THE ATTEMPTED PLASTICIZATION OF CELLULOSE FROM CELLULOSE XANTHATE

by

Dewey H. Stallard, Jr.

B. S. Emory and Henry College

A Thesis Submitted to the Graduate Committee of the Virginia Polytechnic Institute in Partial Fulfillment of The Requirements for the Degree of

MASTER OF SCIENCE

IN

CHEMISTRY

Approved:

_____

Supervisor

_____

Head of Chemistry Department

_____

Chairman of Graduate Committee

Virginia Polytechnic Institute
Blacksburg, Virginia
February 2, 1944

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. P. C. Scherer for the many helpful suggestions throughout this work.

TABLE OF CONTENTS

INTRODUCTION

This investigation was started at the suggestion of Dr. P. C. Scherer who suggested that a film prepared from a cellulose xanthate, in which the fiber form had been destroyed by some action other than by dilute alkali, should have interesting properties. The possibilities of such a material might be much greater if the destruction of the fiber form were brought about by a kneading action.

This investigation was purely a qualitative one and no attempt has been made to test any of the products other than by appearance and general properties.

The main object was that of finding ways and means of handling the material in an attempt to prepare a product of some strength and plasticity.

HISTORICAL

A search of the chemical literature revealed that no published work existed on the kneading effect applied to cellulose xanthate. Some references were found referring to the use of a ball mill in the production of pulp sheets.(1) Also no references could be found as to the plasticization of cellulose xanthate as such.

An investigation carried out by F. B. Sutphin(2) on the forming of a sheet, or film, from cellulose xanthate indicated that plasticization of a regenerated film from xanthate was possible.

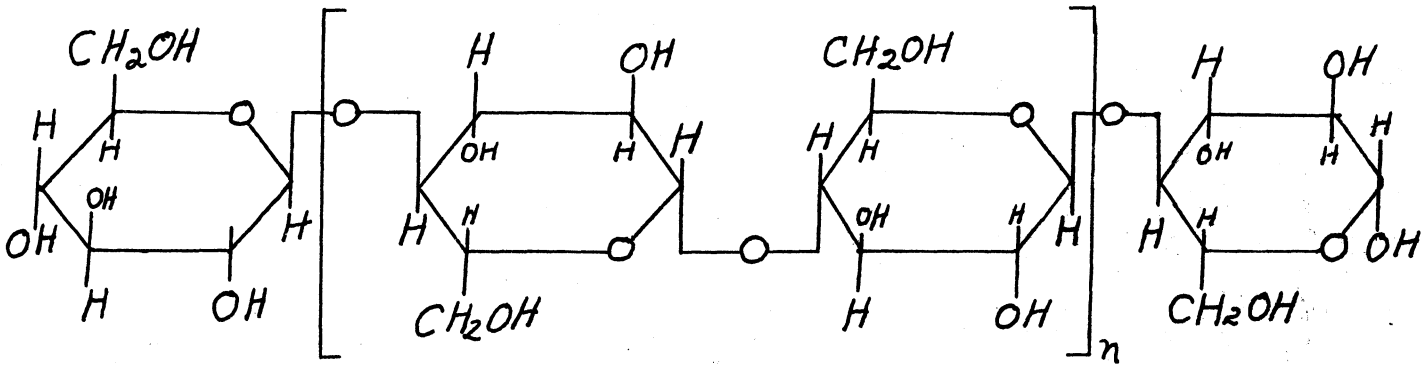

Fig. 1 The Cellulose Chain Molecule

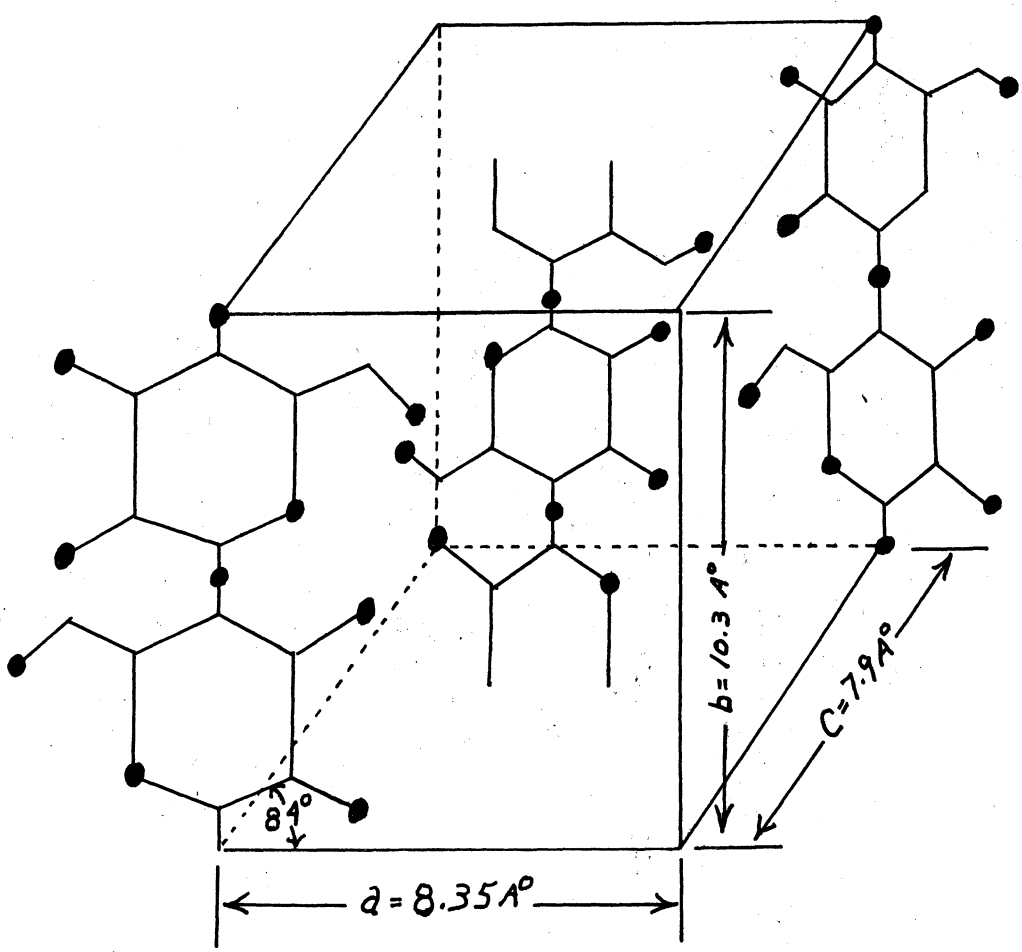

Fig. 2 Meyer and Mark's Model for the Unit Cell for Cellulose

THEORETICAL

Structure of Cellulose

The modern concept of the structure of the cellulose molecule is depicted in Figure 1. This shows that cellulose is made up of anhydroglucose units all of which are connected by glycosidic linkages between the individual glucose anhydrides. Thus the reactions of cellulose are due chiefly to the available hydroxyl groups. The glucose anhydrides all possess three free hydroxyl groups except the end unit which possesses four free hydroxyl groups. The hydroxyl groups are: One in the sixth position being of primary nature and one each in the second and third positions of secondary nature. The fourth hydroxyl group on the end unit is in the fourth position.

