

SULFUR FORMS IN CRUDE VISCOSE RAYON

BY

J. R. LEONARDS

A Thesis submitted to the faculty of the  
Virginia Polytechnic Institute in Partial  
Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

in

CHEMISTRY

August 31, 1940

Approved:

Advisor in Major Work

Head of Major Department

Dean of Graduate School

## TABLE OF CONTENTS

### Part I - STUDIES IN THE DESULFURIZATION OF CRUDE VISCOSE RAYON

	Page
I. INTRODUCTION	1
II. HISTORICAL	2
III. METHOD OF ATTACK	4
IV. DETERMINATION OF SULFUR FORMS	6
V. MISCELLANEOUS EXPERIMENTS	17
VI. INSOLUBILITY OF THE SULFUR IN ORGANIC SOLVENTS	41
VII. METHODS OF DESULFURIZATION	52
VIII. DISCUSSION OF RESULTS	61
IX. SUMMARY	66
X. CONCLUSIONS	68
XI. LITERATURE CITED	69

### Part II - THE EFFECT OF ALCOHOL ON VISCOSE

I. INTRODUCTION	1
II. HISTORICAL	2
III. EXPERIMENTAL	4
IV. DISCUSSION OF RESULTS	29
V. SUMMARY	35
VI. APPENDIX	36
VII. LITERATURE CITED	39
VIII. ACKNOWLEDGMENT	40

PART I

STUDIES IN THE DESULFURIZATION OF CRUDE VISCOSE RAYON

## I. INTRODUCTION

During the manufacture of rayon by the viscose process a certain quantity of sulfur or sulfur compounds is deposited in the crude rayon filament. Since such sulfur content detracts from the clarity and dying properties of the product, a desulfurizing step must be used to remove it. The method of desulfurization has been developed in an empirical manner but little attention has been paid to the form or forms in which this sulfur exists in the rayon.

The purpose of this investigation was to determine the form or forms of the sulfur in crude viscose rayon, that is the manner in which sulfur is combined in rayon. It was hoped that the results of this investigation would lead to a better understanding of the reactions that take place during the spinning of viscose rayon and also of the mechanism of the commercial removal of these sulfur compounds.

## II. HISTORICAL

A search of the literature revealed that very little work had been done on this subject. Kawata<sup>(15)</sup> analyzed the desulfurizing bath which is widely used in commercial practice, that is, an aqueous solution of 0.5% to 1% sodium sulphide by weight. After the bath had been used to desulfurize crude viscose rayon, it contained sulfide, sulphite, thiosulfate, and sulfate ions. The analysis did not distinguish between sulfides and polysulfides and was of little value in the determination of the sulfur forms.

Scherer<sup>(24)</sup> has shown that the sulfur in crude viscose rayon is present in two forms, one of which is readily removed by almost any aqueous solution and the other removed only by hot alkaline reagents. He also speculated on the possible sulfur compounds in the rayon. The following is an extract

from his paper: "During the spinning of the rayon the reaction between the viscose and the acid spin bath may be assumed to result in the production of the following compounds: cellulose, carbon disulfide, hydrogen sulfide, sodium sulfide, sodium sulfate, colloidal sulfur, and sodium thiocarbonates of various compositions; and, when the regeneration of the cellulose is not complete, some cellulose xanthate remains. It is also possible that any or all of the products might react with the newly regenerated cellulose to form organic sulfur compounds or complexes. There is also the possibility that the sulfuric acid of the bath might also react with the cellulose. It may therefore be assumed that the rayon on the spool probably contains the above possible forms of sulfur. After the spinning step the wet spool is placed in a washing

machine and pure water circulated through the threads until no more salts or acids are detectable. This procedure should largely eliminate the water soluble salts. The rayon is then dried. The crude dry rayon may then be assumed to have present a mixture of colloidal free sulfur and organic sulfur derivatives of an unknown nature."

Scherer then suggests as a result of his investigations that colloidal sulfur does not appear to be present in the rayon, basing this suggestion on the incomplete removal of sulfur from the rayon by extraction with known solvents for colloidal sulfur.

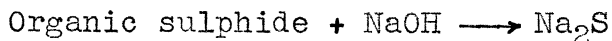
## III. METHOD OF ATTACK

The method for investigation of the sulfur forms in crude viscose rayon which was used in this thesis was divided into two general sections:

(1) Treatment of the rayon with reagents that will convert the sulfur forms into soluble sulfur compounds that may be more easily and conveniently analyzed.

(2) Extraction of the sulfur forms from the rayon with solvents that will not react with these forms. Evaporation of the solvent should allow these forms to be directly analyzed and identified, without interference from the cellulose.

The first procedure used was the extraction of crude viscose rayon with 1% sodium hydroxide solution with subsequent analysis of the extract. On adding hydrochloric acid to the alkaline extract, hydrogen sulfide was evolved and colloidal sulfur separated out. This indicated the possibility of the presence of elementary sulfur in the rayon and also that of an organic sulfide, since the following reactions may have taken place during the extraction:



The sodium sulphide thus formed would dissolve a further

quantity of the elementary sulfur to give a true solution, or would perhaps result in the formation of polysulfides. It is such sulfur in solution which is precipitated on adding acid.

With this point in mind the second method of attack was then tried. The rayon was extracted with a large variety of organic solvents for sulfur. It was found that methyl alcohol would completely dissolve or extract all the sulfur. When the solvent was evaporated it was found that the residue consisted of pure elementary sulfur in an amount equal to the original sulfur content of the rayon. This indicated that all the sulfur in the rayon was in the elementary form, and thus all succeeding experiments were designed to confirm this result.



#### IV. DETERMINATION OF SULFUR FORMS

##### A. Methods of Analysis and Results

###### 1. Total sulfur

The basic principal of the available methods for the analysis of total sulfur in crude undesulfurized viscose rayon is the simultaneous oxidation of the cellulose part of the rayon to volatile products and the conversion of the sulfur to sulfates. This may be brought about by various methods, of which two are:

(1) Combustion in a bomb<sup>(26)</sup>

(2) Oxidation with perchloric acid<sup>(25)</sup>

Both methods yield accurate results but they are rather time-consuming and the danger of an explosion is always present.

Scherer<sup>(24)</sup> has shown that treatment of the crude rayon with 1% sodium hydroxide solution at 80°C. for one hour will remove all the sulfur forms from the rayon. This was verified by so extracting a rayon sample and then analyzing the extracted rayon for sulfur by the perchloric acid method. This was then used as the basis for a method of analysis of total sulfur. The sodium hydroxide extract was oxidized with bromine which converted all the sulfur compounds to sulfates and also destroyed any organic matter which may have interfered.

with the precipitation of barium sulfate. After the solution was acidified and the bromine boiled off, the sulfate ions were precipitated as barium sulphate and weighed. This method was found to be satisfactory in all respects and is the one that was used in all the analyses in this study.

The crude viscose rayon used in this investigation was obtained from different sources and was rayon which was washed and dried after spinning but was undesulfurized and unbleached. These rayons will be designated in the remainder of this work by the following numbers, according to their source:

#1. American Viscose Corporation

#2. North American Rayon Corporation

#3. Rayon Division, E. I. Du Pont de Nemours & Co.

Since most of the original investigations were made with rayon "number one" and later extended to the other two samples, this rayon will be the one referred to when no other designations are made.

Procedure: About 25 grams of rayon were covered with 200 ml. of 1% NaOH solution in a 500 ml. Erlenmeyer flask and the solution boiled gently on the hot plate for about one hour. The extract was then filtered by decantation into a one liter volumetric flask, and the rayon pressed with a flattened stirring rod to expell absorbed solution. The rayon was then

washed once with hot water and again extracted with 1% sodium hydroxide for about twenty minutes. Washing with hot water was then continued until the volumetric flask was filled to the mark. This was the standard procedure for extraction with sodium hydroxide except that where smaller samples of rayon were analyzed, one extraction followed by thorough washing was found to be sufficient.

A 100 ml. aliquot portion of the sodium hydroxide extract was measured out with a pipette into a 250 ml. Erlenmeyer flask. One to two ml. of bromine were added and the solution boiled gently under the hood for fifteen minutes. While the solution was still boiling it was acidified with hydrochloric acid and the excess bromine boiled off. This took about five minutes. (Note: If the solution is acidified while cold and then brought to a boil, the bromine is much harder to boil off and may take anywhere from one-half to one hour.) The colorless oxidized solution was then filtered hot into a 400 ml. beaker and 10 ml. of 10% barium chloride solution was added. The precipitate of barium sulfate was digested on the edge of the hot plate for one hour and allowed to cool overnight. The barium sulfate was filtered on a weighed Gooch crucible, washed with water until the washings were no longer acid, dried at 105°C. for five minutes and ignited to constant weight at 800°C. The results were

expressed as % S.

To avoid errors due to variations in sulfur content from skein to skein of rayon from the same source, a control analysis was made for each skein or batch of rayon investigated. The results given here are the average of about fifteen determinations.

<u>Rayon Sample</u>	<u>Percent Total Sulfur</u>
#1	2.40
#2	0.25
#3	0.168

The maximum deviation from the average value was about five percent. Duplicate analyses of the same skein of rayon checked to one percent.

## 2. Analysis of sulfide, sulfite and sulfate ions in the sodium hydroxide extract

The procedure for this analysis is a standard one<sup>(16)</sup> and was modified only in the amounts and concentrations of the reagents in order to compensate for the small amounts of these ions present in the solution. The total reducing sulfur was determined by pouring an aliquot portion of the sodium hydroxide extract into an excess of acidified standard iodine solution (about 0.025 N.) and back titrating the excess iodine with standard sodium thiosulfate. This was assumed to

be composed of sulfite and sulfide ions. The sulfite ion was determined by precipitating the sulfide as cadmium sulfide, filtering and titrating the filtrate with iodine. The sulfide content was then obtained by difference. In order to determine the sulfate ion, the solution was acidified with hydrochloric acid, boiled for one-half hour and filtered. This removed any sulfide and sulfite. After oxidation with bromine to destroy organic matter the sulfate ions were determined gravimetrically as barium sulfate. The results, expressed as %S., are given in the following table and are the average of four determinations.

Table I

Analysis of Sodium Hydroxide Extract of Rayon

Rayon Sample	Total Sulfur	Total Reducing Sulfur	Sulfate	Sulfide	Sulfite
#	%S	% S	% S	% S	% S
1.	2.40	1.19	0.51	0.63	0.56
2.	0.25	0.15	0.08	0.10	0.05

These results are not of much significance on account of the following factors.

- a. The total reducing sulfur, as determined by

titration with standard iodine solution, was shown to be too high due to the presence of reducing substances other than sulfur compounds. These foreign reducing substances were probably sugars which were formed by the hydrolysis and degradation of the cellulose. This was demonstrated by extracting sulfur free rayon with one percent sodium hydroxide solution and titrating the extract with standard iodine. The amounts of these interfering compounds were nearly equal in magnitude to the reducing sulfur itself, thus rendering invalid the use of a blank determination. Thus it is probable that there are no sulfite ions in the sodium hydroxide extract, the values given in the above table being due to these interfering compounds.

b. When the sodium hydroxide extract of rayon was acidified with hydrochloric acid in order to remove sulfide and sulfite ions, there was noted a precipitate which appeared to be colloidal sulfur. This was coagulated by boiling and identified as elementary sulfur. The following two criteria were used in this and in all following experiments to identify an unknown material as pure sulfur:

- (1) Burns with a pale blue flame liberating sulfur dioxide, the latter being recognized by its characteristic odor.
- (2) Sharp melting point of sulfur.

When the acidified sodium hydroxide extract was boiled to coagulate the colloidal sulfur and boil off hydrogen sulfide, part of the sulfur forms may have been oxidized to soluble non-volatile forms. Also the colloidal sulfur may not have been completely coagulated and would pass through the filter paper. These sulfur forms would then have been analyzed as sulfate ions even though the latter were not originally present. This explanation was supported by the observation that the analytical results obtained for sulfate ions varied widely in different determinations and depended on the time of boiling of the acidified solution.

#### B. Extraction of Rayon with Organic Solvents

The next phase in this investigation was the extraction of the sulfur forms by organic solvents which presumably would not react with them. This procedure should separate the sulfur compounds from the rayon thus allowing them to be more conveniently analyzed.

The extractions were carried out in either Soxhlett or Cavanaugh extractors. No extraction thimbles were necessary since the rayon was used in threads at least four or five inches long and thus were placed directly in the glass extraction cup. The extraction was run continuously. The time required for the

solvent to fill the extraction cup and then be siphoned off was about five minutes. All the rayon samples were dried for one hour at 105°C. before being extracted and care was taken to use dry solvents and dry extractors. After extraction the rayon residues were dried, weighed, and analyzed for total sulfur by the sodium hydroxide method.

The results are expressed in Table II.



Table II  
Solvent Extractions of Rayon

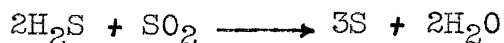
Rayon Sample	Solvent	Time of Extraction	Original Total S.	Total S. After Extraction	Percent S. Extracted	% of Total Sulfur Extracted	Melting Point of Extracted S.
#		hrs.	%S.	%S.	%S.	%	°C.
1	Acetic Acid----	32	2.40	0.00	2.40	100	---
1	Toluene -----	24	2.40	1.35	1.05	44	---
1	Chloroform ----	24	2.40	1.79	0.61	25	---
1	Acetone -----	24	2.40	1.86	0.54	23	114
1	Carbon -						
	Disulfide-----	24	2.40	1.92	0.48	20	---
1	Benzene -----	9	2.40	2.15	0.25	10	---
1	Ether -----	12	2.40	2.40	0.00	0	---
1	Methyl						
	Alcohol-----	24	2.40	0.00	2.40	100	121
1	Ethyl Alcohol--	30	2.40	1.45	0.95	40	---
1	n-Butyl Alcohol-	24	2.40	2.19	0.21	9	---
1	n-Amyl Alcohol--	24	2.40	2.21	0.19	8	---
1	t-Butyl Alcohol-	24	2.40	1.76	0.64	27	---
2	Benzene-----	8	0.25	0.19	0.06	24	---
2	Benzene-----	70	0.25	0.21	0.04	16	---
2	Methyl Alcohol--	24	0.25	0.00	0.25	100	121
3	Benzene-----	24	0.168	0.12	0.048	24	---
3	Methyl Alcohol--	4	0.168	0.00	0.168	100	112-113*

\* Melting point was determined after solution of the extract in benzene.

### C. Discussion

The formation of colloidal sulfur on acidification of the sodium hydroxide extract of rayon may be explained in two ways.

1. If the sodium hydroxide extract of rayon contained sulfide and sulfite ions then on acidification there would be produced hydrogen sulfide and sulfur dioxide respectively. These gases are known to react in the following manner to produce colloidal sulfur.



2. The sodium hydroxide extract may have consisted of a solution of elementary sulfur in sodium sulfide and when the solution was acidified this sulfur was precipitated. The reaction that took place during the extraction of the sulfur compounds in the rayon was probably



and then this sodium sulfide dissolved a further amount of elementary sulfur. However, the sulfide ions present in the sodium hydroxide extract may have been derived from organic sulfides in the rayon since these sulfides would probably be hydrolyzed to sodium sulfide.

