

A STUDY OF THE CREASE-RESISTANCE  
“

OF

VISCOSE RAYON

by

NATHAN SUGARMAN  
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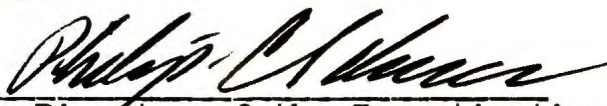
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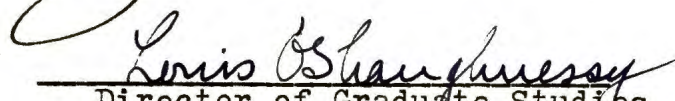
in

CHEMISTRY

Approved:

  
\_\_\_\_\_  
Director of the Investigation

  
\_\_\_\_\_  
Head of the Department

  
\_\_\_\_\_  
Director of Graduate Studies

Virginia Polytechnic Institute  
May, 1942

## BIOGRAPHICAL SKETCH

### Nathan Sugarman

Nathan Sugarman was born in Brooklyn, N. Y., on January 11, 1912. When he was six months old, his parents moved to La Grange, Georgia, where his father became established in business as a merchant.

He received his elementary education in the public schools of La Grange, Ga. After graduating from high school in 1928, he entered the Georgia School of Technology as a student in Chemical Engineering. After completing the five-year Co-operative Plan course, he was graduated with the degree of B. S. in Chemical Engineering in 1933.

After a period of unemployment during the depression, in 1934 he became connected with a project undertaken at Georgia Tech for the utilization of Georgia pine pulp for the production of viscose rayon. The following year he began work toward his Master's degree, and in June, 1937, was graduated with the degree of M. S. in Chemical Engineering.

After receiving the M. S. degree, he became a full-time member of the staff of the Georgia State Engineering Experiment Station, located at Georgia Tech. During his employment in this capacity, he was engaged in research work on the spinning of viscose rayon.

On August 29, 1937, he was married to Miss Esther Goldstein, of Atlanta, Georgia.

During the Spring of 1940, he applied for and received an appointment as a Research Fellow in the Chemistry Department of the Virginia Polytechnic Institute, in order to become a candidate for the degree of Doctor of Philosophy. The work was successfully completed in the Spring of 1942, and the degree awarded on May 30, 1942.

After receiving his Doctorate, he entered the employ of The Standard Register Company, of Dayton, Ohio, as a research chemist.

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## INTRODUCTION

Crease-resistance is a very greatly desirable property in textile fibers. Of the natural fibers, wool exhibits this property to the greatest degree, followed by silk, cotton, and flax, which has a very low crease-resistance. The artificial cellulose fibers fall considerably below wool and silk in this respect.

The improvement of the crease-resistance of rayon and other fibers has been sought in various after-treatment processes, in which substances are either deposited within the fiber, or react with it. There are numerous patents (22) for such methods of imparting crease-resistance.

It would be highly desirable if the crease-resisting powers could be achieved by a modification of the intrinsic properties of a fiber, that is, by producing a fiber which already is crease-resistant.

The purpose of the work reported here was to attempt to produce a viscose rayon fiber with better crease-resisting properties, and to study the effect of a variation in the cellulose chain length distribution in the rayon upon this property.

This work was done under a Fellowship of the Behr-Manning Corporation, Troy, New York. This company has developed a method for producing pile fabrics by an electrodeposition

process (18). Rayon flock (very short cut rayon fibers) is sprinkled upon an adhesive-coated fabric backing material. This is then run between two plates charged by a high frequency alternating current. The rayon fibers acquire a charge and literally dance up and down perpendicularly to the fabric, upon which the ends of the fibers become imbedded in the adhesive. This process produces the pile fabric.



## HISTORICAL AND LITERATURE REVIEW

### Creasing

Creasing in a fiber is the deformation which a fiber undergoes upon being subjected to a bending stress. Conversely, the resistance to creasing is the power of recovery from this deformation which the fiber possesses.

