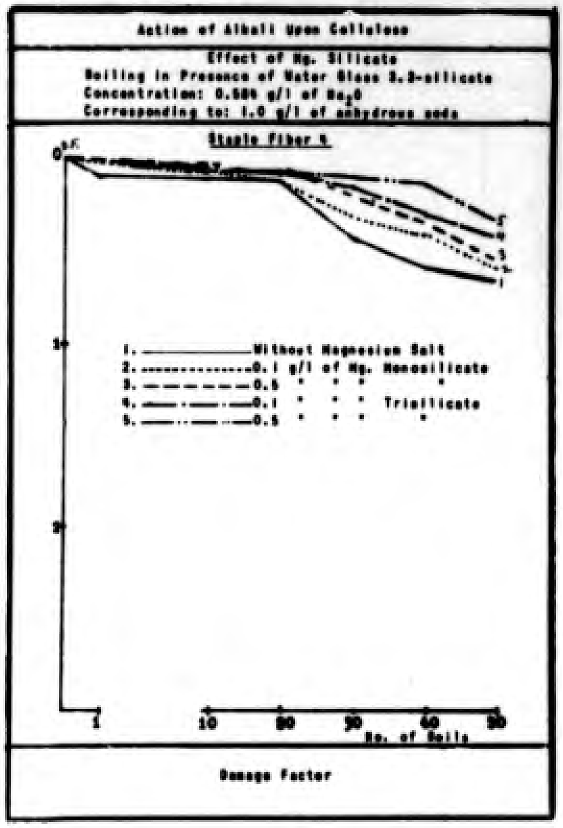
Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Water Glass 3.3-silicate
Concentration: 0.584 g/l of Na_2O
Corresponding to: 1.0 g/l of anhydrous soda

Staple Fiber 4

Total Quantity of Dissolved Cellulose Obtained by Consecutive Treatments.
Gram per 100 g of Fiber

Figure 137



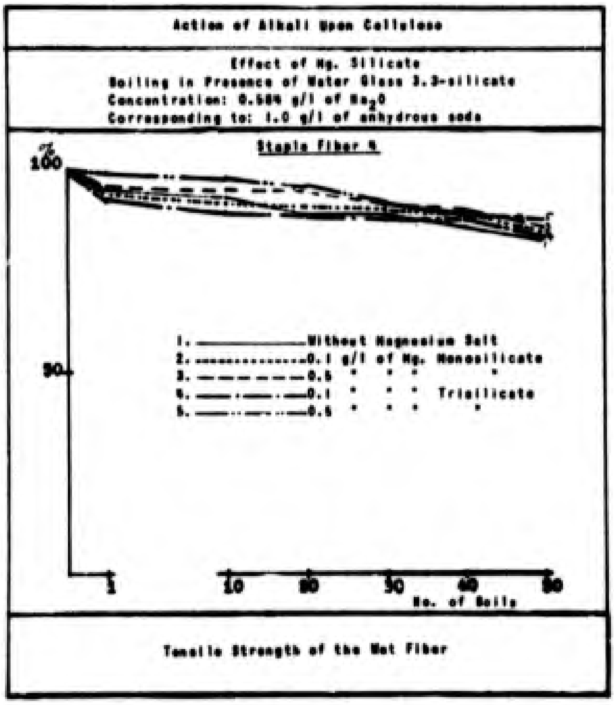
Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Water Glass 3.3-silicate
Concentration: 0.584 g/l of Na_2O
Corresponding to: 1.0 g/l of anhydrous soda

Staple Fiber 4

Damage Factor

Figure 138



Action of Alkali Upon Cellulose

Effect of Mg. Silicate
Boiling in Presence of Water Glass 3.3-silicate
Concentration: 0.584 g/l of Na_2O
Corresponding to: 1.0 g/l of anhydrous soda