The solvent extractions of the crude viscose rayon showed that methyl alcohol was the only organic solvent that completely removed all the sulfur from the rayon. After boiling off all the methyl alcohol the residue was a light yellow powder

which was identified as pure elementary sulfur (Melting Point  $121^{\circ}\text{C}.$ ) The weight of this sulfur corresponded to 96% of the total sulfur originally present in the rayon, the other four percent probably being lost in the handling. This indicated that the sulfur in crude viscose rayon was present entirely in the elementary form. Thus it would be expected that other known solvents for sulfur should also completely extract it from the rayon, but the above table shows that this was not the case. The explanation of this phenomenon will be considered later.

Although the results of the extraction of crude viscose rayon with methyl alcohol indicated that the sulfur is all present in the elementary form, there exists another possibility. In addition to elementary sulfur in the rayon there may have been present a possible organic sulfur compound which reacted with the methyl alcohol to give elementary sulfur. At present no such compound is known but the possibility could not be excluded, since the compounds of cellulose and sulfur are not very well known. Thus a series of experiments were performed which confirmed the conclusion that the sulfur in rayon is present only in the elementary form. These experiments were also designed to yield information about the reactions and behavior of this sulfur.

## V. MISCELLANEOUS EXPERIMENTS

A. Extraction of Crude Viscose Rayon with Liquid Ammonia

Franklin<sup>(10)</sup> has shown that elementary sulfur is soluble in liquid ammonia at a temperature of  $-33^{\circ}\text{C}$ . It was suggested that an extraction of rayon made with liquid ammonia should remove all the sulfur from it, and due to the low temperature there would be very little danger of decomposition of any organic sulfur compounds that may have been present. The extractions were carried out in the following manner using the apparatus shown in Figure I.

Procedure: A weighed rayon sample was placed in the Dewar flask (a) and all joints and stoppers were carefully sealed with a mixture of beeswax and rosin. The valve (c) which led to the ammonia storage tank was cautiously cracked with the pinch cocks (d & e) open. The pressure in the ammonia tank forced ammonia into the first Dewar flask (b). The ammonia was let in slowly so as to allow enough time for the apparatus to cool. About five hundred ml. of ammonia were let in. The valve (c) was then closed and the tube leading to the other Dewar flask was pushed down into the ammonia. By closing the pinch cock (e) the ammonia was forced into the

Dewar flask containing the rayon sample. The water-white ammonia turned light green almost instantly. As the ammonia remained in contact with the rayon the color became darker and finally turned a reddish brown. These color changes are known to take place when elementary sulfur is dissolved in liquid ammonia. The rayon was extracted for fifteen minutes to one hour depending on the amount of rayon extracted and its sulfur content. The ammonia was then siphoned over into the Erlenmeyer flask. The rayon was then washed with fresh ammonia until the washings were no longer colored green, this being a good indication of the completeness of the extraction. The ammonia was evaporated off and the extracted material remained in powdered form which was easily scraped out of the flask.

Analysis of the extracted rayon showed that the ammonia had removed all the sulfur from the rayon. The results of these extractions are given in table III.

The extract of rayon "number one" was a brown powder, while that of "number two" and "number three" was brownish black flakes. The extract appeared to contain some material other than sulfur and so was divided into two portions by solution in benzene.

1. Fraction soluble in benzene.

This was identified as pure elementary sulfur. This evidence therefore supports the results obtained from the

methyl alcohol extractions.

2. Fraction insoluble in benzene.

This was in the form of a black powder which was shown by analysis to contain a small amount of sulfur or sulfur compounds. In "number one" rayon this represented about 25% of the total sulfur content. This material probably consisted of small particles of elementary sulfur that were surrounded by a film of tarry material which prevented their solution in the benzene. This fraction did not melt but decomposed at a temperature of 200°C. The nature of this material which was obtained only in very small amounts warrants further investigation.

Table III

## Extraction of Sulfur in Crude Viscose Rayon by Liquid Ammonia

Rayon Sample	Wt. of Rayon Before Extraction	Wt. of Rayon After Extraction	Loss in Wt. of Rayon	% Loss in Wt.	Original Total S.	Total S. After Extraction	Melting * Point of Extracted S.
#	gms.	gms.	gms.	%	%S.	%S.	°C.
1	13.65	---	---	---	2.46	0.00	---
1	68.72	68.06	0.66	0.97	2.46	0.07	---
1	50.44	49.08	1.36	2.70	2.46	0.00	114
2	16.59	16.52	0.07	0.44	0.24	0.00	113-114
3	59.11	58.97	0.14	0.24	0.168	0.00	113

\* The melting point was taken after the sulfur in the extract was dissolved in benzene and the solvent evaporated.

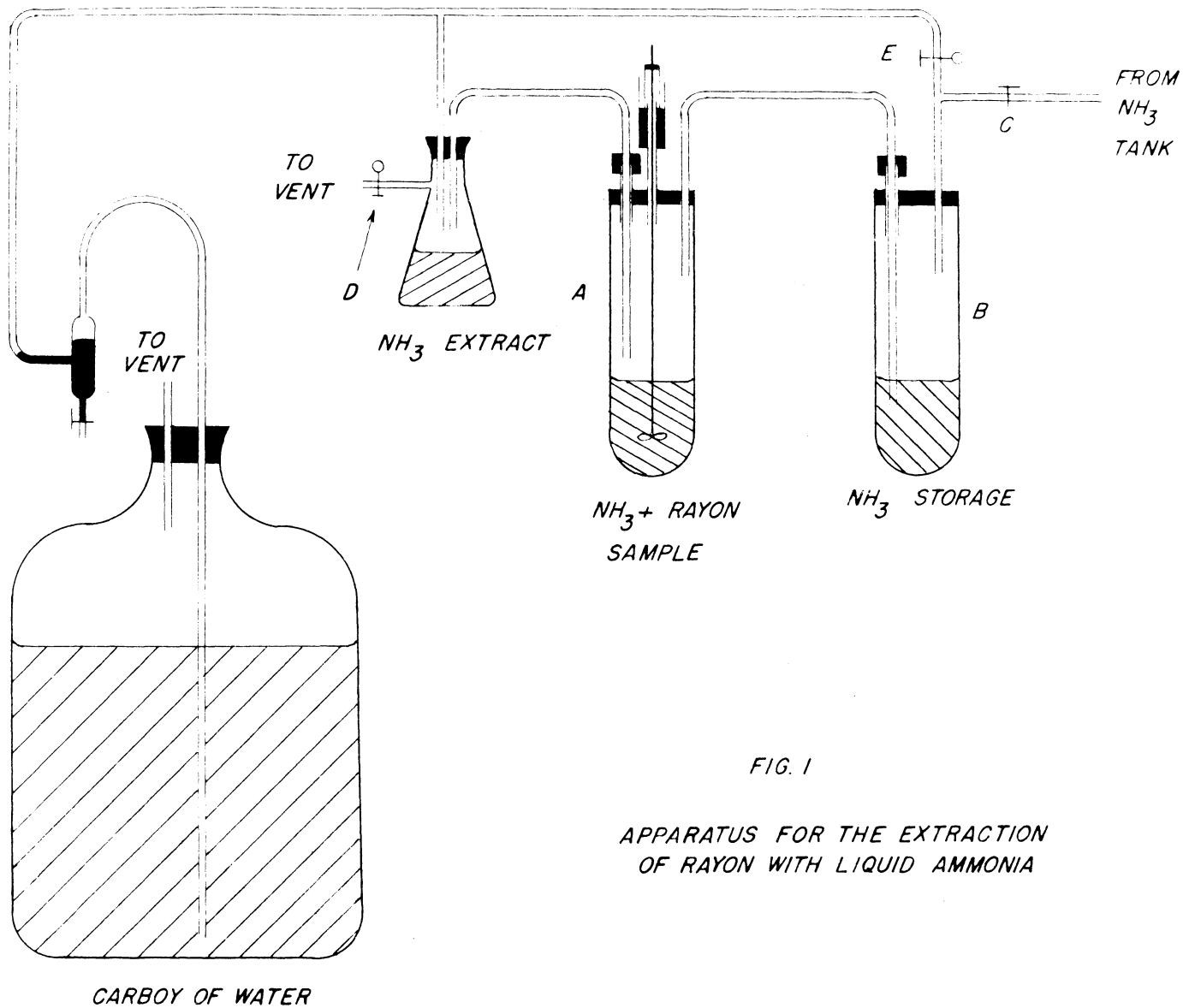


FIG. 1

APPARATUS FOR THE EXTRACTION  
OF RAYON WITH LIQUID AMMONIA



B. Extraction of Rayon with Water

Scherer<sup>(24)</sup> has shown that extraction of rayon with water at 100°C. would remove all the sulfur. This experiment was repeated with rayon "number one" and the results are given in the following table:

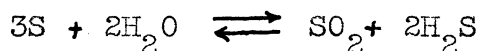
Table IV

Extraction of Crude Viscose Rayon with Water

Time of Extraction	%S. in Water Extract	%S. in Rayon after Extraction	% of Total S. Extracted
Hours	%	%	%
0	0.00	2.40	0.0
12	0.02	1.48	38
24	0.20	1.32	45
72	----	0.14	94

Table IV shows that an appreciable time is required to remove all of the sulfur, in fact even after 72 hours extraction there was still some sulfur left in the rayon. Since sulfur is almost completely insoluble in water, and since almost no sulfur was found in the water extract, the sulfur must have been removed by a hydrolytic reaction, the

products of which were volatile. The following reaction is suggested as having taken place<sup>(21)</sup>.



The small amount of sulfur in the water extract may have been due to the oxidation of these gases by the air to sulfates. This hydrolytic reaction takes place only very slowly, and thus the amount of hydrogen sulfide and sulfur dioxide given off could not be measured. The rate of this hydrolysis was increased in the following experiment by the use of an acid solution, and thus the gases given off could be collected and analyzed.

At this point the effect of the water extraction on the physical appearance of the rayon itself may be noted. The crude viscose rayon was a dull opaque thread. After being extracted and dried it was white, transparent and lustrous. The lustre was probably due to the swelling effect of the water, followed by shrinkage on drying.

#### C. Hydrolysis of the Sulfur in Rayon by Dilute Hydrochloric Acid

The apparatus and procedure used in this experiment were almost identical with that used in the analysis of sulfur in steel. The rayon was placed in a 500 ml. Erlenmeyer flask fitted with a two hole rubber stopper containing a separatory funnel through which the hydrochloric acid was introduced.

The gases evolved in the hydrolysis were passed through a trap and then bubbled through a solution of ammoniacal cadmium chloride solution. The time of hydrolysis varied from fifteen min. to one hour. The cadmium chloride solution was then poured into an excess of standard iodine solution which had been previously acidified with sufficient glacial acetic acid so that the resulting solution was acid. The excess of iodine was then titrated with standard sodium thiosulfate using starch as the indicator.

The results are expressed in Table V

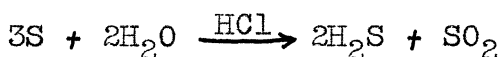
Table V

Hydrolysis of Sulfur in Rayon with Dilute Hydrochloric Acid

Weight of Rayon	Time of Hydrolysis	Net Vol. $I_2$	Normality of $I_2$	Original %S In Rayon	%S Hydrolyzed
gms.	min.	ml.	N.	%	%
1.231	15	12.0	0.026	2.40	0.40
1.231	30	24.2	0.026	2.40	0.82
0.569	15	6.1	0.026	2.40	0.45
0.569	30	9.1	0.026	2.40	0.67
* 0.376	30	14.1	0.026	1.86	1.56
* 0.376	50	15.6	0.026	1.86	1.73

\* These rayon samples had been previously extracted for 24 hours with acetone.

Table V shows that the amount of sulfur which was hydrolyzed by the dilute hydrochloric acid to sulfur dioxide and hydrogen sulfide depended on the time of the hydrolysis. None of the rayon samples investigated were boiled long enough in hydrochloric acid to completely hydrolyze all the sulfur, but in the case of the rayon which had been previously been extracted with acetone, 93 percent of the total sulfur content was hydrolyzed. The titrations were not very accurate due to the difficulty in determining the end point. The maximum error was estimated as being 0.1 % S. which corresponds to about five percent of the total sulfur content. However, there is every indication of a hydrolytic reaction of the sulfur in the rayon, the reaction being:



This is a reversible reaction which is known to take place<sup>(21)</sup>. It proceeds to completion in this case due to the removal of the gaseous products.

#### D. Extraction with Glacial Acetic Acid

About eight grams of crude rayon (#1) were extracted with glacial acetic acid in a Cavanaugh extractor. After 15 minutes of extraction the acetic acid had turned light yellow and after 24 hours it had a dark reddish-brown color. At this time the acid in the extraction flask was replaced with fresh acid and

the extraction continued. After eight hours the acetic acid had turned only a faint yellow color. The extraction had a marked effect on the rayon itself. The filaments were almost completely broken up into a white powder. Analysis of this residue showed that the acetic acid had completely removed the sulfur from the rayon. This reaction was not investigated any further.

E. Treatment of the Rayon with Dilute Ammonium Hydroxide

1.521 grams of rayon were treated with 100 ml. of dilute ammonium hydroxide (50 ml. concentrated  $\text{NH}_4\text{OH}$  and 50 ml. water) in a 250 ml. Erlenmeyer flask fitted with a reflux condenser. The solvent was then boiled gently for one hour. After a few minutes of boiling the solution turned yellow but this color slowly disappeared until at the end of the experiment the solution was again colorless. One hundred ml. of water were added and the solution was filtered. The rayon was then washed several times with cold distilled water, the washings being added to the original filtrate. The rayon residue, which did not appear to be affected by the treatment, was analyzed for total sulfur by the sodium hydroxide method.

Weight of  $\text{BaSO}_4$  --- 0.116 grams

Percent S in residue -- 1.05 %

The ammonium hydroxide removed only about one-half of the total

sulfur content of this particular rayon sample.

F. Extraction of Rayon with Benzoyl Chloride

Elementary sulfur is readily soluble in hot benzoyl chloride. Thus this reagent would be expected to remove all the sulfur from rayon.

1. 0.772 grams of rayon were treated with 50 ml. of benzoyl chloride in a 250 ml. Erlenmeyer flask and heated gently for about ten minutes. At first the rayon fibres could be seen turning black and then the whole mass turned a dark brown color. The rayon fibres were definitely damaged by this treatment and appeared to be disintegrated. The benzoyl chloride was then decanted off through a filter and extraction repeated with 30 ml. more of benzoyl chloride. The rayon was then washed with cold ether and analyzed for total sulfur.

Weight of  $\text{BaSO}_4$  -----0.040 grams

Percent S in Residue ---0.71 %

This indicated that the elementary sulfur in rayon is soluble in benzoyl chloride. However, as with many solvents for sulfur, only a fraction of the total sulfur was removed from the rayon. In this case the incomplete removal of the sulfur may have been due to insufficient extraction so that the experiment was repeated using a longer extraction time.

2. Ten grams of rayon were treated with 100 ml. of benzoyl

chloride and warmed gently at 100°C. After half an hour the benzoyl chloride was decanted off and the rayon extracted with 100 ml. more of benzoyl chloride at 100°C. for half an hour. The rayon was then washed twice with ether and several times with cold acetone. 207 grams of the rayon residue were analyzed for total sulfur.