If a fiber is bent, the outer layer is stretched, the inside of the bend is under compression, and the core of the fiber remains relatively unchanged. In a perfectly elastic fiber, when the bending stress is removed the fiber recovers completely its original form. However, if the fiber exhibits plastic flow and the stretch exceeds the elastic limit of the fiber, it will not completely recover, but will remain permanently deformed.

In rayons, the elastic stretch is small and amounts to about one or two percent (27). The plastic stretch can reach to twenty-five percent of the fiber length. The too low elastic stretch and the too high plastic stretch are primarily the causes of the permanent deformation, or creasing, of rayon. Schwarzkopf (28) has discussed mathematically the creasing of elastic fibers, considering the cases of (a) bending a round fiber of diameter  $d$  around a round rod of diameter  $2R$  and (b) bending the same fiber around an edge.

He arrived at the following equations for the stretch of the outer layers:

$$(a) \quad \% \text{ Stretch} = \frac{100 d}{2R + d}$$

$$(b) \quad \% \text{ Stretch} = \frac{100 d \sin \alpha}{L + d \sin \alpha}$$

where L is the thickness of the edge and  $\alpha$  is the angle the fiber makes with the flat edge. It is pointed out that for  $R = 0$  and  $L = 0$ , in both cases the stretch is 100%.

#### Theories of Creasing

A. J. Hall (10, 11) was among the first to investigate the creasing of rayons. Previous to his work there were no methods described for measuring the crease-resistance. Hall proposed the method of winding the rayon fiber about a card and placing a weight of twenty pounds upon it for five minutes. At the end of the time the weight was lifted from the card, and the winding was carefully removed. The greater the resistance against creasing, the more the winding recovered. Hall measured the angles in the winding, and called them the crease angles.

Using this method, Hall studied the effect of stretching on the crease-resistance of rayon. He stretched rayons to varying degrees and found that with increased stretching the resistance to creasing decreased.



Hall and Mark (14) explained the creasing properties of rayon on the basis of the orientation of the micelles in the rayon. As has already been indicated, in creasing, a bending occurs in which the outer fiber layer is stretched, the middle hardly strained, and the inner layer is compressed. By stretching, an orientation of the micelles, heretofore disordered, occurs. When the strain is released, the micelles spring back to their unoriented position and the crease disappears. If, however, the micelles are already oriented originally, then by creasing, the micelles will not be able to resist the pull and will slide off from one another. In this case the stretch becomes plastic and the crease remains.

Mark believed that the ideal fiber with regard to crease-resistance was one which had an unoriented outer layer and a highly oriented core to give it strength. To prove this, a viscose thread of high orientation was dipped in viscose which was regenerated on the surface of the first thread. This should give an unoriented outer layer. It was found that the crease-resistance of the second fiber was greater than that of the first. Further evidence of the effect of orientation was given in an experiment with a silkworm. Natural silk, which has a high crease-resistance, is known to have a highly oriented inner core with a less oriented outer layer. Mark made fibers of extremely oriented silk by forcing a silk-worm to spin its thread under tension. This was done by means of an electric



motor, which wound up the silk while drawing it out of the worm. This procedure resulted in a silk which was very strong, but which was as creasable as ordinary rayon.

Ohl (19) spun a fiber of one denier under stretch, and a similar one without stretch from the same viscose solution. The measurement of the crease-angles gave for the better oriented fibers  $52^\circ$ , and for the less oriented fibers  $110^\circ$ . These results are in accord with the theories of Hall and of Mark.

In contrast to these views on the effect of stretching and orientation, Elod and Etzkorn (4) found that rayon which had been swollen in water, stretched, and dried under tension had a greater crease-resistance than the original. This increase was not very great, but in no case did they find any decrease in the crease-resistance.