Meyer and Mark's[3] concept of the basic cell is depicted in Figure 2. Their dimensions are based on the work done and established by Polanyi[4] in 1921, and further calculations are based on Haworth's[5] cello-biose model. The dimensions are shown on the model which, for clarity, only shows three chains. The cello-biose residues lie parallel to the b axis and the glucose residues lie alternately pointing in opposite directions.

The chains were first thought to lie in micellar arrangements which terminated at regular intervals but this concept has now been changed and the same chains are now assumed to pass through

both the crystalline and amorphous regions. The chains vary in length but some measurements show them up to 3600 glucose units in length for native cellulose.

Formation of Soda Cellulose

Caustic soda solution containing about 18 percent sodium hydroxide by weight exerts a considerable swelling effect upon cellulose. Such an effect is commercially used in the process of mercerization. This swelling effect is exothermic in nature and it seems that a definite chemical compound is formed. According to Vieweg and Heuser[6] the formation of a compound $(C_6H_{10}O_5)_2 \cdot NaOH$ is confirmed.

General Theories of Xanthate Formation.

1. The Chemical Theory.

The chemical theory assumes that only one of the hydroxyl groups on each $C_6H_{10}O_5$ unit reacts to form the xanthate and that the reaction occurs in definite molecular proportions as represented in the equation:

$$\text{Cell} - \text{ONa} + CS_2 = \text{Cell} \quad \begin{matrix} S \\ | \\ O\text{-}C\text{-}SNa \end{matrix}$$

2. The Physical Theory.

A continuation of the swelling first exhibited in the mercerization effect is brought about by the addition of the carbon disulfide until the secondary valences are broken and the cellulose separates into colloidal particles, which go into solution with certain solvents such as water and sodium hydroxide solution.

3. The Combination of the Two Theories

This theory assumes that only a part of the cellulose reacts to give a monoxanthate with the rest of the cellulose being unaffected. The mono-xanthate formed acts as a dispersing agent for the rest of the unreacted cellulose and thus goes into solution.

Scherer and Miller[7] found that aging has no effect on the rate of xanthation.

Scherer and Lin[8] verified the above and also found that temperature had a marked effect on the rate of xanthation.

Pulp Used

The pulp used in this investigation was a special alpha-cellulose pulp made by Brown Company

Pulp Analysis

Alpha cellulose	95.60%
Moisture	5.81%
Ash.....	.14%
Lignin	.27%

Properties of the Plasticizers Used

Plasticizer	Specific Gravity	Action in Cold 18% NaOH	Mol. Wt.
Castor oil	.968	Some reaction	933.40
Dimethyl pthalate	1.192	Insoluble	194.18
Hercolyn	1.020	Reacted	
Oleic acid	.854	Some Reaction	282.46
Linseed oil	.934	Insoluble	--
Santicizer 8	1.268	Soluble	199
Stearic acid	.847	Insoluble	284.47
Tricresyl phosphate	1.180	Insoluble	368.36
Benzyltrimethyl ammonium Hydroxide	1.07	Soluble	168

Description of Equipment Used and Where Located

Ball Mill — This piece of equipment has a 3' overall length and is equipped with two porcelain jars. The jars are 8" in diameter and 7" in height. The power used is a 1/12 h.p. electric motor which rotates the jars at 65 revolutions perminute. The equipment is made by the Fischer Scientific Company. Located in the Coal Laboratory.

Kneading Rolls - The kneading rolls used are a set of experimental kneading rolls located in the Unit Operations Laboratory. This set of rolls has three rolls on a horizontal plane which turn at three different speeds thus giving the kneading action. The dimensions of the rolls are: 10" in length and 4" in diameter and they can be heated with low pressure steam. Manufactured by Chas. Ross & Son Company.

Steam Vessel - This vessel is a welded iron cylinder having the dimensions: 3' in height and 1.5' in diameter. The vessel is equipped with cover, steam inlet, and condensed steam outlet and is located in the Rayon Laboratory.

Driers — Two driers were used. One a cabinet drier and heated by a steam coil. This drier is located in Rayon Laboratory. The other drier, a box-type drier, is heated electrically and is located in the Physical Chemistry Laboratory. A constant temperature of 45° C. was maintained in both driers.

Xanthating Drum — Glass jar of four-liter capacity with screw top.

Grinder - Located in the Rayon Laboratory and was also used as a kneading machine. Inside dimensions are 10" x 11" x 8". This machine contains a pair of blades which carry on their faces sets of serrated shoes. The bottom of the trough of this machine curves to form two half-cylinders at the junction of which is inserted a saddle. The cooling jacket is cast integral with the trough shell and carries off heat generated and keeps the temperature constant. Manufactured by Werner and Pfleiderer.

Meaning of Terms and Phrases

Acid - Ten percent sulfuric acid.

Crumbs - Soda cellulose prepared by dipping pulp into 18 percent sodium hydroxide for one hour and then pressing to 3.3 times its original weight of pulp. This pressed pulp was then ground in grinder for 3.5 hours to form crumbs.

Xanthate - The compound formed on addition of carbon disulfide to the soda cellulose. The amount of carbon disulfide added was 37 percent of the total weight of cellulose present. This mixture was rotated in an air-tight drum for 1.5 hours.

Xanthation - The above reaction.

Water Washed - Samples were placed in beakers containing 600 cc. of water and the water was changed when it became colored. This procedure was continued until the sample imparted no color to the water.

Acid Washed - The samples were placed in beakers containing ten percent sulfuric acid and were allowed to remain until all color was removed from the sample.

Experiment 1

The Kneading Action

Two-hundred and twenty-two grams of xanthate was kneaded on the kneading rolls until it became too stiff to handle.