Weight of  $\text{BaSO}_4$  ----- 0.011 grams

Percent S. in Residue -- 0.07 %

In this case the benzoyl chloride removed very nearly all the sulfur from the rayon.

An attempt was made to distill off the benzoyl chloride from the extract and thus analyze the extract but the benzoyl chloride attacked the corks and rubber stoppers and since no "all-glass" distilling apparatus was available, this work was abandoned.

#### G. Distillation of the Sulfur from Crude Viscose Rayon

The following table shows the vapor pressure of elementary sulfur at various temperatures. (13)

Table VI

## Vapor Pressure of Sulfur

Temperature	Vapor Pressure
°C.	mm.
250	12.00
200	2.10
170	0.59
130	0.07

Since rayon may be heated in vacuum to 200°C. and even higher without decomposition or charring, it was thought possible that the sulfur in crude viscose rayon might be distilled off by using a suitable vacuum system. The apparatus used is shown in Figure II.

Procedure: The rayon was well packed into the 125 ml. distilling flask, the apparatus sealed with rosin-beeswax compound and the Cenco Hy-vac pump started. The pressure was indicated by the manometer and varied only slightly during the course of the experiment. The pressure was about 0.5 to one mm. The temperature of the oil bath was gradually raised by moving the electric heater closer to the oil bath. The effect of the heat on the rayon threads was to give them a



golden brown color but they did not appear to be otherwise affected.

Rayon Sample #1

The temperature of the oil bath heating the rayon was raised gradually within a period of two hours to 175°C. and then kept for one hour at 190 to 210°C. When the temperature of the oil bath reached 140°C., yellow crystals could be seen collecting on the cool neck of the distilling flask just above the level of the oil. After the "distillation" was stopped, 0.08 grams of these crystals were recovered and identified as pure elementary sulfur, (m.p. 118-119°C.) The melting point indicates that the sulfur condensed in the monoclinic form. These crystals corresponded to about 20 percent of the total sulfur content of the rayon.

Rayon Sample #2

The temperature of the oil bath was kept as follows:

1 hour at 100° to 175°C.  
1 hour at 175° to 185°C.  
2½ hours at 210°C.  
6 hours at 210° to 220°C.

At the higher temperatures a yellow tarry material condensed on the upper part of the neck of the distilling flask. The amount was too small to be identified but was dissolved in hot two percent sodium hydroxide solution. After bromine oxidation, a white precipitate was obtained with barium chloride, indicat-

ing a sulfur compound. The distillate was probably pure sulfur mixed with a small amount of tarry decomposition products of the rayon.

Rayon Sample #3

The distillation was carried out for five hours at 190°C. to 200°C. at a pressure of 0.5 to one mm. The tarry yellow material which deposited on the cool upper part of the neck of the distilling flask was dissolved in hot two percent sodium hydroxide, oxidized with bromine and gave a heavy precipitate of barium sulfate. The original distillate was too small to be identified as such but it appeared to be pure sulfur as was found with rayon sample number one. The results of the distillation of sulfur from crude rayon are given in Table VII.

These results indicated that the sulfur in crude viscose rayon may be distilled off at a suitable temperature and pressure without apparent harm to the rayon fibres.

Table VII  
Distillation of Sulfur from Crude Viscose Rayon

Rayon Sample	Wt. Rayon Before Distillation	Wt. Rayon After Distillation	Loss in Wt. of Rayon	% Loss in Wt.	Original Total Sulfur	Total Sulfur in Residue	% of Total S. Distilled
#	gms.	gms.	gms.	%	%S.	%S.	%
1	18.717	18.433	0.284	1.52	2.40	1.89	21
2	20.33	19.40	0.93	4.5	0.25	0.00	100
3	25.21	24.52	0.69	2.54	0.168	0.106	37

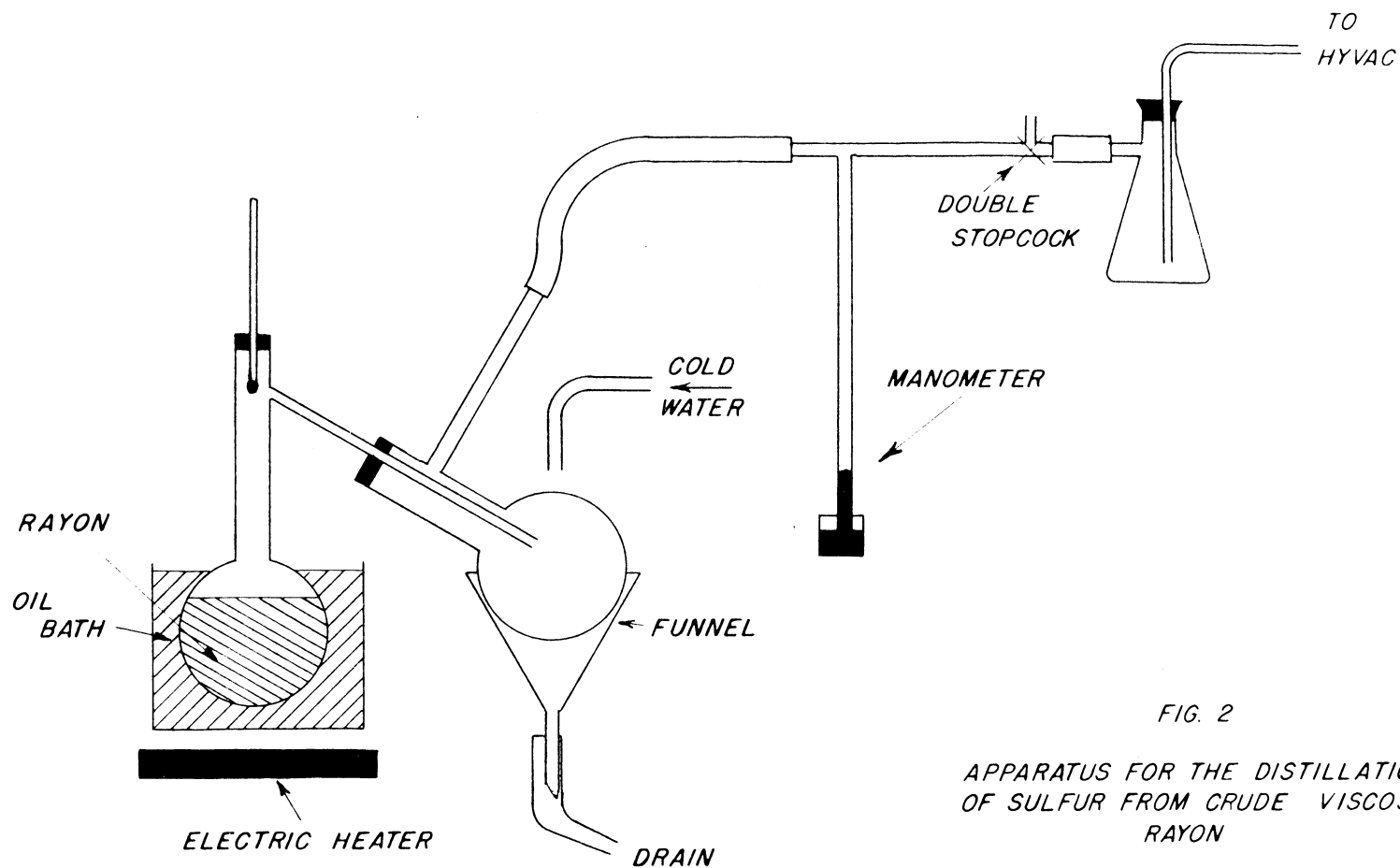


FIG. 2

APPARATUS FOR THE DISTILLATION  
OF SULFUR FROM CRUDE VISCOSE  
RAYON

#### H. Reaction of the Sulfur in Crude Viscose Rayon with Sodium Sulfite

Elementary sulfur is soluble in a hot dilute solution of sodium sulfite, the following reaction taking place:



This reaction was used to confirm the presence of elementary sulfur in rayon.

Procedure: The dry weighed sample of rayon was treated with one percent sodium sulfite and kept near the boiling point or gently boiled for two hours. (20 ml. of sodium sulfite per gram of rayon was used. This was a large excess.) The solution was decanted off and the rayon washed twice with hot water. The excess sodium sulfite is almost completely prevented from reacting with iodine during analysis by the formation of an addition compound with formaldehyde. Ten ml. of formalin solution and five ml. of glacial acetic acid were added and the solution allowed to stand ten minutes. The sodium sulfite was then titrated with standard iodine solution. A blank was run to account for any sodium sulfite that does react with iodine since the sodium sulfite-formaldehyde addition compound will react with iodine at a slow but appreciable rate. The results are shown in Table VIII.

Table VIII

Reaction of Sulfur in Rayon with Sodium Sulfite

Rayon Sample	Wt. of Rayon	Volume of $I_2$	Normality of $I_2$	% S in Rayon that Reacts	Mean % S.	Original Total S in Rayon
#	gms.	ml.	N.	% S.	%S.	% S.
1	0.870	20.0	0.026	1.92	1.88	2.40
1	0.461	10.1	0.026	1.83		
2	6.22	18.5	0.026	0.248	0.25	0.25
2	8.15	25.2	0.026	0.258		
3	4.85	9.0	0.026	0.155	0.14	0.168
3	5.03	7.8	0.026	0.129		

Sample Calculation:

$$\% S = \frac{32 \times \text{ml. of } I_2 \times .026}{\text{Weight of Rayon} \times 10}$$

$$= \frac{32 \times 20.0 \times 0.026}{0.870 \times 10}$$

$$= 1.92 \% S.$$

The low results in the case of sample number one may have been due to the reaction of the sulfur with sodium sulfite being incomplete, or, perhaps, due to the oxidation of some sodium thiosulfate by the air during the long time of boiling.

The method in general is not very accurate due to the difficulty of getting a good end point in the titration. The estimated accuracy is about five percent. However, this method is recommended as a method of analysis of the total sulfur in crude viscose rayon which may be used in the control laboratory of a rayon plant, since it was the simplest and most rapid encountered during this work.

In general the results indicate that the sulfur in the rayon reacted with sodium sulfite according to the reaction



### I. Ash Content of Rayon Samples

In order to investigate whether the sulfur in rayon may be present as an inorganic sulfur compound, the ash content of the rayon samples were determined by burning down the rayon in porcelain crucibles over an electric heater. The residue was then ignited at 900°C. to constant weight in a muffle furnace. The results are given in Table IX.

Table IX

## Ash Content of Crude Viscose Rayon

Rayon Sample	Wt. of Sample	Wt. of Ash	% Ash	Mean % Ash
#	Grams	Grams	%	%
1	5.55	0.008	0.14	0.18
1	5.57	0.012	0.22	
3	10.79	0.037	0.34	0.32
3	10.57	0.032	0.30	

In rayon sample number one the ash content is small compared to the total sulfur but in sample number three the ash exceeded the sulfur content. The amount of ash was too small to be conveniently analyzed and a much larger rayon sample would have to be burned down to make an analysis of the ash.

J. Analysis of Rayon after Benzene Extraction

Samples of rayon were extracted with benzene for eight hours in a Soxhlett extractor. An extraction of the rayon residue was then made with two percent sodium hydroxide solution in the usual manner and the extract analyzed for the various forms of sulfur as previously described. The results are given in the following table.



Table X

## Benzene Extraction of Crude Viscose Rayon

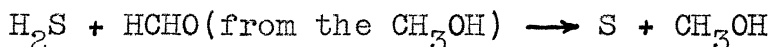
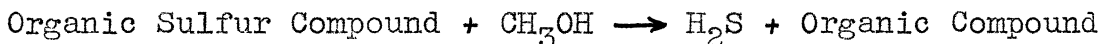
	Sample	Total S.	Total Reducing S.	Sulfide
	#	%S.	%S.	%S.
Before Extraction	1	2.40	0.67	1.10
After Extraction	1	2.15	0.68	1.08
Before Extraction	2	0.24	0.15	0.10
After Extraction	2	0.19	0.20	0.09 <sub>6</sub>

These results are in substantial agreement with those of Scherer (24) who found that the "free sulfur" (which corresponds to the sulfide ion in these experiments) was little affected by extraction with benzene, acetic acid in alcohol, sulfuric acid or hydrochloric acid solutions, and indicated that the "free sulfur" is in a form difficult to remove by any except hot alkaline reagents. However a better explanation may now be offered. The mechanism of removal of the sulfur from rayon by sodium hydroxide is that of the formation of sodium sulfide followed by solution of more sulfur in the sodium sulfide. Extraction with benzene removes some of the elementary sulfur, and on further extraction of the same sample with sodium hydroxide, approximately the same amount of sodium sulfide

would still be formed even though the total sulfur present was decreased. Thus the analytical value of the "free sulfur" or sulfide ion would be nearly the same before and after the solvent extraction.

#### K. Reaction of Hydrogen Sulfide and Formaldehyde

Since it might be argued that some possible organic sulfur compound might exist which could, in some unknown manner, react with methyl alcohol to form elementary sulfur, the following equations were postulated as a mechanism by which elementary sulfur could result:



There being no known organic sulfur derivative at hand which would be alcoholized to hydrogen sulfide by methyl alcohol, a series of experiments, attempting to duplicate the postulated reaction between hydrogen sulfide and formaldehyde in methyl alcohol, was tried.

1. Hydrogen sulfide was bubbled through boiling methyl alcohol for nine hours. Evaporation yielded only a trace of residue, which was not sulfur.

2. Hydrogen sulfide was passed over the surface of a solution of formaldehyde and the mixture of gases was bubbled

through boiling methyl alcohol for 12 hours. Again the evaporation of the alcohol gave no residue.

However, the hydrogen sulfide reacted with the formaldehyde to give a white voluminous precipitate. This was filtered, washed with cold water and divided into two portions. One portion was recrystallized from water and the other from methyl alcohol. The product decomposed into volatile products on prolonged boiling in water. The product, recrystallized from water, retained part of the water and could not be dried without decomposition. Crystallization from alcohol gave a dry white powder having an objectional odor and a melting point of  $99^{\circ}$  to  $101^{\circ}\text{C}$ . It has as yet not been identified but has been found to have several peculiar properties. One such property is the formation of yellow insoluble silver salt which turns brown on exposure to light. This silver salt was insoluble in hydrochloric acid or ammonium hydroxide.

The results of the solvent extractions of rayon have shown that the sulfur is present in the elementary form. This was substantiated by the series of experiments just described. The next phase of this investigation was to determine the reason for the observed insolubility of the sulfur in the rayon in organic solvents for sulfur and to discuss the methods by which this sulfur may be removed.

## VI INSOLUBILITY OF THE SULFUR IN CRUDE VISCOSE RAYON IN ORGANIC SOLVENTS

Table II on page 14 shows the results of the extraction of crude viscose rayon with various solvents for sulfur. Although methyl alcohol will extract all the sulfur from the rayon, other solvents for sulfur will remove only a small fraction of it. This is the case with acetone, carbon disulfide, benzene, toluene and the other organic solvents listed in Table II. This peculiar behavior may be due to several reasons:

- A. Incomplete extraction
- B. Insoluble physical modifications of sulfur
- C. Inability of the solvents to penetrate into the rayon structure.

