

"A STUDY OF THE SULFUR - CELLULOSE
RATIO OF VISCOSE AT MATURITY"

by

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I wish to express my sincere appreciation to
Dr. Philip C. Scherer for his sound advice and friendly
counsel during this investigation.

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INTRODUCTION

The purpose of this investigation was to find the Sulfur-Cellulose ratio at spin time or the so called maturity, which is assumed to be reached by viscose when an ammonium chloride number of ten is reached. In industry this particular value of ammonium chloride number is arbitrarily taken to indicate that a viscose is ready to be spun. Because of this industrial application, interest in this investigation was centered on the study of the Sulfur-Cellulose ratio at spin time.

STATEMENT OF THE PROBLEM

In this work an attempt was made to investigate the effect of different initial degrees of substitution on the maturity Sulfur-Cellulose ratio. In other words, xanthates with various initial sulfur-cellulose ratios were to be prepared and the rates of decomposition were to be studied until an ammonium chloride number of ten was reached. From the results it was hoped to deduce whether the maturity sulfur-cellulose ratios are dependent on the initial sulfur-cellulose ratios or if the same sulfur-cellulose ratios are attained when an ammonium chloride number of ten is reached, regardless of initial ratios.

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From the work of Scherer and Miller it was known

that the rate of xanthation is ^afunction of time, temperature and the amount of carbon disulfide used. In this investigation, the factor of time and temperature of xanthation were controlled to one and one-half hours and 40° C respectively. By varying the amounts of carbon disulfide to 9%, 25%, and 37% by weight, based on alpha cellulose, the required different initial sulfur-cellulose ratios were obtained.

LITERATURE REVIEW

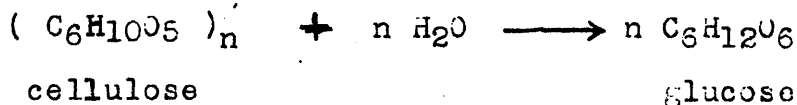
(A) Structure of Cellulose

Cellulose is the most abundant of all naturally occurring organic compounds and probably makes up at least a third of all the vegetable matter in the world. It is the main constituent of the cell walls of the higher plants, having received its name for this reason.³⁴

There is no generally accepted theory on the formation of cellulose. According to one hypothesis⁹ cellulose is formed in large plastids occurring in the cytoplasm of the living cell. There is practically no information as to the essential chemical mechanism of the photosynthesis of cellulose, but it is presumably enzymatic.

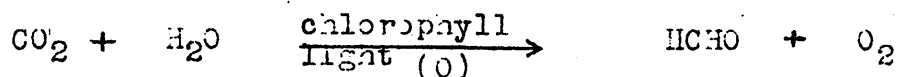
It has been known for long time that cellulose is composed of glucose residues. The purest available form

of cellulose (cotton) yielded glucose on hydrolysis.⁴⁰

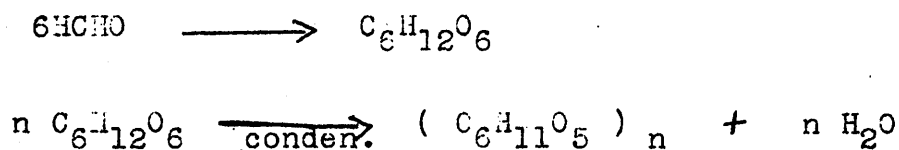


Thus cellulose is anhydro-glucose.

Recent studies have indicated that carbon dioxide reacts with a molecule of water in the presence of light and chlorophyll as follows:



Formaldehyde formed polymerizes to give glucose:



The generally accepted chemical constitution of the cellulose chain molecules (fig. 1) is the result of more than one hundred years of research on the behaviour of cellulose with most varied treatments.¹¹ The reactions of cellulose resemble those which are observed to occur with simple sugars. Since, however, all but one of the potential reducing groups of the glucose residues (the one terminating unit of the open chain) are involved in glycosidic linkages between individual members of the chain, cellulose lacks the pronounced reducing power of the most of the sugars, and its chief reactions are those of its hydroxyl groups. The formula shows that all glucose

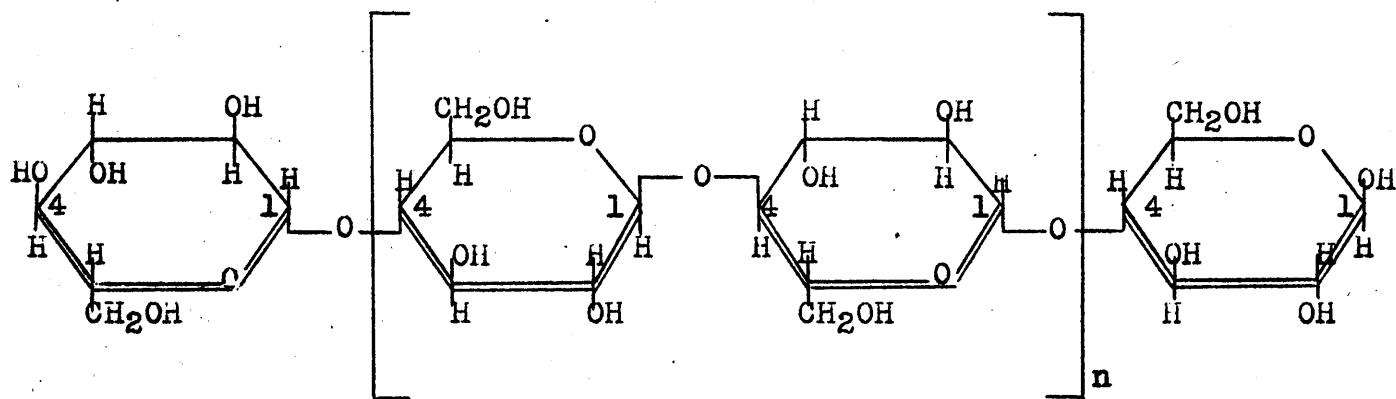


Figure A(1).

Molecular Chain Formula of Cellulose

residue except one (terminating unit) possess three free hydroxyl groups, the one in 6- position being primary and those in 2 and 3 positions being of secondary nature. The free hydroxyl groups in cellulose react as in alcohols to form addition compounds with alkalis and certain complex salts.

Experimental evidence has shown that the individual cellulose molecule is composed of glucose residues united by 1,4 glucosidic linkages of the beta type. Sponsler and Dore⁵² stated that cellulose consists of long parallel chains of glucose residues linked by primary valences and held together by the secondary valences. Haworth¹⁰ has shown that the primary valences are between the number 1 carbon of one glucose unit and the oxygen of number 4 carbon atom of the adjoining glucose residue. This requires inversion of every other one of the glucose units as shown in figure 1.

(B) Chemistry of Viscose

(a) Dipping of the pulp

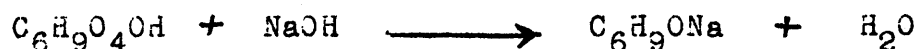
Reaction of cellulose with aqueous NaOH is technically known as mercerization after John Mercer who discovered the process in 1844.³⁸

There are two important objectives in treating cellulose

with alkalies, namely, to modify the physical and chemical properties of natural fibers such as in mercerization and to obtain intermediates as alkali cellulose for conversion to cellulose derivatives.

The first step in the production of viscose from cellulose requires treatment of cellulose pulp with 19% NaOH solution at normal temperature. This step is often spoken of as dipping, or mercerization.

The action of NaOH on cellulose is^a combination of both physical and chemical reactions. The physical view is that simple swelling phenomenon takes place upon treatment with aq. NaOH. The alkali solution, entering between the micelles, pushes the units apart and loosens interconnecting secondary bonds, giving rise to swelling. According to the chemical view, cellulose reacts with aq. NaOH in a definite proportion forming soda cellulose:



The physical swelling phenomena which all celluloses undergo when treated with aq. NaOH are probably much more important than the purely chemical aspects of the changes involved. Whatever the reactions are, they are accompanied by swelling of the fiber.

Water is the fundamental swelling agent but water can penetrate only intermicellar spaces giving rise to only

superficial swelling and for complete dissolution, water must penetrate intramicellar spaces. In order to obtain such a complete dissolution, or maximum swelling with water, some device must be used by which water can penetrate to individual chain bundles. One way is to increase temperature. At high temperature surface tension of water decreases and a better degree of penetration may be obtained. Another way is to use somekind of agent that may provide ^{which} ions [^] are capable of penetrating intramicellar spaces by loosening the crystalline structure of cellulose. Sodium ion is often used for this purpose.

Sodium hydroxide as a swelling agent

With low concentration of NaOH, swelling effect is similar to that of water. With concentration of about 14% to 19% maximum swelling can be obtained and with higher concentrations, swelling is again decreased very rapidly almost to zero. The swelling with different concentrations of aq. NaOH is best explained by the Donann membrane ¹² equilibrium theory.

Swelling differences observed in caustic solutions of varying concentration can perhaps be explained as either having inter or intra micellar character as first pointed out by Katz. ²⁴ X-ray evidence indicates no change in spacing between individual cellulose chains when cellulose

is treated with solution of NaOH below 12% concentration. In solution above 12% concentration, NaOH enters intramicellar spaces and a definite change occurs in the crystal lattices as determined by X-rays. However, the phenomenon is explained by Donnan membrane equilibrium and is supported by X-ray evidence.

Another explanation is that the swelling is caused by hydration, i.e., by the cohesive forces between the alkali cellulose compound and the water molecules. Detail discussion can be found in any standard text book.³⁵

The factors that may effect degree of swelling are (1) concentration of NaOH (2) temperature (3) nature of cellulose (4) time of contact (5) hysteresis and equilibrium (6) changes in solvent and (7) addition of salts.³⁶

Solubility of cellulose obtained from wood pulp in aq. NaOH depends partly upon kind of pulp and process of conversion etc. However in general it is found that maximum solubility is near 10% concentration. For higher and lower concentrations of NaOH the solubility decreases.¹³

The following characteristic changes upon treatment of cellulose with about 18% NaOH are observed:¹⁴

(1) The tensile strength had become greater than that of original material, (2) The treated material showed greater affinity for dyestuff and salts, (3) The sensitivity of the materials to chemical treatment had increased,¹⁵ (4) The hygroscopicity was higher.

That the reactivity of mercerized cellulose has greatly increased by the treatment with 13% NaOH may be demonstrated in various ways: for example the hydrolysis by acids is faster and by the determination of the copper number which is the degree of oxidation measure, etc.¹⁶

Heat of swelling

When cellulose is treated with NaOH solution of sufficient concentration to produce swelling, heat is developed. According to Neale³⁰ the heat of reaction evolved is composed of (1) positive heat of neutralization of the OH⁻ ions of NaOH by H⁺ ions of the cellulose (2) the negative heat of dissociation of the salt (cellulosate) formed and (3) the positive heat of dilution of the NaOH solution. The dilution is due to removal of alkali from the solution by the cellulose and of the liberation of water of reaction as sodacellulose is formed.¹⁷

(b) Aging of alkali cellulose

After the required time of contact of cellulose pulp with alkali solution is over, the excess alkali is removed by pressing, or by centrifuging. The soda cellulose is next ground in a water cooled kneading machine to a specified Bulk Number^{*} or till constant Bulk Number is attained.