Staple Fiber 4

Tensile Strength of the Wet Fiber

Figure 139

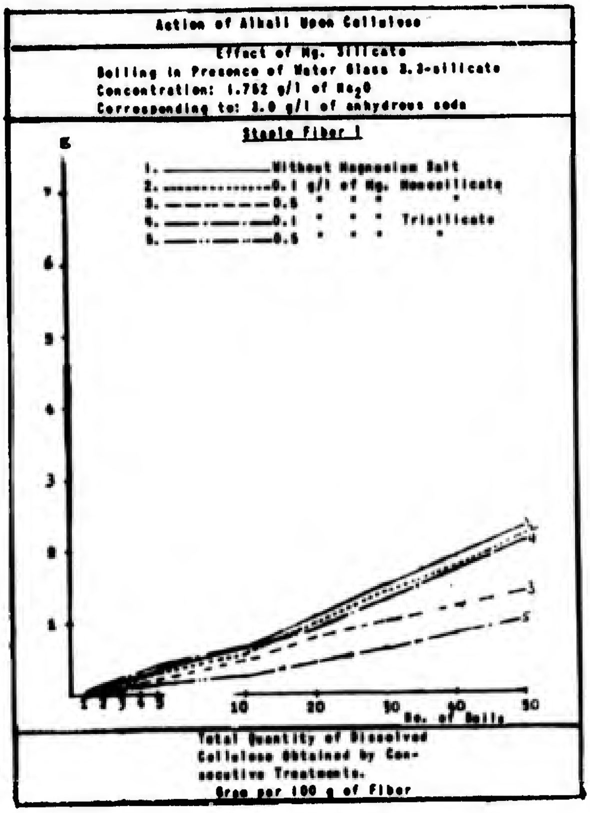


Figure 140

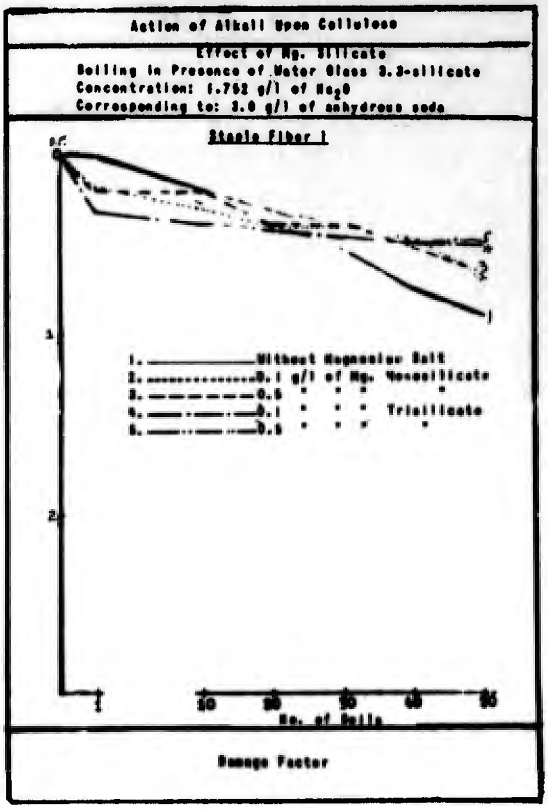


Figure 141

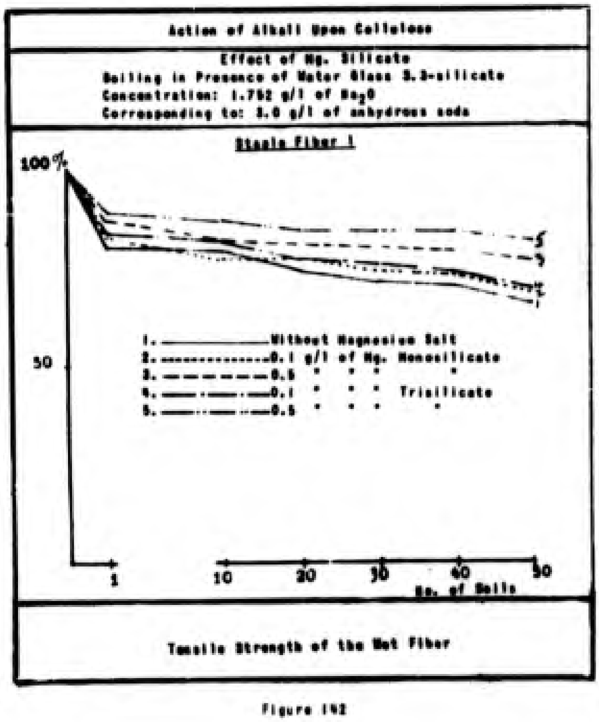


Figure 142

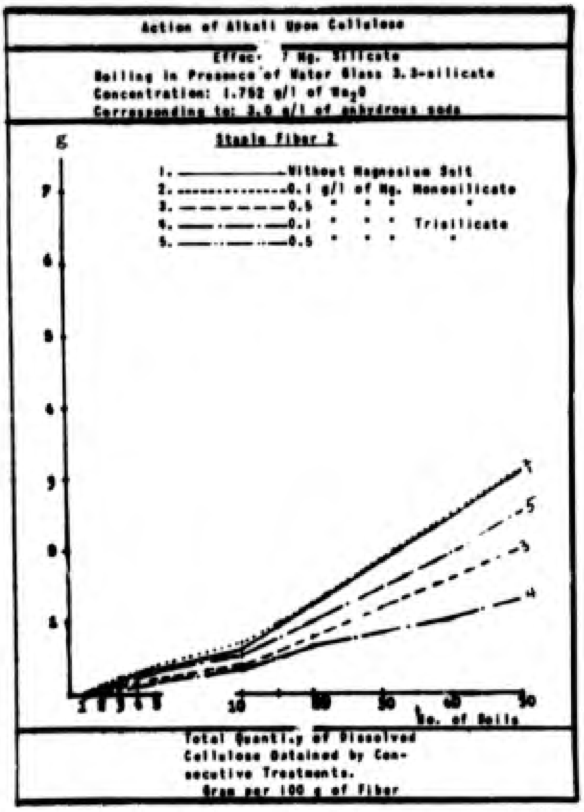


Figure 143

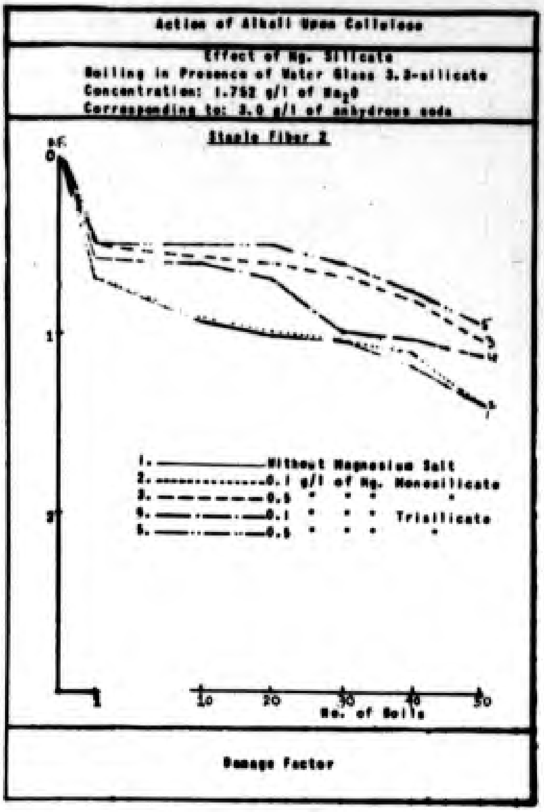


Figure 144

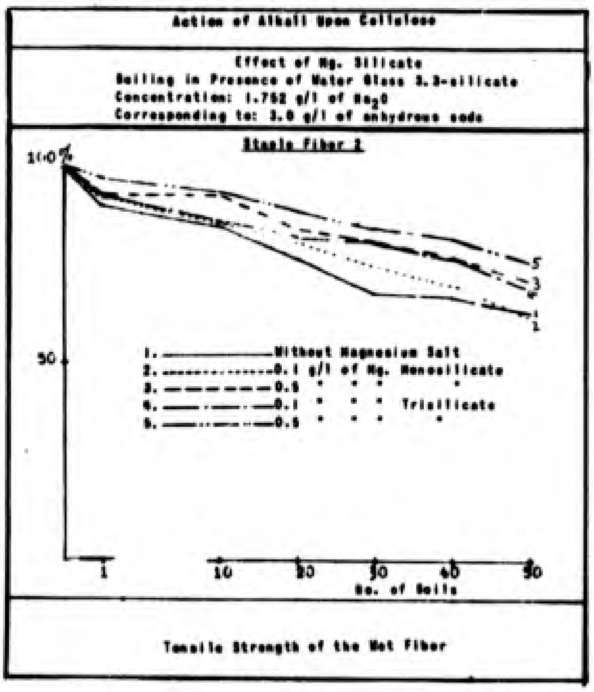


Figure 145

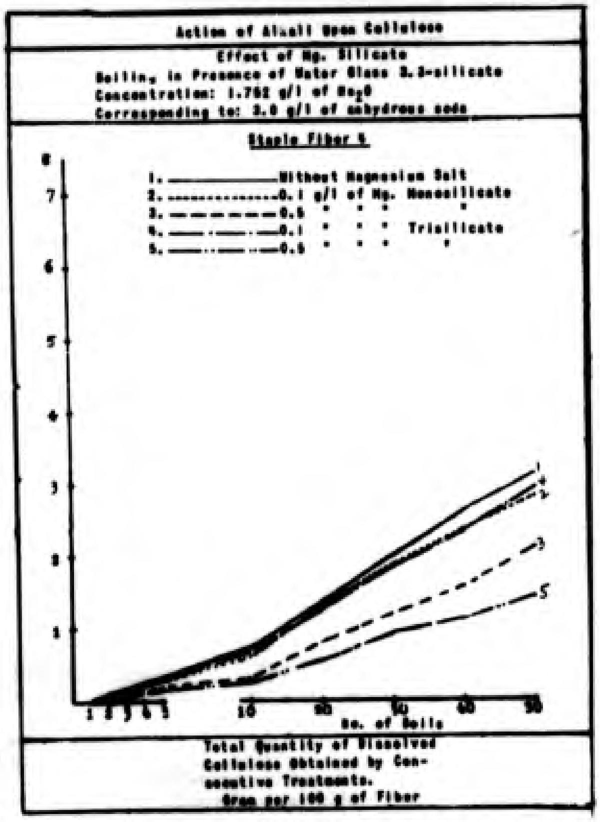


Figure 146

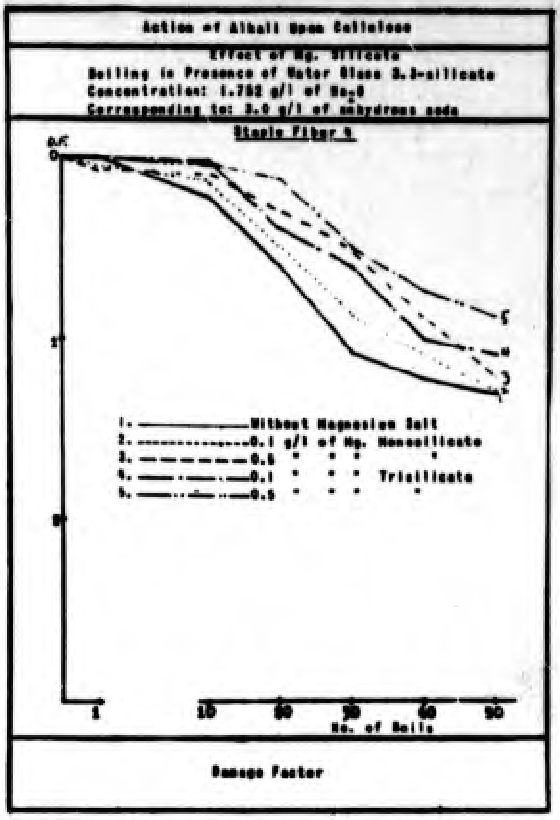


Figure 147

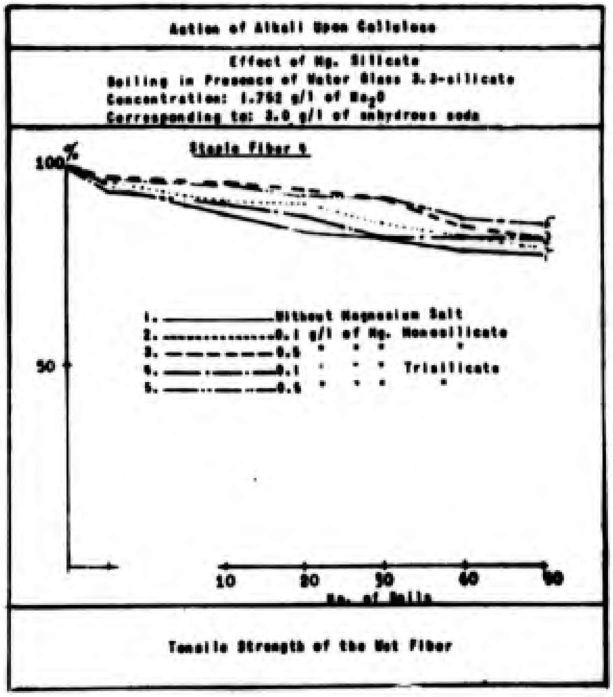


Figure 148

Part V

Thermal Decomposition of Cellulose in the Course of the Drying Process

In the following series of experiments an investigation was made of the behavior of cellulosic fibers in the drying process at different temperatures. Since, in normal washing the fibers are frequently not rinsed until completely free from alkali, studies were made of fibers which had been rinsed until neutral as well as those which still contained free alkali.

Procedure

The cellulosic fibers were subjected to 50 boils, each of one-half hour, in presence of different alkalies and in different concentrations. After the treatments the fibers were rinsed with distilled water until neutral and then divided into two lots, one of which was dried and examined without further treatment. The other was put into an alkaline solution for 10 minutes at room temperature, using the same alkali as in the boiling treatment, but in a concentration one-tenth as strong. The fibers were centrifuged after the boiling treatment without rinsing and then dried.