These explanations will now be considered in order.

### A. Incomplete Extraction of the Sulfur in Crude Viscose Rayon by Organic Solvents

The first assumption as to why carbon disulfide, acetone, benzene and other organic solvents for sulfur only remove part of the sulfur from the rayon would be that the extraction was incomplete. A series of extractions was carried out in Cavanaugh extractors for a long period of time in order to test the

above statement.

Care was taken to exclude all water from the rayon and solvents.

The extraction apparatus was thoroughly cleaned and dried.

The rayon was dried in small aluminum cans, at 110°C. for several hours.

The acetone and toluene were dried over anhydrous potassium carbonate and distilled, and the middle fraction, boiling at a constant temperature, was used. The ethyl alcohol was absolute. The results are given in the following table. (Table XI page 43)

The results, shown in Table XI, indicated that extraction of rayon for a long time with these organic solvents would not remove all the sulfur. Thus the incomplete removal of the sulfur from crude viscose rayon by organic solvents cannot be attributed to incomplete extraction.

Table XI

## Solvent Extraction of Crude Viscose Rayon

Solvent	Time of Extraction	% S. in Rayon After Extraction	% of Total Sulfur Extracted
	hours	% S.	%
----	0	2.40	----
Toluene	36	2.16	10.0
	48	1.96	18.3
	60	2.36	1.6
	90	2.23	7.1
Ethyl Alcohol	30	1.45	39.6
	80	1.14	52.5
Acetone	24	1.86	22.5
	115	1.82	24.2

### B. Physical Form of Sulfur in Rayon

Many physical or alloptopic forms of sulfur are known. Thus the insolubility of the sulfur in rayon in carbon disulfide, acetone, etc. may be explained by the assumption that the sulfur is in some physical form which is insoluble in these organic solvents. There are however several objections to this assumption.

1. All known modifications of sulfur will revert back to the rhombic form if kept at room temperature<sup>(6)</sup>. The rayon under investigation had been exposed to the air for several months before use and thus it was to be expected that all the physical forms of sulfur would have been converted to the most stable rhombic form. It was also postulated from a consideration of the possible reactions during the regeneration of cellulose from viscose that the sulfur in the rayon might be present as colloidal sulfur, which should be readily soluble in the organic solvents under consideration.

2. All known physical modifications of sulfur are slightly soluble in carbon disulfide, benzene, etc. even though some physical forms are usually classed in handbooks as insoluble. Hence even though the solubility of the sulfur in the organic solvent is very small, the long time extraction of the rayon in a Soxhlett extractor should eventually dissolve out all the sulfur.

3. Microscopic examination of the sulfur particles in the rayon filaments did not reveal any differences in the physical forms. This work will be described in the following sections.

#### Microscopic Examination of the Sulfur in Crude Viscose Rayon

The microscope is a very important tool in the identification of the various types of rayon and other textile fabrics. Many of the individual characteristics of the various fibres may also be brought out under the microscope and thus the techniques involved have been highly developed. (11; 12; 17; 22)

The purpose of the microscopic examination of the rayon filaments in this investigation was to determine whether or not the sulfur in the rayon was present in more than one physical form and, if so, to find out if possible what these physical forms were. Since acetone and other organic solvents will extract a fraction of the sulfur from the rayon, it might be possible that the sulfur extracted by these solvents would be in a different physical form than the sulfur which was not extracted. In this work it was attempted to compare microscopically the sulfur particles in the original crude viscose rayon with those in rayon which had been extracted with acetone and other organic solvents for sulfur.

Neither a sectioning plate nor a microtome was available and thus no cross sections of the rayon filaments could be made. Lateral views were used exclusively.



The preparation of a lateral mount of a rayon filament was very simple.<sup>(23)</sup> The individual filaments of the twisted rayon thread were separated and several filaments about one-half inch long were laid on a clean slide. A drop of mounting medium, (alpha-bromonaphthalene) was added from a medicine dropper and the specimen was covered with a clean cover glass, taking care that no air was trapped underneath it. This mount was not permanent but the mounting medium evaporated only very slowly so that the mount could be kept for several weeks. Slides were made in this manner of crude rayon, desulfurized rayon and a series of rayons which had been extracted with various solvents.

At a magnification of 440 times the sulfur particles could be distinguished but were too small to observe their crystalline form. Desulfurized rayon was outstanding by the absence of sulfur particles. (It may be mentioned here that the microscope may be used in the routine examination of crude viscose rayon. An experienced operator may very rapidly determine the approximate sulfur content of the rayon. The microscope is even more sensitive than chemical analysis in determining whether or not the rayon is completely desulfurized.)

The sulfur particles of rayon "number one" were very much larger than those of the other two rayons, and at 440 x the sulfur particles in rayons "number two" and "number three" were just barely visible.

At a magnification of 2500 (1.9 mm. oil immersion objective and 25 x eyepiece) the sulfur in all the filaments could be clearly seen but still no shape, or form, could be noted. In rayon "number one" which contained the largest sulfur particles, these were just large enough to determine their shape but at this magnification detail was poor and depth of focus was limited. These limitations coupled with the interference of sulfur particles just out of focus, yet close to those being examined, did not allow any distinction to be made between the sulfur particles in undesulfurized rayon and those in rayon which had been previously extracted with solvents for sulfur.

Polarized Light: The mounted lateral sections of the rayon filaments were examined under the microscope using polarized light. This was attained by the use of a Nicol prism in the Abbe' substage condenser holder of the microscope. As far as this investigator could determine the rayon filaments, including the sulfur particles, looked identical under polarized light as they did under ordinary illumination.

The source of light in this experiment was a hand-fed carbon arc used on the 110 Volt A.C. line. A resistance in series with the arc limited the current to about six amperes.

Ultramicroscopic Examination of Rayon Fibres: It was suggested

that the ultramicroscope might show up differences in the physical forms of the sulfur particles in the rayon. The available equipment consisted of a Cardiod condenser, quartz chamber and cover glass, and accessories.

The Cardiod condenser (1) might reasonable be called an aplanatic dark field illuminator. It is much superior as a dark field illuminator to the ordinary Paraboloid condenser, but it is also more sensitive to maladjustment, the slightest departure from correct focus being enough to throw all illumination out of the object plane. Thus the medium between the condenser and the objective must be of the highest degree of homogeneity and everything must be scrupulously clean. When parallel light from an extended surface such as an arc lamp is focused on the cardiod condenser, it is imaged by it as a small surface, with little or no depth, in the focal plane of the condenser. The quartz chamber and cover glass is so designed that the liquid is in a thin film having a thickness of two microns. Since the diameter of a rayon filament is much larger than two microns, this condenser could not be used for the ultramicroscopic examination of the sulfur particles in rayon unless sections of that thickness could be made.

However, some pictures of the sulfur in rayon have been made using an ultramicroscope.<sup>(12)</sup> Examination of these gave no indication that different physical forms may be distinguished.

It must be remembered that the ultramicroscope does not give direct image of the particles but really a diffraction pattern; thus the shape of the particle cannot be determined.

In general it may be stated that the available evidence appears to indicate that the incomplete solubility of the sulfur in rayon in carbon disulfide, acetone, etc., is not due to the presence of an insoluble physical modification of sulfur, and some other explanation must be sought.

### C. Penetration of Solvents into the Rayon Structure

The incomplete desulfurization of rayon by extraction with organic solvents may be postulated as due to the inability of these solvents to penetrate into the rayon filaments and reach the sulfur which is present near the center of the filament.

This may be investigated by several methods:

1. The penetration of a solvent into the rayon filaments may be measured by dissolving a dye in the solvent, immersing the thread in the solution for a given time and then making a microscopic examination of the fiber for penetration of the dye. However, an objection to this method is that although the solvent itself might penetrate into the rayon, the molecules of the dye which are much larger would not penetrate. This method was therefore eliminated.

2. Ernst Kuhnel (18) states that liquids which do not

produce a swelling action of cellulose cannot penetrate into the fiber structure. For example, it was not possible to remove the oil drops from an oil-containing viscose fiber, obtained by spinning of a viscose-oil emulsion, by extraction with a solvent for the oil, no matter how long and at what temperature the extraction was carried out. The situation was entirely different, however, when the oil containing fiber was extracted not when dry, but in a state swollen with water. In this case it was possible to quantitatively remove the oil from the fiber especially if the solvent is water soluble. The water serves as a "pathmaker" for the extracting medium or solvent.

These results were directly applied to the extraction of sulfur from rayon by organic solvents. Water was used to swell the cellulose fibers and open up its structure so that the solvent would penetrate.

Procedure: a. A sample of rayon was immersed in cold distilled water for 10 minutes, and the water wrung out by hand. Extraction of the rayon for one hour with acetone (using a Cavanaugh extractor) removed all of the sulfur.

b. The following experiment was designed to swell the cellulose fibers of the rayon by immersion in water, to remove the water, and leave the rayon in a swollen state. This

was to be followed by extracting with a water insoluble solvent.

A sample of rayon was soaked for one-half hour in cold distilled water. It was then dipped into cold acetone for five minutes, and again for two minutes in fresh acetone. It was then immersed in ether for two minutes to remove the acetone and then two minutes in cold benzene. Extraction of the rayon in a Soxhlett extractor for 20 minutes with benzene removed all of the sulfur.

These results indicate that the reason for the incomplete desulfurization of rayon by organic solvents is due to inability of these solvents to penetrate into the inner parts of the rayon filaments. Methyl alcohol, appears to be able to get into the rayon filament and is the only organic solvent found that would remove all of the sulfur from unswollen rayon.

## VII METHODS OF DESULFURIZATION OF CRUDE VISCOSE RAYON

The discussion of this problem was divided into three sections:

- A. The general method in use at the present time.
- B. Methods proposed and patented but not in general use.
- C. A new method of desulfurization using organic solvents, which was developed as a result of this investigation.

A. The most widely used method at the present time for the desulfurization of crude viscose rayon consists of treating the rayon in skein form with a solution of an alkaline sulfide. A much used treatment is with a one percent solution of sodium sulfide or ammonium sulfide at forty to fifty degrees Centigrade for one hour. Many variations in this procedure are also in use. This treatment removes all the sulfur from the rayon, the mechanism of the reaction being, apparently, the solution of the sulfur in the alkaline solution to give the higher polysulfides. (20) After washing, the skein is dipped into a solution of 0.1 percent hydrochloric acid for five minutes to neutralize any excess sodium sulfide and is then bleached.

A disadvantage of this method is that the rayon cannot be desulfurized on the aluminum spool on which it was spun, since the alkaline solution reacts with the aluminum. Another more important disadvantage is the degrading action on the cellulose by the hot alkaline solution. The tensile strength and elongation of the finished rayon is somewhat less than that of the crude rayon, but it is possible that the harmful effect of the desulfurizing bath is not completely indicated by the above two properties. Also the alkaline solutions swell the cellulose, convert it partially to hydrocellulose, which on subsequent washing and drying, imparts a smooth lustrous surface to the filament. The desulfurization by means of organic solvents, which will be later described, will not degrade the rayon in this manner and will also remedy the other deficiencies of the sodium sulfide bath.

B. Many methods have been proposed for the desulfurization of crude viscose rayon. They are mentioned here for the purpose of comparison.

Kami<sup>(14)</sup> treated raw viscose rayon in a closed vessel with a solution of ammonia under controlled conditions (1 hour at 70°C. with 150 grams  $\text{NH}_3$  per liter). The rayon was washed free of ammonia and dried below forty degrees centigrade. This



treatment increased the tearing strength and extensibility of the material and the increase was roughly proportional to the time of treatment and inversely proportional to the temperature. The rayon generally became whiter, softer and more lustrous, but a disadvantage was that the process must be carried out in an air tight apparatus.

Articles made from viscose may be desulfurized<sup>(8)</sup> by substances which exert little or no swelling action on the articles and which contain only a very little water. Examples are phenol, pyridine, sodium sulfide in alcohol, glucose in alcohol, or glycerine in methyl alcohol. The thread in these cases has a more subdued luster and the dry and wet strengths are 50 percent higher than usual.

Rayon may be desulfurized by a physical method<sup>(4)</sup> which consists of treating it with an aqueous solution of a wetting or washing agent.

Many other methods for desulfurization have been proposed.  
(3;5;7;9)

### C. Desulfurization of Rayon by Organic Solvents

In a previous section, it has been shown that if crude viscose rayon is first swollen with water, extraction for one hour with acetone would remove all the sulfur. It appeared possible to use an organic solvent as a desulfurizing agent and

several experiments were run to test the properties of the rayon after this type of desulfurization. The removal of sulfur by organic solvents probably takes place in an entirely different manner than the desulfurization with sodium sulfide and it would thus be expected that the properties of the finished rayons might be different.

Procedure: The tensile strength and elongation of a sample of crude viscose rayon, wound on a bobbin, was first measured. The bobbin was then immersed for 15 minutes in distilled water in order to swell the rayon. It was then placed in a can of acetone which could be tightly covered and which was fitted with a reflux condenser and the acetone was gently boiled for 20 minutes. After cooling, the rayon was rinsed in cold water and dried at 60°C. The rayon was then wound into a skein. After the desulfurization and during skeining three samples of the rayon were taken, one from each end of the bobbin and one from the center. Microscopic examination did not reveal the slightest trace of sulfur particles and thus even the above short extraction with acetone was sufficient for complete desulfurization. After skeining, the rayon was bleached in the normal manner and dried. The finished rayon looked very similar to rayon processed in a normal manner, although it was of a dull luster. The tensile strength and elongation were again measured.

The results are given in Table XII.

Table XII

Physical Properties of Rayon Desulfurized with Acetone

Tensile Strength		Elongation	
Before Desulfurization	After Desulfurization	Before Desulfurization	After Desulfurization
1840	1630	14	16
1940	1680	15	19
1680	1640	18	17
1440	1810	18	14
1850	1700	13	18
<u>1750 *</u>	<u>1690</u>	<u>16</u>	<u>17</u>

\* Average

Note: Tensile strengths are expressed in grams necessary to break five strands at once. Elongation is expressed in percent.

The above results are not very accurate, but within the limits of experimental error it appears that the desulfurization of crude viscose rayon with acetone has very little if any effect on the tensile strength and elongation. The differences noted in the above experiment are probably due mainly to the lack of sufficient data and to the handling of the rayon in the finishing steps.

Further work in this direction seemed interesting, and so this problem was made the subject of a B. S. thesis for T. C. McCaleb of Virginia Polytechnic Institute<sup>(19)</sup>. The results of this investigation will now be described.

Procedure: A sample of crude rayon was divided into two skeins and two bobbins. One skein and one bobbin were desulfurized in the normal manner with sodium sulfide and the other skein and bobbin with methyl alcohol for one hour. The rayon on the skeins was also bleached, while the rayon on the bobbins was not bleached. The tensile strength and elongation were measured before and after desulfurization and the average results of two distinct experiments are given in Table XIII.

