

THE EFFECT OF VARIOUS SPINNING BATHS ON THE CROSS-SECTION
AND PHYSICAL PROPERTIES OF VISCOSE RAYON
FROM PINE PULP

A Thesis
Submitted for the Degree
of
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by
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Abstract

The effect of various concentrations and combinations of salts in the spinning bath on the physical properties and cross-section of rayon fibers is shown. Photomicrographs of the cross-sections are shown. The breaking strength and elongation of the fibers are improved by the addition of zinc and magnesium sulfates.

Purpose

This thesis was undertaken as a phase of the work of the State Engineering Experiment Station on the suitability of pine pulp for the production of viscose rayon. Previous to the work contained herein, only two types of spinning baths were used. These were a sulfuric acid - sodium sulfate - glucose bath and a sulfuric acid - sodium sulfate - zinc sulfate - glucose bath. The effect of the variations of the spinning bath on the serimetric properties of the rayon was not studied. The purpose of this thesis is to show the types of cross sections of the fiber that may be obtained with varying concentrations of different salts and to study the effect on the breaking strength and elongation of the pine rayon.

Introduction

The effects of the spinning process on the properties of the rayon is linked up with the colloidal properties of the viscose. Moore (1), in his review of viscose coagulation, explains the mechanism of coagulation. He states that the colloidal condition of the viscose just before spinning approaches the state of auto-coagulation. The dispersed cellulose is just adequately protected by the cellulose xanthate, which acts as a protective colloid. The colloidal particle consists of regenerated cellulose together with cellulose xanthate which has not been decomposed during the ripening period. The mechanism of hydration may be regarded as a localized swelling of the particle together with the retention of a surrounding film of water. Hydration in this case is the orientation of dipolar water molecules of which the first layer is firmly attached to the colloidal particle, and is called the concrete layer. The succeeding layers of water are attached and oriented to an increasingly less extent. As the distance from the particle increases, the orienting forces become weaker and there is a gradual change from oriented to unoriented water. This volume is named the diffuse water layer. The condition of the dispersion is stable because in a physical arrangement of this type the drop of free

(1) C. L. Moore, Silk and Rayon, 19 (1925).

surface energy is small, the particles possessing a concrete and a diffuse water layer. Upon the loss of the hydration centers, caused by the regeneration of the cellulose at the expense of the cellulose xanthate, or by direct dehydration, the diffuse water layer will be removed first. There is formed between the oriented and unoriented water an interface in which there is a large drop in free energy. The dispersion thereby loses stability. The colloidal particles enveloped in a concrete water layer only unite, and on continued dehydration finally coagulate.

In spinning, the ripened viscose is forced through the fine holes of the spinneret into the coagulating bath. Hase (2) states that the fine viscose streams change immediately into viscose gel by neutralization, dehydration, and decomposition. The above changes are in the first instance confined to the surface of the filament. The gel so formed is then further dehydrated and decomposed inward from the outer skin of regenerated cellulose. Reinthaler (3) states that in the acid spinning bath the dehydration effect is due to the astringent action of the salts present. This effect causes gelation, which is followed by a decomposition effect of the free acid which results in the regeneration of the

- (2) Shin-ichiro Hase. J. Soc. Chem. Ind., Japan 35, Suppl. Binding, 459(1932).
- (3) Franz Reinthaler-F. M. Rowe. Artificial Silk, p. 87.

cellulose. Sobue(4) believes that the mechanism of the spinning process consists of the decomposition of the viscose, the regeneration of the cellulose at first in the contacting layer, then the diffusion of the alkali in the viscose thread into the bath and the beginning of the coagulation of the viscose at the surface on account of a decrease in alkali, and finally of the mutual neutralization of the alkali of the inner part and the acid of the outer part by diffusion.

The first type of viscose spinning bath used was the coagulation of the viscose in a bath of ammonium sulfate, followed by decomposition in dilute sulfuric acid. As this process was imperfect and too expensive, it was replaced by the so-called "acid spinning process." The use of sulfuric acid alone did not give the best results. Mueller(5) introduced the "acid-salt spinning process", and added to the acid bath soluble sulfates of the type of sodium sulfate, ammonium sulfate, magnesium sulfate, and zinc sulfate. In general, the acid liquor consists of the acid and the above mentioned salts added singly or in combination. A carbohydrate is also added in the majority of cases. This is usually added in the form of glucose, and its function, according to Reinthaler(6), is to protect the surface of the cellulose

(4) Hiroshi Sobue. J. Soc. Chem. Ind., Japan 38, Suppl. Binding 474-7(1935).

(5) G. P. 187497 of 1905.

(6) Reinthaler-Rowe, Artificial Silk, P. 88.

from the persistent action of the acid, to prevent salts from crystallizing on the filaments, and to assist in the solution of the gases evolved during spinning.

The composition of the spinning bath liquor has an important effect on the coagulated filaments. The speed of coagulation and the complexity of the shape of the cross sections of the filaments are related to the percentages of constituents used.

Hase(7) has shown that the coagulation velocity of viscose is retarded in sulfate coagulation liquors. The retarding effect is in the increasing order of $Mg < Na < NH_4 < Fe < Zn$. The effect of glucose is approximately the same as that of ammonium sulfate. The effect of a mixture of sulfates is greater than the additive effect.

It has been shown by Hase(8) that the speed of coagulation increases according to the following conditions:

(1) A minimum quantity of alkali is used in the dispersion of the cellulose to form viscose.

(2) The ripening of the viscose is allowed to proceed for the maximum time; in other words, the nearer the colloidal condition of the viscose approximates to the stage of auto-coagulation.

(7) Shin-ichiro Hase. J. Soc. Chem. Ind., Japan 35. Suppl. Binding 277-9(1932).

(8) Ibid., P. 393.

(3) The higher the temperature of the spinning bath.

(4) The longer the distance that the filaments are immersed in the bath.

(5) The acid content of the spinning liquor is higher.

The cross sections of the rayon filaments are influenced by the composition of the spinning bath. When the bath contains metallic sulfates the outline of the cross sections are irregular and indented. This irregularity is due to the astringent action exerted by the salts of the spinning liquor. Lattermose and Schiel(9) state that a thread of viscose upon immersion in the spinning bath immediately becomes covered with a skin of precipitated cellulose which acts as a semi-permeable membrane. The high osmotic pressure of the bath solution causes an outward migration of liquid from within the fiber, whereupon the fiber wall is pressed together. As the osmotic pressure of the bath is increased (by addition of salts) the outer pressure on the fiber is increased, tending to form an irregularly shaped fiber. At the same time the porosity of the fiber is increased.

The irregularity of the cross section can be given a numerical value. This may be done in any agreed manner.

(9) A. Lattermose and Carl Schiel. Z. angew. Chem. 42, 80-1(1930).

Hase(10) has suggested a method that has much to recommend it. Hase's complexity number, λ , is the ratio of the periphery of the section to the circumference of a circle with the same area as that of the cross section. This may be expressed as

$$\lambda = L/L_1 \quad \text{or} \quad \lambda = 0.282 \times L/\sqrt{A}$$

where λ is the complexity, L is the periphery of the section, A is the sectional area, and L_1 is the circumference of a circle having the same area as A . According to Hase(11), the effect of the sulfates on λ is to increase it in the order $\text{NH}_4 < \text{Na} < \text{Mg} < \text{Fe} < \text{Zn}$.

(10) See ref. (7).

(11) Ibid.

Procedure

A. Materials.

Pine pulp from the Pulp and Paper Laboratory, Savannah, Georgia, was used as the cellulose raw material. The constituents of the spinning baths were sulfuric acid, sodium sulfate, magnesium sulfate, zinc sulfate, ammonium sulfate, and glucose. The only other materials necessary for the production of the rayon were sodium hydroxide and carbon disulfide.

B. Apparatus.

No special apparatus was necessary for the preparation of the viscose, the regular experimental equipment being used. A small circulating water bath was attached under the bobbin shaft so that the bobbin could be immersed during spinning. Hard rubber boxes with a capacity of about five liters were used as spinning bath containers.

For the cross-section work, a Spencer rotary microtome, a microscope, and a camera were used.

A Suter Serimeter was used for the physical tests on the rayon.

C. Method.

1. Preparation and spinning of the viscose.

The schedule for the preparation of the viscose was as follows:

Weight of pulp: 600 gms. per batch.

Soaking: 1 hr. at 20°C. in 18% NaOH.

Press Ratio: 2.84

Shredding: 2 hrs. with temp rise to 24 - 26° C.

Aging of Alkali - Cellulose: 92 - 94 hrs. at 20°C.

Xanthation: 3 hrs. Temp. rise to 25 - 28 °C. 1 cc. of CS₂ for each 10 gms. of alkali-cellulose; half added at beginning of xanthation and half at end of first hour.

Dissolving: 2 hrs. at temp of 15°C.

Ripening: 95-97 hrs. at 20°C.

The viscose was spun on the five-jet spinning machine, but only one jet was used in order to keep the conditions constant. The spinning rate was 80 meters per minute. Each bobbin was spun for 15 minutes. The bobbin rotated in a water bath in order to facilitate washing. The temperature of the spinning baths was kept at 45°C. The rayon was washed by placing the bobbins in a large pan of running water and allowing to remain for 24 hours. The yarn was then allowed to air dry.

The spinning liquor was made up in the rubber boxes. The bath with the lowest concentration of acid and salts was made up first. After being used, additions were made to the bath to bring it up to the next concentration. Calculated additions were made to each bath during spinning to keep the concentration as constant as possible.

A sample of the bath was taken for analysis prior to spinning.

With the sulfuric acid content held as constant as possible, runs were made using varying concentrations of a single added salt. Such runs were made using three concentrations each of sodium, magnesium, zinc, and ammonium sulfates, and glucose. Runs were made holding the sulfuric acid and sodium sulfate concentrations constant and varying the amounts of zinc and magnesium sulfates, singly and in combinations. A run was made holding the concentrations of the sodium, zinc, and magnesium sulfates as constant as possible and varying the concentration of the sulfuric acid.

2. Testing of the rayon.

The rayon was twisted with a twist of 2.5 - 3.0 turns per inch. A skein of 450 meters was reeled for denier determinations. Another skein was reeled for the breaking strength determinations. The yarn was conditioned at 70% relative humidity and the breaking and weighing was done in that atmosphere. Twenty breaks were made and the average taken. For the wet strengths, the strands were tied in the clamps and the yarn was wetted by a brush with water containing a little pine oil. All the tests were made on undesulfurized rayon.

3. Cross-section preparation and Photo-micrography.

The thread to be sectioned was first dyed a deep shade with Congo Red. The thread was tied to a wire frame and dipped into a solution of celluloid in acetone. The thread was then allowed to dry.

A candle was then built up on the thread with paraffin. The paraffin was melted in a test tube on a water bath. When all was melted, the paraffin was allowed to cool until the liquid became cloudy about an inch from the bottom of the test tube. The thread on the frame was put in the paraffin and allowed to stay until the whole tube became cloudy. The thread was quickly removed and plunged into ice water. When hardened, the thread was removed and the water wiped off. The same process was repeated over and over until the desired thickness was reached. The candle was kept in water and allowed to season.

The candle was sectioned on a microtome, cutting sections of ten microns thickness. The ribbon that was formed was floated in warm water (lower than the melting point of the paraffin) to flatten out the ribbon. A glass slide was smeared with a thin coating of Meyer's albumen, and the slide was slipped under the ribbon in the water so as to lay the ribbon flat on the slide. The water was allowed to dry off and the slide was warmed gently to allow the albumen to coagulate. Then it was heated further to melt the paraffin and the paraffin was allowed to run off. The remaining paraffin was then dissolved off with benzol.