* Bulk Number is the measure of mechanical subdivision of soda cellulose crumbs. Bulk Number is the weight in grams of 1000 c.c. of loosely packed soda cellulose crumbs.

The resulting crumbs are allowed to stand or age in a closed vessel under controlled temperature for a definite time. During this aging soda cellulose undergoes certain changes; the most important of which are: increase of its alkali solubility and decrease of its solution viscosity. Both these effects are due to oxidation produced by the air oxygen which is present in the system and alkaline hydrolysis resulting in cleavage of glycosidic linkages. There is also slight increase in the reducing power of the soda cellulose and formation of carboxylic acid groups.

In commercial practice, the aging of alkali cellulose is an important step in the manufacture of viscose (cellulose xanthate). Its purpose is to decrease the viscosity of the cellulose and consequently of the viscose prepared therefrom to such an extent that a solution is obtained which may be filtered and thereafter forced through the spinning nozzle without difficulty. Experimental results show that the greatest degradation (drop in viscosity) during aging process occurs in the early stages. ¹⁸ This drop in viscosity indicates that the average chain length of the cellulose decreases as aging proceeds. For example

<u>D.P.</u>	<u>Time of Aging</u>
1000	0 hours
900	4 hours
300	113 hours

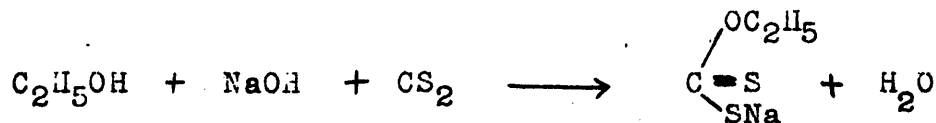
The process of aging is influenced by a number of factors; (1) origin and previous history of cellulose (2) concentration of oxygen (3) conditions under which the alkali cellulose is prepared: (a) time of contact between cellulose and NaOH solution (b) concentration of NaOH used (c) ratio of alkali to cellulose (degree of pressing) and (d) time and temperature of aging.

Experiments have shown that the aging process is essentially a process during which the cellulose is degraded by oxidation.¹⁹ More recently, Staudinger and Jurisch⁵³ have shown that in a high vacuum no aging of alkalicellulose occurs even after eight days at 20° C.

The mechanism of the chemical process by which the cellulose chains are ruptured during aging is still not fully known. Plausible hypotheses can be found in any standard text book.³⁷

(c) Xanthation of alkalicellulose

On the basis of analogy between cellulose and ordinary alcohols, the reaction between sodacellulose and carbon disulfide was first represented in a manner similar to the reaction between carbon disulfide and alcohols in the presence of alkali:



Cellulose xanthates are prepared by allowing carbon disulfide to act upon alkali cellulose, either as such or after it has been aged for a certain period. According to Cross and Eevan, cellulose in the form of sheets is steeped in aqueous NaOH of mercerizing strength and freed of excess alkali by pressing or centrifuging until it has acquired about three times its original dry weight. The alkali cellulose thus obtained is defibered and subjected to the action of carbon disulfide in a closed vessel which is being frequently shaken by hand or slowly rotated on a mechanical device. Under the influence of the carbon disulfide, the mass swells considerably and changes color from white to yellow and finally to deep orange. Completion of reaction can be judged from the color by experts or by noting the change in the pressure in the xanthating drum.⁴⁵ During xanthation, temperature tends to rise but only a few degrees and may be kept constant by cooling.

If the time of xanthation is extended, the crumbly mass tends to become peptized and if stirred may lose fibrous structure and become a more or less homogenous paste.

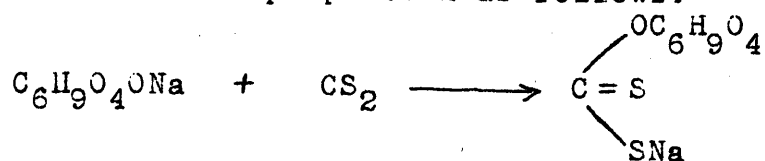
The solution of the xanthate crumbs in water or dilute alkali is an orange colored highly viscous liquid which Cross and Eevan have termed "Viscose."

The function of excess alkali is probably physical because as with other reactions, the degree of diffusion

of the agents into the fibrous structure and the degree of swelling accomplished under the action of the alkali are essential prerequisites in approaching completion of reaction. Excess of NaOH is therefore required in the preparation of alkali-cellulose in order to avoid poor xanthation yield.

There are three general theories of xanthate formation:

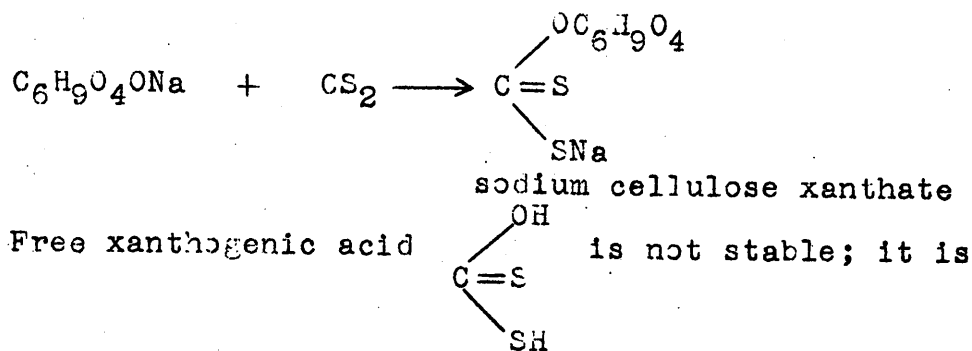
(1) The chemical theory: assumes that the reaction occurs in definite molecular proportion as follows:



(2) The physical theory: refers to the dispersion of highly swollen cellulose to an extent that the secondary valences are entirely overcome and the micelle separates into colloidal particles which apparently go into solution in water or dilute alkali.

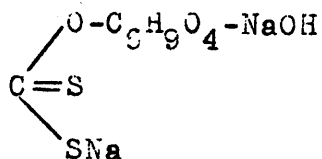
(3) Combination of the physical and the chemical theory: assumes that only a portion of the alkali cellulose reacts to give xanthate, the remaining being unaffected. The xanthate formed acts as a dispersing medium for the unconverted soda cellulose, taking the whole mass into solution.

Of the many esters obtained from cellulose, the dithiocarbonic acid ester is of special theoretical and practical importance. This compound is obtained when soda-cellulose is treated with carbon disulfide. The formation of this ester of cellulose is broadly represented as follows:

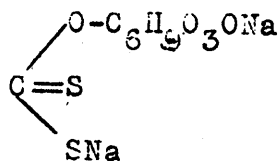


obtained only in the form of sodium salt. The same is true for cellulose compound.

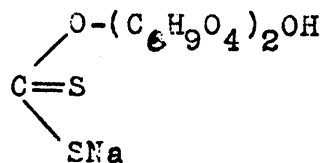
Cross and Eevan are of the opinion that cellulose xanthate contains a second atom of sodium in the form of sodium hydroxide bound to the cellulose radical as shown: ²⁰



According to Ost, Westhoff and Gessner ³¹ the second Na atom is present in cellulosate form:



Experimental results show that in purified xanthate the ratio of sulfur to sodium to cellulose derived from analysis is in agreement with the formula.



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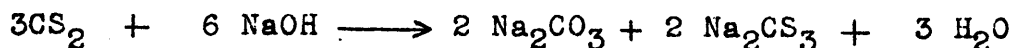
Lieser has confirmed this by producing purified xanthate in another way.

Degree of substitution in cellulose xanthate obtained by the step wise procedure already described in the previous part can be summarized as follows:

Investigator	⁶ De Wyss	Faust	Geiger	Scherer & Miller
Ratio of xanthate group : C ₆ H ₁₀ O ₅ unit	0.85:1.0	1.8:1.0	1.0:1.0	0.93 : 1.0

These results were obtained by using very large excess of carbon disulfide (100 - 200 % by weight based on Stock %)

Theoretical calculations indicate that only 23.4% CS₂ is required to attain 1:1 xanthate group to C₆H₁₀O₅ unit. However, the course of the reaction of cellulose with carbon disulfide is complicated by the fact that CS₂ also reacts with NaOH to form sodium carbonate and sodium thio-carbonate according to equation:



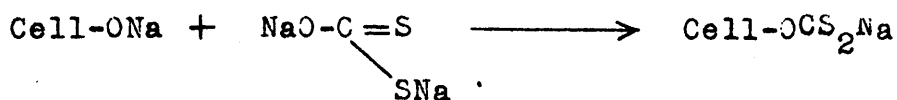
Thus, the formation of secondary compounds necessitates use of nearly 37% CS₂ when complete xanthation reaction is carried out at room temperature.

The degree of substitution which cellulose reaches within a certain set of conditions will depend upon the rate of substitution and by product formation and thus will be the result of competition between the two reactions.

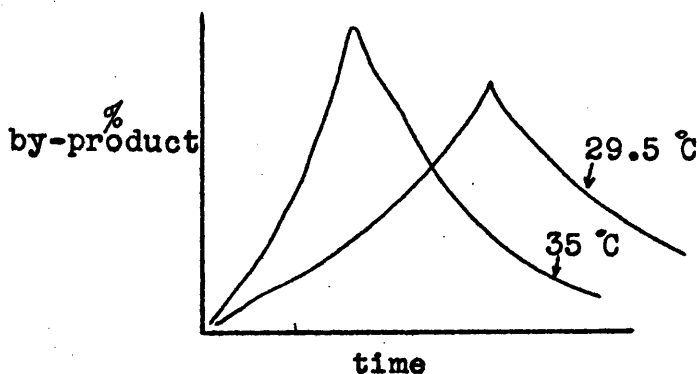
Judged by the results obtained by Kita and Tomihisa it was found that the rate of the side reaction was high at the beginning but slowsdown as the time of contact between mixture of NaOH solution and CS₂ becomes longer. It appears that on xanthation of alkalicellulose between 1/4 and 1/3 of the CS₂ employed is consumed for the formation of by-products.

The rate at which both reactions proceed was determined by Scherer and Lin.⁴³ They found that at the end of three hours, as much as 96.2% of the carbon disulfide used was present in the form of xanthate and 2% in the form of by-product.

Attempts made at investigation of the distribution of CS₂ show that at low temperature by-product formation is very high at first and this decreases as the time of contact increases. The reaction may be represented as:⁴¹



Graphically it may be shown as:



In the year 1933 Scherer and Miller⁴⁶ undertook an investigation of the xanthation process used, in the preparation of viscose solution. The direction of their attack was to measure rate of xanthation of sodacellulose i.e., to measure the rate at which carbon disulfide reacts with sodacellulose crumbs prepared in normal fashion by treatment of cellulose with 18% NaOH for one hour. Study was made of the effect of temperature on the rate of xanthation. Three runs were made with very large excess of CS₂ (152.4%) by weight, using temperatures 25° C, 29.5° C and 35° C. Thus from their investigation it was possible to get any desired sulfur:cellulose ratio by xanthating for the corresponding length of time, depending upon the temperature used. From their results:⁴⁷

<u>Temperature</u>	<u>Time</u>	<u>Sulfur:Cellulose</u>
25 °C	113 min.	0.25
29.5°C	90 min.	0.25
35 °C	52 min.	0.25

25 °C	200 min.	0.322
29.5°C	200 min.	0.324
35 °C	200 min.	0.338

This showed that the rate of reaction is higher in the beginning and finally reaches almost constant values. By this method Scherer and Miller obtained maximum values of xanthate group to C₆H₁₀O₅ unit as 0.93 : 1.00.