A sample of the kneaded material was treated with ten percent sulfuric acid until completely regenerated. The sample was then washed with water until free of acid and allowed to dry.

A second sample was treated in the same manner and was boiled in a .5 percent water solution of sodium sulfide.

A third sample was allowed to dry in air without treatment except the drying action.

Results:

Sample 1 was plastic while wet but on drying became hard and brittle.

A part of sample 1 was examined under the microscope. This examination showed that the fiber form had been destroyed.

Sample 2 could not be cleared up by the boiling solution.

Sample 3 became very hard, had no plasticity, and the sodium salts reacted with the CO_2 in the air to give a film of sodium carbonate.

Experiment 2

Kneading Form Required to Destroy Fiber Form

Four fifty-gram samples of xanthate were used and each sample was kneaded on the rolls for different lengths of time. The kneaded samples were treated with ten percent sulfuric acid until completely regenerated. The samples were then washed free of acid and examined under the microscope.

Sample	Kneading Time in Minutes
1	5
2	10
3	15
4	20

Results:

Samples 1 and 2 on examination under the microscope showed that the fiber form had not been completely destroyed while samples 3 and 4 showed that the kneading time was sufficient to completely destroy the fiber form.

The above samples were dried in the drier at 45° C. and tested for strength by hand examination. The samples showed increased strength as the kneading time increased.

Experiment 3

Effect of Adding Water on Kneading Time

Four fifty-gram samples of xanthate were used and to each sample a varying amount of water was added. The samples were each kneaded on the rolls for a period of 20 minutes, a small sample was taken every five minutes while the material was kneading. This was regenerated in ten percent sulfuric acid, washed, and then examined under the microscope. The time that each sample was kneaded to completely destroy the fiber form was noted.

Sample	CC. Water Added	Kneading Time In Minutes
1	5	15
2	10	10
3	15	5
4	20	5

Results:

The kneading time required to destroy the fiber form decreased as the amount of water added increased.

It required at least five minutes of kneading action before the material became thoroughly plastic.

The above samples were allowed to dry after treatment with the acid and examined for strength. The dried samples indicated that the strength increased as the amount of water added increased.

Experiment 4

The Effect of Kneading with Heated Rolls

Four fifty-gram samples of xanthate were used and each sample was kneaded at different temperatures.* When the samples became too stiff to knead the time was recorded.

Sample	Approx. Temp. ° C.	Time in Minutes
1	40	8
2	75	5
3	90	3
4	100	Too hot

Results:

Sample 4 could not be kneaded due to the rapidity of regeneration of the cellulose.

Sample 1 was regenerated in ten percent sulfuric acid and washed after the sample had been completely regenerated. The sample on examination showed that the fiber form had not been completely destroyed.

The above samples were also treated with ten percent sulfuric acid until completely regenerated, washed free of acid and allowed to dry at 45° C. On examination Sample 1 had the greatest strength with decreasing strength in Samples 3 and 4.

* These rolls could be heated with low pressure steam.

Experiment 5

The Effect of Adding Glycerine

Five forty-gram samples of xanthate were used and to each sample a quantity of glycerine was added. These samples were then kneaded on the kneading rolls for 15 minutes. The kneaded samples were regenerated in ten percent sulfuric acid and by heat at a temperature of 45° C.

Sample	c.c. Glycerine Added	Total Wt. Glycerine in Gms.	$\frac{\text{Glycerine}}{\text{Cellulose}} \times 100$
1	2	2.52	21.2
2	5	6.30	52.5
3	10	12.60	105.0
4	15	18.90	157.4
5	20	25.20	Would not knead

Results:

The glycerine added to the samples prevented to some degree the kneading action on the rolls and this was especially so in samples containing the larger amounts of glycerine.

Sample 5 could not be kneaded due to excess glycerine.

The effect of adding glycerine permitted a much better kneading action without becoming dry.

The glycerine had no noticeable effect on the plasticity of either the acid treated samples or the heat treated samples.

Experiment 6

Attempt to Plasticize with Mineral Oil

This experiment was carried out in the same manner as Experiment 5 with the exception that mineral oil was used instead of glycerine.

Results:

No kneading action could be obtained on the kneading rolls.

Experiment 7

The Characteristics of the Pulp Grinder When Used as a Kneading Machine

One-thousand grams of xanthate were used in this experiment. Two-hundred gram portions were added to the grinder in an effort to determine the minimum amount of xanthate that could be used and still get a maximum kneading action. It was found that it required between 800 and 1000 grams of xanthate to obtain satisfactory results. Also the amount of kneading time required to completely destroy the fiber form was determined by taking samples every ten minutes. This time was found to be between 50 and 60 minutes

In the following work 888 grams of xanthate was used since that was the capacity of the xanthating drum employed.

Experiment 8

Attempt to Plasticize with Mineral Oil

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. Mineral oil was added in five c.c. portions and small samples were withdrawn after each addition had been thoroughly kneaded.

The withdrawn samples were divided into three portions for regeneration:

Portion A - Regenerated with ten percent sulfuric acid, washed with water, dried at 45° C.

Portion B - Regenerated by heat at 45°C. washed with water, dried at 45° C.

Portion C - Regenerated by drying in air at room temperature.

The procedure was adopted as standard regeneration in all subsequent experiments.

Note. When the kneading action was lost due to the addition of the oil, water was added in five c.c. portions until the kneading action reappeared.

Sample	Total c.c. Oil Added	Total Weight Oil Added in Grams	$\frac{\text{Oil}}{\text{Cellulose}} \times 100$
1	5	4.8	2.0
2	10	9.7	4.0
3	15	14.5	6.0
4	20	19.3	8.0
5	25	24.1	10.0
6	30	28.9	12.0
7	35	33.7	14.0

Results:

None of the samples showed increased plasticity, although increased strength was shown in all of the samples. This was assumed to be due to the addition of water to the kneading mixture.

The heat regenerated and water washed sample had the greatest strength.

The air-dried sample was very brittle and reacted with the CO_2 in the air.

Experiment 9

The Effect of Adding Soap

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. Ordinary household granulated soap was added in ten gram portions and small samples were withdrawn after each addition had been thoroughly kneaded.

The samples were treated in the standard manner.

Sample	Total Weight of Soap in Grams	$\frac{\text{Soap}}{\text{Cellulose}} \times 100$
1	10	4.2
2	20	8.3
3	30	12.4
4	40	16.7
5	50	20.9
6	60	25.0
7	70	29.1
8	80	33.3
9	90	37.5
10	100	41.6

Results:

The material showed decreased strength as the weight of the soap increased. This was especially true in the acid treated (A) samples after 50 grams of soap had been added.