A drop of Canada Balsam was placed on a cover glass, and this was inverted and placed over the specimen.

The photo-micrographs were taken at a magnification of 1000 diameters. A low light intensity and an exposure of about 15 seconds were used to give greater contrast. Eastman

Commercial Ortho film was used.

An opisometer, or map-measuring instrument, was used to measure the periphery of the cross sections. A planimeter was used to measure the area. Three measurements were made on each section and three sections, where possible, on each photograph were used.

Hase's complexity number is used for irregularity evaluation.

Data Sheets and Photomicrographs

All values for strengths^{*} are given in grams per denier. The values for elongation are in percentages of original length. Spinning bath composition is given in per cent.

Data Sheet No. 1

Fig.	Sample	<u>Spinning Bath Composition</u>				<u>Complexity</u>
		H ₂ SO ₄	Na ₂ SO ₄	MgSO ₄	ZnSO ₄	
1.	E-3-3(4)	9.01				1.025
2.	E-6-16(1)	9.02	11.72			1.122
3.	E-6-16(2)	9.75	20.53			1.129
4.	E-7-8(1)	9.57	28.92			1.092
5.	E-7-5(7)	11.40			(NH ₄) ₂ SO ₄ 11.10	1.098
6.	E-7-5(8)	11.33			21.40	1.093
7.	E-7-5(9)	11.15			32.35 Glucose	1.059
8.	E-7-5(4)	9.98			4.82	1.081
9.	E-7-5(5)	10.16			10.18	1.020
10.	E-7-5(6)	10.11			21.00	1.050
11.	E-7-5(1)	9.44			0.65	1.022
12.	E-7-5(2)	9.62			1.59	1.047
13.	E-7-5(3)	10.01			8.10	1.124
14.	E-7-3(3)	9.79		6.45		1.034
15.	E-7-3(1)	10.12		10.90		1.128
16.	E-7-3(2)	9.73		17.50		1.370
17.	E-7-6(1)	9.42	19.91		0.86	1.656
18.	E-7-6(2)	9.83	19.99		1.55	1.476
19.	E-7-6(3)	10.20	19.85		7.34	1.409
20.	E-7-6(4)	9.24	20.08	3.15		1.335
21.	E-7-6(5)	9.22	20.48	5.74		1.350
22.	E-7-6(6)	9.22	20.53	2.95	1.02	1.566
23.	E-7-6(7)	9.24	20.57	5.75	1.25	1.614

Data Sheet No. 1, Continued

<u>Fig.</u>	<u>Sample</u>	<u>Spinning Bath Composition</u>				<u>Complexity</u>
		H_2SO_4	Na_2SO_4	$MgSO_4$	$ZnSO_4$	
24.	E-7-6(8)	9.43	19.95	3.05	1.79	1.485
25.	E-7-6(9)	9.43	20.16	5.57	2.14	1.651
26.	E-7-7(2)	7.76	21.18	3.19	1.17	1.398
27.	E-7-7(3)	8.82	20.79	3.16	1.15	1.616
28.	E-7-7(4)	10.52	19.78	2.98	1.21	1.464
29.	E-7-7(5)	11.45	20.06	3.08	1.14	1.630
30.	E-7-7(6)	12.69	19.82	3.20	1.13	1.478
31.	E-7-7(7)	14.38	19.65	3.32	1.11	1.264
32.	E-7-7(8)	16.02	19.47	2.98	1.09	1.239
33.	E-7-7(9)	17.92	18.85	2.86	1.05	1.175
34.	E-7-7(10)	19.65	18.29	2.58	1.10	1.165
35.	Commercial Rayon					1.180
36.	Commercial Rayon					1.472

Data Sheet No. 2

Fig.	Spinning Bath Composition				Denier	Strength		Elongation	
	H ₂ SO ₄	Na ₂ SO ₄	MgSO ₄	ZnSO ₄		Dry	Wet	Dry	Wet
1.	9.01				139.0	1.63	0.57	7.4	10.8
2.	9.02	11.72			133.9	1.52	0.55	9.5	16.1
3.	9.75	20.53			133.4	1.71	0.61	9.6	14.5
4.	9.57	28.92			134.7	1.99	0.77	9.2	13.3
5.	11.40			(NH ₄) ₂ SO ₄ 11.10	137.7	1.61	0.53	9.8	13.5
6.	11.33			21.40	136.0	1.62	0.60	8.5	14.2
7.	11.15			32.35 Glucose	136.4	1.69	0.60	9.1	16.3
8.	9.98			4.82	137.1	1.59	0.60	7.2	11.6
9.	10.16			10.18	138.7	1.62	0.59	7.8	11.1
10.	10.11			21.00	134.0	1.64	0.60	8.6	12.4
11.	9.44			0.65	150.6	1.55	0.59	8.7	13.0
12.	9.62			1.59	138.4	1.23	0.56	10.8	16.2
13.	10.01			8.10	139.1	1.60	0.63	11.1	16.3
14.	9.79		6.45		134.1	1.64	0.57	8.1	14.0
15.	10.12		10.90		138.8	1.49	0.53	10.8	20.3
16.	9.73		17.50		141.5	1.81	0.76	7.7	12.4
17.	9.42	19.91		0.86	132.6	1.81	0.69	14.6	25.4
18.	9.83	19.99		1.55	133.5	1.52	0.66	14.9	25.5
19.	10.20	19.85		7.34	136.0	1.77	0.74	14.6	22.8
20.	9.24	20.08	3.15		138.7	1.78	0.62	8.8	11.8
21.	9.22	20.48	5.74		135.0	1.65	0.67	10.6	15.8
22.	9.22	20.53	2.95	1.02	138.1	1.51	0.73	14.9	26.8
23.	9.24	20.57	5.75	1.25	137.9	1.72	0.81	15.4	27.5

Data Sheet No. 2, Continued

Fig.	Spinning Bath Composition				Denier	Strength		Elongation	
	H ₂ SO ₄	Na ₂ SO ₄	MgSO ₄	ZnSO ₄		Dry	Wet	Dry	Wet
24.	9.43	19.95	3.05	1.79	140.6	1.66	0.80	15.9	22.4
25.	9.43	20.16	5.57	2.14	136.6	2.00	0.84	14.6	28.8
	6.49	21.05	3.11	1.04	(Xanthate gel not decomposed).				
26.	7.76	21.18	3.19	1.17	(Rayon too bad to twist).				
27.	8.82	20.79	3.16	1.15	140.9	1.73	0.74	11.6	18.6
28.	10.52	19.78	2.98	1.21	142.8	1.54	0.78	14.7	25.4
29.	11.45	20.06	3.08	1.14	147.0	1.43	0.69	13.3	27.6
30.	12.69	19.82	3.20	1.13	143.8	1.41	0.58	12.9	21.3
31.	14.38	19.65	3.32	1.11	143.9	1.24	0.47	14.9	28.6
32.	16.02	19.47	2.98	1.09	139.9	1.24	0.48	14.4	28.4
33.	17.92	18.85	2.86	1.05	140.7	1.32	0.45	11.2	26.6
34.	19.65	18.29	2.58	1.10	140.8	1.07	0.42	12.2	23.1
35.	Commercial Rayon				151.7	1.19	0.72	18.3	32.7
36.	Commercial Rayon				153.4	1.36	0.79	21.4	30.7

Data Sheet No. 3

Analyses of Viscoses

Batch	NaOH %	Cellulose %	Sulfur %	Viscosity seconds (Taken at	Maturity cc. 10% NH ₄ Cl spinning)
E-7-3	6.47	6.85	2.37	29.0	8.3
E-6-16	6.57	6.81		18.0	10.0
E-7-5	6.57	6.84	2.26	36.8	7.6
E-7-8	6.23	6.62	2.19	19.0	7.1
E-7-6	5.78	6.93		18.0	8.1
E-7-7	6.94	6.89		33.0	8.6

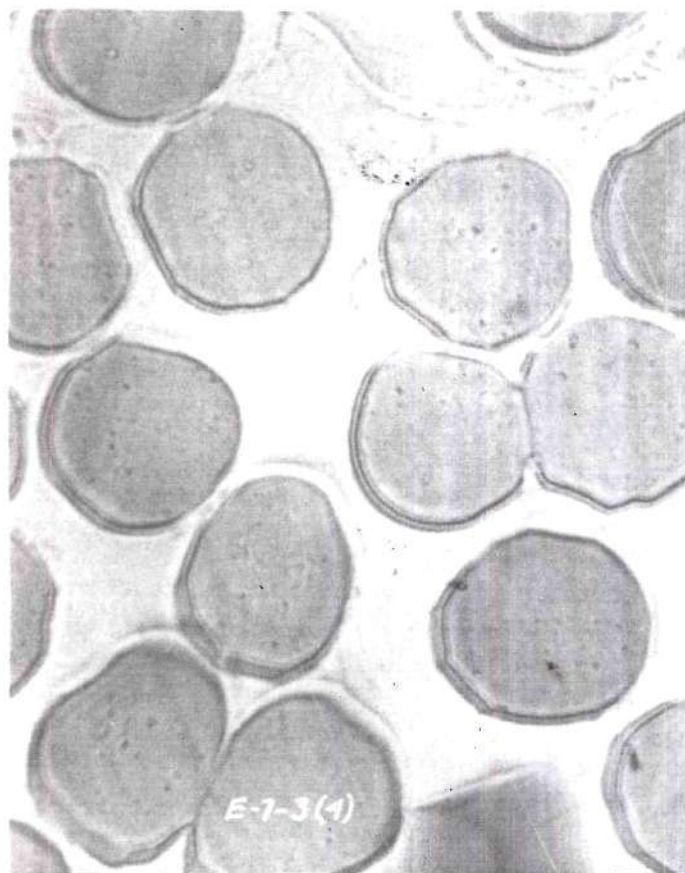


Fig. 1

Sample E-7-3(4)

 H_2SO_4 - 9.01%

Denier - 139.0

Dry Strength - 1.63

" Elong. - 7.4%

Wet Strength - 0.57

" Elong. - 10.8%

Complexity - 1.025

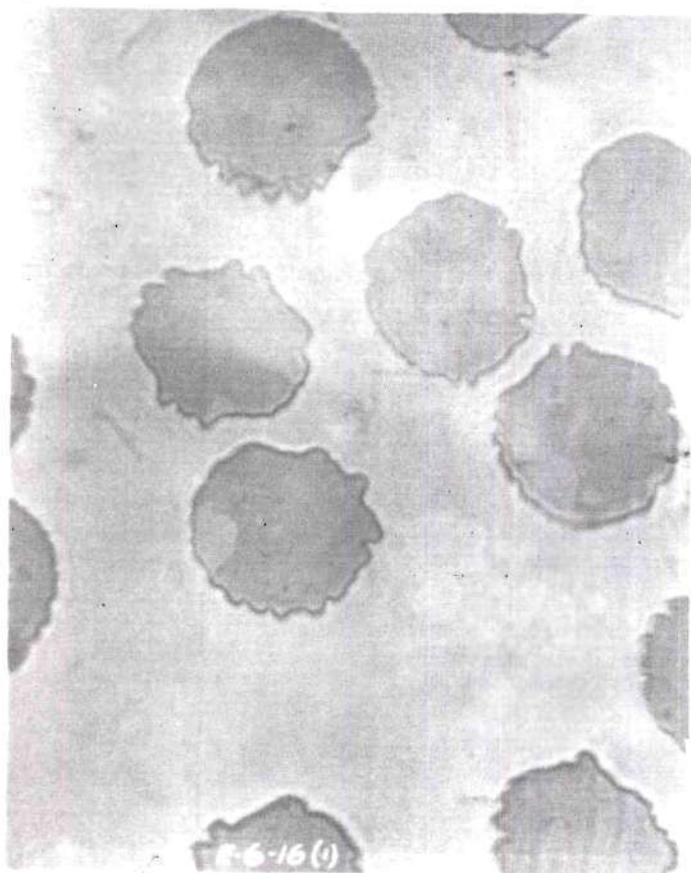


Fig. 2

Sample E-6-16(1)