Scherer and Miller also carried out investigation at different temperatures of the time required to use up all of the carbon disulfide.⁴⁸ It was found that with increasing temperature, time required to use up all the carbon disulfide decreases.

<u>% CS₂</u>	<u>Temp.</u>	<u>Time</u>
20	25 °C	120.0 min.
20	29.5 °C	69.0 min.
22	35 °C	54.5 min.
37	25 °C	191.0 min.
37	29.5 °C	117.0 min.
37	35 °C	78.5 min.

This clearly showed that time and temperature used in this investigation were sufficient for complete reaction.

Scherer and Miller have also shown that there is no effect of aging⁴⁹ and bulk number⁵⁰ upon xanthation time. However, viscosity of viscose is markedly affected due to alkaline hydrolysis and oxidation taking place. In industry soda cellulose crumbs are aged for a period of about 48 hours so as to get satisfactory viscosity of viscose. In this study crumbs were aged for 60 hours. This gave viscose that could be easily handled.

Formation of soluble xanthate Work done by Scherer and Miller⁵¹ showed that whenever the ratio of combined sulfur to cellulose exceeded 0.16, formation of soluble xanthate occurred.

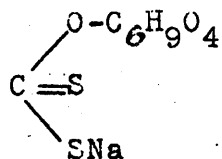
(d) The ripening of viscose

The hydrolytic changes which viscose undergoes on standing are described by the term "ripening". Viscose syrup is allowed to stand at constant temperature for a period of time so that chemical and colloidal changes can occur.

The chemical changes during ripening:- Chemically, ripening may be regarded as the reverse of xanthation. Whereas xanthation represents the substitution of hydroxyl groups, the ripening process embodies the regeneration of hydroxyl groups and hence eventually of cellulose.

Cross and Ewan⁵ first advanced the theory that a chemical change takes place during the ripening of viscose. They assumed²¹ that the xanthate passes through three intermediate stages before cellulose appears. (Xanthate is dissolved in water after standing for certain time.)

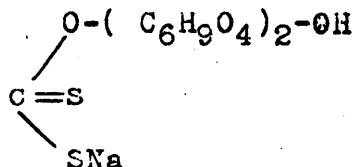
(1) The first product of the reaction is



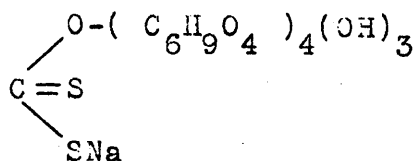
This compound follows from the ratio of
Na:S:Cellulose = 1:2:1.

(2) After standing twenty four hours a product is present in which the ratio of Na:S:Cellulose is 1:2:2 i.e., there are present for each two simple cellulose molecules one atom of sodium and two atoms of sulfur. Therefore the

formula:



(3) After six or seven days in air, the ratio changes to 1:2:4.



(4) After long standing ratio becomes 0:0:Cellulose. This cellulose is of the empirical composition $\text{C}_6\text{H}_{10}\text{O}_5$.

The method of analysis in which Cross and Bevan separated by-product sulfur from xanthate sulfur by the use of a salt solution, showed a constant decrease of xanthate sulfur, which led them to conclude that the cellulose xanthate more correctly termed the cellulose ester of dithio-carbonic acid, loses dithio-carbonic acid groups during the ripening and that cellulose is finally regenerated.

By different methods of analysis Ost, Westhoff and Gessner³² and Wolffenstein and Oser⁵⁵ came to the same conclusion.

On the other hand Leuchs²⁷ published experiments which led him to a different view of the subject. He decomposed viscose with sulfuric acid and determined the amount of carbon disulfide and hydrogen sulfide liberated. Assuming that all the carbon disulfide set free has its origin in the decomposition of cellulose xanthate and that all the byproduct sulfur is liberated as H_2S and sulfur and from the fact that he obtained practically constant values for

the carbon disulfide : $C_6H_{10}O_5$, he concluded that no chemical change takesplace during the ripening of viscose.

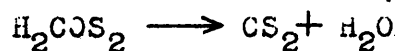
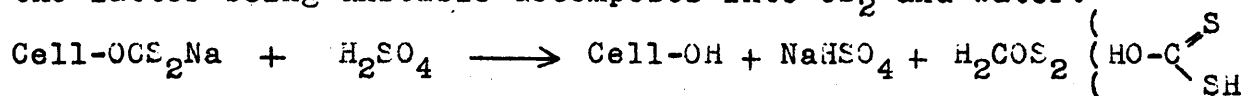
(C) Theoretical discussion:

As the ripening of viscose is important in its technical use, it was sought to clear away the differences of opinion that existed as to chemical changes involved. Reflection led to the conviction that Leuchs was wrong in his conclusion that only cellulose xanthate can produce carbon disulfide when viscose is decomposed by a mineral acid.

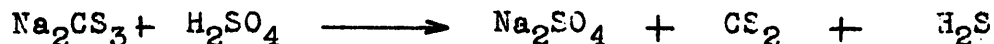
Viscose is a solution of cellulose xanthate, in which we find besides cellulose compounds, NaOH and the products of the reaction between CS_2 and excess NaOH; chiefly: Na_2CS_3 , Na_2CO_3 , and Na_2S .

If viscose be decomposed by a mineral acid, the following main reactions takesplace:

Cellulose xanthate is hydrolysed with the formation of regenerated cellulose and dithiocarbonic acid of which the latter being unstable decomposes into CS_2 and water.



Sodium thiocarbonate reacts with the acid to form the sodium salt, carbon disulfide and H_2S .



On treatment with mineral acid, thiocarbonate therefore

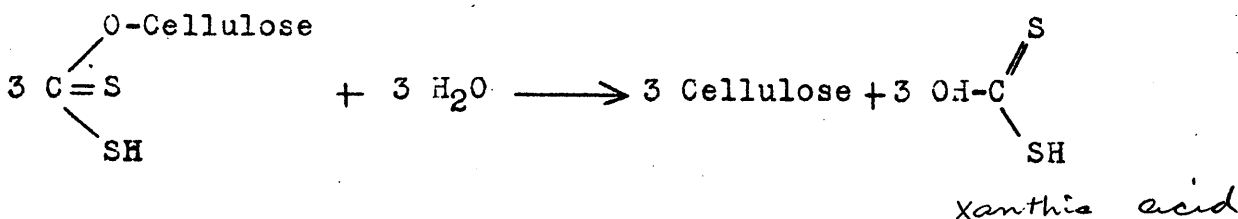
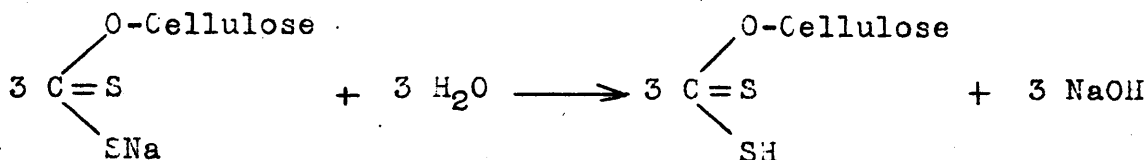
produces carbon disulfide just as well as does the cellulose xanthate, and the proportion xanthate sulfur to cellulose can by no means be ascertained by simply decomposing viscose with a mineral acid and determining the amount of CS_2 liberated.

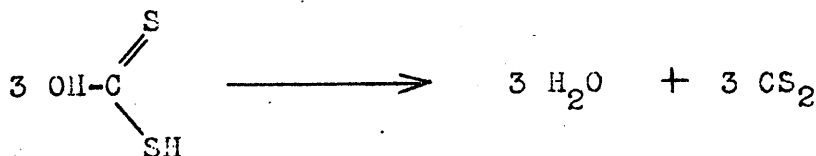
De Wyss⁷ in his method made use of Cross and Ewan's⁴ discovery that cellulose xanthate remains unattacked if treated with a weak acid such as acetic acid or lactic acid, whereas thiocarbonate are unstable in the presence of these acids. De Wyss used this property of viscose to modify Leuschs' procedure so as to distinguish between xanthate carbon disulfide and thiocarbonate carbon disulfide. If a dilute solution of viscose be acidified with acetic acid, its color gradually changes from a deep yellow to a very light yellow. This change in color was assumed to be an indication of the disappearance of the thiocarbonates. At this point all the CS_2 and practically all the H_2S set free by the action of acetic acid can be removed by extracting the viscose with ether. When treated with mineral acid the purified viscose solution still produced CS_2 , which could have had no other origin than cellulose xanthate. By its determination, the true amount of xanthate sulfur could be obtained. De Wyss applied this method to samples taken at intervals from viscoses which were ripened at $18^\circ C$ over a total period of 200 hours. His results showed

a decided decrease of the sulfur cellulose ratio during the time of ripening with about 50% of the total decrease occurring during the first third of the time of observation.

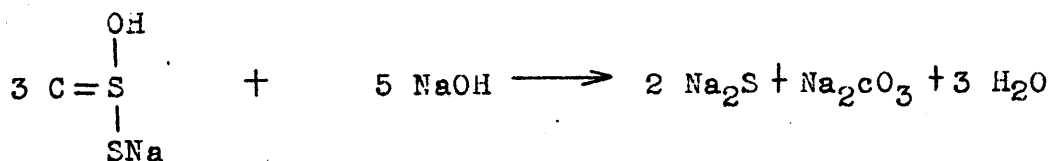
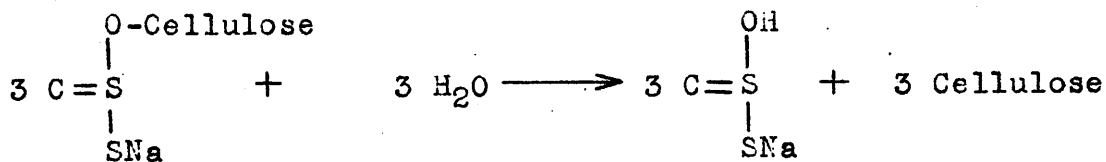
Fink and co-workers^{9(a)} developed an interesting method for estimating the xanthate sulfur and its decrease during ripening process. When ultra filtration is applied to viscose, suitably diluted, only the inorganically combined "electrolytic" sulfur enters the ultrafiltrate, whereas the sulfur combined with the xanthate ('Colloidal' sulfur) remains upon the filter so that if the total sulfur content of the viscose be known, the xanthate sulfur be calculated. The method was applied to viscose which was continuously stirred during ripening period in order to reduce in-homogeneity and consequently erratic results. The results obtained for xanthate sulfur agree very well with those derived from the diethyl chloracetamide method.²⁶

According to Klauditz²² there are two reactions which comprise the viscose ripening process: (1) Hydrolysis





(2) Saponification:



According to reaction (1), the hydrolysis reaction, presence of NaOH stabilizes the xanthate and results in minimum decomposition of cellulose xanthate. According to reaction (2), the saponification reaction, presence of NaOH increases the rate of decomposition of cellulose xanthate. At lower concentration of NaOH (6% - 8%), hydrolysis reaction predominates over saponification reaction. Working with normal viscose solution which contains 3.5% NaOH, it was found that only 15% to 20% of the total decomposition of the cellulose xanthate was a result of saponification.