The water treated (B) samples showed little change in strength and it was assumed that the soap was dissolved out.

The dry soap was not completely dissolved in the kneading mixture above Sample 6.

Experiment 10

The Effect of Adding Soap Solution

This experiment was conducted in the same manner as Experiment 9 with the exception that the soap was added to the kneading mixture in solution.

The soap solution was made by adding water to 100 grams of soap until a very viscous solution was formed.

Sample	Total Weight Soap Added in Grams	$\frac{\text{Soap}}{\text{Cellulose}} \times 100$
1	10	4.2
2	20	8.3
3	30	12.4
4	40	16.7
5	50	20.9
6	60	25.0
7	70	29.1
8	80	33.3
9	90	37.5
10	100	41.6

Results:

The material was very plastic throughout the experiment while kneading was handled with greater ease.

The greatest strength was exhibited in the acid treatment (A) Sample 5 with decreasing strength thereafter.

There was no apparent increase in plasticity in any of the regenerated samples.

Experiment 11

Attempt to Plasticize with Mineral Oil

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading mixture was added soap solution containing 50 grams of soap. Mineral oil was then added in 10 C.C. portions.

Sample	Total C.C. Oil Added	Total Weight Oil Added in Grams	$\frac{\text{Oil}}{\text{Cellulose}} \times 100$
1	10	9.7	4.0
2	20	19.4	8.0
3	30	28.9	12.0
4	40	38.6	16.0
5	50	48.3	20.0
6	60	58.0	24.0
7	70	67.7	28.0
8	80	Kneading action lost	

Results:

The addition of the soap solution permitted a greater amount of oil to be added to the kneading mixture.

The maximum amount of oil added was 70 C.C. and on the next addition the plastic form was lost and could not be restored by the addition of water.

Sample 6 showed that the oil had been added to excess, shown by an oil film formed on top of the water.

Experiment 12

Effect of Adding an Aluminum Salt

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading mixture was added 50 grams of soap in solution. Ten-gram portions of aluminum sulfate were then added to the kneading mixture but after the second addition the dry salt would not "knead in." The first addition did show that there was a definite reaction.

Experiment 13

Effect of Adding an Aluminum Salt

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading mixture was added 50 grams of soap in solution, and a saturated water solution of aluminum sulfate in portions containing ten grams of the dissolved salt.

Samples were taken and treated in the standard manner.

Sample	Total Weight of Salt in Grams	$\frac{\text{Salt}}{\text{Cellulose}} \times 100$
1	10	4.2
2	20	8.3
3	30	12.4
4	40	16.7
5	50	20.9
6	60	25.0
7	70	29.1
8	80	Plasticity destroyed

Results:

There was a definite reaction between the aluminum salt noted by the hydrogen sulfide gas given off and the change in color of the material.

Increasing amounts of salts decreased the strength noticeably in all samples. Sample 3 (A) showed some strength but samples 4, 5, and 6 rapidly decreased in strength.

No plasticity was shown in any of the dried samples.

Experiment 14

Attempt to Plasticize with Dimethyl Phthalate

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. Dimethyl phthalate was added to the kneading mixture drop by drop and samples were taken after five C.C. portions had been added.

Sample	Total CC Plasticizer Added	Total Wt. Plasticizer in Gms.	$\frac{\text{Plasticizer}}{\text{Cellulose}} \times 100$
1	5	5.95	2.50
2	10	11.90	4.95
3	15	17.85	7.43
4	20	23.80	9.92
5	25	29.75	12.38
6	30	35.70	14.85
7	35	41.65	Plasticity destroyed

Results:

30 C.C. was the maximum amount of plasticizer that could be added. The kneading action was lost and could not be restored by addition of water.

No plasticity was shown in any of the dried samples and all tended to be brittle.

Increasing amounts of plasticizer did not alter the character of the dried samples.

Experiment 15

Attempt to Plasticize with Dimethyl Phthalate and Soap Solution

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To this was added 50 grams of soap in solution. Dimethyl phthalate was added drop by drop to the kneading mixture and samples were taken after five C.C. portions had been added.

Samples were treated in the standard manner.

Sample	Total CC Plasticizer Added	Total Gms. Plasticizer Added	$\frac{\text{Plasticizer}}{\text{Cellulose}} \times 100$
1	5	5.95	2.50
2	10	11.90	4.95
3	15	17.85	7.43
4	20	23.80	9.92
5	25	29.75	12.38
6	30	35.70	14.85
7	35	41.65	17.37
8	40	47.60	19.83
9	45	53.55	22.30
10	50	59.50	Plasticity destroyed

Results:

The addition of the soap solution permitted a greater amount of the plasticizer to be added.

No plasticity was shown in any of the dried samples and all were more brittle than samples from Experiment 14.

Increasing amounts of plasticizer did not alter the character of the dried samples.

Experiment 16

Attempt to Plasticize with Dimethyl Phthalate, Soap Solution and an Aluminum Salt

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To this was added a water solution containing 50 grams of soap and 30 grams of aluminum sulfate. Dimethyl phthalate was added drop by drop to the kneading mixture and samples were taken after five C.C. portions had been added.

Samples were treated in the standard manner.

Sample	Total CC Plasticizer Added	Total Gms. Plasticizer Added	$\frac{\text{Plasticizer}}{\text{Cellulose}} \times 100$
1	5	5.95	2.50
2	10	11.90	4.95
3	15	17.85	7.43
4	20	23.80	9.92
5	25	29.75	12.38
6	30	35.70	14.85
7	35	41.65	17.37
8	40	47.60	19.83
9	45	53.55	22.30
10	50	59.50	24.75
11	55	65.45	Plasticity destroyed

Results:

The addition of the aluminum salt permitted an even greater amount of plasticizer to be added than in Experiment 15.

No plasticity was shown in any of the dried samples and all were more brittle than samples from Experiment 15.

Samples 9 and 10 (B) cleared up well and were of a waxy tough nature.

Experiment 17

Attempt to Plasticize with Tricresyl Phosphate

This experiment was conducted in the same manner as Experiment 14 with the exception that tricresyl phosphate was used as the plasticizer.

Sample	Total CC Plasticizer Added	Total Gms. Plasticizer Added	$\frac{\text{Plasticizer}}{\text{Cellulose}} \times 100$
1	5	5.90	2.45
2	10	11.80	4.90
3	15	17.70	7.35
4	20	23.60	9.80
5	25	29.50	12.40
6	30	35.40	14.75
7	35	41.30	17.20
8	40	47.20	19.65
9	45	53.10	Plasticity destroyed

Results:

The samples had less strength than did the samples from Experiment 14.