Alkalies

The treatment was carried out with the following alkalies:

1) Anhydrous sodium carbonate, analytically pure.
2) Sodium monosilicate (sodium metasilicate) $Na_2O \cdot SiO_2 \cdot 4\ H_2O$.
3) Technical water glass 38 - 39° Be, containing 35.95% of $Na_2O \cdot 3 \cdot 3\ SiO_2$.

Concentration of Alkali

The boiling treatments of the fibers were carried out in three different concentrations:

Concentration 1: 0.584 g/l of Na_2O corresponding to 1 g/l of Na_2CO_3
Concentration 3: 1.752 g/l of Na_2O " " 3 g/l of Na_2CO_3
Concentration 5: 2.920 g/l of Na_2O " " 5 g/l of Na_2CO_3

The alkaline baths, for the ten-minute treatment at room temperature were of the following concentrations:

Concentration 0.1: 0.0584 g/l of Na_2O cor. to 0.1 g/l of Na_2CO_3
Concentration 0.3: 0.1752 g/l of Na_2O " " 0.3 g/l of Na_2CO_3
Concentration 0.5: 0.2920 g/l of Na_2O " " 0.5 g/l of Na_2CO_3

Drying Temperature

1) 65°)
2) 100° : with variations of ±5° C.
3) 120°)

Time of Drying

One hour in each case.

Fibrous Material

Spun rayon No. 6.

Methods of Examination