The colloidal changes during ripening. Viscose represents a typically colloidal solution and the colloidal changes which viscose undergoes on ripening consists chiefly of changes in viscosity and in its behavior with electrolytes. These have been known for a long time and have been confirmed more recently.³ They may be summarized as follows:

Immediately after solution of the crude xanthate in dil. NaOH solution, the viscosity drops over a certain length of time. It reaches a minimum, then slowly increases over a long period, and eventually increases rapidly. When this last state has been reached, the viscose coagulates and finally a gel results which shows the phenomena of syneresis. A typical ripening curve of viscose may be found in any standard test book.

Important factors that can effect the rate of decomposition are temperature, cellulose and alkali concentration. As would be expected, temperature increase is a very efficient means of increasing the rate at which colloidal phenomena occur.² At high temperature the rate of hydrolysis increases and there occurs rapid gelation. At 0 °C the colloidal chains are slowed down and both coagulation and decomposition are retarded so that viscose may be kept at 0 °C for many days without any changes taking place.⁴²

Cellulose Concentration. It has been found that with increasing cellulose concentration, the viscosity of the viscose not only increases but also tends to increase at

a faster rate. In other words, the time in which the viscose coagulates becomes shorter with increasing cellulose concentration.

Alkali Concentration Viscose shows its greatest stability to coagulation at about 3% - 9% alkali concentration. This fact was first recognised by Ost, Westhoff and Gessner³³ and later confirmed by other investigators.²⁵

Methods for determination of Xanthate Sulfur

(1) Direct titration method - Johann Eggert⁸

Weigh out into a glass plate 1 1/2 to 2 grams of viscose. Spread out well into a thin film and place plate in saturated NaCl solution containing about 2% glacial acetic acid. Strip the film from the plate when clear. Place it in a beaker and cover with 70 c.c. of 19% NaOH. After five minutes dilute with 100 c.c. of distilled water and after three more minutes add 300 c.c. of more distilled water. After the film is completely dissolved, treat the solution with acetic acid to very slight acidity (takes about 25 c.c. $\frac{1}{2}$, add a drop of starch solution, and titrate with 0.1 N iodine solution until first appearance of blue.

This method was tried^{in the present investigation} but did not give satisfactory results due to the fact that the determination of end point during direct titration with iodine solution was quite difficult.

39
(2) Iodine titration method

A solution containing 12 c.c. of N/10 iodine solution, 50c.c. of 1% acetic acid, and 100c.c. of distilled water is cooled to below 15 °C and to this is added an aliquot portion of diluted xanthate solution to be analyzed. After standing for twenty minutes excess iodine is back titrated with N/10 $\text{Na}_2\text{S}_2\text{O}_3$ and the iodine used calculated as total sulfur.

A second aliquot portion of the sample is added to cold saturated brine solution. After fifteen minutes the cold solution is filtered and an aliquot of the filtrate is titrated as above with iodine. The iodine consumed is calculated as impurity sulfur and the difference between total sulfur and impurity sulfur is considered to be xanthate sulfur.

Since quite a major drop in the sulfur : cellulose ratio occurred^r within first few hours this method had to be modified in order to be able to determine initial sulfur: cellulose ratio in the xanthated crumbs. Moreover, the size of the aliquot portions used had to be increased so as to lead to accurate results.

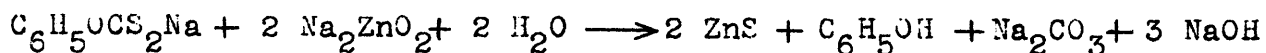
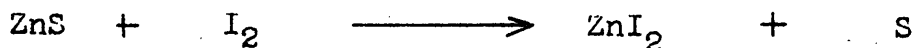
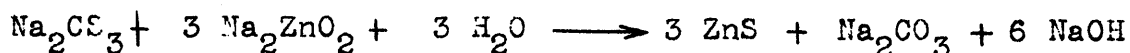
(3) Determination of Xanthate sulfur using Sodium Zincate 1

This procedure was a fairly rapid volumetric determination of xanthate sulfur in viscose. The sulfur in all forms, whether combined as sodium cellulose xanthate, sodium thiocarbonate or sodium sulfide, is quantitatively transformed into zinc sulfide in the presence of sodium zincate.

The zinc sulfide is then titrated iodometrically in the presence of an excess of sulfuric acid. From the amount of iodine used total sulfur is calculated.

A second portion of the sample is taken and to this is added saturated brine solution so that all the xanthate sulfur will precipitate out. Filter and take an aliquot portion to treat with sodium zincate. Impurity sulfur is quantitatively transformed into zinc sulfide in the presence of sodium zincate. The zinc sulfide is titrated as before and the amount of impurity sulfur calculated. The difference between the total sulfur and the impurity sulfur gives the xanthate sulfur.

Reactions



EXPERIMENTAL

(a) Nature of the pulp The pulp used in these experiments was a special high alpha-cellulose pulp.

(b) Preparation of Soda Cellulose

555 grams of air dry pulp were cut into sheets which were 7" by 7" in size. These pulp sheets were placed in a glass vessel and then submerged in 18.02% caustic solution so that they were completely covered and the time and the temperature were noted. They were allowed to remain in the solution for exactly one hour and then were removed and allowed to drain back for one minute. The sheets now swollen with caustic were arranged in an even pile and pressed.

Pressing of the pulp A piece of heavy iron plate from the pan of the hydraulic press was placed under the pile of pulp sheets and the whole mass transferred to the pan of the press. Over the pile of pulp sheets was placed a heavy iron plate and enough blocks of wood were inserted between this iron plate and the top of the press so as to avoid lost motion. The pressure on the sheets was raised to 2000 lbs. per square inch and maintained there for short time. The pressure was released and the moist sheets transferred to the pan of a balance and weighed. The wet weight of the

pulp should be 3.33 times the weight of the dry pulp and, if necessary, correct weight was obtained by addition of sufficient dip liquor to the wet pulp.

Grinding of the Pulp The pressed sheets were ground in a Werner and Pfleider grinder with a current of water passing through the jacket in order to maintain constant temperature. The grinding was continued for three and one-half hours and at the end of this time the machine was stopped and a bulk number test was run as described below. The crumbs were returned to the grinder and the grinding continued for fifteen minutes longer and another bulk number test was run. Grinding was continued until two test agreed. At this point the grinding was complete and the bulk number was usually about 238. The contents of the grinder were transferred into a large tin can provided for the purpose.

Aging of the crumbs The crumbs were then transferred into stoppered bottle and were placed in the constant temperature room at 15 °C for a period of sixty hours. After the required tests had been run the crumbs were ready for xanthation at the end of this period.

Alkali Cellulose Tests

Bulk Number Test By means of a liter beaker the weight in grams of loosely packed soda-cellulose crumbs was determined. From this weight, the weight in grams of 1000 c.c. of loosely packed soda-cellulose crumbs was calculated by simple proportions. This weight in grams of 1000 c.c. of loosely packed soda-cellulose crumbs was then recorded as the Bulk Number.

NaOH % By means of a weighing bottle, five grams of the moist crumbs were weighed into a beaker and covered with 150 c.c. of distilled water. After standing and stirring for five minutes the mixture was titrated with standard acid HCl using phenolphthalein and the % NaOH calculated.

Stock % To the neutralized sample from the above test, was added about ten ml. of glacial acetic acid and the residue was filtered on a Buchner funnel provided with a weighed filter paper. The pad on the paper was washed with about a liter of hot distilled water and dried at 105 °C to constant weight. The residue was calculated as % Stock.

(c) Preparation of Cellulose Xanthate The crumbs, properly aged, were then placed in a weighed mason jar which was about half filled so as to get satisfactory mixing. 25% by weight of carbon disulfide based on stock % was then added to the jar which was stoppered tightly. The jar was next transferred to a constant temperature xanthation box at 40 °C in which the contents of the jar were mechanically mixed for a period of one and three-quarters hours. At the end of this xanthation time, the rotation was stopped and vacuum was applied for about five minutes in cases where very large excess of CS₂ was used. About 30 grams

of xanthated cellulose was removed at this point to determine initial sulfur:cellulose ratio in the crumbs. Rest of the xanthated crumbs were used to make viscose as described below:

(d) Preparation of Viscose By means of the tests already run the proper amount of NaOH and water required to give a syrup containing 6.5% NaOH and 7.0% cellulose was calculated and placed in the reaction vessel. The jar and its contents was placed under a propellor blade driven by the large electric motor and stirred for forty-five minutes so as to get homogeneous solution. The jar at the end of stirring was covered and placed in the cold room at 15 °C to ripen.

(e) Ripening of Viscose The ripening of the syrup was carried out at 15 °C in the constant temperature room for a period of 200 hours. Samples were taken out every 24 hours for a study of the chemical changes taking place.

(f) Typical example showing the calculations involved in the preparation of viscose

Weight of the dry pulp.....545 gms.
Weight of the wet pulp.....1815 gms. (3.33 times wt.
of dry pulp.)

Bulk Number..... 238 (constant after five hours of grinding)

Alkali %

Weight of weighing bottle plus crumbs.....23.9766 gms.
Weight of weighing bottle alone.....23.5088 gms.
Weight of crumbs alone..... 5.4678 gms.

10.30 ml. of 0.1975 N HCl were used to titrate above sample:

Therefore:
$$\frac{10.30 \times 0.1975 \times 0.04 \times 100}{5.4678} \equiv 14.86\% \text{ NaOH}$$

Stock %

Weight of filter paper plus residue.....1.8300 gms.
 Weight of filter paper alone.....0.3476 gms.
 Weight of the residue alone.....1. 4824gms.

Therefore:

$$\frac{1.4824 \times 100}{5.4678} = 28\% \text{ Stock.}$$

Xanthation

Weight of the bottle plus crumbs.....979.6 gms.
 Weight of the bottle alone.....699.6 gms.
 Weight of the crumbs alone.....280.0 gms,

Amount of Carbon Disulfide used:- 25% by wt. based on Stock%

Therefore: $280 \times 0.28 \times 0.25 = 19.6 \text{ gms. CS}_2$

$$\frac{19.600}{1.263} = 15.52 \text{ ml. CS}_2 \text{ used.}$$

40 gms. of xanthated cellulose used for determination of initial ratio of sulfur:cellulose in crumbs.

Amount of Xanthated Cellulose.....255 gms.
 Amount of Original Cellulose250 gms.

Amount of alkali in 250 g. of crumbs..250 X 0.148 = 35.7 g. NaOH
 Amount of cellulose in 250 g. " ..250 X 0.230 = 70.0 g. Cell.

$$\frac{70}{0.07} = 1000.0 \text{ gms. Total wt. of viscose to give 7\% cellulose and 6.5\% NaOH.}$$

Amount of alkali required is 6.5%, therefore:

$$1000.0 \times 0.065 = 65. \text{ gms. NaOH required in 1000 g. of viscose}$$

$$\frac{35.7 \text{ gms. NaOH already present in crumbs}}{29.3 \text{ gms. to be added to get 6.5\% NaOH content}}$$

$$\frac{29.30}{0.18} = 163 \text{ gms. of 18\% NaOH to be added or}$$

$$\frac{163}{1.2} = 136 \text{ ml. of 18\% NaOH required.}$$

Final Composition of Viscose: (7% Cellulose & 6;5% NaOH)

255 gms. Xanthated Cellulose

163 gms. NaOH

582 gms. H₂O distilled.