Elod and Etzkorn (4) also attempted to test Mark's theory concerning the orientation of the micelles in the outer layers. It was attempted to unorient the outer layers of viscose and cuprammonium fibers by a topochemical, or surface, acetylation followed by saponification. Also, acetate fibers were saponified. It was shown that rayon treated in this manner had an increased creasing tendency, which was contrary to what would be expected according to Mark's theory.

Quehl (25) has advanced the theory that the crease resistance of the different fibers is bound up in the relative

amounts of crystalline and amorphous material present in the fibers. According to him, the creasing increases with the increasing proportion of crystallites to amorphous material making up the fiber, with increasing crystallite size, and with increasing degree of orientation of the crystallites in the fiber. These conclusions were based largely on a review of the micellar structure of various textile fibers.

In order to have a better conception of the terms crystalline and amorphous in the above connection, it is well to consider the more recent views on the inner structure of cellulose fibers. Clark (2) has given a good review of these theories.

The cellulose molecule itself is a primary valence chain of polymerized anhydro-glucose units linked together through oxygen bridges at the 1 - 4 positions.

According to the Micellar Theory, a cellulose crystallite is a parallel bundle of cellulose chains. The dimensions of the micelles are around 600 A. U. long and 55 A. U. thick. Primary-valence forces hold the glucose residues in the form of a chain; the chains are held together alongside each other by secondary valence forces (perhaps hydrogen bonds); and the micelles are held together in a fiber by tertiary forces or amorphous cementing material.

The Macromolecular Theory views the cellulose



filament as a lattice of macromolecules with no intermediate stages of aggregation. This theory is best applicable to synthetic polymers.

The newest theory, known as the Net and Fringe Structure, is a compromise, but one that has found wide acceptance. In this theory, the "brick" structure representing regular termination of cellulose chains is discarded in favor of an essentially continuous network of longer chains. Over occasional areas these chains may be nearly parallel to form ordered regions corresponding to crystallites, or micelles, which therefore are not continuous "bricks" but are bound together with the same long cellulose chains in disorder. These disordered regions may be considered as the amorphous portion of the fiber. Mark (15) has shown that stretching increases the amount of crystalline material and diminishes the amount of amorphous region.

The moisture relations of the fibers appear to have an important bearing on the crease-resistance. Elod and Etzkorn (5) have shown that the resistance to creasing decreases with increasing relative humidity of the air and with increasing moisture content of the rayon.

The ability of a fiber to resist creasing has been shown by Elod and Hass-Wittmuss (9) to be directly connected with the swelling capacity of the fibers. The resistance



against creasing decreases with viscose, cuprammonium and acetate rayon with increasing degree of swelling in the state of equilibrium.

In addition to the relations depending upon the internal construction of the fibers, external factors also play a part in the crease-resistance. Thus (6) fine-filament rayons are less inclined to bending than thicker ones. It is also stated that the crease-resistance increases with increasing titer of the threads. This agrees with the fact that thicker fabrics crease less than thin ones.

The crease-resistance is further dependent upon the shape of the fiber cross-section. Fibers with round cross-sections crease more than those with flat cross-sections, since with a flat fiber the surface of the section is smaller than that of a round cross-section (7).

#### Crease Resisting Processes

Practically all of the crease-resisting processes make use of the impregnation of the fiber with foreign substances. These processes seem to be in conformity with the theory proposed by Quehl on the amorphous-crystalline relationship. The substances added are resins and inorganic salts which increase the amount of amorphous substance in the fiber. The addition of resins also reduces the swelling capacity of the fiber, and hence acts to increase the crease-resistance

in this way.

The best known crease-resisting process is the one originated by the Tootal Broadhurst Lee Company in 1926 (21). In this process, the material is impregnated in a water-soluble urea-formaldehyde resin, the excess squeezed out, and the resin polymerized by heating. The German I. G. (22) patented a similar process, but mentioned only its use in decreasing the swelling of the fibers. Here it is seen that the two effects, resistance to swelling and resistance to creasing, seem to go hand in hand. A great many other processes involving the use of resins have been patented (23), but their action is fundamentally the same.