The plasticity could not be restored on the addition of water after 40 C.C. of plasticizer had been added.

No plasticity was shown in any of the dried samples and strength decreased slowly as the amount of plasticizer added increased.

Experiment 18

Attempt to Plasticize with Tricresyl Phosphate and Soap Solution

This experiment was conducted in the same manner as Experiment 15 with the exception that tricresyl phosphate was used as the plasticizer.

Sample	Total CC Plasticizer Added	Total Gms. Plasticizer Added	$\frac{\text{Plasticizer}}{\text{Cellulose}} \times 100$
1	5	5.90	2.45
2	10	11.80	4.90
3	15	17.70	7.38
4	20	23.60	9.80
5	25	29.50	12.40
6	30	35.40	14.75
7	35	41.30	17.20
8	40	47.20	19.65
9	45	53.10	22.10
10	50	59.00	24.50
11	55	64.90	27.00
12	60	70.80	Plasticity destroyed

Results:

The soap solution permitted a greater amount of the plasticizer to be added to the mixture.

No plasticity was observed in any of the dried samples. Also the samples had less strength than did the samples of Experiment 17.

Experiment 19

Attempt to Plasticize with Tricresyl Phosphate, Soap Solution and an Aluminum Salt

This experiment was conducted in the same manner as Experiment 16 with the exception that tricresyl phosphate was used as the plasticizer.

Sample	Total CC Plasticizer Added	Total Gms. Plasticizer Added	Plasticizer / Cellulose x 100
1	5	5.90	2.45
2	10	11.80	4.90
3	15	17.70	7.35
4	20	23.60	9.80
5	25	29.50	12.40
6	30	35.40	14.75
7	35	41.30	17.20
8	40	47.20	19.65
9	45	53.10	22.10
10	50	59.00	Plasticity destroyed

Results:

The dried samples had little strength and were very brittle.

Samples 8 and 9 (A) and (B) crumbled on touch.

No plasticity was observed in any of the samples.

Experiment 20

Effect of Adding Casein (Powdered)

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading xanthate casein was added in ten-gram portions.

Samples were taken and treated in the standard manner.

Samples	Total Grams Casein Added	$\frac{\text{Casein}}{\text{Cellulose}} \times 100$
1	10	4.16
2	20	8.33
3	30	12.50
4	40	16.66
5	50	20.83

Results:

On regeneration of the samples (A) and (B) it was observed that the casein had not been completely dissolved.

The samples had no strength.

Experiment 21

Effect of Adding Casein in Solution

The experiment was conducted in the same manner as Experiment 20 with the exception that ten-grams, portions of the casein in solution was added to the kneading mixture. The casein solution was made by dissolving 100 grams casein in hot 18 percent sodium hydroxide. The solution was cooled and then added.

The samples were treated in the standard manner

Sample	Total Grams Casein Added	$\frac{\text{Casein}}{\text{Cellulose}} \times 100$
1	10	4.16
2	20	8.33
3	30	12.50
4	40	16.66
5	50	20.83
6	60	25.00
7	70	28.16
8	80	33.35
9	90	37.50
10	100	41.66

Results:

The samples increased in strength up to a maximum of 60 grams of casein added after which the strength decreased.

The (B) samples had the greater strength but required a greater length of time for treatment than in any of the previous experiments.

No plasticity was observed in the dried samples.

Experiment 22

Attempt to Plasticize With Dimethyl Phthalate And Casein

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading xanthate was added 60 grams of casein in solution. The plasticizer was added in five C.C. portions to the kneading mixture.

The samples were treated in the standard manner.

Sample	Total CC Plasticizer Added	Total Gms. Plasticizer Added	$\frac{\text{Plasticizer}}{\text{Cellulose}} \times 100$
1	5	5.95	2.50
2	10	11.90	4.95
3	15	17.85	7.43
4	20	23.80	9.92
5	25	29.75	12.38
6	30	35.70	14.85
7	35	41.65	17.37
8	40	47.60	19.83
9	45	53.55	Plasticity destroyed

Results:

The treated samples (A) and (B) had less strength than the samples from Experiment 21 and were very brittle when dry.

The strength of the samples decreased as the amount of plasticizer added increased.

No plasticity was observed in any of the samples when dry.

Experiment 23

Attempt to Plasticize with Tricresyl Phosphate And Casein

This experiment was conducted in the same manner as Experiment 22 with the exception that tricresyl phosphate was used as the plasticizer.

Sample	Total CC Plasticizer Added	Total Gms. Plasticizer Added	$\frac{\text{Plasticizer}}{\text{Cellulose}} \times 100$
1	5	5.90	2.45
2	10	11.80	4.90
3	15	17.70	7.35
4	20	23.60	9.80
5	25	29.50	12.40
6	30	35.40	14.75
7	35	41.30	17.20
8	40	47.20	19.65
9	45	53.10	22.10
10	50	59.00	24.60
11	55	64.90	Plasticity destroyed

Results:

The treated samples (A) and (B) had less strength than the samples from Experiment 21 and were very brittle when dry.

The strength of the samples decreased as the amount of plasticizer added increased.

No plasticity was observed in any of the samples when dry.

Experiment 24

Attempt to Plasticize with Santicizer 8*

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading mixture was added the plasticizer in 10 C.C. portions; the samples were withdrawn and treated in the standard manner.

Sample	Total CC Plasticizer Added	Total Gms. Plasticizer Added	$\frac{\text{Plasticizer}}{\text{Cellulose}} \times 100$
1	10	12.68	5.28
2	20	25.36	10.56
3	30	38.04	15.84
4	40	50.72	21.12
5	50	63.40	26.40
6	60	76.08	31.68
7	70	88.76	36.96
8	80	101.44	42.24
9	90	114.12	47.52
10	100	126.80	52.80

Results:

The plasticizer did not destroy the kneading action at any time-appearing to be soluble in the xanthate.

The (B) samples were unaffected since the plasticizer is soluble in alkaline solutions.

The (A) samples were brittle and strength decreased as the amount of plasticizer added increased.

No plasticity was observed in any of the dried samples.

* Mixture of o and p toluene ethylsulfonamides.

Experiment 25

Attempt to Plasticize with Santicizer 8 and Soap Solution

This experiment was conducted in the same manner as Experiment 24 with the exception that 50 grams of soap in solution was added to the kneading mixture. The plasticizer was then added as in Experiment 24.