1000 gms. Total weight of Viscose.

Procedure for Analysis

(a) Cellulose content of Viscose Into a cold 150 ml. beaker exactly 25gms. of viscose was weighed to ^{nearest} centigram. It was then transferred to a 250 ml. volumetric flask with cold distilled water and the volume was completed. A 20 ml. aliquot sample of the diluted syrup was placed in a 600 ml. beaker and to this was added glacial acetic acid in double the quantity of the sample and the xanthate was precipitated in shreds. The sample was then diluted with distilled water and boiled until all the xanthate has been converted to cellulose. The cellulose was then filtered in a Gooch crucible containing a mat of asbestos and washed five times with boiling distilled water. After drying to constant weight at 105 °C the crucible was placed in an oven at temperature of 1400 °F and the cellulose was ignited. From the difference between the weight of crucible plus asbestos plus cellulose (before heating in an oven at 1400 °F) and the weight of crucible plus asbestos (after heating at 1400 °F), the weight of cellulose was determined.

(b) Xanthate sulfur content of Viscose

(1) Initial xanthate sulfur in the xanthated crumbs

On completion of the xanthation, 30 gms. of the crumbs were placed in a liter beaker containing 200 ml. of a solution of 70% CH₃OH & 30% H₂O . The sample was vigorously agitated and with a high speed propeller after two minutes of agitation

sufficient glacial acetic acid was added to make concentration of 2% , agitation ^{was} continued for one more minute and then the excess solution was decanted. The crumbs were next washed thrice on a suction filter with 900 ml. solution of 85% CH₃OH plus 15% HOH plus 2% glacial acetic acid using high speed propeller for vigorous stirring. Next the crumbs were washed thrice ^{with} 300 ml. of solution of 85% CH₃OH plus 15% HOH as indicated. Finally the crumbs were washed with pure CH₃OH. The use of 70% CH₃OH was decided upon after finding that this concentration permitted sufficient swelling of the crumbs to ensure proper washing out of impurities. The use of 85% CH₃OH was decided upon after finding that pure methyl alcohol did not give quite as complete removal of impurities, probably since the crumbs were not swollen and could not be dispersed into easily purified separate fibers. The product was dried by drawing through it a current of dry air at room temperature and was used immediately in the experiment.

Preparation of Xanthate Solution Six grams of purified xanthate were dissolved in 300 ml. of 12% NaOH by stirring for about ten minutes. A 20 ml. aliquot was used to determine cellulose content as described before. Other aliquot portions were kept for the determination of xanthate sulfur.

Xanthate Sulfur Determination To a solution containing 20 ml. of N/10 iodine solution, 100 ml. of 10% acetic acid and 200 ml. of distilled water was added a 20ml. aliquot portion of the prepared xanthate solution to be analyzed. After standing for 30 minutes excess iodine was back titrated with N/10 $\text{Na}_2\text{S}_2\text{O}_3$ and the iodine used calculated as total sulfur.

A second aliquot portion of the sample was added to 200 ml. CH_3OH plus cold saturated brine solution. After 15 minutes the solution was filtered and an aliquot of the filtrate was titrated as above with iodine. The iodine consumed was calculated as impurities sulfur and the difference between total and impurity sulfur was considered to be xanthate sulfur.

Xanthate Sulfur in the Viscose

Into a 150 ml. beaker exactly 25 gms. of viscose was weighed to the ^{nearest} centigram. It was then transferred to a 250 ml. volumetric flask with cold distilled water and the volume was completed. The diluted viscose was used to determine cellulose content and xanthate sulfur exactly as described in previous part.

Determination of Xanthate Sulfur using Sodium Zincate

(a) Determination of total sulfur

Reagents A sodium zincate reagent composed of 10 gms. of C.P. zinc oxide, 100 gms. C.P. caustic soda and distilled water to 1000 ml. ; 0.1 N Iodine ; 0.1 N thiosulfate and 1 M sulfuric acid.

Procedure Into a cold 150 ml. beaker there was weighed 25 gms. of viscose to the ^{nearest} centigram. It was transferred to a 250 ml. volumetric flask with cold distilled water and the volume was completed. Into a 500 ml. Erlenmeyer flask there was introduced in the order given, 100 ml. distilled water, 10 ml. sodium zincate, and 10 ml. aliquot of the diluted viscose; and the flask was covered with a 5 cms. diameter funnel to avoid spattering. No immediate precipitate occurred. The mixture clouded between 65 °C and 70 °C and flocculation started at 75 °C (a yellow ppt. appeared overnight if the solution was kept at room temperature.) The contents were brought to a boil and after 30 minutes of gentle boiling, the contents of the flask were cooled in ice and then flushed into a 600 ml. beaker containing a cold solution of 50 ml. of M/H₂SO₄ and 20 ml. of 0.1/N iodine. The mixture was immediately transferred back into Erlenmeyer flask quantitatively and a minimum of 20 minutes of contact to decompose the ZnS entirely was allowed. The

excess iodine was titrated with 0.1 N solution of sodium thiosulfate in the presence of a few drops of starch solution as indicator. From this amount of total sulfur was determined.

(b) Determination of Impurity sulfur

Reagent Saturated NaCl solution plus others already mentioned in part (a).

Procedure 100 ml. of diluted viscose prepared for the determination of the total sulfur (25 gms. in 250 ml.) was pipetted into a 500 ml. volumetric flask packed in ice and the volume completed with an iced saturated NaCl solution. This was mixed well and allowed to stand for 15 minutes. (in case of unripe viscose, the rate of settling of coagulated xanthate was likely to be low. A centrifuge may be advantageously used to hurry the settling and speed up analytical procedure). The sample was filtered through a dry fluted paper of rapid filtering characteristic and a 50 ml. portion of the filtrate was pipetted into a 500 ml. Erlenmeyer flask and its sulfur content determined; exactly as for total sulfur above.

The difference between total sulfur and impurity sulfur gives the xanthate sulfur.

Reactions refer to page 27 .

Ammonium Chloride Number of Viscose

Into a 125 ml. Erlenmeyer flask 20 gms. of viscose was weighed to the nearest centigram. To this was added 30 ml. of distilled water which was mixed well until complete dilution was obtained. This sample was then titrated with an aqueous ammonium chloride solution (10% by weight) adding about 1 ml. at a time until the viscosity of the mixture becomes fairly high. From this point on NH_4Cl was added a few drops at a time with vigorous shaking after each addition, until the mixture becomes so thick that it will no longer flow easily on inverting the flask. This point was taken as the end point and the number of ml. of NH_4Cl required was recorded as the NH_4Cl number. Considerable practice was required to obtain check results.

Effect of Acetic Acid on cellulose content upon standing

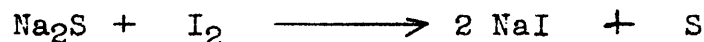
Procedure for analysis given on page 34 was followed until the samples were diluted with distilled water and boiled until all the xanthate has been converted to cellulose. The beaker was then allowed to stand for required length of time to study the effect of acetic acid on cellulose content, upon standing.

Analytical Method ³⁴ of analysis for checking conversion factor Determination of S in Na_2S by (1) Gravimetric method and (2) Volumetric method (Iodine titration method)

(1) Gravimetric Method. Nearly 12 gms. of $\text{Na}_2\text{S}, 9\text{H}_2\text{O}$ was dissolved in water and diluted to one liter. A ten ml. aliquot was taken in 400 ml. beaker and to this was added a few drops of liquid bromine to bring about oxidation. The sample was made acid with excess conc. HNO_3 which gave rather strong oxidizing effect. The solution was kept hot for half an hour and was partly covered with watch glass. More liquid bromine was added to keep solution slightly yellowish; to insure complete oxidation. The solution was next taken to dryness; more conc. HNO_3 was then added and sample was again taken to dryness. Excess conc. HCl was added and taken to dryness on a hot plate. More conc. HCl was added and again brought to dryness. At this point water was added and solution was made slightly acid using 4% HCl solution. By this treatment all the sulfide was converted to soluble sulfate. Ten ml. of 10% BaCl_2 solution was then added slowly and the beaker was allowed to stand overnight to let crystals of BaSO_4 grow. The following day the precipitate was transferred quantitatively to a filter paper and washed with hot water. The filter paper was put in a weighed crucible and gently heated at first; followed by 20 min. at 900°C . Increase in weight was calculated as BaSO_4 .

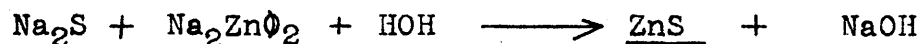
Factor: $\text{BaSO}_4 \times 0.1373 = \text{S gms.}$

(2) Volumetric (Iodine Titration) Method



To a solution containing 20 ml. of N/10 iodine solution, 100 ml. of 10% acetic acid and 200 ml. of distilled water was added 10 ml. aliquot of $\text{Na}_2\text{S}, 9\text{H}_2\text{O}$ solution. After standing for 30 minutes excess iodine was back titrated with N/10 $\text{Na}_2\text{S}_2\text{O}_3$ and the iodine used was calculated as sulfur.

(3) Volumetric Method In this method, 10 ml. of $\text{Na}_2\text{S}, 9\text{H}_2\text{O}$ was taken in 500 ml. Erlenmeyer and to this was added 20 ml. of Na_2ZnO_2 solution ^{-*-} and 100 ml. of distilled water.



The contents were brought to a boil and after 30 min. of gentle boiling, the flask was cooled. To this sample was added a mixture containing 20 ml. of 0.1 N I_2 and 100 ml. of 10% acetic acid. After 30 min. of standing excess iodine was back titrated with N/10 $\text{Na}_2\text{S}_2\text{O}_3$ and the iodine used was calculated as sulfur.

-*- refer to page 37 'reagents'.

RESULTS

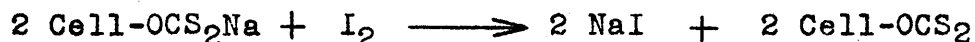
(a) Effect of acetic acid on cellulose content of Viscose:

<u>Time in hours.</u>	<u>Cellulose content.</u>
0	0.0697 gms./ 10 ml. aliquot
0	0.0707 gms./ "
2.5	0.0723 gms./ "
2.5	0.0720 gms./ "
4.5	0.0734 gms./ "

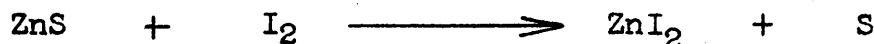
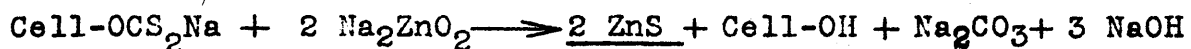
(b) Conversion Factor:

<u>Procedure</u>	<u>Factor</u>	<u>Amount of Sulfur gms.</u>
Gravimetric	S or 0.1373 BaSO ₄	0.01313 & 0.01306
Iodine Titration	S:2I or 16/127	0.01378 & 0.01371
Sodium Zincate	S:2I or 16/127	0.01635 & 0.01690

Conversion factor for reaction:



4 S : 2 I or 2 S : 1 I or 64/127 for Iodine titration



S : 2 I or 16/127 for Na₂ZnO₂ method.