 H_2SO_4 - 9.02% Na_2SO_4 - 11.72%

Denier - 133.9

Dry Strength - 1.52

" Elong. - 9.5%

Wet Strength - 0.55

" Elong. 16.1%

Complexity - 1.122

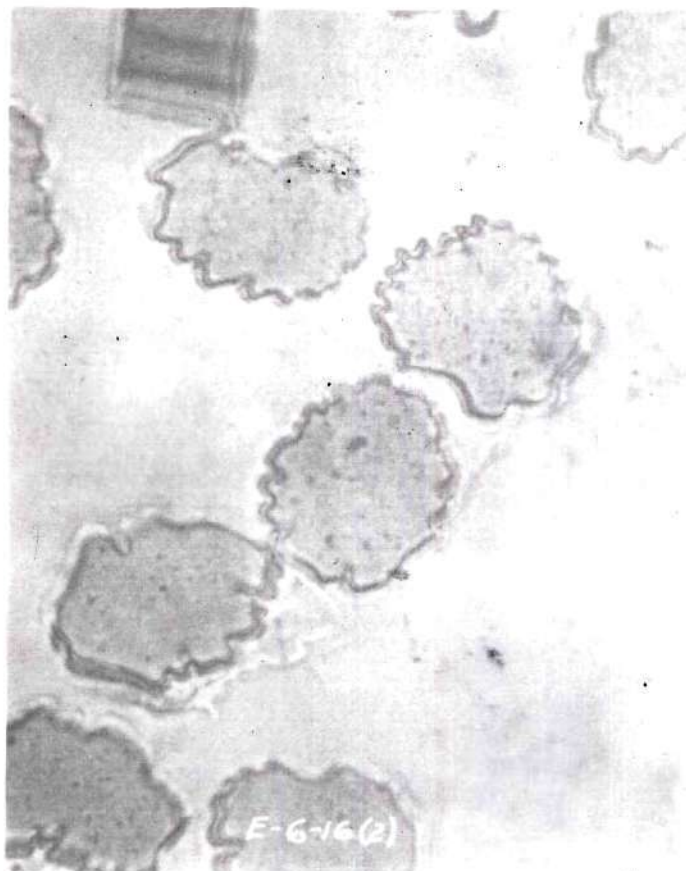


Fig. 3

Sample E-6-16(2)

 H_2SO_4 - 9.75%
 Na_2SO_4 - 20.53%

Denier - 133.4

Dry Strength - 1.71
" Elong. - 9.6%Wet Strength - 0.61
" Elong. - 14.5%

Complexity - 1.129

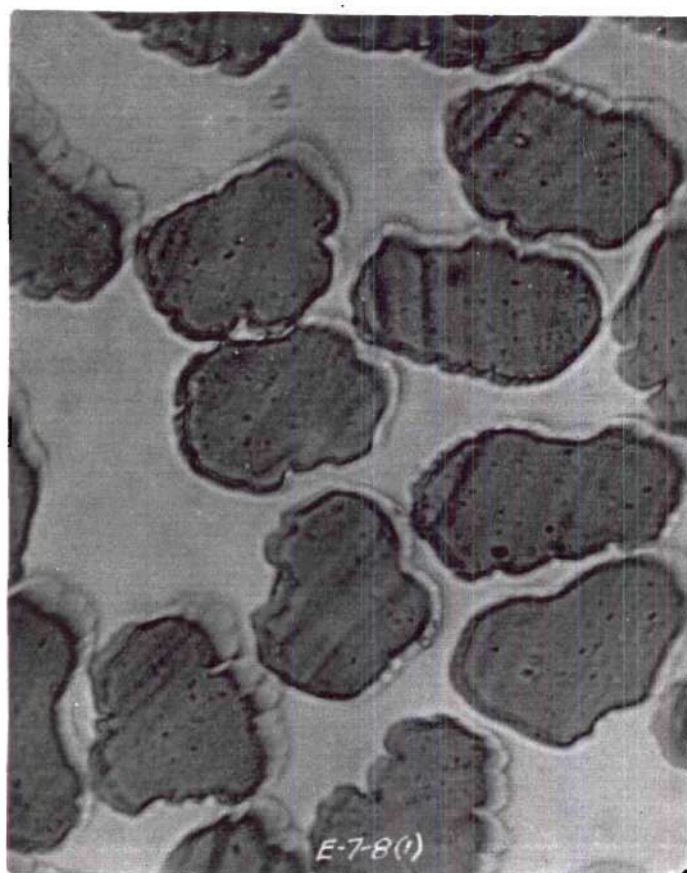


Fig. 4

Sample E-7-8(1)

 H_2SO_4 - 9.57%
 Na_2SO_4 - 28.92%

Denier - 134.7

Dry Strength - 1.99
" Elong. - 9.2%Wet Strength - 0.77
" Elong. - 13.3%

Complexity - 1.092

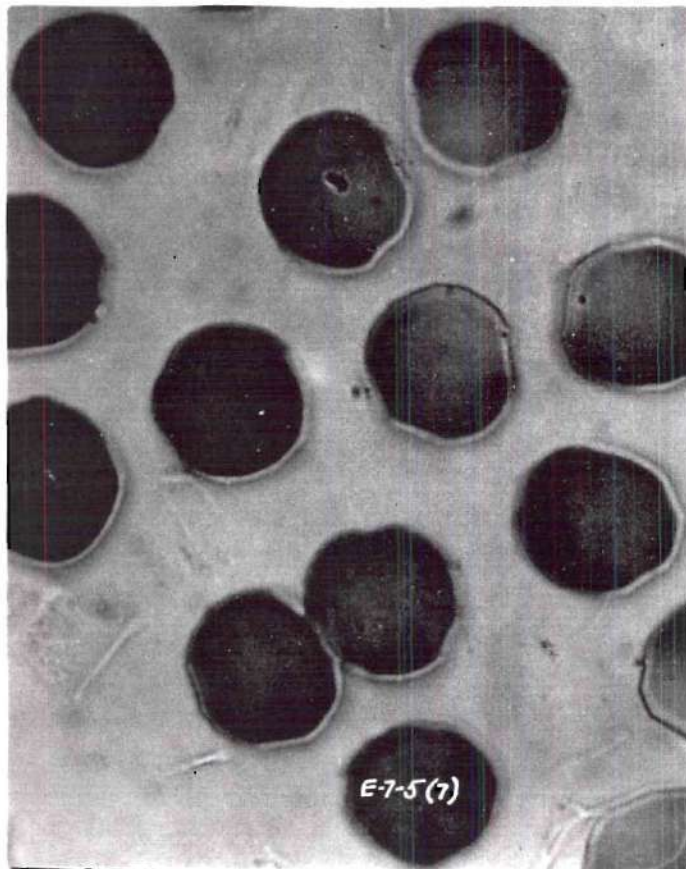


Fig. 5

Sample E-7-5(7)

 H_2SO_4 - 11.40%
 $(\text{NH}_4)_2\text{SO}_4$ - 11.10%

Denier - 137.7

 Dry Strength - 1.61
 " Elong. - 9.8%

 Wet Strength - 0.53
 " Elong. - 13.5%

Complexity - 1.098

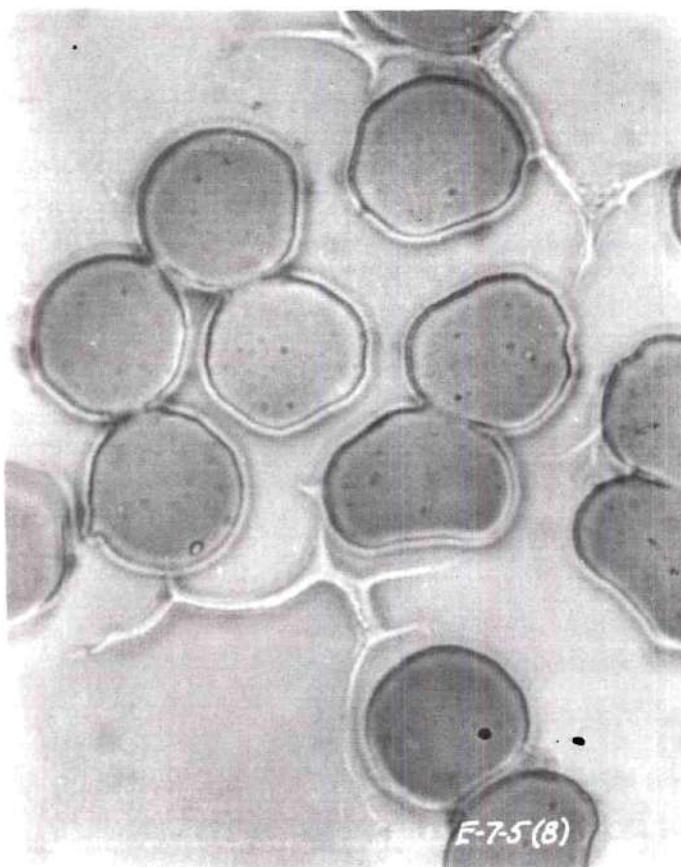


Fig. 6

Sample E-7-5(8)

 H_2SO_4 - 11.33%
 $(\text{NH}_4)_2\text{SO}_4$ - 21.40%

Denier - 136.0

 Dry Strength - 1.62
 " Elong. - 8.5%

 Wet Strength - 0.60
 " Elongation - 14.2%

Complexity - 1.093

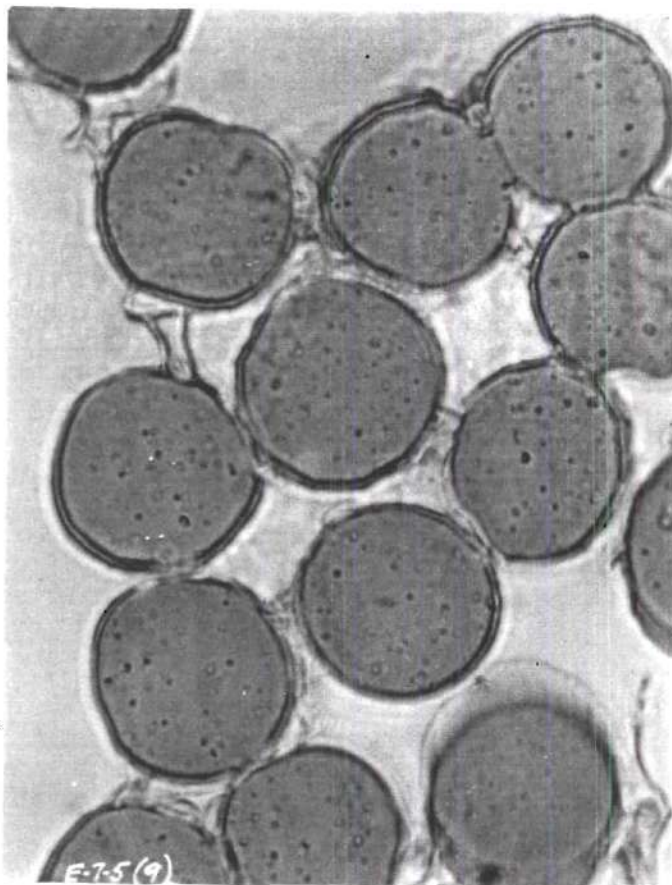


Fig. 7

Sample E-7-5(9)