Table XIII

Effect of Desulfurization on the Physical Properties of Rayon

Desulfurizing Agent	Tensile Strength Grams per denier		Elongation percent	
	Dry	Wet	Dry	Wet
<u>SKEIN</u>				
Undesulfurized	2.19	0.93	13.6	17.2
Sodium sulfide	1.58	0.91	11.0	17.0
Methyl alcohol	2.02	0.91	14.0	17.6
<u>BOBBIN</u>				
Undesulfurized	2.19	0.93	13.6	17.2
Sodium sulfide	1.66	0.88	11.0	17.0
Methyl alcohol	2.05	0.87	10.8	16.6

These results appear to indicate that rayon desulfurized with methyl alcohol had a dry tensile strength which was twenty-five per cent greater than rayon finished in the normal manner. The other properties were very nearly the same with both methods. As was previously stated, the tensile strength and elongation do not fully indicate the harmful effects of the finishing steps on the rayon. In the above experiments, although the number of tests run were insufficient to allow any general conclusions to be drawn, they do indicate that the use of methyl alcohol as a desulfurizing agent is at least as good as sodium sulfide. Since, however, it is known that organic solvents do not have the same degrading action on cellulose as do the alkali sulfides, the methyl alcohol should be a better desulfurizing agent in this respect.

No comparison will be made of the cost of equipment necessary for the two methods of desulfurization (sodium sulfide and alcohol) but it should be noted that the alcohol may be recovered more easily than can the sodium sulfide.

The rayon desulfurized by methyl alcohol was much less lustrous than the rayon treated with sodium sulfide. The sulfide solution exerts a much greater swelling action on the cellulose and this is probably the factor which is responsible for the luster. Thus the use of organic solvents would be of value

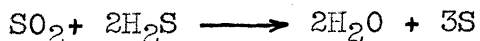
when a dull luster yarn is desired since no oil or inorganic pigments need be incorporated into the rayon.

It is suggested that further work be done on the desulfurization of rayon using other organic solvents, making use of more sensitive tests to determine the degradation of the cellulose or the other harmful effects on the rayon.

## VIII. DISCUSSION OF RESULTS

A. General Discussion

The analysis of total sulfur in the three types of rayon under investigation showed that rayon "number one" had a very much higher total sulfur content than rayon "number two" and "number three". The explanation for these large differences is interesting. The high sulfur content of rayon "number one" may be explained in the following manner. It is known that hydrogen sulfide is liberated in the regeneration of the cellulose when the viscose is spun. This hydrogen sulfide, escaping from the interior of the rayon filaments, may cause fissures and holes to be formed and so reduce the strength of the filament. This is prevented by the addition of sodium sulfite to the viscose so that on spinning, there is formed both hydrogen sulfide and sulfur dioxide which react to form sulfur.

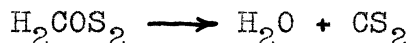
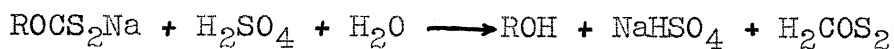


If this type of treatment were used, it would account for the high sulfur content of the rayon. This high sulfur content is not objectionable since it may easily be removed. The low sulfur content of rayons "number two" and "number three" may be attributed to the incorporation of a wetting agent in low concentrations in the spin bath. Lauryl pyridine hydrochloride

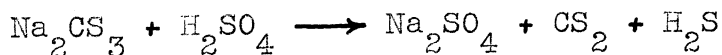
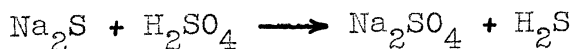
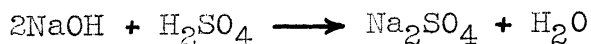


is a common agent. The interfacial surface tension between the cellulose and spin bath is lowered, thus allowing the hydrogen sulfide to escape from the rayon filaments and accounting for the low sulfur content.

During the spinning of the rayon the following reactions may be assumed to have taken place between the viscose and the acid spin bath: Cellulose xanthate is hydrolyzed with the formation of regenerated cellulose and dithiocarbonic acid, which latter being unstable decomposes into carbon disulfide and water<sup>(27)</sup>.

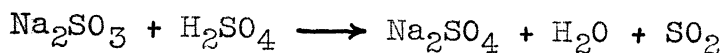


However, viscose is a solution of cellulose xanthate, in which we find, besides the cellulose compound, sodium hydroxide and the products of the reaction between carbon disulfide and the excess sodium hydroxide - chiefly sodium thiocarbonate, sodium carbonate, and sodium sulfide. These constituents would also react with the acid spin bath in the following manner:



There are also several other possibilities. Sodium sulfite if often added to viscose and a small amount may also be formed

by the oxidation of sodium sulfide. Hence:



All the products of the above regeneration reactions, except sulfur, are either volatile or water soluble, which is consistent with the results of this investigation.

It is also possible that the sulfuric acid or any of the products of the decomposition of cellulose xanthate might react with the newly regenerated cellulose to form organic sulfur compounds or complexes. Since only sulfur is found in the crude rayon then the above reactions do not take place or else result only in water-soluble products.

Thermal treatment of cellulose in the presence of unchanged cellulose xanthate or thiocarbonates must result in organic sulfur compounds. Since no such compounds were found in the rayon, it may be assumed that the regeneration of the cellulose was complete and the removal of the products of regeneration, except sulfur, was also complete before the crude rayon was dried.

## B. Recommendations

The following items are suggested as suitable for further work:

1. That an investigation be made on the material extracted from crude viscose rayon by liquid ammonia.
2. To study the effect of abnormal spinning conditions on the sulfur forms. In this connection may be mentioned the work carried out by Baylor<sup>(2)</sup> on the sulfur content of rayon which had been spun through various acid spin baths. Viscose was spun through baths containing sulfuric acid, hydrochloric acid nitric acid, phosphoric acid, and acetic acid. After washing and drying the rayon was analyzed for total sulfur. The results are given in Table XIV.

Table XIV

Effect of the Spinning Bath on the Total Sulfur Content of Crude Viscose Rayon

Acid Spin Bath	Total Sulfur Content
	% S
$\text{H}_2\text{SO}_4$	1.96
HCl	0.54
$\text{CH}_3\text{COOH}$	0.52
$\text{HNO}_3$	0.47
$\text{H}_3\text{PO}_4$	0.31

Although in this investigation it appears that the sulfuric acid spin bath caused the rayon to have a high sulfur content, it is probable that the acid was not completely washed out of the rayon. The problem warrants further investigation.

The determination of the sulfur forms in Lillienfeld rayon would also be of interest.

3. To identify the product of the reaction between hydrogen sulfide and formaldehyde.

4. To investigate more fully the possible advantages of the use of organic solvents as desulfurizing agents.

## IX SUMMARY OF RESULTS

A method of analysis of the total sulfur in crude viscose rayon was developed. This consisted of extraction of the sulfur with sodium hydroxide solution, oxidation to sulfates with bromine, and precipitation as barium sulfate. This method is accurate to one percent.

A more rapid method for the analysis of total sulfur consists of boiling the rayon in a dilute solution of sodium sulfite followed by titration of the sodium thiosulfate produced.

The total sulfur may also be roughly estimated by observation under the microscope. The presence of even a trace of sulfur may be observed by this method.

The form of the sulfur in the crude viscose rayon was shown to be entirely elementary sulfur. This was accomplished by extracting the sulfur with methyl alcohol and showing that the extract consisted of pure elementary sulfur. This result was supported by the series of experiments in Section V.

The reason for the incomplete removal of the sulfur from the rayon by organic solvents for sulfur was shown to be due to the inability of the solvent to penetrate into the cellulose structure. When the rayon was swelled by soaking in water, the solvents were able to penetrate into it and thus remove all

the sulfur.

Extraction of rayon in a swollen condition for 20 minutes with acetone completely desulfurized it. This treatment did not appear to have any effect on the tensile strength or elongation. The use of acetone or methyl alcohol as a desulfurizing agent was shown to be feasible.

## X. CONCLUSIONS

The sulfur in the three types of crude viscose rayon investigated, was present entirely in the elementary form.

This sulfur cannot be completely extracted by organic solvents for sulfur, except methyl alcohol. This is due to the inability of these solvents to penetrate into the cellulose structure. Swelling the cellulose fibers with water will allow these solvents to penetrate, and under such conditions, all of the sulfur may be removed.

Organic solvents do not have a harmful effect on the rayon and their use as a desulfurizing agent is preferable to that of sodium sulfide. The use of organic solvents in this connection may be commercially feasible.

The presence of sulfur in crude viscose rayon and its approximate amount may be rapidly determined by a microscopic examination.

## XI LITERATURE CITED

1. Bausch and Lomb Catalogue, (1929) pp. 102
2. Baylor, B. S. Thesis, Virginia Polytechnic Institute (1940)
3. British Patent, 428955 \*
4. British Patent, 466,757 \*
5. British Patent, 432,692 \*
6. Caven and Lander, Systematic Inorganic Chemistry, p. 361
7. Cellulose Ind., 8 21-24 (Tokyo)\*
8. French Patent, 783,563 \*
9. French Patent, 655,729 \*
10. Franklin, Am. Chem. J., 20 822 (1898) \*
11. Herzog, Kunstseide, 10 281-3 (1928) \*
12. Herzog, Die Microscopische Untersuchung der Seide und der Kunstseide
13. Handbook of Chemistry and Physics (22nd. edition)
14. Kami, Cellulose Ind. 6 99 (Japan)\*
15. Kawata, Cellulose Ind. 8 48-52 (Tokyo)\*
16. Kolthoff & Furman, Volumetric Analysis, pp.400
17. Lawrie, J. Soc. Dyers Colorists, 44 73-8 \*
18. Kuhnel, Kunstseide and Zellewolle, January 1940 \*
19. McCaleb, B. S. Thesis, Virginia Polytechnic Institute (1940)
20. Marsh and Wood, Introduction to Cellulose Chemistry, p.338



21. Mellor, A Comprehensive Treatise on Inorganic & Theoretical Chemistry
  22. Preston, Rayon Record, 4 947-51 \*
  23. Rayon Sub Committee Publications, Rayon Identification
  24. Scherer, Ind. Eng. Chem., 25 1319 (1933)
  25. Smith, Perchloric Acid, Bulletin of the G. F. Smith Chemical Company
  26. Vitale & Marisca, Ann. Chim. Applicata, 18 461-4 (1928)\*
  27. Wyss, George de, Ind. Eng. Chem. 17 1043 (1925)
- \* Indicates that original article was not available.

Part II - THE EFFECT OF ALCOHOL ON VISCOSE

## INTRODUCTION

In recent years there has been considerable interest in the colloidal nature of viscose and its relation to the reactions that take place when the viscose is ripened and spun. It is assumed (1) that the viscose sol is at first very hydrated and should be classed as a lyophilic sol. Ripening consists in dehydration of the colloidal particles followed by coagulation, and it is known that temperature increases the rate of ripening (9). However the actual reactions that take place in the ripening of viscose are at present unknown.

The general purpose of this investigation was to obtain further information about the colloidal nature of viscose but the specific problem was to determine the effect of alcohol in viscose on the viscosity, ammonium chloride number, and other properties of the viscose.

It was expected that if viscose is a lyophilic sol that alcohol would dehydrate the colloidal particles and convert the viscose into a lyophobic sol. If the viscose could be so changed then it would be expected to have a lower viscosity and would also be coagulated more easily by the acid spinning bath. This would be valuable since the alkali cellulose would not have to be aged as long as in the normal process, thus avoiding the degrading action on the cellulose during this step and also there is the possibility that a more dilute acid spin bath may be used. It is possible that there might also be a chance that much, if not all, of the sulfur content of the spun yarn would be eliminated.

## II HISTORICAL

It is known that the addition of an excess of alcohol to viscose will cause the precipitation of the cellulose xanthate. This procedure is used as a method of purifying and isolating cellulose xanthate (6). However no mention was found in the literature on the effect of alcohol on the properties of viscose when the alcohol was present in amounts which were insufficient to precipitate the cellulose xanthate.

There is however considerable information concerning the colloidal nature of viscose. Blanco (32) states that a freshly prepared solution of cellulose xanthate appears to have characteristics somewhat similar to those of a true solution. On standing it undergoes certain changes, gradually assuming the properties of a colloidal solution. Freshly prepared xanthates are soluble in strong alcohol and salt solutions but become insoluble on standing. More evidence of the colloidal nature of viscose is available as a result of ultramicroscopic studies (20). Such studies have shown that fresh viscose contains the cellulose dissolved in colloidal dispersion. This was shown by a slow Brownian movement which constantly became less distinct as the viscose ripened and was limited by the high viscosity of the solution. Also as the viscose ripened the number of particles decreased and caused the growth of the mass of single particles to such an extent that coagulation of the dispersed phase to a gel took place and a coherent net shaped film became recognizable in the microscope.

This is in agreement with the generally accepted physico-chemical theory of viscose formation (5) which stated that only a small amount of cellulose xanthate is actually formed, which acts as a dispersing agent for unchanged cellulose.

However Sweet (10) states that the particles that he observed under the ultramicroscope were foreign particles which could not be filtered out, and did not appear to be dispersed cellulose.

### III EXPERIMENTAL

#### A. Method of Procedure

Two general methods of procedure were used in this investigation.

(1) Ethyl alcohol was added in varying amounts to normal viscose and the change in the ammonium chloride number was determined.

(2) Ethyl alcohol was added to the sodium hydroxide solution which was used to dissolve the cellulose xanthate crumbs. This yielded a viscose containing a definite amount of alcohol. The effect of the alcohol on the properties of the viscose was then determined.

#### B. Procedures and Results

Run No. 1. A viscose syrup containing 7% cellulose and 6.5% NaOH was made up in the normal manner (7). Samples of this viscose of about twenty grams each were weighed out in 125 ml. Erlenmyer flasks. To these flasks were added 0, 2, 5, and 10 ml. of 95% (by volume) ethyl alcohol. These were stirred up and water was added with rapid stirring until the total weight of the solution was about fifty grams. This total weight was recorded and stirring continued until a homogeneous "solution" was obtained. On the addition of the alcohol a portion of the cellulose xanthate of the viscose was precipitated out but this was redispersed on stirring in the water. Ammonium chloride, 10.29%, was added from a burette until coagulation occurred. This was done in the regular manner as described in the Appendix. An approximate value of the ammonium chloride number was then calculated. The results are expressed in table I:

Table I

The Effect of the Addition of Alcohol to Viscose on the Ammonium Chloride Number.

Weight of viscose	Volume of alcohol added	Weight of alcohol added	Total weight of viscose + alcohol	Total weight water viscose alcohol	Volume of NH <sub>4</sub> Cl	NH <sub>4</sub> Cl number	Percent alcohol
Grams	ml.	Grams	Grams	Grams	ml.		%
20.72	0.0	0.0	20.72	50.72	20	19.3	0.0
19.51	2.0	1.5	21.0	51.0	18	17.6	7.1
19.70	5.0	3.8	23.5	49.5	17	16.4	16.2
22.80	10.0	7.5	30.3	52.3	18	14.6	24.8
50.0	35	26	76	Precipitation of xanthate			34

The ammonium chloride numbers given in Table I, were calculated in the following manner.