% CS₂ = 37%

<u>Procedure for Analysis</u>	<u>Factor</u>	<u>Time hrs.</u>	<u>Av. Cell.</u>	<u>Av. S</u>	<u>S/Cell.</u>
2 Cell-OCS ₂ Na + I ₂ → 2 NaI + 2 Cell-OCS ₂ .	64/127	0	0.1326	0.0376	0.283
ZnS + I ₂ → ZnI ₂ + S.	16/127	0	* Fails completely.		
2 Cell-OCS ₂ Na + I ₂ → 2 NaI + 2 Cell-OCS ₂ .	64/127	24	0.0650	0.00753	0.117
ZnS + I ₂ → ZnS ₂ + S.	16/127	24	0.0641	0.00700	0.109

During the analysis it was found that in the determination of initial sulfur : cellulose ratio the results obtained by the modified Iodine titration method were quite different from those obtained by the Sodium Zincate method. It was also found that the results obtained by the Sodium Zincate method were not reproducible, and that the range of the results obtained was quite wide. In order to ascertain the correctness of the gravimetric factor analysis were carried out in which sulfur content of Na₂S, 9H₂O solution was determined by the modified Iodine titration method and by the Sodium Zincate method. From the results the correctness of the conversion factor was established. The correct factors for each reactions are shown above. Once the correct factor was found, the inability of the Sodium Zincate method to give satisfactory results was concluded to be due to the failure of the method.

TABLE (1)

"Change in Sulfur:Cellulose ratios on ripening of viscose."

Xanthation: CS₂ : 37% by wt. based on alpha cell. content.
Time : one and three-quarter hours.
Temp.: 40 °C.

Ripening: Temp.: 15 °C.

<u>Time in hours</u>	<u>S:Cell. ratios</u>	<u>Av. Time</u>	<u>Av. S:Cell.</u>
0	.356, .364, .370	0	0.3630
26	.175, .184		
30	.185, .190	28	0.1835
50	.168, .175		
54	.161, .174	52	0.1695
71	.153, .166		
72	.155, .157		
74	.166	72	0.1594
93	.142, .147		
94	.139, .139, .146	93.6	0.1426
116	.130, .132, .135, .139	116	0.1340
140	.117, .118, .120, .128	140	0.1210
165	.105, .120	165	0.1125
195	.097, .098	195	0.0975

TABLE (2)

"Change in Sulfur:Cellulose ratios on ripening of Viscose "

Xanthation: CS₂ : 25% by wt. based on alpha cell. content.
 Time : one and three-quarter hours.
 Temp. : 40 °C

Ripening: Temp. : 15 °C

<u>Time in hours</u>	<u>S:Cell. ratios</u>	<u>Av. Time</u>	<u>Av. S:Cell.</u>
0	.254, .258, .261	0	0.2580
22	.124, .130		
23	.120, .125	22.5	0.1247
54	.109, .116		
55	.111	54.4	0.1120
78	.111, .0994		
79	.102, .1180	78.5	0.1040
102	.0700, .0934		
103	.1050	102.4	0.0953
150	.0802, .0803	150	0.08025
198	.0683, .0696	198	0.06890

TABLE (3)

Xanthation: CS₂ : 9% by wt. based on alpha cell. content.
 Time : one and three-quarter hours.
 Temp. : 40 °C.

Ripening : Temp. : 15 °C.

<u>Time in hours</u>	<u>S:Cell. ratios</u>	<u>Av. Time</u>	<u>Av. S:Cell.</u>
0	.140, .161, .169	0	0.1570
24	.0650		
26	.0650, .0698	25	0.0666
72	.0484		
75	.0436	73	0.0460
148	.0360, .0368	148	0.0364
195	.0300, .0340	195	0.0320

TABLE (4)

"Change in Ammonium Chloride Number on ripening of Viscose"

Xanthation: CS₂ : 37% by wt. based on alpha cell. content.
 Time : one and three-quarter hours.
 Temp. : 40 °C

Ripening: Temp. : 15 °C

<u>Time in hours</u>	<u>NH₄Cl #</u>	<u>Av. Time</u>	<u>Av. NH₄Cl #</u>
0	infinity	0	infinity
26	23.6, 25.6		
34	25.5		
45	21.3, 22.4	35.2	23.68
54	13.6, 16.8		
55	17.0, 20.4	54.5	16.95
74	13.0, 13.0		
76	12.6, 12.8		
78	12.4, 12.6	76	12.73
102	11.8, 12.05		
104	11.2, 11.5	103	11.64
114	11.2, 11.2	114	11.20
124	10.8, 10.9		
130	10.5, 10.65	127	10.71
165	9.7, 9.7, 9.8, 9.7	165	9.73
195	8.9, 8.9	195	8.90

"Changes in Ammonium Chloride Number on ripening of Viscose "

TABLE (5)

Xanthation: CS₂ : 25% by wt, based on alpha cell. content
 Time : one and three-quarter hours
 Temp. : 40 °C

Ripening: Temp. : 15 °C

<u>Time in hours</u>	<u>NH₄Cl #</u>	<u>Av. Time</u>	<u>Av. NH₄Cl #</u>
0	infinity	0	infinity
25	11.80,12.00		
28	11.70,12.00	26.5	11.97
56	10.35,11.10		
59	10.35,10.90	57.5	10.92
80	9.90,10.30		
83	10.10,10.15	81.5	10.11
104	9.70,9.70		
107	9.00,9.55	105.5	9.49
150	8.45,8.50	150	8.47
198	7.30,7.10	198	7.20

TABLE (6)

Xanthation: CS₂ : 9% by wt, based on alpha cell. content
 Time : one and three-quarter hours
 Temp. : 40 °C

Ripening: Temp. : 15 °C

<u>Time in hours</u>	<u>NH₄Cl #</u>	<u>Av. Time</u>	<u>Av. NH₄Cl #</u>
0	infinity	0	infinity
24	10.0,10.4		
26	10.2	25	10.20
75	8.0, 8.2		
77	8.2	76	8.10
148	6.0,6.0	148	6.00
195	4.8,4.8	195	4.8

TABLE (7)

" Sulfur : Cellulose Ratio vs. Ammonium Chloride Number "

From Graphs:- Figure (1) and Figure (2)

<u>Time hours</u>	<u>S:Cellulose</u>	<u>NH₄Cl #</u>	<u>% CS₂</u>
200	0.096	8.8	37
160	0.114	9.8	37
140	0.123	10.4	37
120	0.132	11.0	37
100	0.140	11.8	37
80	0.151	12.6	37
60	0.163	14.3	37
50	0.163	23.0	37
45	0.172	33.0	37

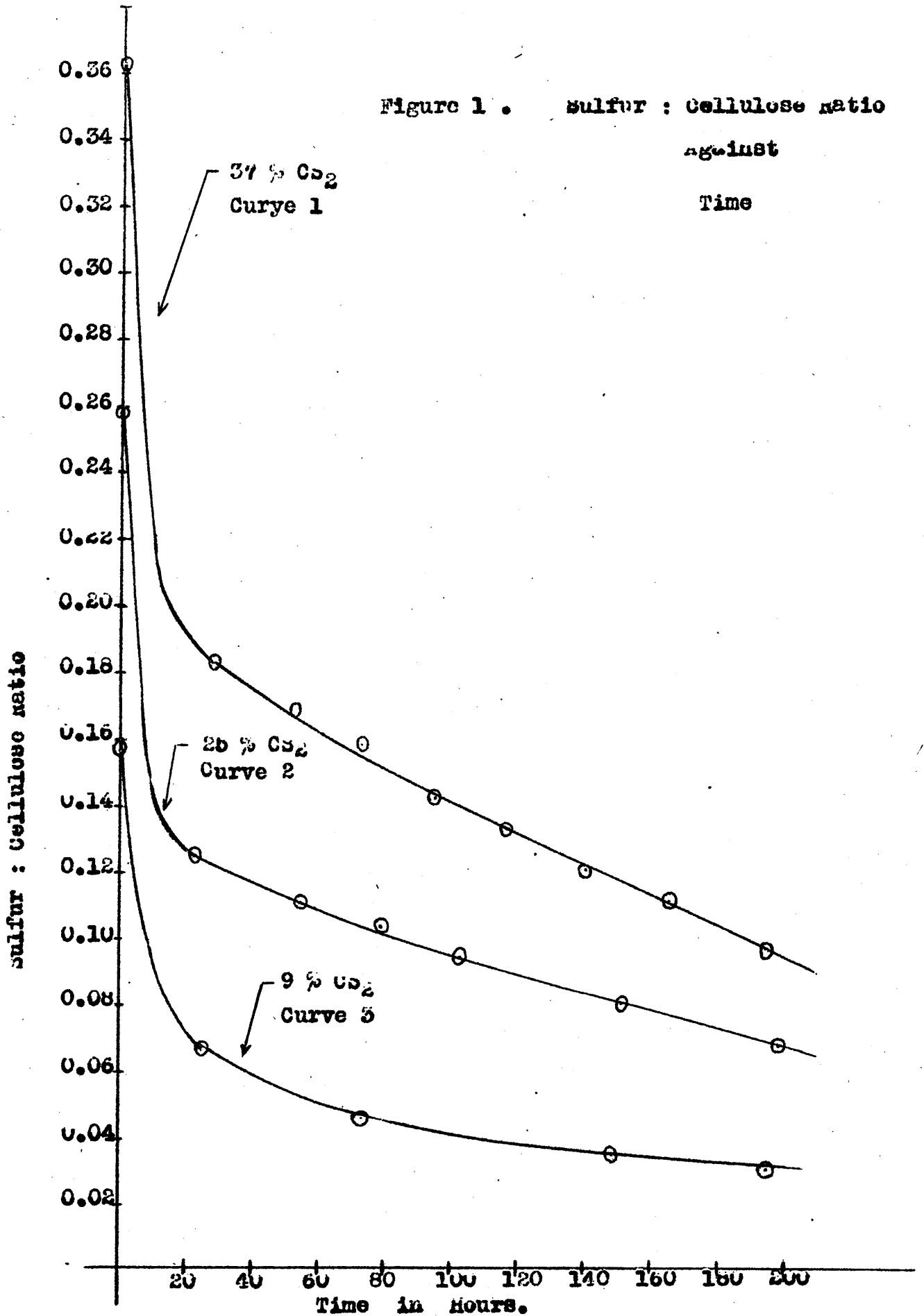
200	0.063	7.2	25
160	0.079	8.2	25
140	0.084	8.6	25
120	0.090	9.1	25
100	0.096	9.6	25
80	0.102	10.1	25
60	0.109	10.7	25
40	0.117	11.4	25
20	0.127	12.3	25
10	0.142	13.9	25
7	0.160	20.0	25