 H_2SO_4 - 11.15%
 $(\text{NH}_4)_2\text{SO}_4$ - 32.35%

Denier - 136.4

 Dry Strength - 1.69
 " Elong. - 9.1%

 Wet Strength - 0.60
 " Elong. - 16.3%

Complexity - 1.059

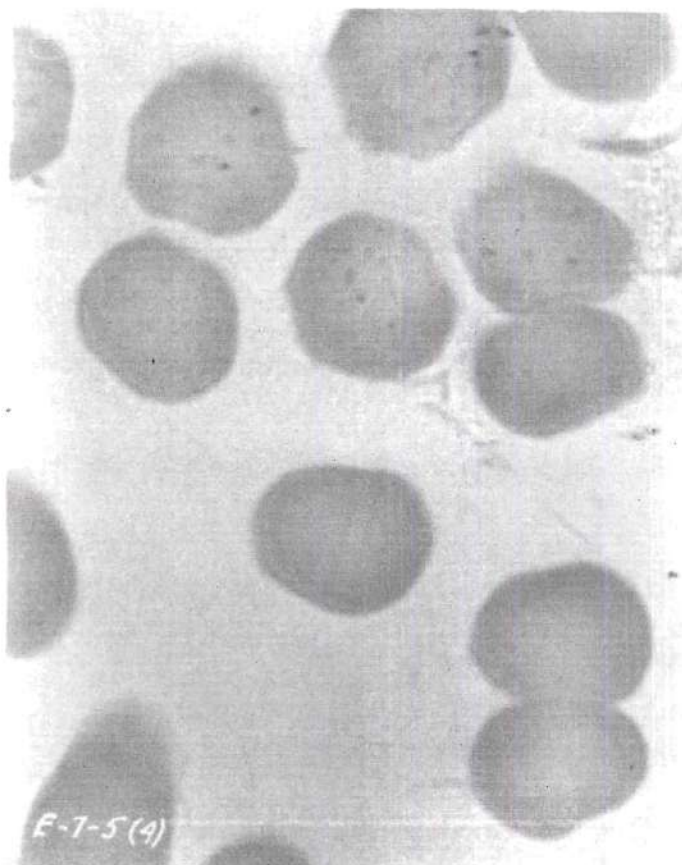


Fig. 8

Sample E-7-5(4)

 H_2SO_4 - 9.98%
 Glucose - 4.82%

Denier - 137.1

 Dry Strength - 1.59
 " Elong. - 7.2%

 Wet Strength - 0.60
 " Elong. - 11.6%

Complexity - 1.081

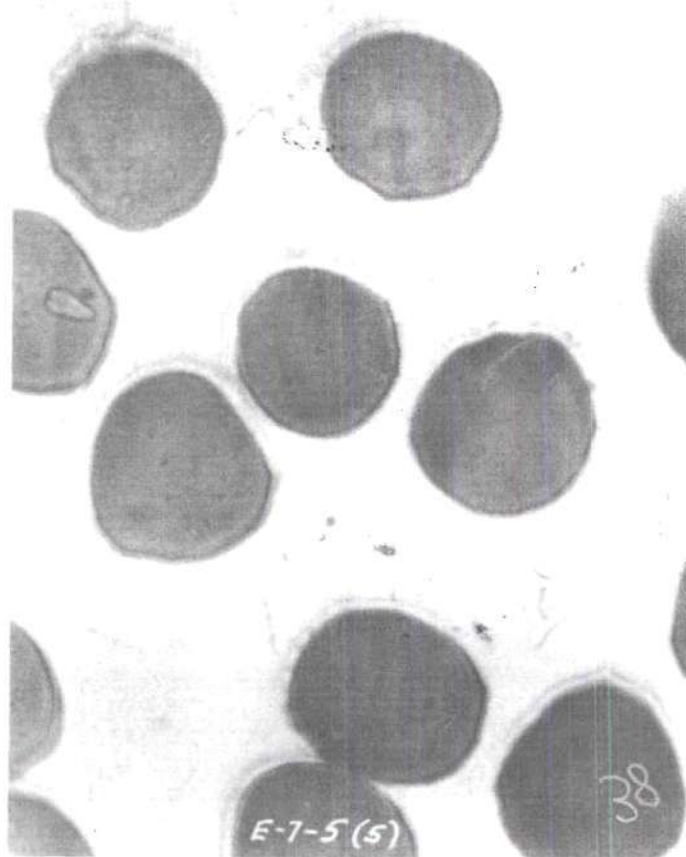


Fig. 9

Sample E-7-5(5)

H_2SO_4 - 10.16%
Glucose - 10.18%

Denier - 138.7

Dry Strength - 1.62
" Elong. - 7.8%

Wet Strength - 0.59
" Elong. - 11.1%

Complexity - 1.020

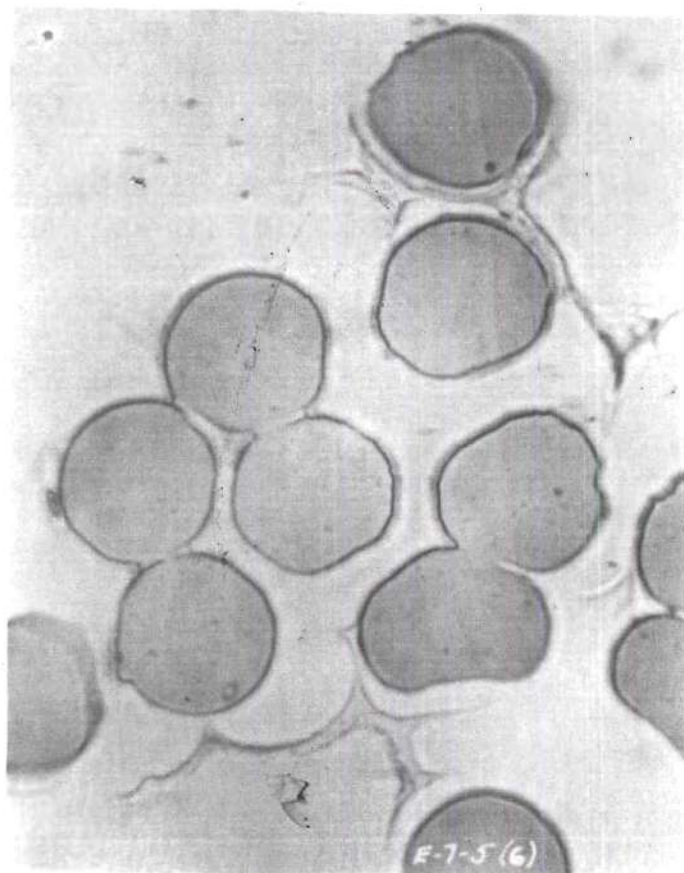


Fig. 10

Sample E-7-5(6)

H_2SO_4 - 10.11%
Glucose - 21.00%

Denier - 134.0

Dry Strength - 1.64
" Elongation - 8.6%

Wet Strength - 0.60
" Elong. - 12.40%

Complexity - 1.050

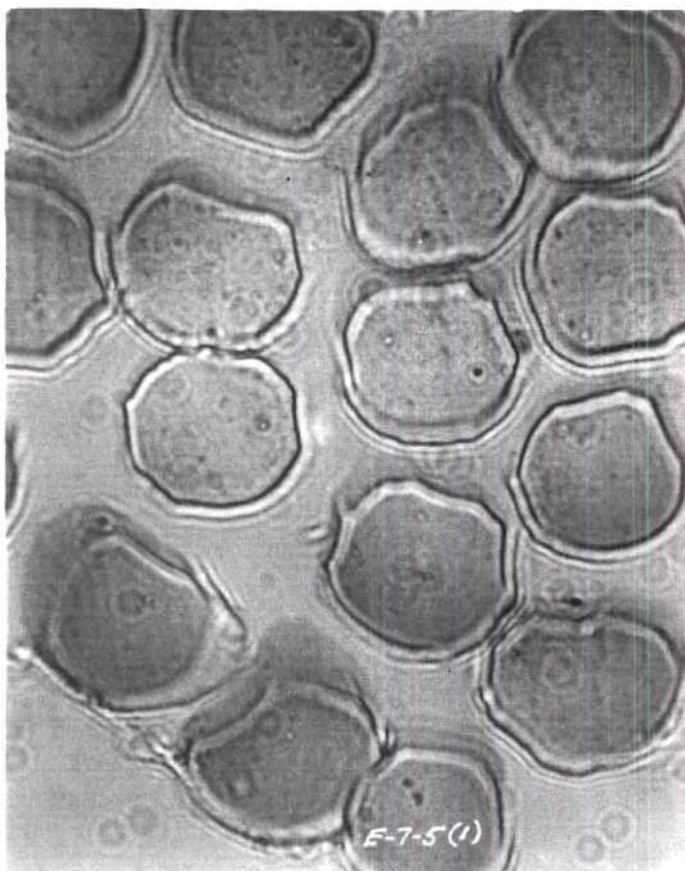


Fig. 11

Sample E-7-5(1)

 H_2SO_4 - 9.44% $ZnSO_4$ - 0.65%

Denier - 150.6

Dry Strength - 1.55

" Elong. - 8.7%

Wet Strength - 0.59

" Elong. - 13.0%

Complexity - 1.022

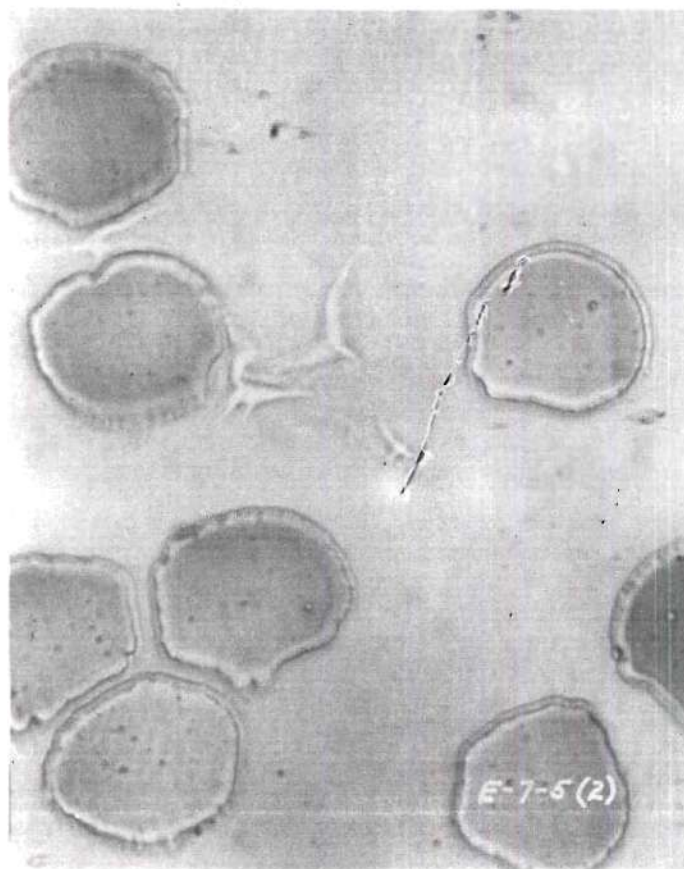


Fig. 12

Sample E-7-5(2)