1. Fiber Decomposition. After each of the first five boils, then after each tenth boil, the bath was filled up to the original volume and the quantity of dissolved and decomposed cellulose was quantitatively determined by oxidation with potassium bichromate and sulfuric acid. In the analytical calculation these decomposition products were considered as cellulose $(C_6H_{10}O_5)x$.

2. Damage Factor (Schädigungszahl). The examinations were made after the first and after each tenth boil. (Results are incomplete.)

3. Tensile Strength of the Wet Fiber. Determinations were made after the first and after each tenth boil. (Results are incomplete.)

4. Manner of Representing the Experimental Results. For clarity, the results are presented in the form of curves.

Boiling Treatment in the Presence of Sodium Carbonate (Figures 149 to 153)

These results show that drying temperatures up to 100° C. have no particular influence on the neutral fiber, but drying at 120° C. causes a strong thermal decomposition of fiber under any conditions.

When drying at 65° C. the alkali has little effect upon the fiber, but when the fiber is dried at 100° C. damage by the alkali is clearly perceptible, while at 120° C., decided decomposition is observed on the alkaline fiber as well as on the neutral fiber.

Boiling Treatment in the Presence of Sodium Monosilicate (Figures 154 to 158)

The results are similar to those obtained in the boiling treatment with sodium carbonate. The action of the alkali on the fiber is perceptible at a drying temperature of 100° C.