200	0.031	4.7	9
160	0.034	5.7	9
140	0.036	6.3	9
120	0.038	6.8	9
100	0.041	7.4	9
80	0.045	8.0	9
60	0.050	8.7	9
40	0.059	9.6	9
20	0.072	10.6	9
10	0.092	11.6	9
5	0.116	13.0	9
2	0.140	22.0	9

R = Sulfur : Cellulose ratio.... initial

r = Sulfur : Cellulose ratio.... maturity

<u>R</u>	<u>r</u>	<u>% CS₂</u>
0.157	0.064	9
0.253	0.100	25
0.363	0.118	37



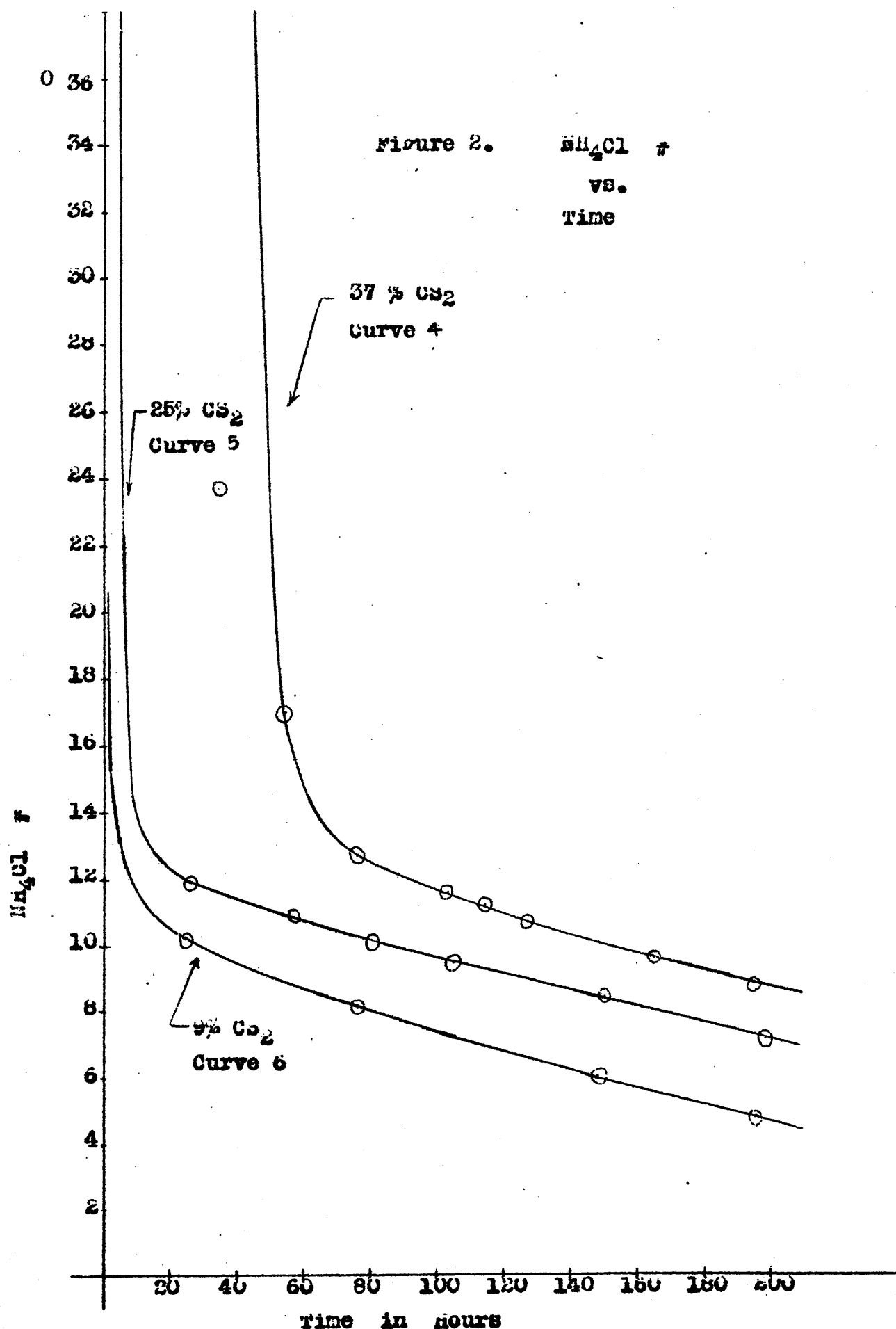
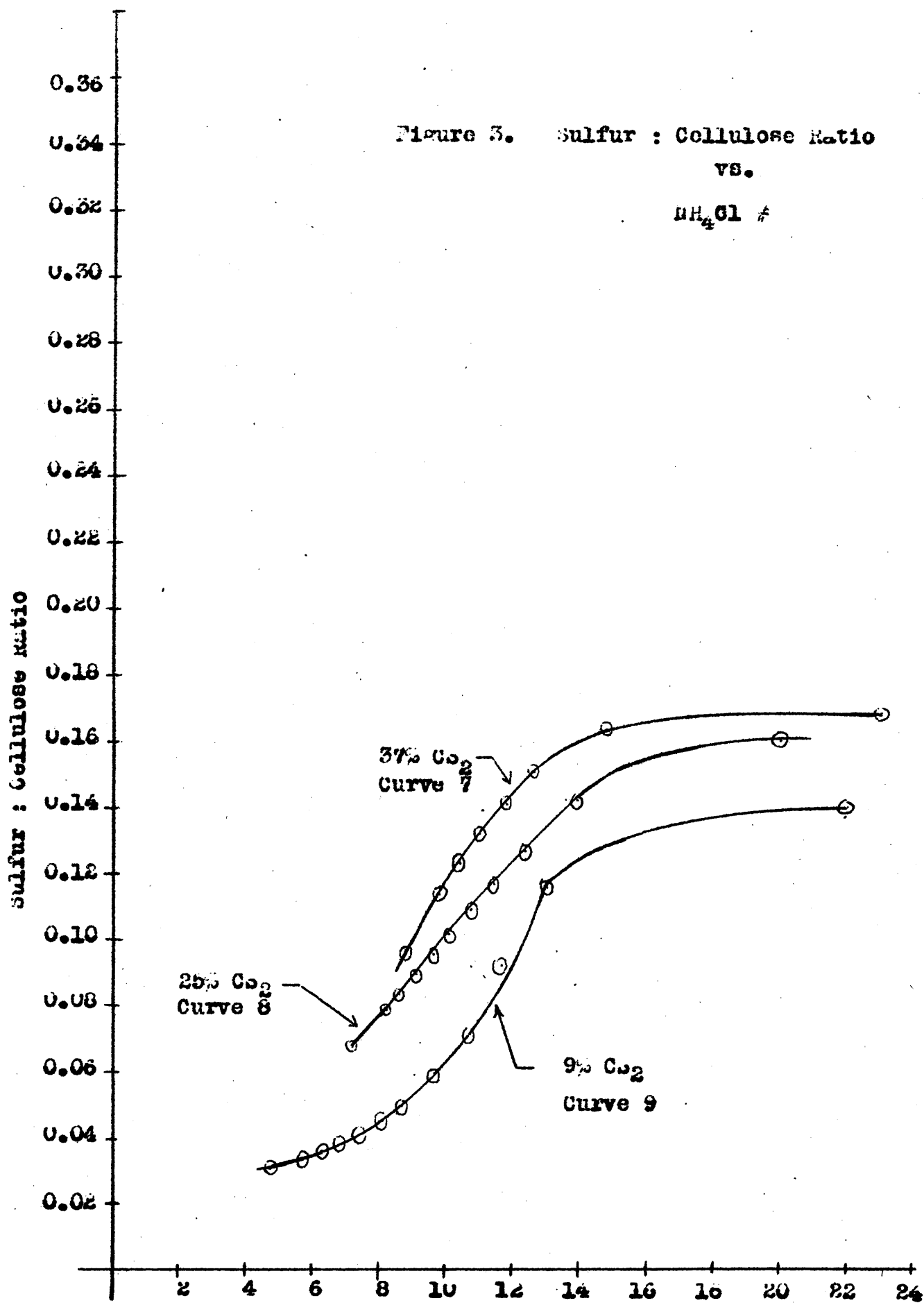