 H_2SO_4 - 9.62% $ZnSO_4$ - 1.59%

Denier - 138.4

Dry Strength - 1.23

" Elong. - 10.8%

Wet Strength - 0.56

" Elong. - 16.2%

Complexity - 1.047

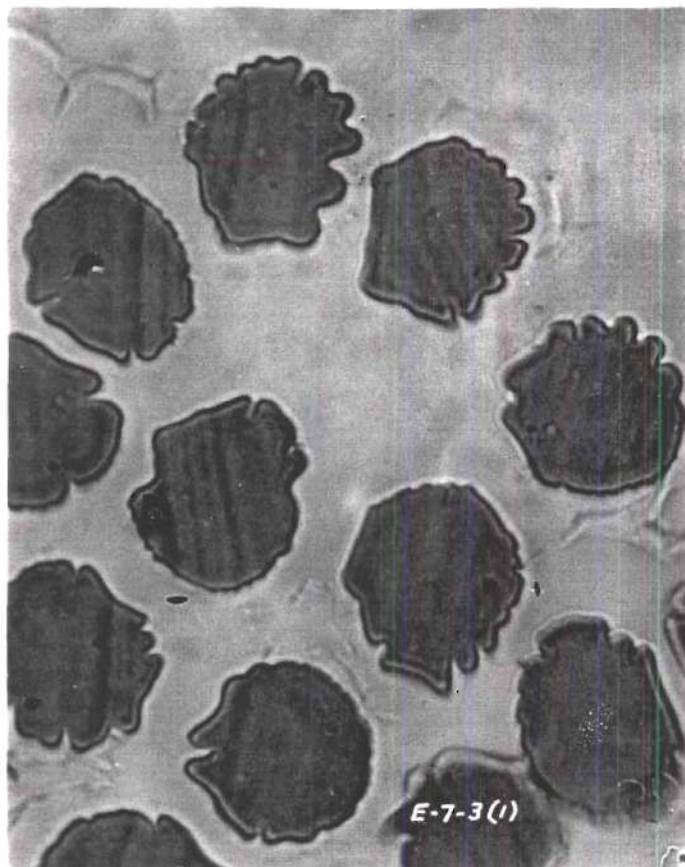


Fig. 15

Sample E-7-3(1)

 H_2SO_4 - 10.12% $MgSO_4$ - 10.90%

Denier - 138.8

Dry Strength - 1.49

" Elong. - 10.8%

Wet Strength - 0.53

" Elong. - 20.3%

Complexity - 1.128

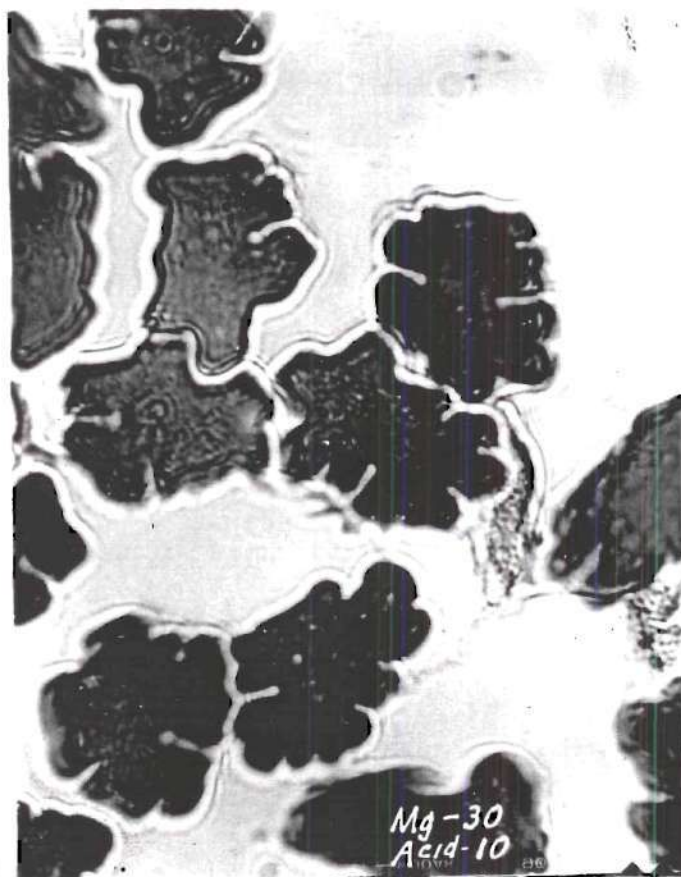


Fig. 16

Sample E-7-3(2)

 H_2SO_4 - 9.73% $MgSO_4$ - 17.50%

Denier - 141.5

Dry Strength - 1.81

" Elong. - 7.7%

Wet Strength - 0.76

" Elong. - 12.4%

Complexity - 1.370



Fig. 17

Sample E-7-6(1)

H_2SO_4 - 9.42%
 Na_2SO_4 - 19.91%
 ZnSO_4 - 0.86%

Denier - 132.6

Dry Strength - 1.81
 " Elong. - 14.6%

Wet Strength - 0.69
 " Elong. - 25.4%

Complexity - 1.656

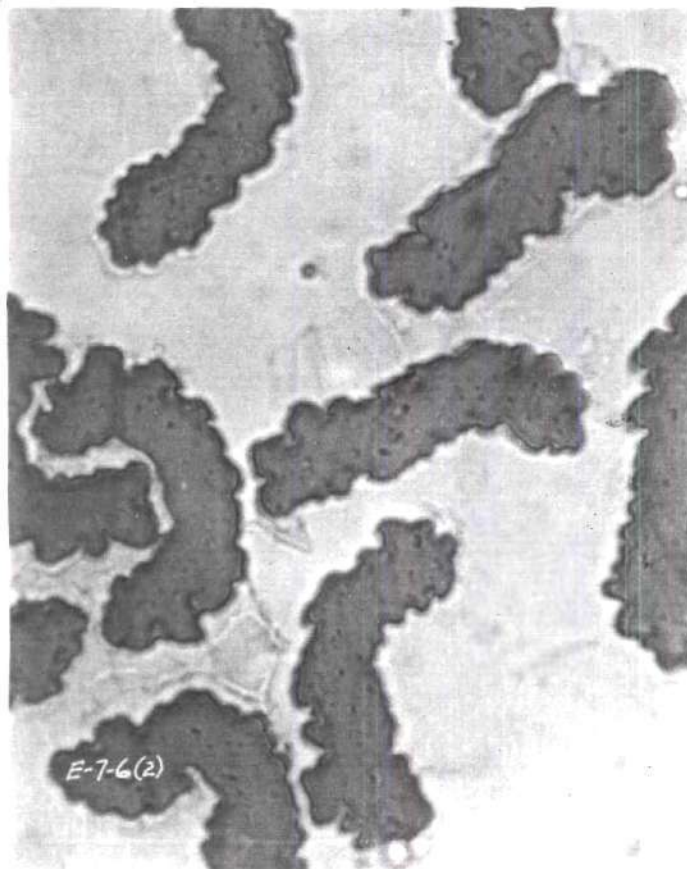


Fig. 18

Sample E-7-6(2)

H_2SO_4 - 9.83%
 Na_2SO_4 - 19.99%
 ZnSO_4 - 1.55%

Denier - 133.5

Dry Strength - 1.52
 " Elong. - 14.9%

Wet Strength - 0.66
 " Elong. - 25.5%

Complexity - 1.476

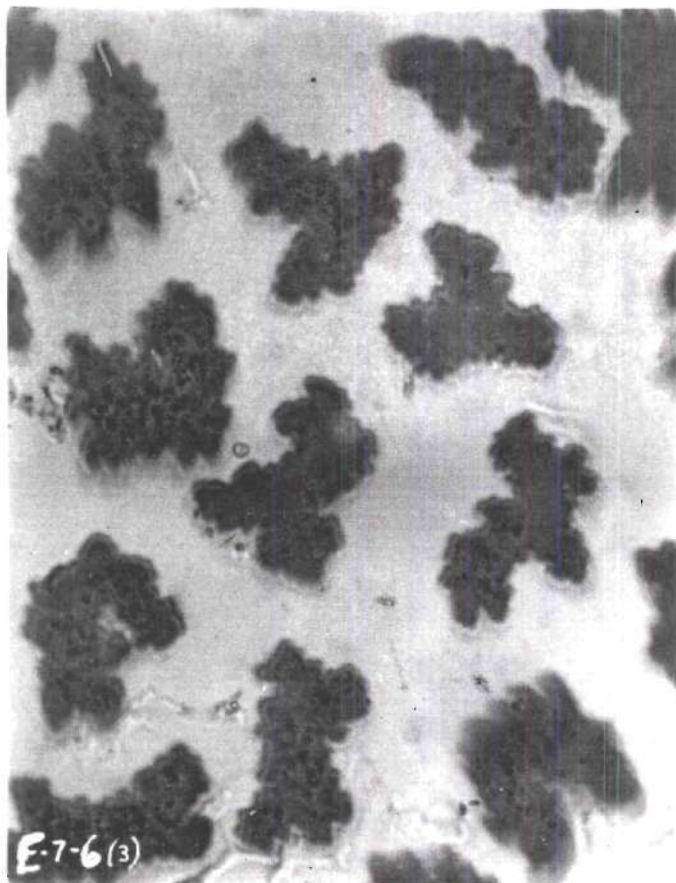


Fig. 19

Sample E-7-6(3)

 H_2SO_4 - 10.20% Na_2SO_4 - 19.85% ZnSO_4 - 7.34%

Denier - 136.0

Dry Strength - 1.77

" Elong. - 14.6%

Wet Strength - 0.74

" Elong. - 22.8%

Complexity - 1.409

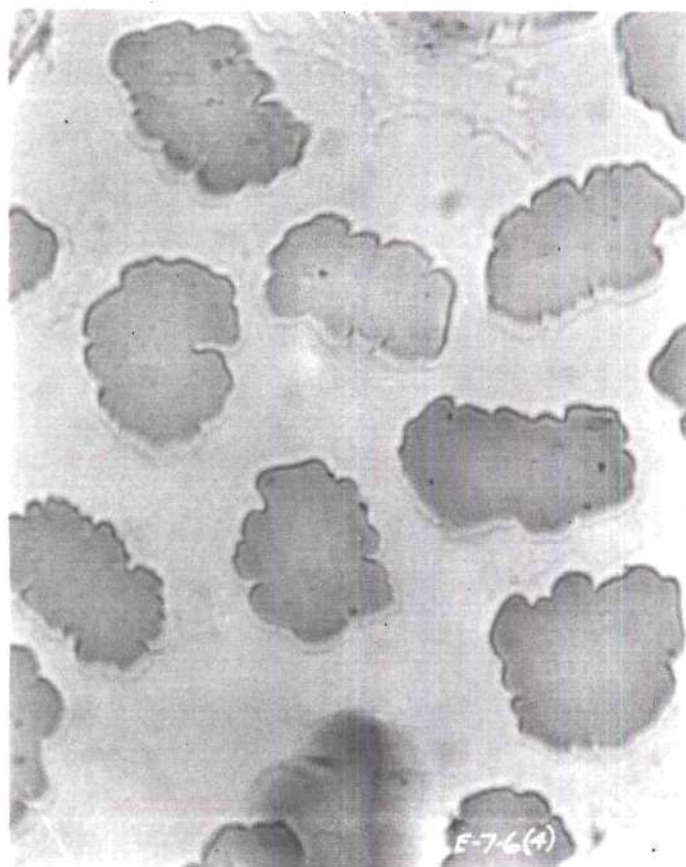


Fig. 20

Sample E-7-6(4)