$\text{NH}_4\text{Cl}$  No. = Number of ml. of 10 percent ammonium chloride that is required to just coagulate 20 grams of viscose diluted with 30 grams of water.

$$= \text{ml. NH}_4\text{Cl} \times \frac{10.0}{10.29} \times \frac{20.0}{\text{Wt. viscose}} \times \frac{50}{\text{Total Wt. of solution (gms.)}}$$

$$= 20.0 \times \frac{10.0}{10.29} \times \frac{20.0}{20.72} \times \frac{50.0}{50.72}$$

$$= 19.3$$



It is evident that the values of the ammonium chloride numbers given in the above table, cannot be compared to the values obtained when using the standard procedure. However they do indicate qualitatively the amount of electrolyte required to coagulate the viscose. They show very roughly that the addition of alcohol to viscose tends to decrease the ammonium chloride number. (This is what is to be expected since addition of an excess of alcohol will precipitate the cellulose xanthate). This experiment was not at all accurate but the following two "runs" were carried out in a more careful manner.

Run No. 2. Eight hundred and thirty-eight grams of air dry pulp, containing 5.32% moisture, was dipped in 17.85% by weight of sodium hydroxide solution for 1 hour at 23°C. and pressed to 2510 grams. The alkali cellulose was ground in the water cooled, Werner and Pfleiderer grinder for three and one half hours and aged in a closed cardboard container at 20°C.

Analysis of Alkali Cellulose Crumbs\*

Bulk Number -----	176
Sodium hydroxide -----	15.0%
Stock (cellulose) -----	31.0%

After aging for 24, 54, and 72 hours respectively, 250 grams of crumbs were xanthated by adding 21.6 ml of carbon disulfide and rotating in a large glass bottle for one and three-fourth hours at 28°C. The xanthations were all carried out under the same conditions, as

\* See Appendix

described in (7) the only change being the substitution of the large glass bottle for the steel drum.

The viscose solutions containing varying amounts of ethyl alcohol were made up in the following manner. All the viscose samples were made up to contain 7% cellulose and 6.5% sodium hydroxide and were modified only by their alcohol content. The viscose was made up in five hundred ml. wide mouth bottles. Solution was affected by slowly rotating the bottles for two hours at room temperature. After this time the cellulose xanthate appeared to be completely dissolved in all cases, except that containing twenty percent alcohol. This viscose was then ripened at 20°C to await viscosity and ammonium chloride ripeness determinations. The data used in the preparation of the viscose is given in the following Table(II).

Table II.

Preparation of Viscose Containing Ethyl Alcohol

Weight of xanthate	Volume of 18% NaOH	Volume of water	Volume of Ethyl alcohol	Percent Ethyl alcohol
Grams	ml.	ml.	ml.	%
46	23.5	101.6	0.0	0
46	23.5	92.0	11.7	5
46	23.5	82.5	23.4	10
46	23.5	72.9	35.2	15
46	23.5	63.3	46.9	20

Sample Calculation Showing How Viscose was Made to Contain  
Varying Amounts of Ethyl Alcohol.

Data.

Specific Gravities

CS <sub>2</sub> -----	1.25
17.9% NaOH -----	1.20
92.5% (by weight) Ethyl Alcohol -----	0.811

Alkali Cellulose Analysis

NaOH -----	15.0%
Stock -----	31.0%
Alpha Cellulose -----	29.5%

Calculations.

Forty-six grams of cellulose xanthate crumbs were used per sample of viscose. This consisted of 4.3 grams of CS<sub>2</sub> and 41.7 grams of the alkali cellulose.

Total weight of Viscose

$$= \frac{41.7 \times 95 \times 31.0}{100 \times 0.07 \times 100}$$

$$= 176 \text{ grams}$$

Total Weight of NaOH Required

$$= 176 \times 0.065$$

$$= 11.4 \text{ grams}$$

Weight of NaOH already present in the  
Cellulose Xanthate

$$= \frac{41.7 \times 15.0}{100}$$

$$= 6.3 \text{ grams}$$

Weight of NaOH to be Added

$$= 11.4 - 6.3$$

$$= 5.1 \text{ grams}$$

Volume of 17.9% NaOH Required

$$= \frac{5.1 \times 100}{17.9 \times 1.2}$$

$$= 11.7 \text{ ml.}$$

For a viscose containing 5% alcohol (based on total weight of viscose)

Weight of alcohol required

$$= 8.8 \text{ grams}$$

Volume of alcohol required

$$= \frac{8.8 \times 100}{0.811 \times 92.5}$$

$$= 11.7 \text{ ml.}$$

Weight of water Required

$$= 176 - (\text{weight of all other materials})$$

$$= 176 - (\text{weight of xanthate crumbs} + \text{weight of alcohol} + \text{weight of NaOH solution})$$

$$= 176 - (46 + 9.5 + 28.4)$$

$$= 92 \text{ grams}$$

Thus the 46 grams of cellulose xanthate crumbs were dissolved in a solution containing

92.0 ml. water

23.5 ml. of 17.9% NaOH

11.7 ml. of 92.5% ethyl alcohol

and the resulting viscose contained

7% cellulose

6.5% Sodium hydroxide

5% Ethyl alcohol

Similar calculations were made for the other concentrations of alcohol in viscose.

Effect of Alcohol on the Viscosity of Viscose

The viscosity of the viscose was measured after it had ripened for 20 hours at 20°C. The results of these measurements are given in Table III.

Table III

Effect of Alcohol on the Viscosity of Viscose

Percent : Alkali cellulose : Alkali cellulose : Alkali cellulose :						
alcohol	aged 24 hours		aged 54 hours		aged 72 hours	
	Viscosity	Gelling	Viscosity	Gelling	Viscosity	Gelling
	of viscose	time	of viscose	time	of viscose	time
%	Seconds	Hours	Seconds	Hours	Seconds	Hours
0	2640	90	683	430	400	--
5	No flow	20	958	310	700	360
10	Gel	20	Gel	20	Gel	20
15	Gel	20	Gel	20	Gel	20
20	The cellulose xanthate was precipitated					

The values of the viscosities given in the above table are entirely relative. They represent the time required for the viscose to be discharged through a given pipette at a given temperature, the actual viscosities being so high that a standard viscosity pipette could not be used.

Effect of Alcohol on the Ammonium Chloride Number  
of Viscose

The ammonium chloride numbers of the viscoses were also measured. After 20 hours ripening none of the viscose samples could be coagulated by ammonium chloride according to the regular method of measuring the ammonium chloride number, (See Appendix). With further ripening the ammonium chloride numbers were readily obtained and are given the following table.

Table IV.

Effect of Alcohol on the Ammonium Chloride Number of Viscose.

Percent Ethyl alcohol	: Alkali cellulose: aged 24 hours		: Alkali cellulose aged 54 hours		: Alkali Cellulose aged 72 hours	
	Viscose ripened	NH <sub>4</sub> Cl number	Viscose ripened	NH <sub>4</sub> Cl number	Viscose ripened	NH <sub>4</sub> Cl number
%	Hours		Hours		Hours	
0	55	12.5	48	11.5	57	12.3
5	76	9.7	48	10.0	57	10.4



Another effect of the alcohol on the viscose was also noted. This was the color of the viscose. After complete solution and 20 hours ripening the sample containing no alcohol was dark brown in color, and there was a gradual lightening of the color with increasing alcohol concentration, the viscose containing five percent alcohol being a light orange color. The significance of this observation will be later discussed.

Table III indicates that viscose containing ten percent by weight of alcohol will gel within 20 hours of ripening at 20°C. Twenty percent alcohol is sufficient to precipitate the cellulose xanthate. It has also been shown that the presence of the alcohol in the viscose increased its viscosity and tends to decrease the ammonium chloride number. The next experiment was therefore designed to measure the properties of viscose containing from 0 to 5% of alcohol since this was found to be the useful working range.

Run No. 3. Four hundred and fifty-one grams of air dry pulp, containing 5.32% moisture was dipped in 17.85% sodium hydroxide solution for one hour at 21°C. and then pressed to 1345 grams. The alkali cellulose was ground in the Werner and Pfleiderer grinder for three hours to a bulk number of 204 and aged in a closed cardboard container at 20°C. The following is the analysis of the alkali-cellulose crumbs made as described in the appendix.

Bulk No. -----	204
Sodium Hydroxide -----	15.2%
Stock -----	29.9%

After aging for 25, 54 and 73 hours respectively, 360 grams of crumbs were xanthated by adding 29.4 ml of carbon disulfide and rotating for one and three-fourth hours at 28°C.

Viscose was then made up to contain seven percent cellulose, six and five tenths percent sodium hydroxide and varying amounts of Ethyl alcohol. Sample calculations were given in the previous experiment and the data for making up the viscose is given in Table V.

Table V.  
Preparation of Viscose

: Weight of xanthate crumbs	: Volume of 18% NaOH	: Volume of water	: Volume of Ethyl alco- hol	: Percent Ethyl alcohol	:
Grams	ml.	ml.	ml.	%	
<u>63</u>	29.5	132.5	0.0	0	
63	29.5	130.0	3.1	1	
63	29.5	127.5	6.2	2	
63	29.5	125.0	9.2 <sub>5</sub>	3	
63	29.5	122.5	12.3	4	
63	29.5	120.0	15.4	5	

The viscose was allowed to ripen at 20°C. After 18 hours ripening, the viscosities of the viscose samples were measured. Ammonium chloride numbers were determined after ripening for various intervals of time (see appendix). The results are given in Tables VI - IX, and are plotted in Figures I to V respectively.

Table VI

The Effect of Alcohol on the Viscosity of Viscose

Percent Ethyl alcohol	Alkali cellulose f aged 24 hrs.	Alkali cellul- ose aged 54 hrs.	Alkali cellulose aged 73 hrs.
	Relative viscosity	Relative viscosity	Relative viscosity
0	41.5	26.0	15.3
1	50.0	---	18.5
2	---	---	22.6
3	---	42.0	---
4	107	84.0	61.5
5	The viscose does not flow through pipette		---

Table VII

The Effect of Ethyl Alcohol on the Ammonium Chloride Number  
of Viscose.

Alkali Cellulose Aged 25 Hours at 20°C.

Percent Ethyl alcohol	:	:	Ammonium Chloride Number	:
%	Viscose ripened 46 hrs.	Viscose ripened 75 hrs.	Viscose ripened 95 hrs.	Viscose ripened 118 hrs.
0	12.5	10.8	9.8	8.8
1	11.6	----	9.1	-----
2	11.5	9.3	8.6	-----
3	10.7	----	---	7.1
4	10.5	----	7.9	-----
5	10.1	8.2	7.4	6.0

Table VIII

The Effect of Ethyl Alcohol on the Ammonium Chloride

Number of Viscose.

Alkali Cellulose Crumbs aged 54 hours			
Percent Ethyl alcohol	Ammonium Chloride Number		
%	Viscose ripened 47 hrs.	Viscose ripened 76 hrs.	Viscose ripened 113 hrs.
0	12.5	11.0	9.3
1	11.5	10.1	---
2	11.1	----	8.1
3	12.6	9.1	---
4	12.5	----	---
5	12.2	8.5	7.2

Table IX

The Effect of Ethyl Alcohol on the Ammonium Chloride

Number of Viscose.

Alkali Cellulose Crumbs Aged 73 hours		
Percent Ethyl alcohol	Ammonium Chloride Number	
%	Viscose ripened 57 hours	Viscose ripened 94 hours
0	13.0	10.6
1	----	----
2	11.1	----
3	----	9.0
4	----	----
5	10.2	8.5

Table X

The Effect of Ethyl Alcohol on the Rate of  
Ripening of Viscose

Alkali Cellulose aged 25 hours at 20°C.

Ripening time  Hours	Ammonium Chloride Number		
	0 Percent alcohol	2 Percent alcohol	5 Percent alcohol
46	12.7	11.5	10.1
75	10.8	9.3	8.2
95	9.8	8.6	7.4
118	8.8	7.5	6.0



Fig. I The Effect of Ethyl Alcohol on the Viscosity of Viscose

I - Alkali Cellulose aged 24 hours at 20°C.

II - Alkali Cellulose aged 54 hours at 20°C.

III - Alkali Cellulose aged 73 hours at 20°C.

Relative Viscosity

Weight Percent Alcohol

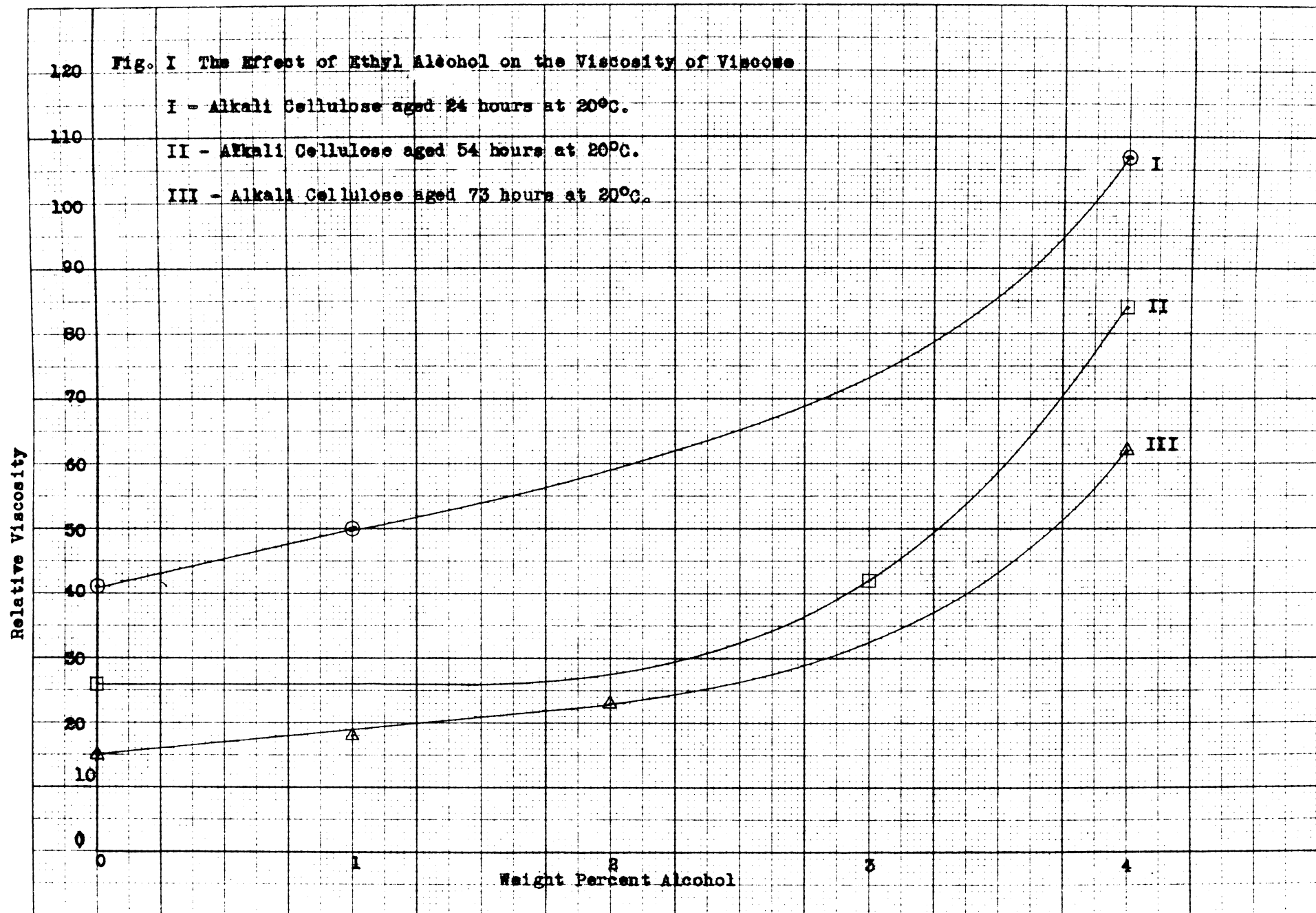


Fig. 2. The Effect of Ethyl Alcohol on the Ammonium Chloride Number of Viscose

Alkali Cellulose aged 25 hours at 20°C.