In connection with the use of formaldehyde containing resins, Quehl (25) cites the use of formaldehyde alone as a crease-proofing agent. The efficacy of this treatment depends upon the fact that the hydroxyl groups are etherified forming a methylene ether of cellulose. This diminishes the hydrophilic properties of the cellulose, but this alone is insufficient to explain the significant increase in the crease-resistance. It is pointed out that hydroxyl groups from two different cellulose chains can be connected through the reaction with formaldehyde. This gives a structure which would keep the micelles from gliding off from one another, as in the case of creasing.

Crease-resistance can also be imparted without the use of resins (24). One method is described as using 200 parts



of sodium borate mixed to a paste with 20 parts of coconut oil, 30 parts of water. This mixture is worked to a paste, and used diluted to impregnate the material. Another method describes the use of borax.

Similarly insoluble salts can be deposited within the fiber by first impregnating with a solution of calcium acetate, squeezing and drying. Then the material is treated with a second solution of sodium silicate, which is removed, and then dried. This treatment is said to impart crease-resistance to rayon fabrics.

#### Chain Length Distribution

It is now recognized that high polymeric systems, such as cellulose, are not homogeneous as regards molecular weight, but consist of mixtures of chains of varying lengths. The molecular weight of a sample of cellulose may be expressed in terms of the average chain length or degree of polymerization. By degree of polymerization (D. P.) is meant the number of basic monomer units, in this case anhydro-glucose, which make up the chain. It is evident that different samples which show the same average degree of polymerization may have entirely different chain-length distribution.

Mark (16) has discussed the experimental methods for fractionating cellulose and its derivatives and the appropriate ways to represent the results of fractionation experi-



ments. Two methods are available, fractional solution and fractional precipitation. Neither of these can be applied to cellulose directly, but the nitrate and acetate can be used for fractionation.

Carothers (1), and Douglas and Stoops (3) were among the first to show the relationship of molecular weight and mechanical properties of high polymers. There is a limiting degree of polymerization below which films and fibers cannot be formed, and above this the mechanical properties increase with increasing D.P. until very high molecular weights are reached.

Less is known about the connection between the chain length distribution and the physical properties. Ohl (20) was the first to point out that cellulose acetates having the same average chain length but different distribution curves seemed to have different tenacity properties.

Spurlin (29) prepared a series of fractions of nitrocellulose, from which he cast films upon which he made tenacity and folding endurance tests. He found little difference in the stress-strain curves of the various fractions, but there was a superiority of the fractions over the blends in the fold tests. Mixtures which contained a comparatively large amount of low molecular weight material proved inferior.

Mark (17) prepared blends of equal average D.P. of

high and low molecular weight fractions of cellulose acetate and spun them into fibers. The fibers with the greater proportion of low chain lengths had the lowest tenacity.

It seems generally that large amounts of low molecular weight material in the fibers have a deleterious effect upon the mechanical properties.

PART I

THE EFFECT OF TENSION DURING SPINNING  
UPON THE CREASE-RESISTANCE

A. Purpose

Since the theories of crease-resistance seemed to emphasize the effect of orientation of the micelles, it was decided to try to spin a rayon under conditions of minimum tension, hence insuring the greatest possible disorientation. At the same time, in order to check the theory, rayon of high spinning tension would also be prepared.

The rayon thus produced would be subjected to a practical crushing test after being fabricated into the Behr-Manning pile fabric. This would show if there was any practical, significant differences as far as the crush resistance was concerned in rayons of such widely different orientation.

B. Experimental

Viscose. The viscose solution contained seven percent cellulose and six and one-half percent sodium hydroxide. It was prepared according to the following schedule:

Weight of pulp: 700 gms. per batch.

Dipping: 1 hr. at 20° C. in 18% NaOH soln.

Press Ratio: 3.33

Shredding: 3 hrs. with temp. rise to 21 - 23°.