Results:

The (A) samples had less strength than the samples from Experiment 24.

The (B) samples were unaffected.

No plasticity was observed in any of the samples.

Experiment 26

Attempt to Plasticize with Santicizer 8, Soap Solution and an Aluminum Salt

This experiment was conducted in the same manner as Experiment 24 with the exception that a solution of 50 grams of soap and 60 grams of aluminum sulfate was added to the kneading mixture. The plasticizer was then added as in Experiment 24.

Results:

The (A) samples had little strength and decreased in strength as amount of plasticizer added increased.

The (B) samples were affected by the addition of aluminum salt and decreased strength was observed as the amount of plasticizer increased.

No plasticity was observed in any of the samples when dried.

Experiment 27

Attempt to Form a Cellulose Gel from Cellulose Pulp

Thirty-two grams of dry pulp, 644 grams water and 136 grams of small flint stones were placed in the ball mill and allowed to beat for 52 hours. The material was examined every four hours under the microscope to determine the degree of beating. This examination was made with small smears of the material placed on a glass slide.

Results:

The material required a total of 52 hours heating time to completely destroy the fiber form.

A white, syrupy material resembling buttermilk was obtained and this material could be filtered by the use of a vacuum filter.

A small sample when placed on a glass slide and allowed to dry at a temperature of 45° C. had great strength but no plasticity.

Experiment 28

Attempt to Plasticize the Material from Experiment 27 with Dimethyl Phthalate

A weight of material from Experiment 27 corresponding to 7.5 grams of actual cellulose, two C.C. dimethyl pthalate, 20 C.C. water, and 200 grams of stones were placed in the ball mill, and allowed to heat for a period of four hours. The beaten material was carefully washed from the ball mill, filtered in a vacuum filter and then dried at 45° C.

Results:

The material crumbled on touch.

Experiment 29

Attempt to Plasticize the Material from Experiment 27 with Tricresyl Phosphate

This experiment was conducted in the same manner as Experiment 28 with the exception that tricresyl phosphate was used as the plasticizer.

The results were the same as in Experiment 28

Experiment 30

Attempt to Plasticize the Material from Experiment 27 with Santicizer 8

This experiment was conducted in the same manner as Experiment 28 with the exception that santicizer 8 was used as the plasticizer.

The results were the same as in Experiment 28.

Experiment 31*

Attempt to Plasticize the Material from Experiment 27 with Santicizer 8 and Sodium Hydroxide

This experiment was conducted in the same manner as Experiment 30 with the exception that 4.5 grams of sodium hydroxide was also placed in the ball mill.

Result:

The dried samples had some strength but no plasticity was observed.

* A new batch of material was made in the same manner as Experiment 27.

Experiment 32

Attempt to Plasticize the Material from Experiment 27 with Santicizer 8 and Soap Solution

This experiment was conducted in the same manner as Experiment 31 with the exception that five grams of soap in solution was also placed in the ball mill.

Results:

The material could not be filtered and no sample could be obtained. The material was discarded.

Experiment 33

A Cellulose Gel prepared from a Viscose Solution and Then Beaten in the Ball Mill

Two-hundred and twenty-two grams of xanthate was made into viscose solution containing 7.5 percent cellulose and 6.5 percent sodium hydroxide (these percentages were calculated.) This solution was allowed to gel by placing in a constant temperature of 55° C. for ten hours. The gel was then broken up into fine crumbs by grinding in the grinder for three hours.

The ground crumbs were placed in a cloth box and water was allowed to continuously run through the bag, thus washing the material. To completely wash the material required about twenty hours.

A weight of this washed material corresponding to 30 grams of cellulose and 200 grams stones was placed in the ball mill and allowed to heat for three hours. The heating time was sufficient to form a dispersion that resembled soft putty in nature. A sample of this material was placed in the drier and allowed to become thoroughly dry. On examination of the dried material considerable strength was observed but no plasticity.

Experiment 34

Attempt to Plasticize the Viscose Gel with Santicizer 8

In this experiment the beaten material obtained from Experiment 33 was used. A weight of material corresponding to 7.5 grams of cellulose, 2 C.C. of Santicizer 8 and 200 grams of stones were placed in the ball mill and allowed to beat for a period of four hours. The material was then washed out carefully with water and filtered in a vacuum filter. The sample was then dried at 45° C.

Result:

The material crumbled on touching.

Experiment 35

Attempt to Plasticize the Viscose Gel with Santicizer 8 and Sodium Hydroxide

This experiment was conducted in the same manner as Experiment 34 with the exception that 4.5 grams of sodium hydroxide was also placed in the ball mill.

Result:

The material had fair strength but no plasticity when dry.

Experiment 36

Attempt to Plasticize the Viscose Gel with Dimethyl Phthalate

This experiment was conducted in the same manner as Experiment 34 with the exception that dimethyl pthalate was used as the plasticizer.

Result:

Material crumbled when dried.

Experiment 37

Attempt to Plasticize the Viscose Gel with Tricresyl Phosphate

This experiment was conducted in the same manner as Experiment 34 with the exception that tricresyl phosphate was used as the plasticizer.

Result:

The material crumbled when dried.

Experiment 38

Treatment of the Viscose Gel by Washing Free of Water with Acetone

The ground and washed material from Experiment 33 was washed free of water with acetone and an amount of this material corresponding to 30 grams of cellulose and 200 grams of stones were placed in the ball mill. This material was beaten for a period of 40 hours. At the end of this time the material was not completely dispersed so the material was discarded.

Experiment 39

Attempt to Knead the Viscose Gel in the Grinder with Soap

A batch of viscose gel was made up and treated in the same manner as in Experiment 33. The entire batch was placed in the grinder with a soap solution containing 50 grams of soap and permitted to grind for four hours.

Result:

No kneading action could be obtained so the material was discarded.

Experiment 40

Attempt to Plasticize a Lime-Viscose(9) Mixture with Dimethyl Phthalate

Two-hundred and fifty grams of crumbs were aged 48 hours and were then xanthated in the standard manner. The cellulose xanthate so formed was made into a viscose solution containing 7.5 percent cellulose and 6.5 percent sodium hydroxide. This solution was allowed to stand for 24 hours in constant temperatured room at 18° C.

One-hundred-gram samples of the above solution were placed in beakers. To the different samples was mixed 50 grams of lime and varying amounts of plasticizer.

The samples were placed on glass slides and allowed to dry at 45° C.