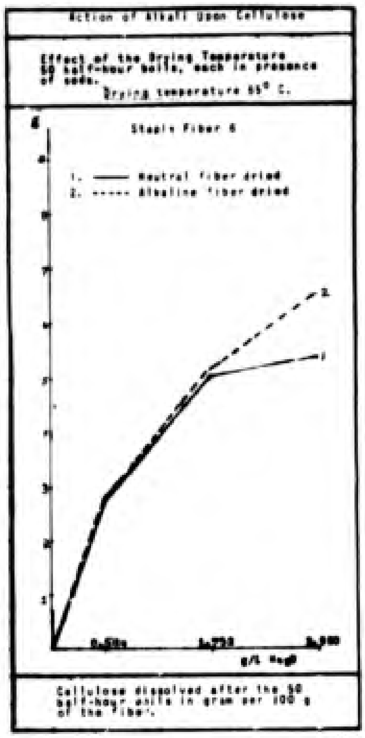


Figure 149

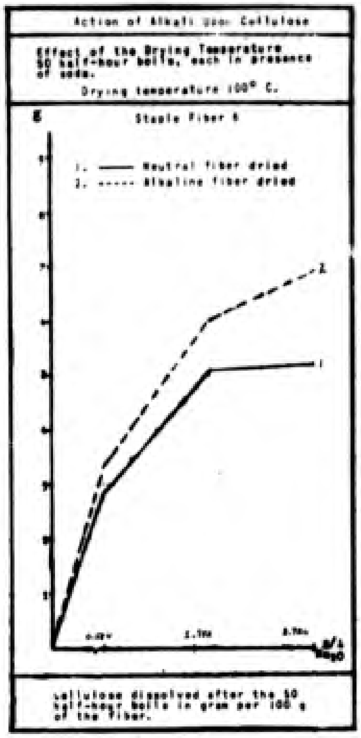


Figure 150

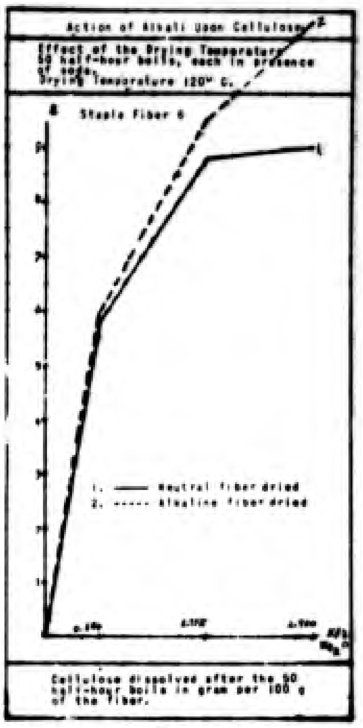


Figure 151

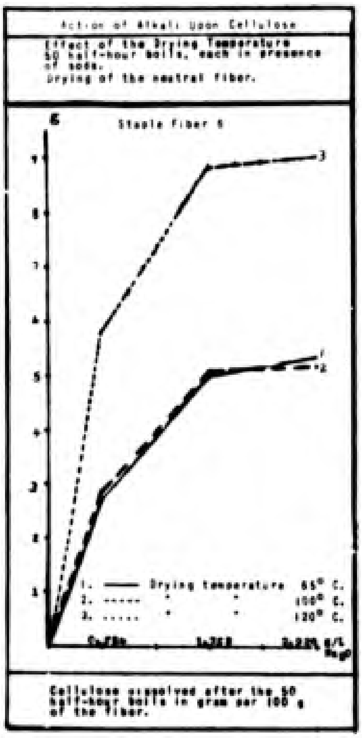


Figure 152

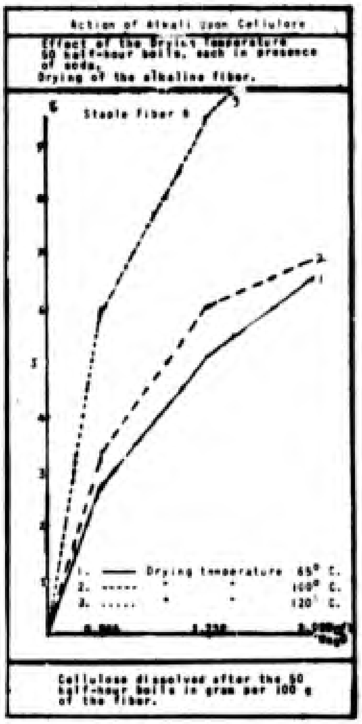


Figure 153

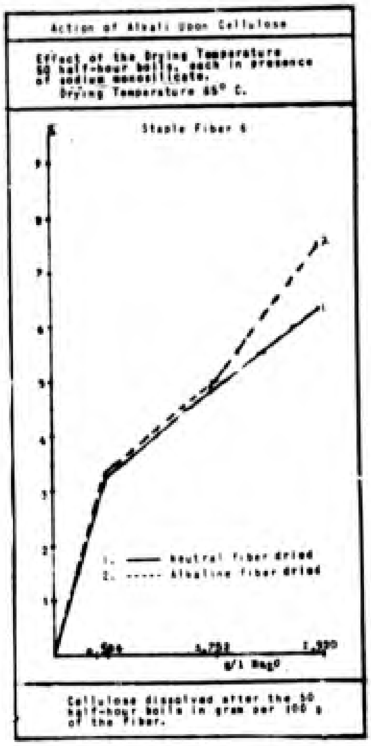


Figure 154

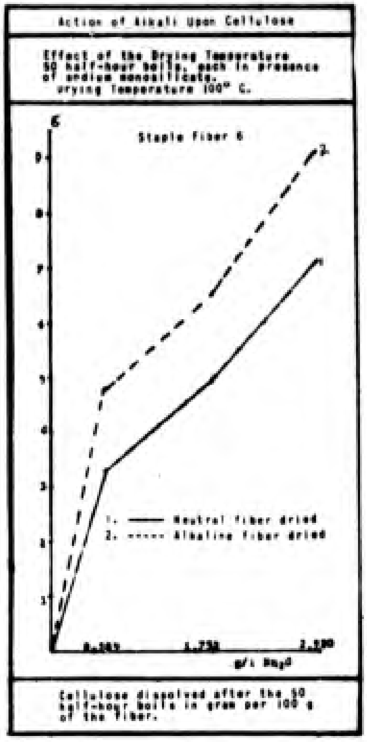


Figure 155

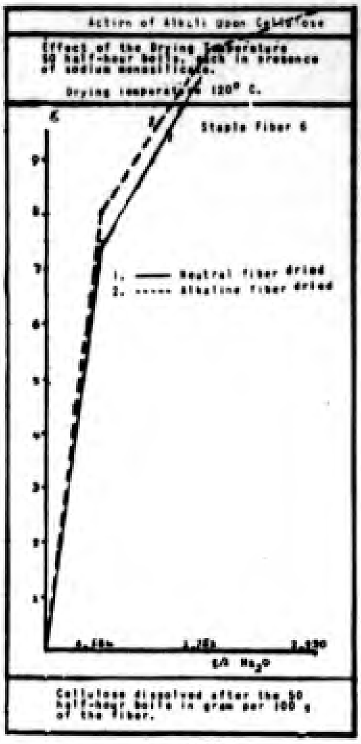


Figure 156

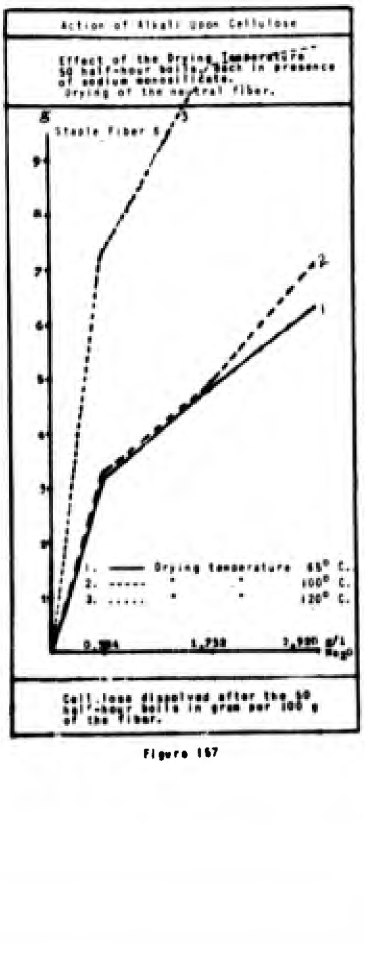


Figure 157

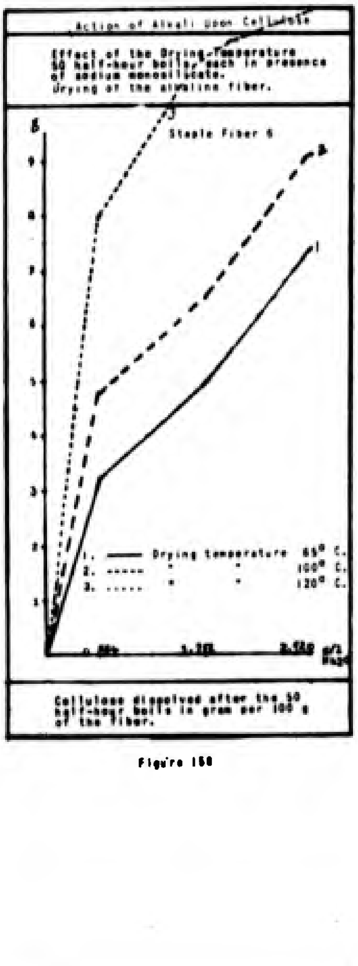


Figure 158

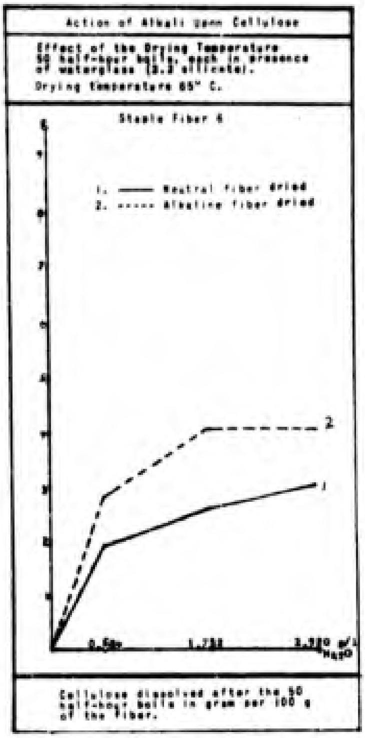


Figure 159

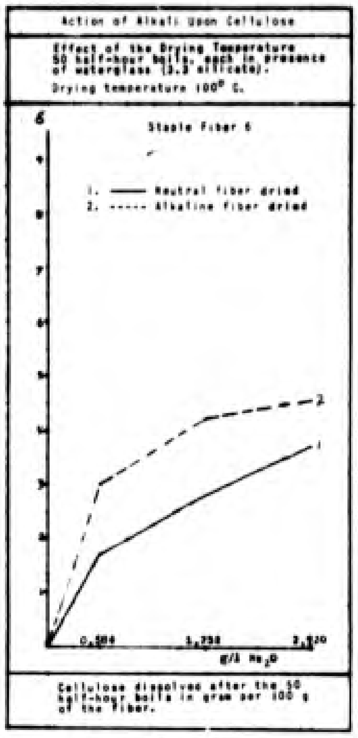


Figure 160

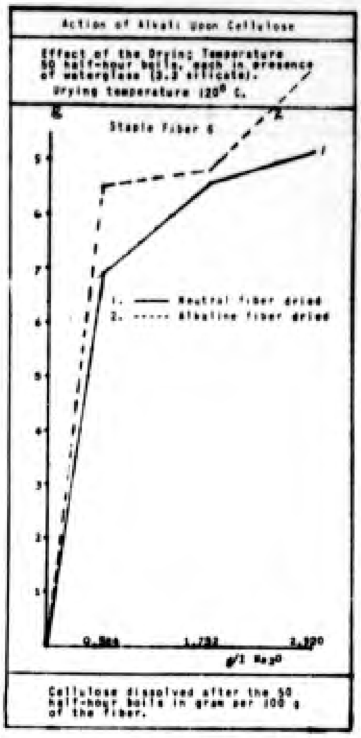


Figure 161

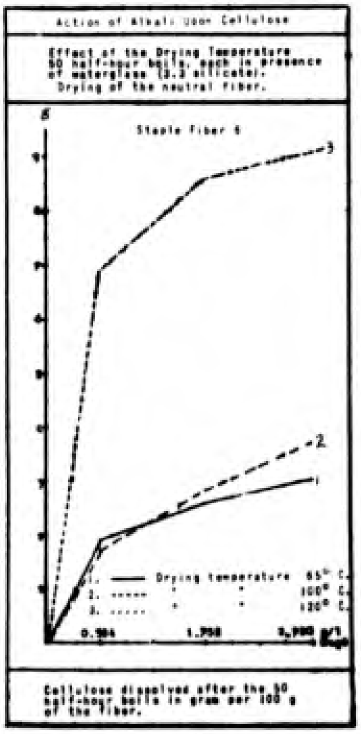


Figure 162

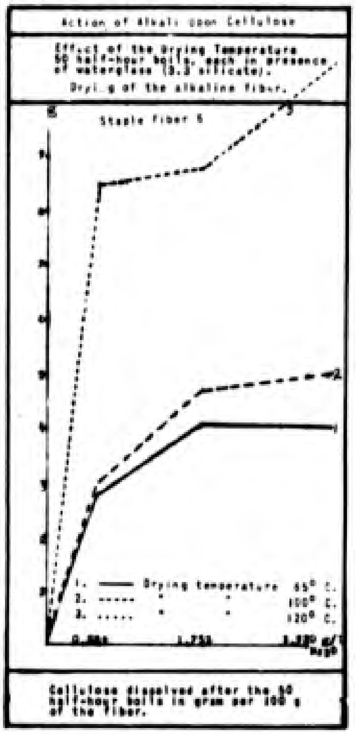


Figure 163

Boiling Treatment in the Presence of Water Glass (Figures 159 to 163)