Aging of Alkali-cellulose: 48 - 50 hrs. at 18° C.



Xanthation: 1 3/4 hrs. at 28° C. 37% CS<sub>2</sub>, based upon weight of cellulose, used.

Dissolving: 2 hrs. with temp. rise to 28 - 30° C.

Ripening: 69 - 71 hrs. at 18° C.

Maturity at Spinning: Average - 8.8 ml.

Viscosity at Spinning: Average - 30.4 sec.

Spinning. In order to achieve minimum tension, the regular glass friction thread-guide was replaced by a small grooved roller, similar to a small pulley. This roller acted as the thread-guide, and, since it was very free-rolling, the thread passed over it with very little friction.

The roller was mounted on a holder which also had attached to it three parallel glass rods mounted horizontally. When the condition of maximum spinning tension was desired, the thread was allowed to pass over these rods in such a manner that a large amount of friction occurred. This, of course, resulted in a high tension between the thread-guide and the spinning bobbin.

The spinneret used in these runs had 24 holes; the diameter of the holes was 0.0045 inch.

The spinning bath used had the following composition:

H<sub>2</sub>SO<sub>4</sub> - 10.0%

Na<sub>2</sub>SO<sub>4</sub> - 18.0%

MgSO<sub>4</sub> - 4.0%  
ZnSO<sub>4</sub> - 1.0%

A total of seven batches were spun in this series, and approximately three pounds each of rayon spun without and with tension were produced.

Testing. The rayon was sent to the Behr-Manning Corporation, where it was made into pile fabric and tested. The test method consisted in pressing a disk into the pile with a definite pressure for a definite length of time. Upon release of the pressure, the crush mark was inspected visually, and the depth of the crush measured with a micrometer.

The tensile properties (breaking strength and elongation) of the yarn were measured with the Suter serimeter.

### C. Results

The tests made on the pile fabrics showed little or no difference in the crush resistance of the high and low tension rayons. Both types showed poor practical crush resistance.

The following average values for the tensile properties were found:

Without tension:	Breaking strength	- 1.76 grams/denier
	Elongation	- 16.6 percent
With tension:	Breaking strength	- 2.61 grams/denier
	Elongation	- 8.0 percent

The above values illustrate the great difference in tensions employed, since it is well known that a low tension in spinning gives low strength with high elongation, and a high tension gives high strength and low elongation.



PART II

THE EFFECT OF TITANIUM DIOXIDE PIGMENT ON THE CREASE-  
RESISTANCE AND THE HIDING POWER FOR CRUSH MARKS  
ON PILE FABRICS

A. Purpose

The visual appearance of crush marks on pile fabrics is due largely to the difference in reflective powers of the sides and of the ends of the fibers. It was hoped to be able to mask the crush marks by incorporating in the rayon amounts of titanium dioxide pigment considerably greater than that ordinarily employed in delustering.

B. Experimental

Viscose. The viscose was prepared in the same manner as described in Part I, except that varying percentages of titanium dioxide, based upon the cellulose content, were added. The desired amount of pigment was added to the dissolving lye and stirred for about 20 minutes before adding the xanthate.

Four batches were prepared, containing 2, 5, 10, and 25% of titanium dioxide, based upon the weight of cellulose.

Spinning. The 24-hole spinneret was used in this series. The regular glass hooked thread-guide was used. This gave a medium, or intermediate, tension. The spinning bath

composition, different from that used in Part I, was as follows:

$\text{H}_2\text{SO}_4$  - 10.0%

$\text{Na}_2\text{SO}_4$  - 16.0%

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  - 30%

Testing. The test methods were the same as those described in Part I.

Resiliency tests were also made on these samples. (See Part III for method).

### C. Results

The crush tests were very poor. The incorporation of the pigment had no practical effect upon the crush-resistance. However, at the higher percentages there appeared to be less contrast between the crushed and uncrushed surfaces than at the lower ones.