 H_2SO_4 - 9.24% Na_2SO_4 - 20.08% MgSO_4 - 3.15%

Denier - 138.7

Dry Strength - 1.78

" Elong. - 8.8%

Wet Strength - 0.62

" Elong. - 11.8%

Complexity - 1.335

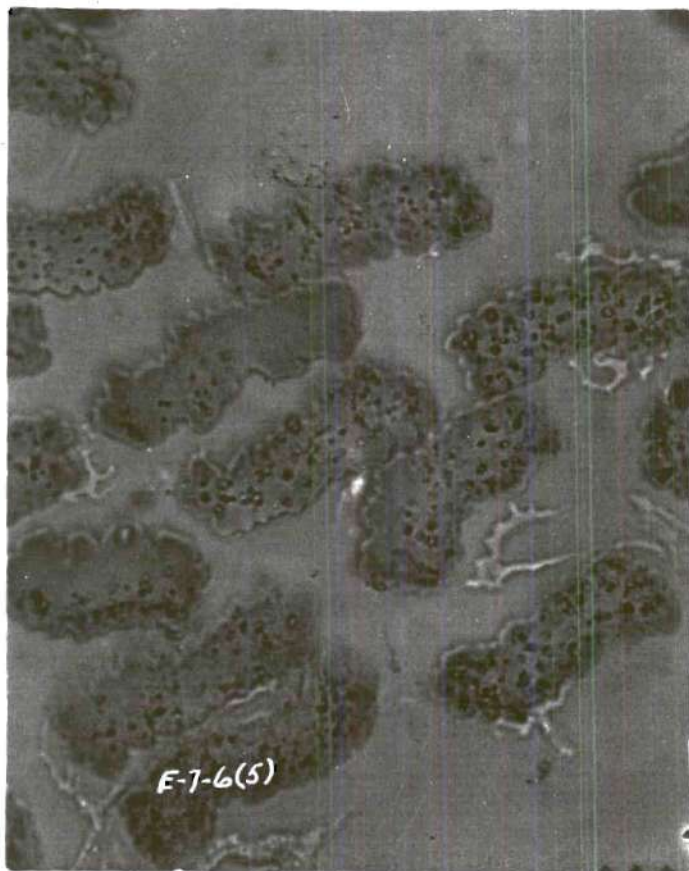


Fig. 21

Sample E-7-6(5)

H_2SO_4 - 9.22%
 Na_2SO_4 - 20.48%
 MgSO_4 - 5.74%

Denier - 135.0

Dry Strength - 1.65
 " Elong. - 10.6%

Wet Strength - 0.67
 " Elong. - 15.8%

Complexity - 1.350

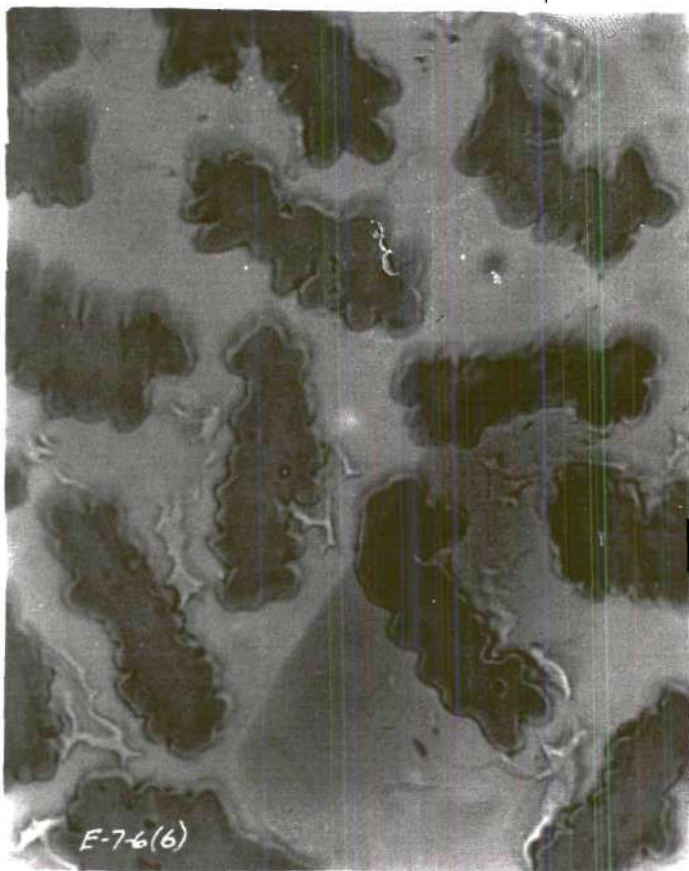


Fig. 22

Sample E-7-6(6)

H_2SO_4 - 9.22%
 Na_2SO_4 - 20.53%
 MgSO_4 - 2.95%
 ZnSO_4 - 1.02%

Denier - 138.1

Dry Strength - 1.51
 " Elong. - 14.9%

Wet Strength - 0.73
 " Elong. - 26.8%

Complexity - 1.566



Fig. 23

Sample E-7-6(7)

H_2SO_4 - 9.24%
 Na_2SO_4 - 20.57%
 MgSO_4 - 5.75%
 ZnSO_4 - 1.25%

Denier - 137.9

Dry Strength - 1.72
 " Elong. - 15.4%

Wet Strength - 0.81
 " Elong. - 27.5%

Complexity - 1.614

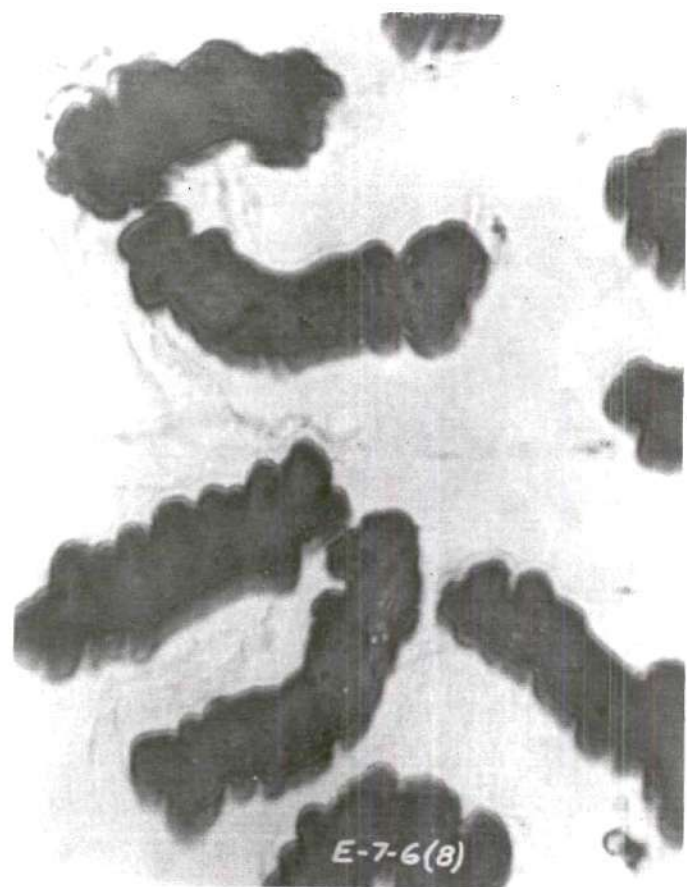


Fig. 24

Sample E-7-6(8)

H_2SO_4 - 9.43%
 Na_2SO_4 - 19.95%
 MgSO_4 - 3.05%
 ZnSO_4 - 1.79%

Denier - 140.6

Dry Strength - 1.66
 " Elong. - 15.9%

Wet Strength - 0.80
 " Elong. - 22.4%

Complexity - 1.485

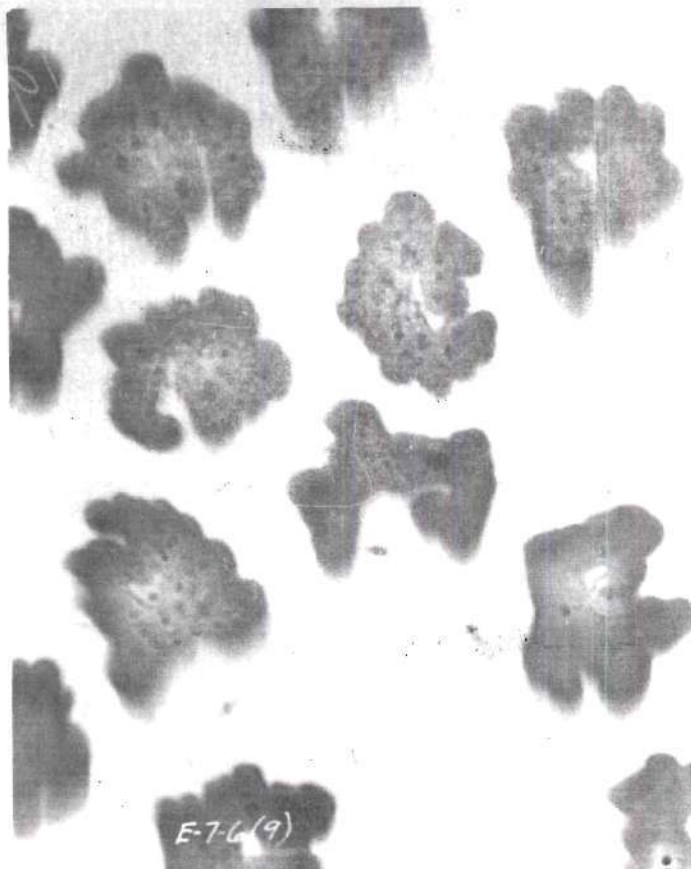


Fig. 25

Sample E-7-6(9)

 H_2SO_4 - 9.43% Na_2SO_4 - 20.16% MgSO_4 - 5.57% ZnSO_4 - 2.14%

Denier - 136.6

Dry Strength - 2.00

" Elong. - 14.6%

Wet Strength - 0.84

" Elong. - 28.8%

Complexity - 1.651

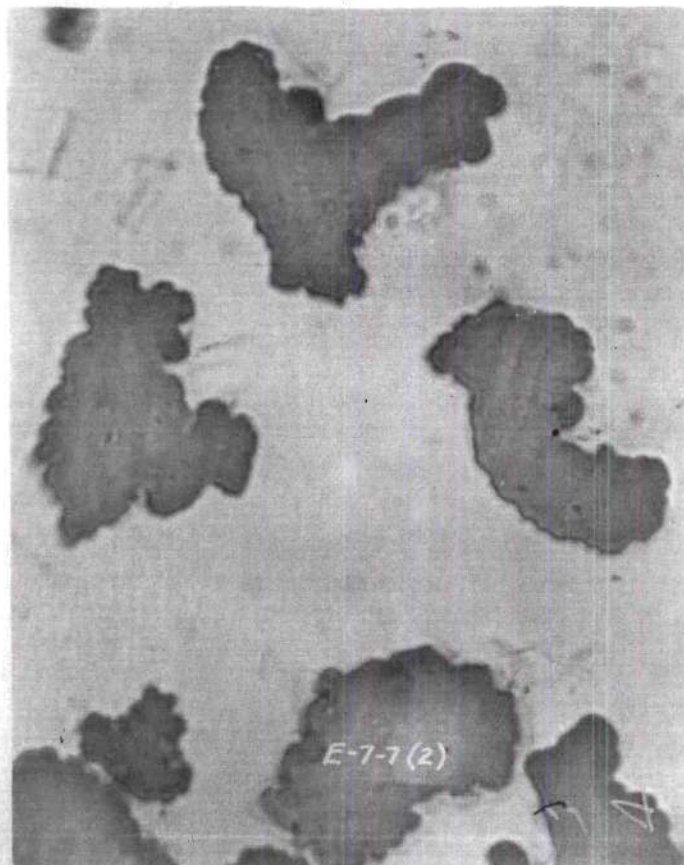


Fig. 26

Sample E-7-7(2)

 H_2SO_4 - 7.76% Na_2SO_4 - 21.18% MgSO_4 - 3.19% ZnSO_4 - 1.17%

Many spin-hooks on
yarn. Too bad to
twist. No sample
for testing.