When using water glass, the alkali causes strong damage to the fiber even at a drying temperature of 65° C., a finding which differs considerably from the results obtained with sodium carbonate and sodium monosilicate. Probably for similar reasons, mineral deposits on the alkaline fiber are considerably greater than those on the neutral fiber. (Figure 164.)

Mineral Ingredients of the Fiber After 50 Boils with Water Glass
Grams of Mineral Ingredients per 100 Grams of Fiber

Drying Temperature		Untreated Fiber	Alkali Concentration 1	3	5
---		0.26	-	-	-
65° C.	Neutral	-	14.61	19.43	26.64
	Alkaline		17.58	24.72	28.91
100° C.	Neutral	-	15.11	24.72	28.91
	Alkaline		18.23	25.13	29.17
120° C.	Neutral	-	17.43	21.32	25.37
	Alkaline		19.61	26.61	31.21

Figure 164

Experiments with Additional Use of Magnesium Silicate

In a former series of experiments it was ascertained that the damaging action of oxygen on the fiber is considerably decreased by the addition of magnesium silicate to the boiling baths. Therefore, it seems advisable to determine whether it would act as a fiber protective agent in the process of drying the neutral or alkaline fiber.

Method of Working. The cellulosic fibers were subjected to 50 half-hour boils in the manner previously described, the same alkalies being used in the same concentrations. Furthermore, the neutral and alkaline fibers were dried in the same manner, using only one drying temperature (100° C.). The following experiments were made:

1) Boiling without the addition of magnesium silicate.
   a) Drying of the neutral fiber.
   b) Drying of the alkaline fiber.
2) Boiling with the addition of magnesium silicate.
   a) Drying of the neutral fiber.
   b) Drying of the alkaline fiber.