Sample	Total CC Plasticizer Added	Total Gms. Plasticizer Added	$\frac{\text{Plasticizer}}{\text{Cellulose}} \times 100$
1	1	1.19	15.85
2	2	2.38	31.70
3	5	5.95	79.45
4	10	11.90	158.85
5	15	17.85	248.05
6	20	23.80	317.00

Results:

The dried samples had a light green color and were easily broken.

The addition of plasticizer had little effect on the strength.

The addition of the plasticizer permitted greater ease of mixing.

Experiment 41

Attempt to Plasticize a Lime-Viscose Mixture with Tricresyl Phosphate

This experiment was conducted in the same manner as Experiment 40 with the exception that tricresyl phosphate was used as the plasticizer.

The results were the same as in Experiment 40.

Experiment 42

Attempt to Plasticize a Lime-Viscose Mixture with Santicizer 8

This experiment was conducted in the same manner as Experiment 40 with the exception that Santicizer 8 was used as the plasticizer.

The results were the same as in Experiment 40.

Experiment 43

Attempt to Plasticize with Linseed Oil

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading xanthate was added commercial linseed oil in five C.C. portions.

The use of the air-dry sample was discontinued and the procedure was to place the sample in the drier at 45° C. until completely dry, and then treat with ten percent sulfuric acid. This will be the standard method in subsequent experiments.

Samples were withdrawn and treated in the standard manner.

Sample	Total C.C. Oil Added	Total Grams Oil Added	$\frac{\text{Oil}}{\text{Cellulose}} \times 100$
1	5	4.65	1.94
2	10	9.34	3.88
3	15	13.99	5.72
4	20	18.64	7.76
5	25	23.29	9.70
6	30	27.90	Plasticity destroyed

Results:

The addition of the linseed oil caused an oily appearance to be imported to the kneading mixture with no indication that the oil was dissolving or reacting with the xanthate.

The acid-treated samples (A) crumbled on touching while the water-treated samples (B) had considerable strength and could be molded or caused to assume different shapes by the treatment under heat and pressure. The treated samples (C) crumbled on touch when dry. No plasticity was found in any of the

Experiment 44

Attempt to Plasticize with Castor Oil

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading mixture was added castor oil in ten C.C. portions.

The samples were withdrawn and treated in the standard manner.

Sample	Total C.C. Oil Added	Total Grams Oil Added	$\frac{\text{Oil}}{\text{Cellulose}} \times 100$
1	10	9.68	4.03
2	20	19.36	8.10
3	30	29.04	12.12
4	40	38.72	16.15
5	50	48.40	20.18
6	60	58.08	24.21
7	70	67.76	28.23
8	80	77.44	32.26
9	90	87.12	36.29
10	100	96.80	40.32
11	120	116.16	48.36
12	140	134.52	56.42
13	160	154.95	64.50
14	180	174.24	72.54
15	200	193.60	80.60

Results:

The oil apparently dissolved in the xanthate as the plasticity was retained throughout the experiment.

The acid-treated samples (A) had considerable strength but no plasticity when dry.

The water-treated samples (B) had some plasticity, the maximum effect being in Samples 8 and 9.

The acid-treated (C) samples had decreased strength.

Experiment 45

Attempt to Plasticize with Oleic Acid

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading xanthate was added oleic acid in ten C.C. portions.

The samples were withdrawn and treated in the standard manner.

Sample	Total C.C. Acid Added	Total Grams Acid Added	$\frac{\text{Acid}}{\text{Cellulose}} \times 100$
1	10	8.54	3.55
2	20	17.08	7.10
3	30	25.62	10.65
4	40	34.16	14.20
5	50	42.70	17.75
6	60	51.24	21.30
7	70	59.88	24.85
8	80	68.32	28.40
9	90	76.86	31.95
10	100	85.40	35.50
11	120	102.48	42.65
12	140	119.56	49.70
13	160	136.64	56.80
14	180	154.72	63.90
15	200	170.80	71.00

Results:

The acid apparently dissolved in the xanthate as the plasticity was retained throughout the experiment.

The acid-treated samples (A) had decreased strength after Sample 7. These samples were very brittle. The water-treated samples (B) had greater strength than the (A) samples. The acid-treated (C) samples had less strength than any of the dried samples.

No plasticity was found in any of the samples when dry.

Experiment 46

Attempt to Plasticize with Hercolyn

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading mixture was added hercolyn in ten C.C. portions until a maximum of 80 C.C. had been added. Then oleic acid was added in ten C.C. portions.

The use of the acid-treated samples (A) was discontinued and only the (B) and (C) samples will be discussed in the following experiments.

Sample	Total CC Hercolyn Added	Total Gms. Hercolyn Added	CC Oleic Acid Added	$\frac{\text{Hercolyn}}{\text{Cellulose}} \times 100$
1	10			
2	20			
3	30			
4	40			
5	50			
6	60			
7	70			
8	80			
9	80		10	
10	80		20	
11	80		30	
12	80		40	
13	80		50	
14	80		60	

Results: The water-treated samples (B) swelled considerably in water and crumbled on touch when dry.

The acid-treated samples (C) did not swell but crumbled on touch when dry.

The addition of the oleic acid restored the strength to both (B) and (C) samples. These samples did not swell but were very brittle when dry.

Experiment 47

Attempt to Plasticize with Stearic Acid

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading mixture was added five grams of stearic acid dissolved in 25 C.C. of carbon disulfide.

The samples were withdrawn in the standard manner, but were regenerated in the steam vessel with low-pressure steam.

The regenerated samples were divided into two portions and treated in the following manner.

Portion A - The salts present were dissolved with ten percent sulfuric acid, the sample was washed with water and dried at 45° C.

Portion B - The salts present were dissolved with water and sample was dried at 45° C.

This procedure was adopted as standard treatment in all subsequent experiments.

Sample	Total Grams Acid Added	$\frac{\text{Acid}}{\text{Cellulose}} \times 100$
1	5	2.08
2	10	4.16
3	15	6.24
4	20	8.32
5	25	10.40
6	30	12.48
7	35	14.56
8	40	16.64
9	45	18.72
10	50	20.80

Results:

The steam regeneration permitted quicker penetration in the (A) and (B) samples. Also the swelling of the samples in the water-treated (B) samples was decreased.

The strength of the samples decreased as amount of acid added increased.

No plasticity was found in any of the samples when dry.