I. Viscose ripened 46 hours at 20°C.

II. Viscose ripened 75 hours at 20°C.

III. Viscose ripened 95 hours at 20°C.

IV. Viscose ripened 118 hours at 20°C.

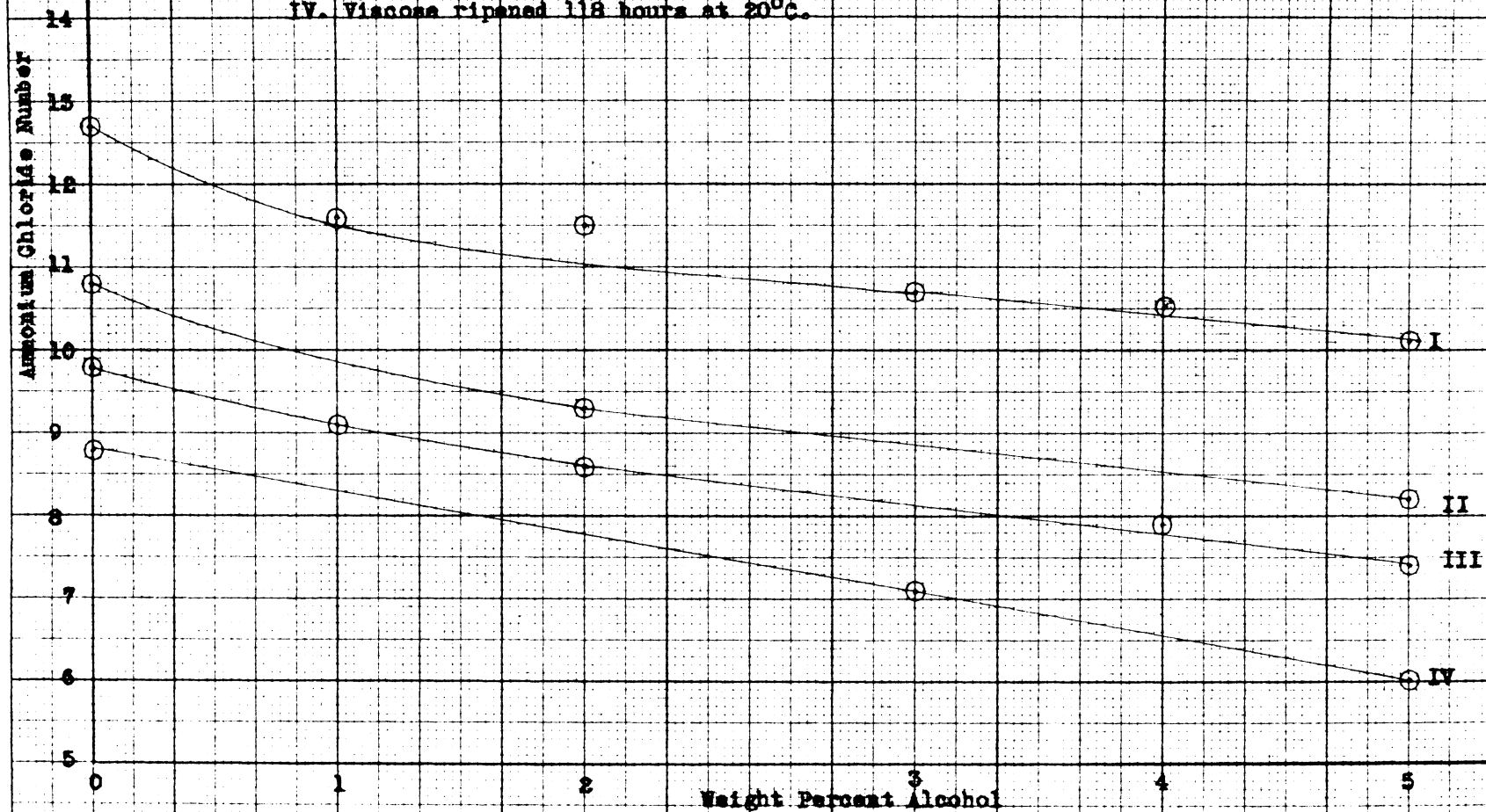


Fig. 3. The Effect of Ethyl Alcohol on the Ammonium Chloride Number of Viscose.

Alkali Cellulose Aged 54 Hours at 20°C.

I. Viscose Ripened 47 hours at 20°C.

II. Viscose Ripened 76 hours at 20°C.

III. Viscose Ripened 113 hours at 20°C.

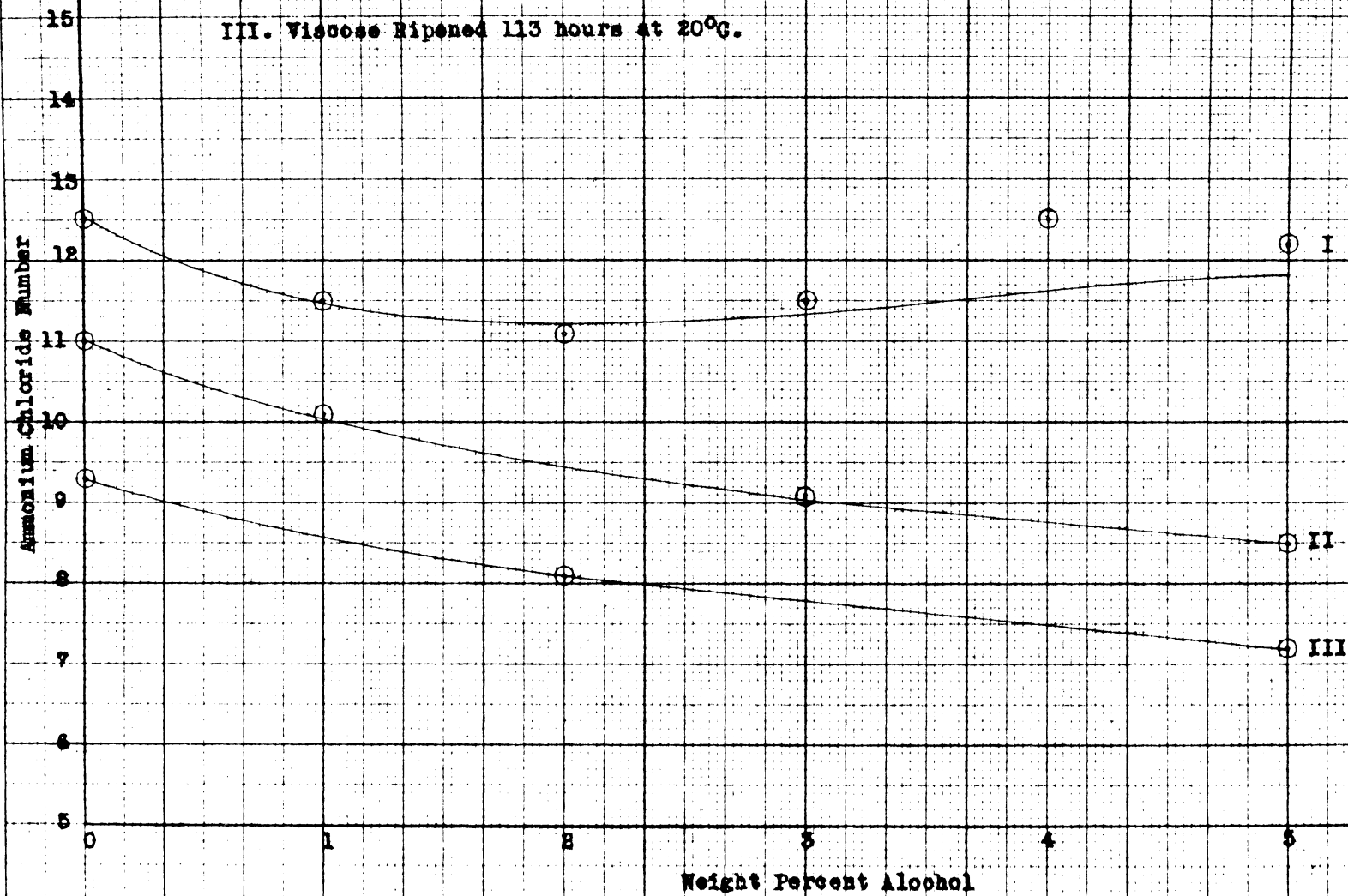


Fig. 4. The Effect of Ethyl Alcohol on the Ammonium Chloride Number of Viscose Alkali Cellulose Aged 73 hours at 20°C.

I. Viscose Ripened 57 hours at 20°C.

II. Viscose Ripened 94 hours at 20°C.

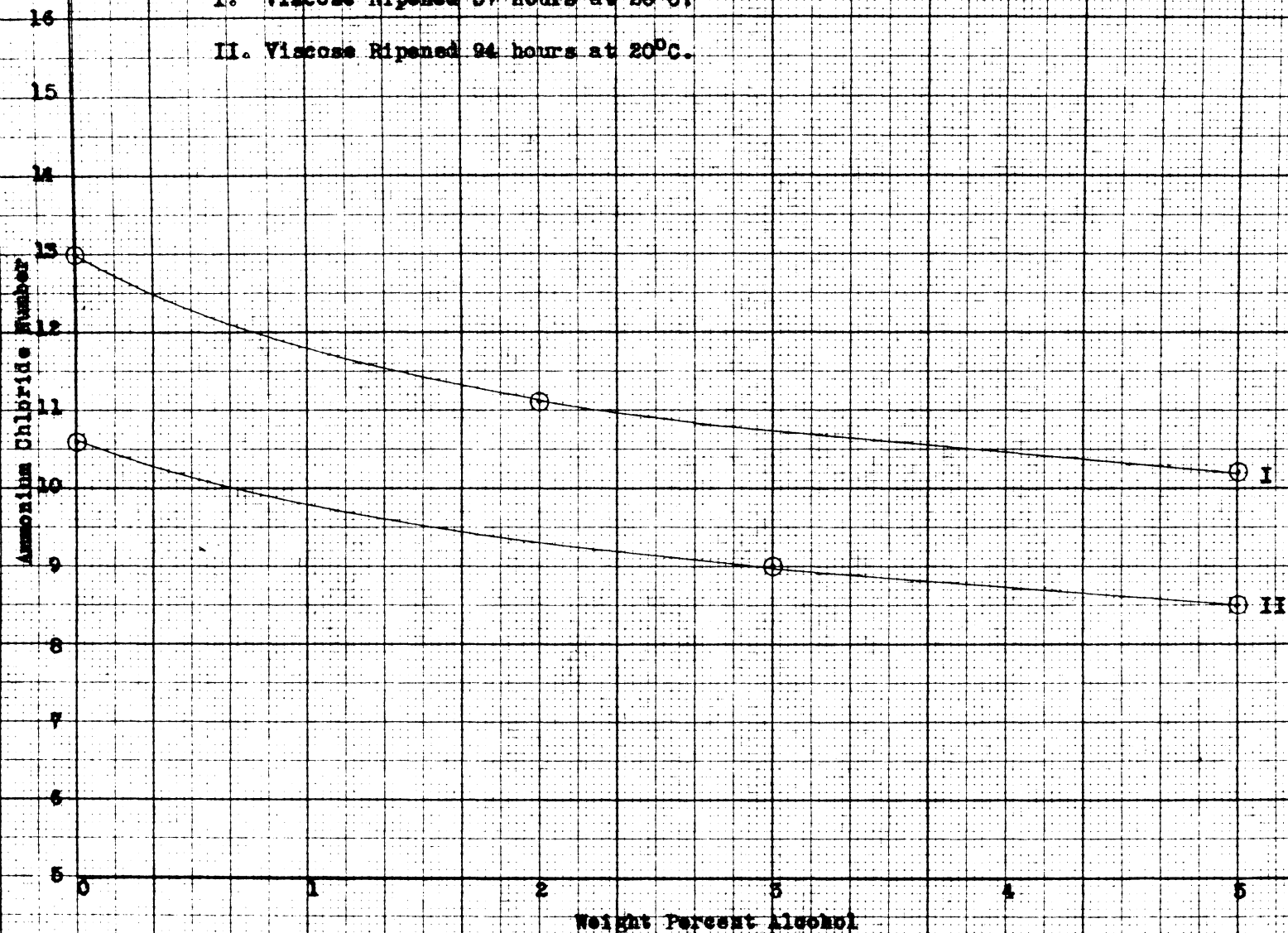


Fig. 5. The Effect of Ethyl Alcohol on the Rate of Ripening of Viscose

Alkali Cellulose Aged 24 hours at 20°C.