Complexity - 1.398

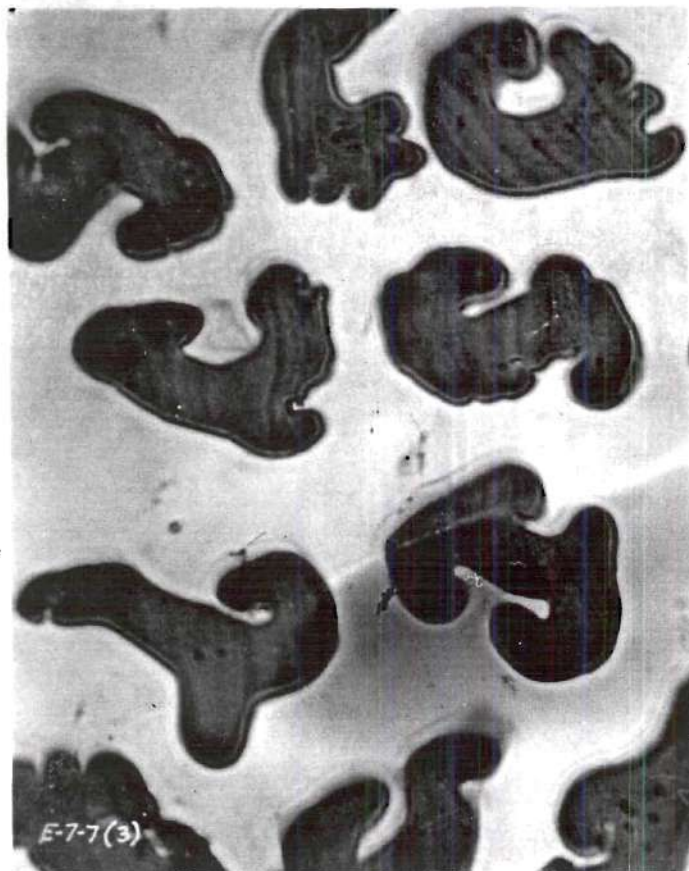


Fig. 27

Sample E-7-7(3)

 H_2SO_4 - 8.82% Na_2SO_4 - 20.79% MgSO_4 - 3.16% ZnSO_4 - 1.15%

Denier - 140.9

Dry Strength - 1.73

" Elong. - 11.6%

Wet Strength - 0.74

" Elong. - 18.0%

Complexity - 1.616



Fig. 28

Sample E-7-7(4)

 H_2SO_4 - 10.52% Na_2SO_4 - 19.78% MgSO_4 - 2.98% ZnSO_4 - 1.21%

Denier - 142.8

Dry Strength - 1.54

" Elong. - 14.7%

Wet Strength - 0.78

" Elong. - 25.4%

Complexity - 1.464

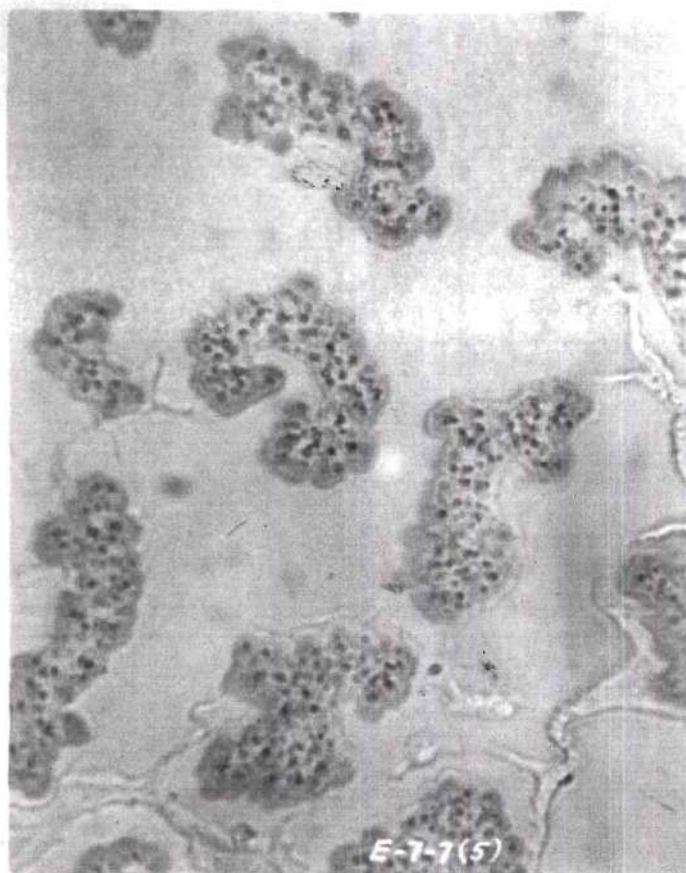


Fig. 29

Sample E-7-7(5)

H_2SO_4 - 11.45%
 Na_2SO_4 - 20.06%
 MgSO_4 - 3.08%
 ZnSO_4 - 1.14%

Denier - 147.0

Dry Strength - 1.43
 " Elong. - 14.3%

Wet Strength - 0.69
 " Elong. - 27.0%

Complexity - 1.630

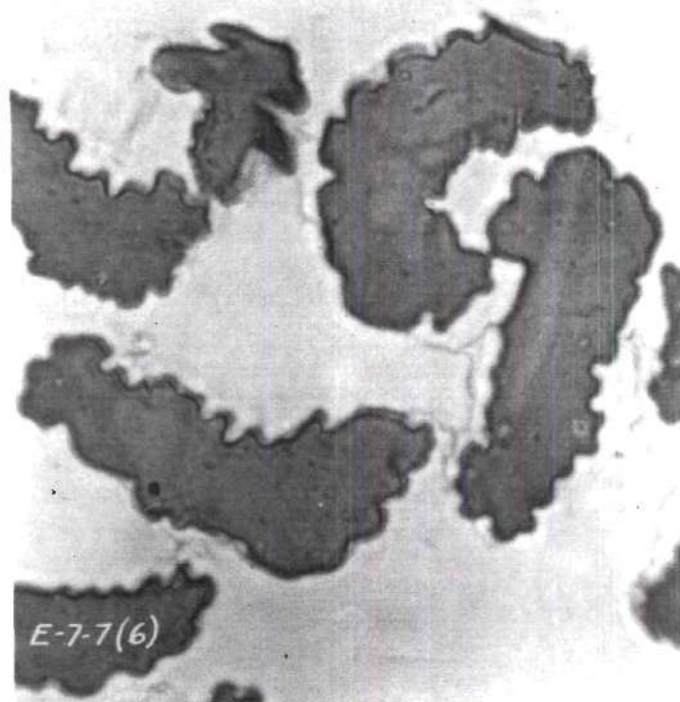


Fig. 30

Sample E-7-7(6)

H_2SO_4 - 12.69%
 Na_2SO_4 - 19.82%
 MgSO_4 - 3.20%
 ZnSO_4 - 1.13%

Denier - 143.8

Dry Strength - 1.41
 " Elong. - 12.9%

Wet Strength - 0.58
 " Elong. - 21.3%

Complexity - 1.478

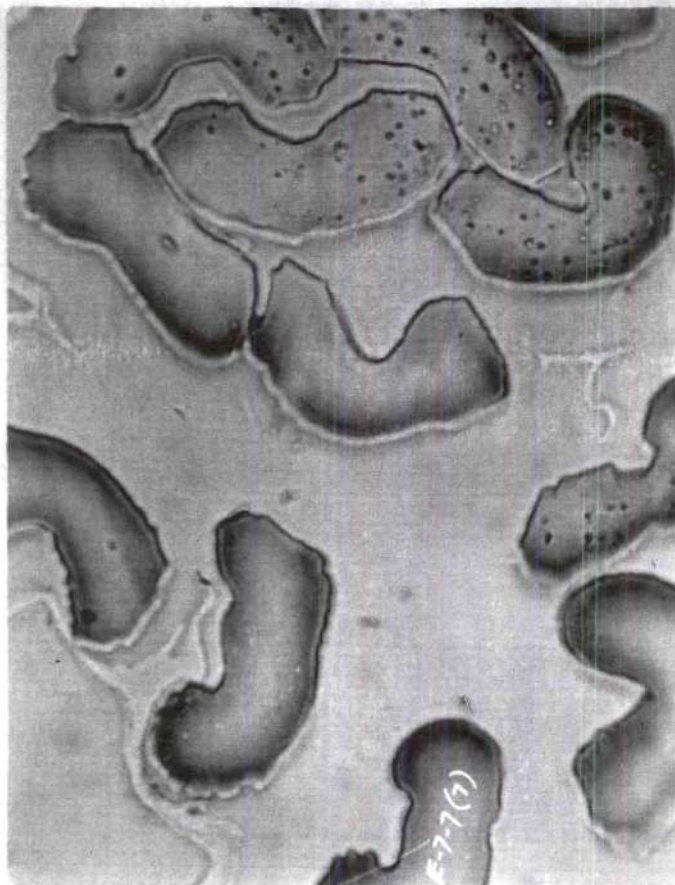


Fig. 31

Sample E-7-7(7)

H_2SO_4 - 14.38%
 Na_2SO_4 - 19.65%
 MgSO_4 - 3.32%
 ZnSO_4 - 1.11%

Denier - 143.9

Dry Strength - 1.24
 " Elong. - 14.9%

Wet Strength - 0.47
 " Elong. - 28.6%

Complexity - 1.264

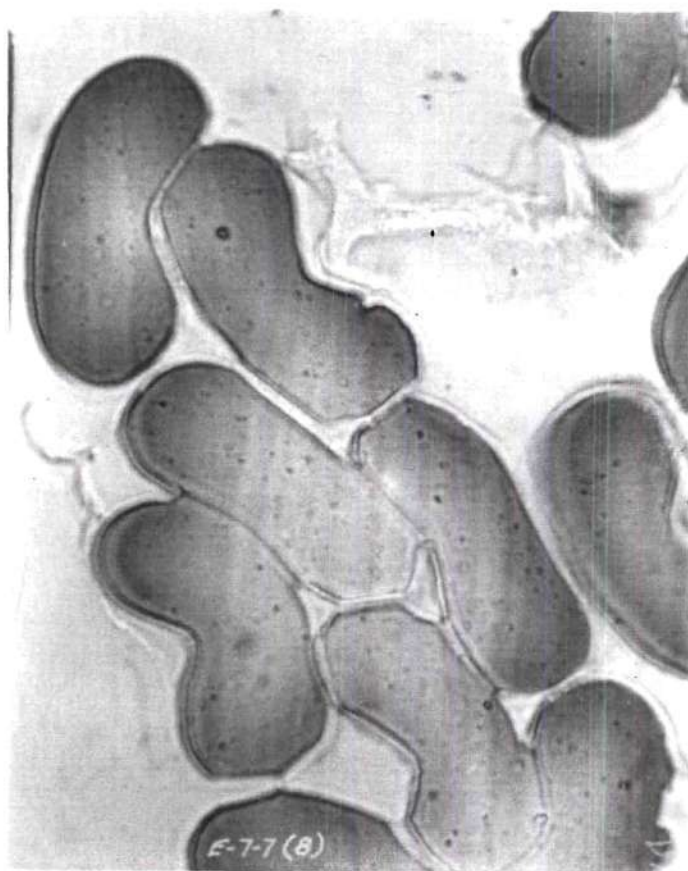


Fig. 32

Sample E-7-7(8)