Figure 3. Sulfur : Cellulose Ratio
vs.
 NH_4Cl %



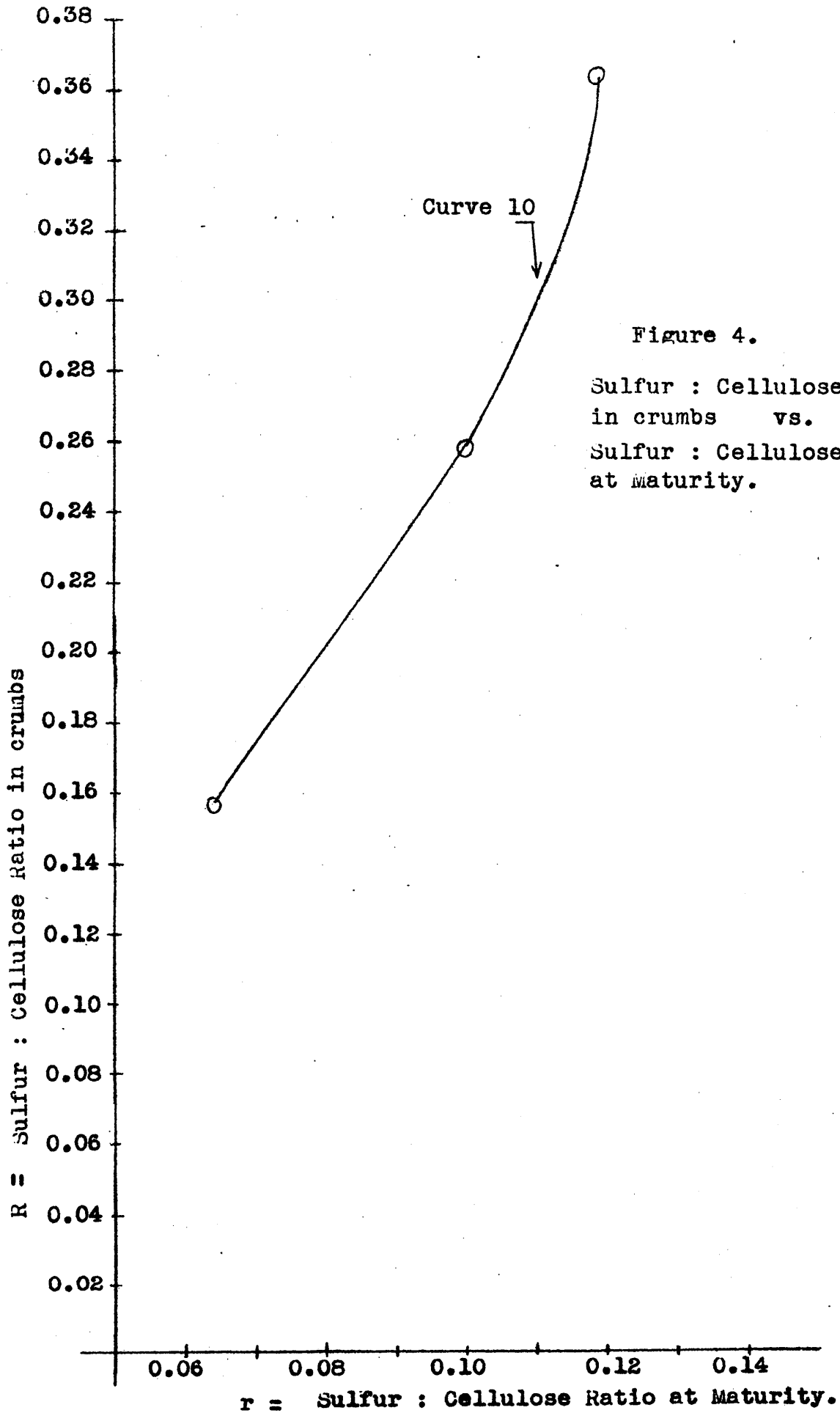
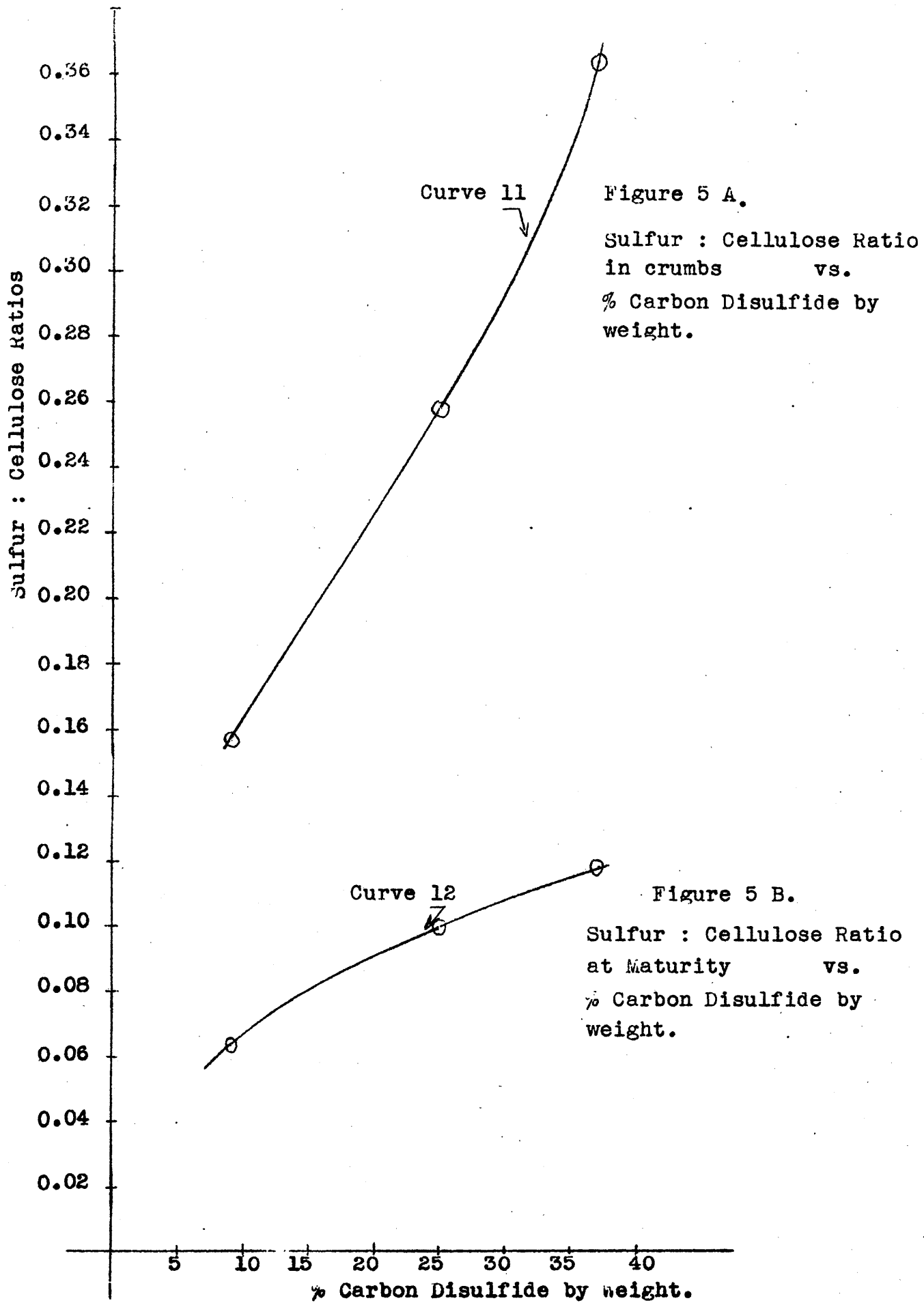


Figure 4.

Sulfur : Cellulose Ratio
in crumbs vs.
Sulfur : Cellulose Ratio
at maturity.



DISCUSSION OF RESULTS

When different viscoses were analyzed during their ripening at 15 °C., fairly concordant results were obtained with viscoses made under practically the same conditions. (Tables 1, 2, & 3) The three curves in figure 1, represents the averages of three to five different viscoses, showing decided decrease in the ratio sulfur:cellulose. Curve 1 represents viscose made with 37 % CS_2 in order to approach a ratio equal to 2:1. Curve 3 represents viscose made with 9% CS_2 in order to approach the soluble xanthate ratio of sulfur:cellulose 0.16 as found from the work of Scherer and Miller.³⁷ However samples of viscoses made with 9% CS_2 contained a large portion of undissolved cellulose fibers. Curve 2 represents viscose made with 25 % CS_2 in order to get a ratio in between the first two, thus covering the range of sulfur:cellulose ratio satisfactorily. Curves 2 & 3 were therefore obtained with less than theoretical amount of CS_2 . All the three curves show that more than 50% of the total decrease occurs within the first twenty four hours of the time of observation. It is apparent, then, that the initial rate of decomposition is faster, probably involving the change of the C_6 stage to the C_{12} stage.

(Tables 4, 5, & 6) The three curves in figure 2, represent change in ammonium chloride number with time

of ripening. The state of ripening was determined by the c.c. of 10% NH_4Cl solution necessary to start coagulation of a viscose solution. Curve 4, 5, & 6 represent viscoses made with 37% CS_2 , 25% CS_2 , 9% CS_2 . All the three curves in figure 2 show a decided decrease in the ammonium chloride number. All the three curves also show that ammonium chloride number approaches infinity at zero hour ripening. At the end of 24 hours it is noticed from the curves that ripening has proceeded to a much greater extent with 9% CS_2 than 25% CS_2 ^{or} than 37% CS_2 .

In accordance with the general acceptance of industry viscose is said to be mature when ammonium chloride number of ten is attained.

The determination of ammonium chloride number method is quite complex and considerable practice is required to get check results. This is especially true of the measurement of ammonium chloride number before 48 hours of ripening so that these are only a rough approach to exactness.

The general nature of curves in figure 1 & 2 are similar. The samples of viscoses were kept at temperature $14^\circ\text{C} - 15^\circ\text{C}$.

(Tables 7) The three curves in figure 3 represent sulfur:cellulose ratios corresponding to ammonium chloride number. These curves were deduced from

the results of figure 1 and 2 so as to study the sulfur : cellulose ratios of viscoses at maturity. Curves 7, 8, & 9 show different sulfur:cellulose ratios at maturity, when ammonium chloride number is ten. The sulfur:cellulose ratios at maturity however decrease with decrease in the amount of CS₂ used; maintaining other conditions constant. The curves 7 & 8 are quite smooth and uniform because the samples of viscoses were completely soluble. The curve 9 is non-uniform possibly because of the incompletely soluble xanthate. The curves also show that after^a certain rapid increase in sulfur:cellulose ratios with ammonium chloride number, there is very slow increase in the sulfur:cellulose ratios with ammonium chloride number. Thus the ratio approaches a limit beyond which it does not show noticeable change.

(Table 7) The curve in figure 4 represents sulfur: cellulose ratio in the crumbs corresponding to sulfur: cellulose ratio at maturity. The curve shows decided decrease in the maturity ratio with decrease in the initial ratio. Thus starting with different initial ratios gives different maturity ratio. The higher the initial ratio, higher will be the maturity ratio. It should however be noticed that the maturity ratio for the soluble xanthate are quite close together compared with wide difference in

the initial ratios.

(Table 7) The curve in figure 5A represents sulfur:cellulose ratio in the crumb corresponding to % CS_2 by weight. The curve 11 shows the initial sulfur : cellulose ratio approach 2;1 (theoretical maximum) with 37% CS_2 . Initial ratio in the crumbs decreases with decrease in the amount of CS_2 used; other conditions being kept constant.

(Table 7) The curve in figure 5E represents sulfur:cellulose ratio at maturity corresponding to % CS_2 by weight. The curve 12 shows that the maturity ratios are different depending upon amount of carbon disulfide used. The higher the amount of CS_2 , the higher is the maturity ratio. There is almost a linear relationship between amount of CS_2 and maturity ratio.

CONCLUSION

(1) The effect of acetic acid on the cellulose content of viscose is negligible upon standing.

(2) The sodium zincate method fails to give satisfactory results in the determination of initial sulfur:cellulose ratio in the crumbs. This may be due to two reasons. Either the amount of sulfur in the initial determination of sulfur content is so high that the procedure of analysis is not suitable or possibly, the coagulated xanthate produced by the zinc sulfide itself acts as a protective colloid and prevents complete precipitation of all sulfur present as zinc sulfide. In consequence of the wide variations in results obtained the method is not applicable to the determination of the initial ratio.

(3) The sodium zincate method is quite satisfactory for the determination of sulfur content in the viscose. This may be due to the lower sulfur content (as already shown that more than 50% of decrease in sulfur content of viscose takesplace within first 24 hours); or it may be that the protective colloid effects are overcome and that all the sulfur is gravimetrically converted to ZnS; giving check results. The results obtained for viscose by the sodium zincate method and the modified iodine titration method are in agreement. This shows that the sodium zincate method is quite satisfactory for the determination of sulfur content in viscose syrup after twenty four hours ripening.

(4) There is a decided decrease in the sulfur:cellulose ratio and the ammonium chloride number with the time of ripening. The major portion of the decrease being within first 24 hours. The time required to attain maturity depends upon amount of CS_2 used during xanthation.

(5) The sulfur:cellulose ratio at maturity depends upon the initial sulfur:cellulose ratio. The higher the initial sulfur:cellulose ratio, the higher will be the maturity ratio.

(6) For wide differences in initial sulfur:cellulose ratio there is relatively little difference in the maturity sulfur:cellulose ratio.

(7) The initial sulfur:cellulose ratio depends upon the amount of CS_2 used; other conditions being kept constant. The higher the amount of CS_2 , the higher will be the initial sulfur:cellulose ratio.

(8) The sulfur:cellulose ratio at maturity depends upon the amount of CS_2 used. The higher the amount of CS_2 used the higher will be the sulfur:cellulose ratio at maturity.

(9) It may be concluded then that the "maturity ratio" may be varied at will within a reasonable range by controlling the "initial ratio" of the xanthate.

Suggestions for further work

(1) A more satisfactory method for determining "maturity" should be developed.

(2) If possible, a wide range of "maturity ratio" should be prepared.

(3) The effect of different "maturity ratio" on the properties of rayons spun from them should be studied.

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