Experiment 48

Attempt to Plasticize with Pure Linseed Oil

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading mixture was added five C.C. portions of linseed oil in an emulsified solution with viscose. This solution was made by adding five C.C. oil to 25 C.C. viscose solution and stirring for five minutes with a high-speed stirrer.

The samples were withdrawn and treated in the standard manner.

Samples	Total C.C. Oil Added	Total Gms. Oil Added	$\frac{\text{Cellulose}}{\text{Oil}} \times 100$
1	5	4.65	1.94
2	10	9.34	3.88
3	15	13.99	5.72
4	20	18.65	7.76
5	25	23.29	9.70
6	30	27.90	11.64
7	35	32.55	13.58
8	40	37.36	15.52
9	45	42.01	17.46
10	50	46.70	19.40
11	55	51.35	Plasticity destroyed

Results: The effect of adding the linseed oil in a mixture with viscose permitted more oil to be added with greater ease. The acid-treated (A) samples had less strength as the amount of linseed oil increased and no plasticity when dry. The water-treated samples (B) had more strength than the (A) samples and could be molded to some degree on heating. All the samples became very brittle when dried.

Experiment 49

Attempt to Plasticize with Oleic Acid

This experiment was conducted in the same manner as Experiment 45 with the exception that the samples were regenerated in the steam vessel.

Results:

The results were the same as in Experiment 45 but the steam regeneration permitted greater ease of penetration in the treatment of the samples. This was especially so with the water-treated (B) samples.

Experiment 50

Attempt to Plasticize with Castor Oil

This experiment was conducted in the same manner as Experiment 44 with the exception that the samples were regenerated in the steam vessel.

The samples were withdrawn and treated in the standard manner.

Results:

The water-treated (B) samples had no plasticity when dried, contrary to the results in Experiment 44. The (B) samples of the experiment were reexamined and no plasticity was observed. It is concluded then that the samples when treated were not completely dry.

Experiment 51

Attempt to Plasticize with Castor Oil and Nonane Glycol

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading xanthate was added 80 C.C. castor oil and varying portions of nonane glycol.

The samples were withdrawn and treated in the standard manner.

Sample	Total C.C. Nonane Glycol Added
1	5
2	10
3	20
4	30
5	50

Results:

The nonane glycol apparently had no effect on the mixture as the samples had the same characteristics as Sample 8 (A), (B) from Experiment 44.

Experiment 52

Attempt to Plasticize with a Mixture of Dimethyl Pthalate and Cellulose Acetate

Eight-hundred and eighty-eight grams of xanthate was placed in the grinder and allowed to knead for one hour. To the kneading xanthate was added ten grams in portions of a mixture of dimethyl pthalate and cellulose acetate.* This mixture was made by adding 25 grams of cellulose acetate to 100 grams of dimethyl pthalate and heating until complete solution. The solution was then cooled before adding.

The samples were withdrawn and treated in the standard manner.

Sample	Total Grams Mixture Added
1	10
2	20
3	30
4	40
5	50
6	60
7	70
8	80
9	90
10	100

Results: The samples when withdrawn from the steam vessel had the appearance of crepe rubber but on treatment with water (B) became very brittle. The acid-treated samples (A) were very brittle and had little strength but the water tested samples (B) had considerable strength but no plasticity. The samples could be molded to some degree with heat. This effect increased as the amount of mixture added increased.

* On addition of some portions the plasticity was destroyed but could be restored by adding 5-10 C.C. water.

Experiment 53

Investigation of a Quaternary Ammonium Compound and Cellulose

The quaternary ammonium compound used in this experiment was benzyl trimethyl ammonium hydroxide in a 42 percent solution which is capable of dispersing cellulose. If this solution is diluted it will swell the cellulose.(10)

Two-hundred grams of pulp was cut into small pieces and placed in a large jar with a mixture of 200 C.C. of water and 200 C.C. of benzyl trimethyl ammonium hydroxide. This was tumbled for one hour and then placed in the grinder and allowed to grind for three hours.

Result: The mixture had swollen only slightly and the fiber form could not be destroyed by the kneading action.

Three 100 C.C. portions of the 42 percent solution was added to the mixture and allowed to grind for one hour each.

Result: The cellulose was still only slightly swollen and fiber form was still present.

The above mixture was allowed to grind overnight and an attempt was made to xanthate this material by the addition of carbon disulfide. The grinder was made airtight and the carbon disulfide added and allowed to grind for two hours. It was then examined and a yellow color had been imparted to the mixture. More carbon disulfide was added and the mixture allowed to grind for 20 hours. The fiber form was still present and could not be destroyed by the kneading action.

CONCLUSIONS

The results obtained in all of the preceding experiments emphasize the difficulty which is encountered in the attempt to plasticize a cellulose xanthate and the removing of the salts formed in the xanthate formation. The removal of the salts in the water treatment (B) required large amounts of water which also seemed to remove the plasticizer. Some of the plasticizers were soluble in alkaline solutions and in the dissolving out of the salts, the dissolved salts caused high causticity, thus removing the plasticizer also.

The acid-treated samples (A) and (C) required from three to four hours to completely dissolve the salts present in the sample. This treatment probably caused a high degree of degradation since all of the samples were brittle and had less strength than the water-treated samples.

Since the results of the investigation are all negative in so far as the main object was concerned, it is concluded that a plasticized cellulose cannot be obtained from cellulose xanthate using the plasticizers and methods set forth in this investigation.

BIBLIOGRAPHY

1. G. A. Richter. Purified Wood Fiber, Industrial And Engineering Chemistry, Vol. 23, No. 3. (1931) p. 266.

2. F. B. Sutphin. B. S. Thesis, presented to Dr. P. C. Scherer, Va. Poly. Inst. (1933) Sheets Manufactured from Pure Xanthate and Viscose Mixed with Pulp.

3. Clark. Applied X-Rays. McGraw Hill Book Co., New York and London (1940), 3rd ed., p. 607.

4. Gilman. Organic Chemistry. John Wiley and Sons, New York (1943) Vol. II, 2nd ed., p. 1712.

5. Meyer and Mark. "Aufbau der Hochpolymeren Organischen Naturstoff," Akad. Verlags-Ges., Leipzig (1930).

6. Doree, C. The Methods of Cellulose Chemistry. D. VanNostrand Company (1933). P. 92.

7. Miller, David W., M. S. Thesis, Va. Poly. Inst. (1938).

8. Scherer and Lin. Rate of Xanthation of Soda Cellulose, Rayon Textile Monthly (1939).

9. Scherer and Radspinner. M. S. Thesis, Study of Insulating Material from Lime and Viscose (1939).

10.