I. 0% Ethyl Alcohol

II. 2% Ethyl Alcohol

III 5% Ethyl Alcohol

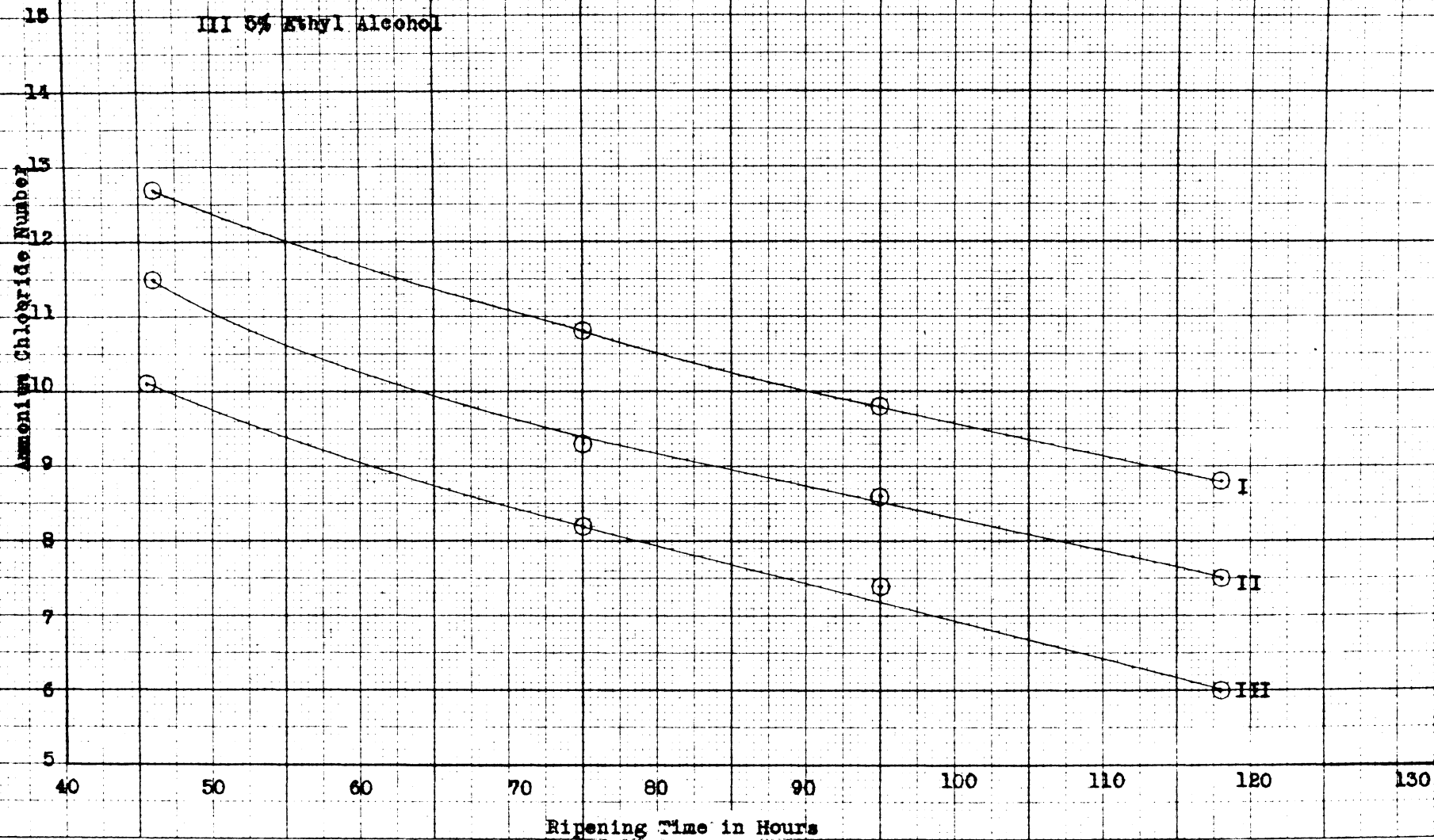
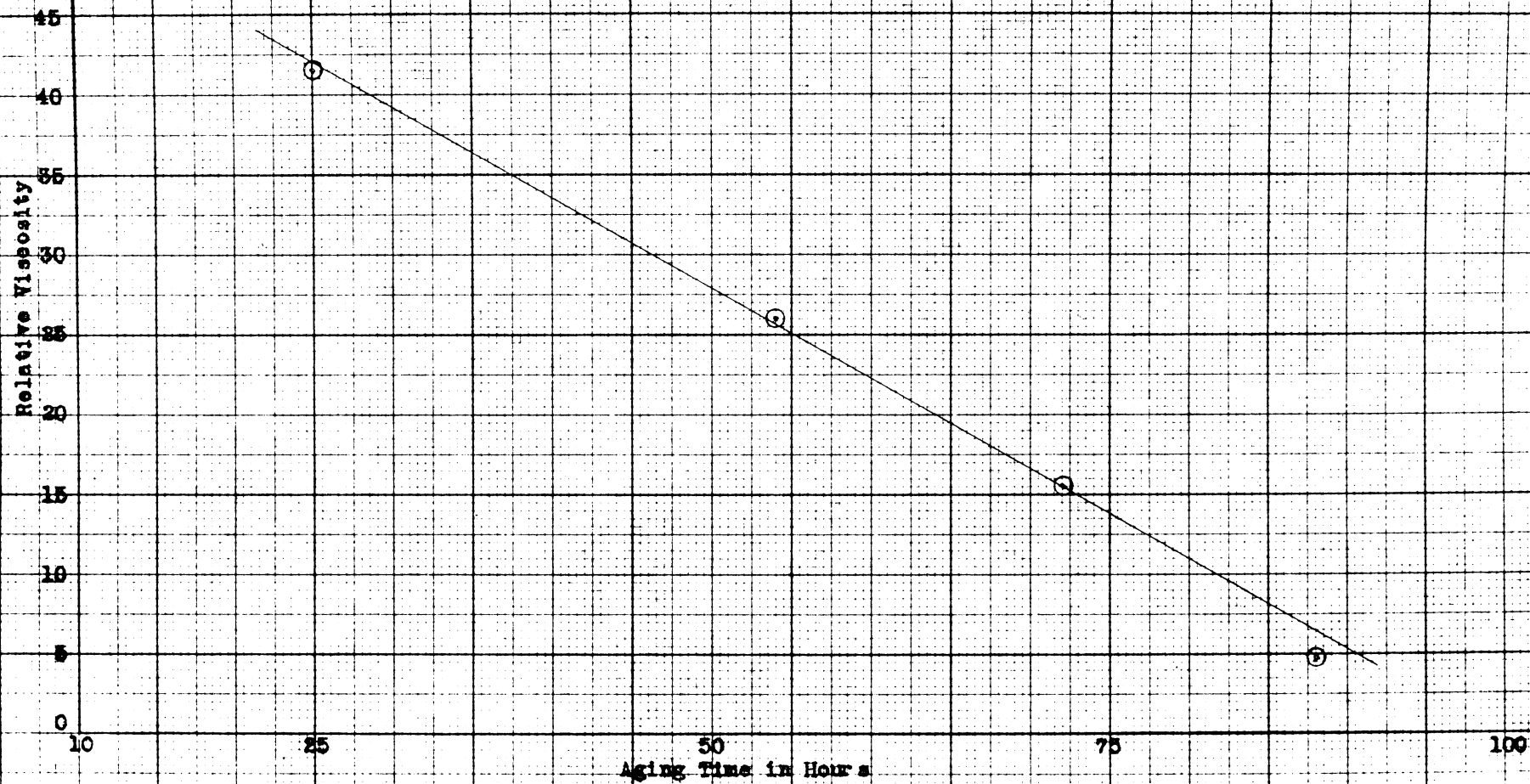


Fig. 6. Effect of Aging of the Alkali Cellulose on the Viscosity of Viscose

Alkali Cellulose Aged at 20°C.

Viscose Refined 20 Hours at 20°C.



#### IV. DISCUSSION OF RESULTS

##### A. Effect of Alcohol on Viscosity and Ammonium Chloride Number.

On the assumption that viscose is a lyophilic sol it would be expected that the addition of alcohol would decrease both the viscosity and ammonium chloride number. The above data, however, show that the presence of alcohol decreases the ammonium chloride number of viscose, as is expected, but the viscosity was increased. The reason for this increase in viscosity will now be considered.

1. Alcohol does not act as a dehydrating agent in concentrations as low as 5% and thus the change in viscosity is probably not due to this factor. However the viscosity of water itself is increased by the addition of alcohol and this may partially account for the increase in the viscosity of the viscose. In this investigation it would have been more appropriate to measure a quantity also called Relative Viscosity which is defined as:

$$\text{Relative Viscosity} = \frac{\text{Viscosity of Viscose}}{\text{Viscosity of water-alcohol solution}}$$

However, the increase in viscosity of water on addition of alcohol is not sufficient to account for the large increase in the viscosity of viscose caused by the presence of alcohol.

2. The increase in the viscosity of viscose may be due to the increased size of the micellae in dispersion. The alcohol must therefore permit, or increase, the tendency for small micellae to

aggregate into larger ones. This would increase the viscosity and decrease the ammonium chloride number. According to the physico-chemical theory of xanthate formation, only a small amount of cellulose xanthate is actually formed which acts as the dispersing agent for the remainder of the unchanged cellulose. The alcohol may have precipitated part of this dissolved cellulose xanthate, thus removing the dispersing agent which keeps the cellulose micellae in dispersion and allowing them to aggregate.

3. Richter\* had demonstrated that when acetone is added to an aqueous solution of sodium hydroxide, the acetone will withdraw water from the aqueous phase with consequent increased alkali concentration. A similar situation may have been present when alcohol was added to viscose. In this case the "effective concentration" of both the sodium hydroxide and cellulose would be increased thus causing an increased viscosity.

It is probable that all three of the above factors contributed to the increase in the viscosity of the viscose.

---

\* Richter and Glidden, Ind. Eng. Chem. 32, 1122.



B. Effect of the Alcohol on the Rate of Ripening of the Viscose.

Table X shows the change in ammonium chloride number with time for viscose containing 0, 2 and 5% ethyl alcohol. The results are plotted in Figure V. The rate of ripening will be given by the rate of change of ammonium chloride number with time. Since the slope of the curves are very nearly the same at all times, it appears as though the presence of alcohol in viscose has very little, if any, effect on the rate of ripening of the viscose.

It is interesting to compare this result with that of Scherer and Miller (8) who showed that the rate of xanthation at a constant temperature is independent of aging. It might therefore be expected that the reverse reaction, ripening, would also be constant at a constant temperature and (with respect to the presence of alcohol), this was shown to be true in this investigation.

C. Effect of Alcohol on Time Required for Viscose to Gel.

Although the data showing the time required for the viscose to gel is not given in this thesis, it was noted that in general the time for gelling increased with aging of the alkali-cellulose crumbs and decreased with amount of alcohol added. This was not due to the alcohol increasing the rate of ripening of the viscose, since Figure V shows that the rate of ripening is constant at a constant temperature. If the alcohol removed some of the dispersing agent as was previously assumed then less remains to be removed by the hydrolysis during ripening and thus the gelling time would be decreased.

D. Effect of Alcohol on the Color of Viscose

At a given ripening time, the presence of alcohol caused the viscose to have a lighter color than it had in the absence of alcohol. The orange color in normal viscose is due to the products of the reaction between  $\text{CS}_2 + \text{NaOH}$  during xanthation and also to the by products of the ripening process. Immediately after solution all the viscose samples were orange in color.

The brown color of the viscose after ripening may be explained as being due to the iron which had gotten in to the alkali cellulose crumbs in the process of steeping and grinding. This would presumably be in the form of  $\text{Fe}(\text{OH})_3$  and  $\text{FeS}$  in the viscose.

The alcohol may have inhibited the formation of dark-colored iron compounds thus explaining why the viscose containing alcohol did not turn brown on ripening.

E. Recommendations.

The pulp used in making all the viscose for this investigation was a high alpha-cellulose pulp obtained from the Brown Company in Berlin, N. H. Its viscosity was so high that even after aging the crumbs 72 hours at 20°C., the viscosity of the resulting viscose was too high for use with the modified standard A.S.T.M. viscosimeter, which was the instrument used in this work. However, since only the relative viscosities were required, the use of this viscosimeter was considered as being suitable, even though the long time of discharge made the measurements tedious.

It is recommended that if any further work involving viscosities of viscose is to be done using this high-viscosity pulp, that the alkali-cellulose crumbs be aged for a longer period of time, at least 100 hours, or else the viscosities should be measured by the falling sphere method.

The degree of ripening, or coagulability of viscose was measured by the ammonium chloride number (Hottenroth method). This method involved the addition of water to the viscose before coagulation by ammonium chloride.

On account of this dilution with water, the Hottenroth number may not give a true measure of the effect of alcohol on the degree of ripening. It is recommended that the ripeness of the viscose be measured by the salt number or by other methods.

## V. CONCLUSIONS

The presence of alcohol in viscose increases the viscosity of the viscose.

The greater the concentration of alcohol in viscose, the greater the viscosity.

The presence of alcohol in viscose decreases the ammonium chloride number at a given ripening time.

The decrease in ammonium chloride number depended on the concentration of alcohol. The greater the concentration of alcohol the greater is this decrease in ammonium chloride number.

The presence of alcohol appeared to have very little, if any, effect on the rate of ripening of the viscose.

Viscose containing 10% by weight of alcohol gels almost immediately after solution of the cellulose xanthate. The gel is transparent.

A viscose containing 20% by weight of alcohol could not be prepared. In this case the cellulose xanthate was precipitated.

The greater the concentration of alcohol in viscose, the shorter is the ripening before the gelation of the viscose.

## VI. APPENDIX

### A.. Alkali Cellulose Tests

#### (1) Bulk Number

The bulk number is the weight of one liter of alkali cellulose crumbs. It was measured by calibrating a one liter beaker with water and weighing the crumbs required to just fill the beaker to the brim without packing.

#### (2) Sodium hydroxide Percent

By means of a weighing bottle 5 grams of the moist crumbs were weighed into a beaker and covered with 150 ml. of water. After standing and stirring for 5 minutes the mixture was titrated with standard hydrochloric acid ( approximately 1 N.) using phenolphthalein as the indicator. The percent sodium hydroxide was then calculated.

#### (3) Stock Percent

To the neutralized sample from the above analysis was added about ten ml. of glacial acetic acid and the residue was filtered on a Buchner funnel provided with a weighed nainsook filter. The pad on the cloth was washed with about a liter of hot water, covered twice with acetone and then dried in a weighing bottle at 105°C. to constant weight. The residue was calculated as percent stock.

B. Tests on Viscose.

(1) Viscosity

The viscosity measurements were made in a room held at a constant temperature of 20°C. The viscosity was measured by the rate of flow through a standard pipette. The pipette was a glass tube about 15" long having an inside diameter of 3/4". At one end was sealed a smaller tube 1" long and 3/16" inside diameter. The pipette was calibrated with glycerine of specific gravity 1.26. The viscose was drawn into the pipette by suction and allowed to flow out by the force of gravity. The relative viscosity was calculated in the following manner:

$$\text{Relative Viscosity} = \frac{\text{Time of discharge of viscose}}{\text{Time of discharge of the glycerine}}$$

The pipette was graduated so that the glycerine flowed through in 100 seconds.

(2) Ammonium Chloride Number

The ammonium chloride number (6) is the number of ml. of 10% ammonium chloride required to coagulate 20 grams of viscose diluted with 30 ml. water under given conditions.

Twenty grams of viscose were diluted with 30 ml. of water and mixed well at room temperature. The ammonium chloride was added slowly from a burette until after stirring for one minute the viscose was just coagulated.

The ammonium chloride ripeness (6) depends on the degree of degradation of the cellulose the number of xanthate groups still retained, the electrolytes in the solution and the temperature.



VII. LITERATURE CITED

- (1)\* Atsuki, J. <sup>c</sup>Faulty of Engineering, Tokyo Imperial University,  
17, 135-44.
- (2)\* Berl and Bitter; Cellulose-chemie, 7, pp. 137-45 (1926).
- (3) Blanco, Ind. Eng. Chem. 18, 1257 (1926).
- (4) Doree, The Methods of Cellulose Chemistry, p. 225.
- (5) Doree, The Methods of Cellulose Chemistry, pp. 237.
- (6) Marsh and Wood, Introduction to Cellulose Chemistry, pp. 335.
- (7) Scherer, Laboratory Directions, Viscose Rayon Production,  
Virginia Polytechnic Institute.
- (8) Scherer and Miller, Rayon Textile Monthly. Aug. 1938. pp. 54.
- (9)\* Suehiro, J. Soc. Chem. Ind., (Japan) 39, 377-378.
- (10) Sweet, M.S. Thesis, Virginia Polytechnic Institute, (1932).

\* Original not available

VIII ACKNOWLEDGEMENT

The author wishes to acknowledge his most sincere appreciation to Dr. P. C. Scherer, Jr. for his suggestion of the problem and for the continual help and advice given throughout this investigation.