The resiliency values were as follows:

Percent Pigment	Degree of Resiliency
2	0.616
5	0.644
10	0.629
25	0.705

These values indicate a trend for the resiliency to increase with increasing pigment content.

### Tensile Properties

% Pigment	Denier	Breaking Strength, dry	Elongation, dry	Breaking Strength, wet	Elongation, wet
2	174	296	9.6	97	19.8
5	178	296	10.4	102	22.0
10	186	284	8.9	91	22.4
25	210	277	10.0	95	26.9

Since the denier increases with increasing loading, the breaking strength in grams is given instead of in grams per denier. It is seen that the dry strength decreases as the amount of pigment increases.



### PART III

## THE RELATION BETWEEN THE CHAIN-LENGTH DISTRIBUTION OF THE CELLULOSE AND THE CREASE-RESISTANCE

### A. Purpose

It has already been pointed out (pages 11 - 13) that the distribution of chain lengths in the cellulose appears to have a definite influence upon the physical properties of the cellulose. Also, the theory has been proposed that fibers containing the larger amount of amorphous material had a higher crease-resistance.

In the light of the conception of the network structure of a filament, it would appear that a structure composed of long chains of fairly equal length (which, of course, is not the case) would have a great many voids between the chains. Now if a viscose solution containing very long and very short chains in definite proportions were spun into rayon, it seemed reasonable to expect the very short chains to fill in the voids between the longer chains. It appeared probable, too, that shorter chains would have less chance of becoming oriented and thereby adding to the crystallinity of the fibers.

The purpose of the work discussed in this part was to prepare rayon fibers with artificial chain-length distributions and to determine the effect upon the crease-resistance of

the fibers. Also, the effect of spinning tensions was again studied, since it was thought that rayons of different distributions might be affected differently by a given spinning tension.

## B. Experimental

### 1. Method for Producing Rayon of Varying Distributions.

The different chain length distributions were achieved by mixing varying proportions of alkali-cellulose of different aging periods. This method of obtaining artificial distributions in viscose rayon fibers is believed to be new, no reference to this having been found.

During the aging of alkali-cellulose, a depolymerization of the cellulose chains occurs, with a consequent lowering of the average degree of polymerization. An alkali-cellulose aged for a short period gives a viscose with a high viscosity, while with increased aging time, the viscosity decreases.