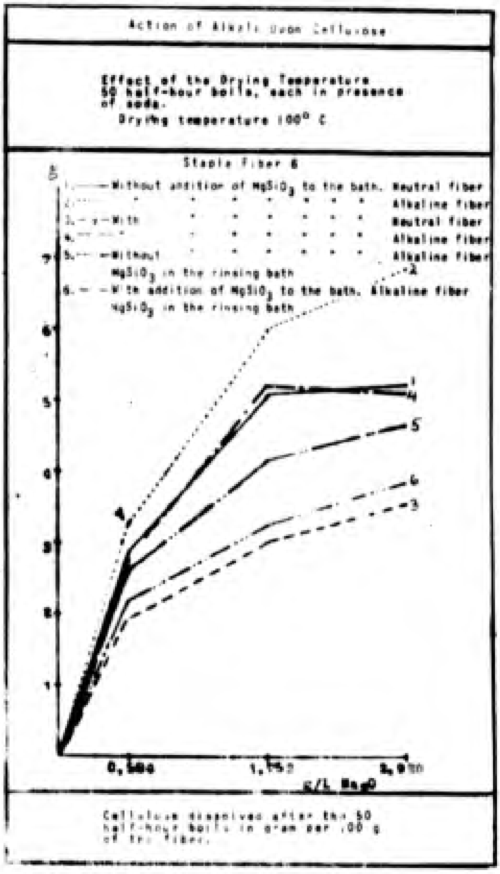


Figure 165

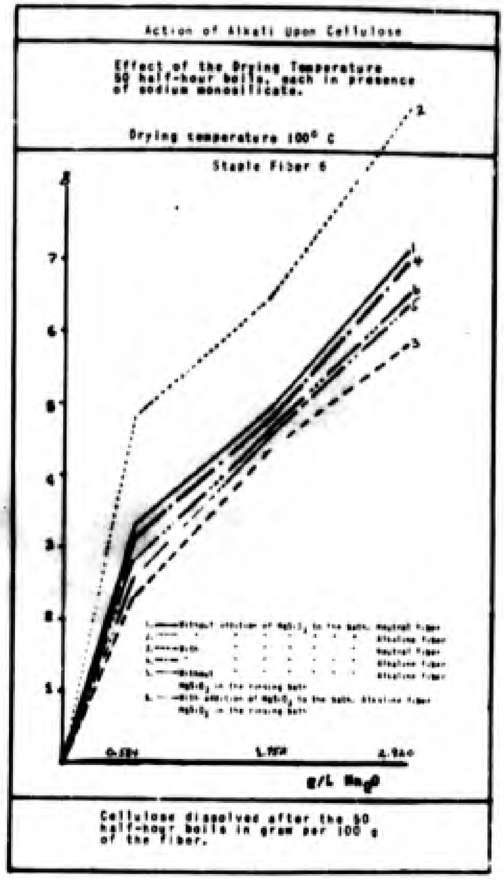


Figure 166

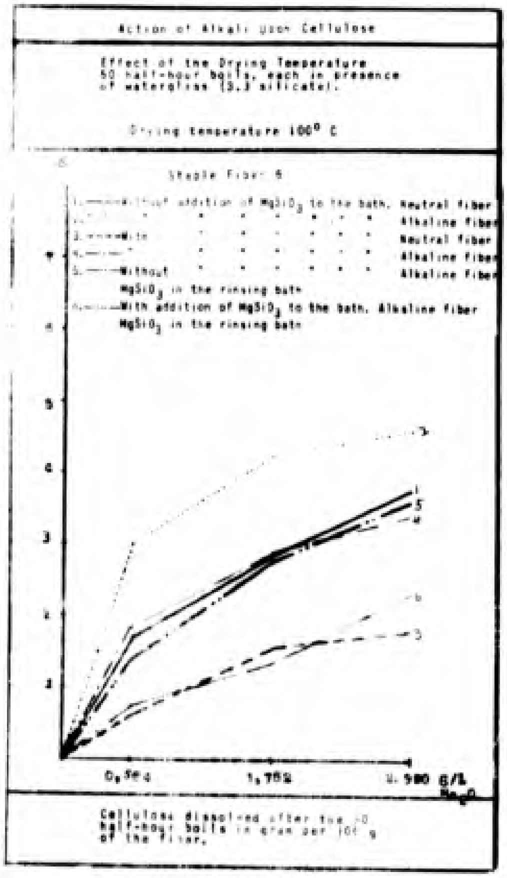


Figure 167

3) Boiling without the addition of magnesium silicate, rinsing with an alkaline bath containing magnesium silicate, and drying in an alkaline condition.
4) Boiling with the addition of magnesium silicate, rinsing with an alkaline bath containing magnesium silicate, and drying in an alkaline condition.

The magnesium silicate used in these experiments was prepared by precipitating water glass ($Na_2O \cdot 3 \cdot 3\ SiO_2$) with magnesium sulfate and corresponds with the formula: $MgO \cdot 3 \cdot 3\ SiO_2$.

It was used in all cases in a concentration of 0.5 g per liter.

The results of the boiling treatment with sodium carbonate are shown in Figure 165, with sodium monosilicate in Figure 166, and with water glass in Figure 167.

From these three series of experiments, comprising the boiling treatments of cellulosic fibers in presence of sodium carbonate, sodium monosilicate and water glass, with and without magnesium silicate, the rinsing of the fiber with and without magnesium silicate, and the drying of the neutral and alkaline fiber, the following conclusions were drawn:

1) The greatest damage to the fiber is caused by boiling without magnesium silicate and drying in an alkaline condition.

2) Fiber damage caused by the treatment described in Paragraph 1 above, is considerably minimized if the fiber is rinsed until neutral before being dried.

3) About the same damage as described in Paragraph 2 above, takes place when boiling with the addition of magnesium silicate and drying the fiber in an alkaline condition.

4) If magnesium silicate is added to the rinsing bath, but not to the boiling bath, and the fiber is dried in an alkaline condition, damage to the fiber is the same or less than when treated as in Paragraph 3 above.

5) The fiber is protected to an especially high degree when magnesium silicate is added to the boiling bath as well as to the last rinsing bath and when the fiber is dried in an alkaline condition.

6) The least fiber damage is noted when magnesium silicate is added to the boiling bath, and the fiber is rinsed until neutral and dried.

These results indicate that fiber damage caused by alkaline boils is minimized by the addition of magnesium silicate to the boiling and rinsing baths, by rinsing until neutral, and drying below 100° C.