H_2SO_4 - 16.02%
 Na_2SO_4 - 19.47%
 MgSO_4 - 2.98%
 ZnSO_4 - 1.09%

Denier - 139.9

Dry Strength - 1.24
 " Elong. - 14.4%

Wet Strength - 0.48
 " Elong. - 28.4%

Complexity - 1.239

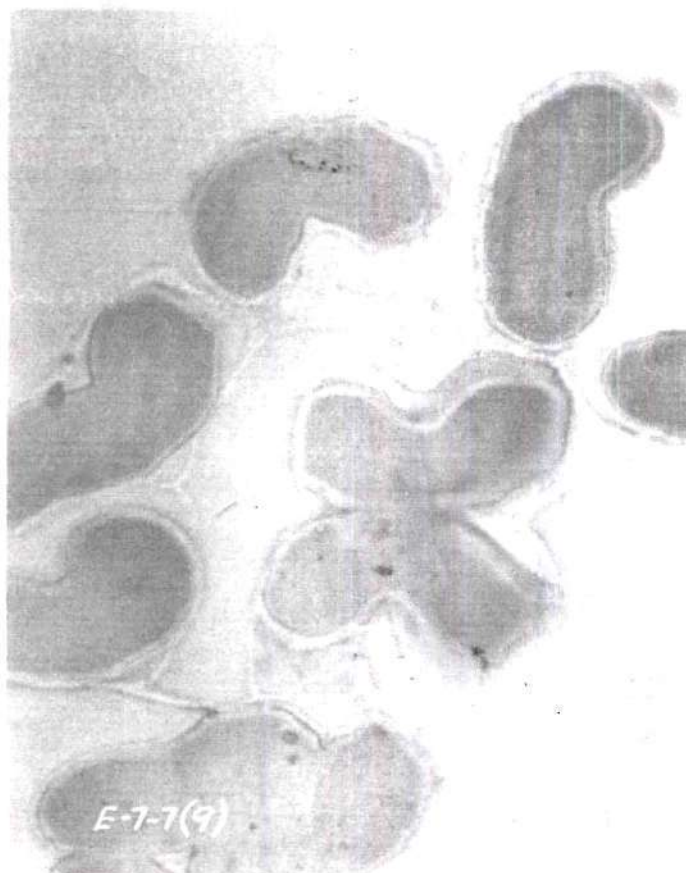


Fig. 33

Sample E-7-7(9)

H_2SO_4 - 17.92%
 Na_2SO_4 - 18.85%
 MgSO_4 - 2.86%
 ZnSO_4 - 1.05%

Denier - 140.7

Dry Strength - 1.32
 " Elong. - 11.2%

Wet Strength - 0.45
 " Elong. - 26.6%

Complexity - 1.175

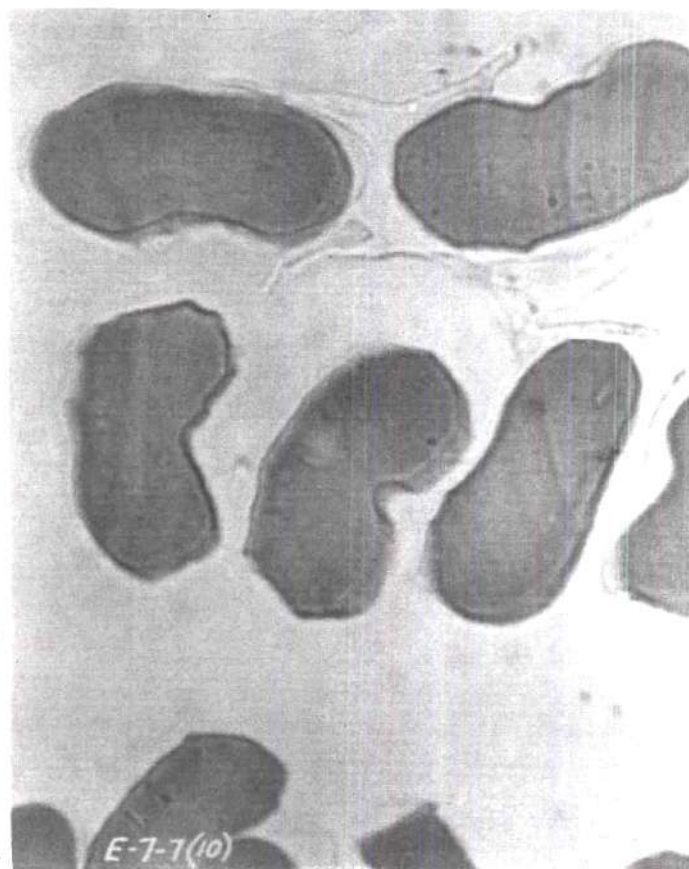


Fig. 34

Sample E-7-7(10)

H_2SO_4 - 19.65%
 Na_2SO_4 - 18.29%
 MgSO_4 - 2.58%
 ZnSO_4 - 1.10%

Denier - 140.8

Dry Strength - 1.07
 " Elong. - 12.2%

Wet Strength - 0.42
 " Elong. - 23.1%

Complexity - 1.165

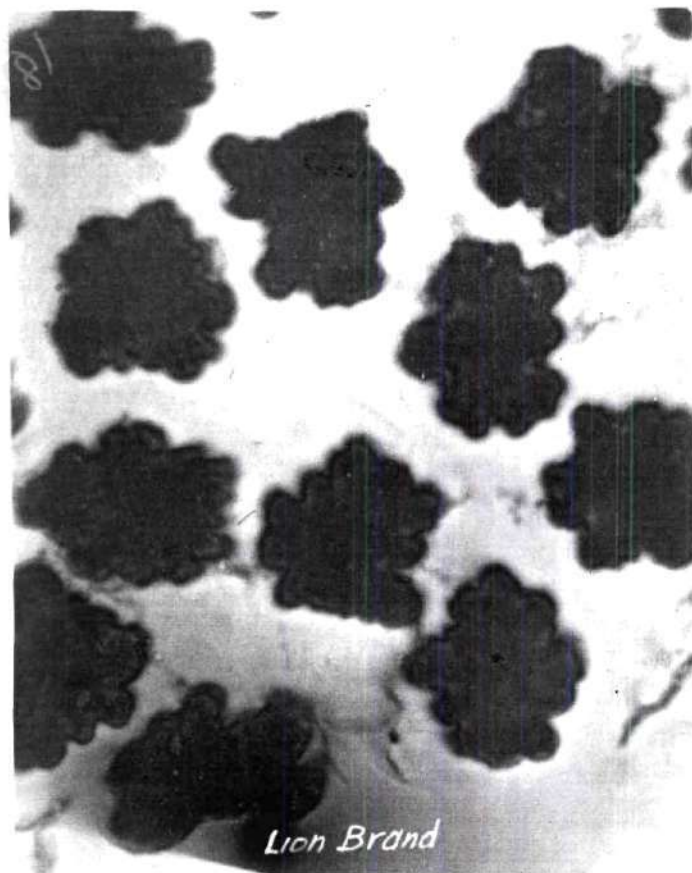


Fig. 35

Sample - Commercial

Denier - 151.7

Dry Strength - 1.19

" Elong. - 18.3%

Wet Strength - 0.72

" Elong. - 32.7%

Complexity - 1.180



Fig. 36

Sample - Commercial

Denier - 153.4

Dry Strength - 1.36

" Elong. - 21.4%

Wet Strength - 0.79

" Elong. - 30.7%

Complexity - 1.472

Discussion of Results

The shape of the cross section of the thread spun into sulfuric acid is nearly circular (Fig. 1). Addition of Na_2SO_4 to the bath causes an indentation in the section, and the higher concentrations of salt cause an elongation of the section (Figs. 2-4). The addition of ammonium sulfate and glucose to the acid bath has little effect on the circularity of the sections, the complexity remaining low (Figs. 5-10). Additions to the acid bath of zinc sulfate in concentrations up to 8% allows the section to retain its circularity, but causes increasing indentations with increasing concentrations of salt (Figs. 11-13). The addition of magnesium sulfate to the acid bath causes an increase in complexity with increasing concentration of salt (Fig. 14-16).

The addition of small amounts of zinc sulfate to a bath containing sulfuric acid and sodium sulfate has a marked effect on the shape of the cross sections. Fig. 17 shows the ribbon-like, serrated structure obtained when 0.86% zinc sulfate is added. Greater additions of zinc sulfate cause a decrease in the complexity number, although the sections are very much indented and serrated (Figs. 18-19). Additions of magnesium sulfate to the acid-sodium sulfate bath causes an increase in the complexity. (Figs. 20-21). A comparison of Figs. 21, 23, and 25, and 20, 22, and 24 shows that with the acid, sodium and magnesium concentrations remaining constant,

the complexity is increased by adding zinc sulfate in increasing concentrations.

In the series Figs. 26-34, the run was made keeping the salt concentrations constant and increasing the concentration of the acid. The first concentration of acid was 6.49%, and this failed to decompose the xanthate, the thread winding up on the bobbin in a jelly-like mass. The increasing acid content after 12% caused the indentations and serrations to disappear, but the section remained elongated.

Figs. 35 and 36 show the cross sections of commercial rayons. It appears that the desired type of cross section is one having a good circularity, but being well indented and serrated.

From an inspection of the strength and elongation data, it is seen that with acid alone and with one - salt combinations, the strength and elongation are both low. It appears that an increase in the salt content causes an increase in the tensile strength, with little change in the elongation. Addition of zinc sulfate to the acid - sodium sulfate bath causes an increase in both strength and elongation. The best properties of the yarn were obtained when both zinc and magnesium sulfates were added to the acid - sodium sulfate bath. The highest strength obtained was 2.00 grams per denier dry, and 0.84 grams per denier wet, with an elongation of 14.6% (Fig. 25). These properties are comparable with some brands of commercial rayon.

The test with increasing acid concentration showed a steady decrease in strength with increase in acid concentration.

Conclusion

This work has shown that an improved rayon results from the addition of magnesium and zinc sulfates to the spinning bath.

No attempt was made to show the effect of small variations in the concentrations of the salts, the concentrations used being at rather wide intervals. In order to show the effect of small changes, greater refinements in procedure would have to be made, particularly in controlling the properties of the viscose and the concentrations of the baths. Further work along this line should include these small variations.

Future work on spinning should be done on the coagulation rate of different spinning baths as measured by the iodine decolorization properties of the rayon. An interesting problem to investigate would be the relation of the coagulation velocity of the rayon to the tension of spinning and the effect on the physical properties of the rayon.

Since it is seen that the addition of salts to the spinning bath improves the quality of the rayon, the question arises as to why the quality is improved. It would be interesting to know if the presence of salts in the bath has any effect on the micellar arrangement in the fiber. This could be determined by an x-ray study.

Another problem along this same line would be to determine

the amount of stretch that should be given the filaments during spinning to obtain optimum tensile properties, and the relation of the spinning bath composition to the stretch.

Continuing with the effect of salts in the spinning baths, other sulfates such as aluminum, chromium and cobalt, may be used. Also the effect of other substances such as organic compounds in the bath, may be studied. Of particular interest would be the use of thermal decomposition products of rosin in the bath, and this should be investigated.

There are innumerable combinations of constituents of the spinning bath that may be used, and the investigation of very many of them would require much work and time. The present work is designed to be a point of departure for further investigations along the same line. The writer hopes that any other work undertaken will profit by this thesis.