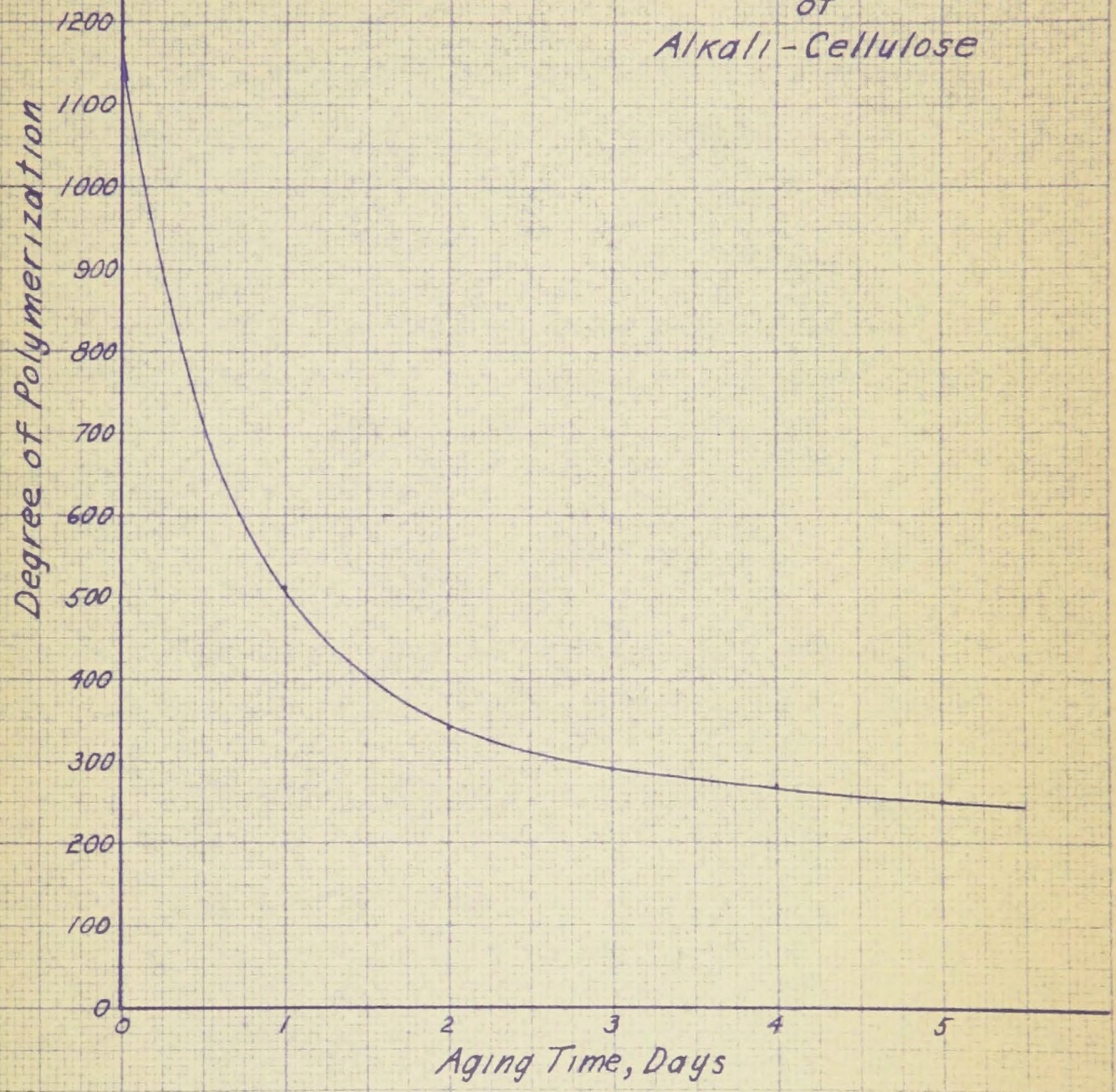
Fig. 1 is a curve taken from Lottermoser and Wultsch (13a), and shows the course of the change of the average degree of polymerization with the aging time. This curve was used as a basis for calculating the mixtures of alkali-cellulose which would maintain a constant average degree of polymerization.

The normal aging time for the alkali-cellulose used



Fig. 1.

Degree of Polymerization  
vs.  
Aging Time  
of  
Alkali-Cellulose





in the preparation of the viscose solutions is two days. From the curve in Fig. 1, the corresponding degree of polymerization of the alkali-cellulose is 340. This value is then the average D. P. to which the various mixtures must be adjusted.

All except one of the components in the mixture are arbitrarily selected. To illustrate the method of calculation, the computations for the preparation of Batch F-5 are given below in detail.

It was desired to combine 2 parts of 2-day aged and 8 parts of 5-day aged with the required amount of 0-day aged alkali-cellulose. From the curve, the corresponding D. P.'s are found to be as follows:

2-day - 340  
5-day - 250  
0-day - 1180

The unknown quantity,  $\underline{x}$ , is the proportion of 0-day aged material necessary to give an average D.P. of 340. Then,

$$\frac{(2 \times 340) + (8 \times 250) + (\underline{x} \times 1180)}{2 + 8 + \underline{x}} = 340$$

Solving for  $\underline{x}$ , there is obtained

$$\underline{x} = 0.858 \text{ parts}$$

Changing into terms of percent, we have

$$\frac{2}{10,858} \times 100 = 18.4\% \text{ 2-day aged}$$

$$\frac{8}{10.858} \times 100 = 73.6\% \text{ 5-day aged}$$

$$\frac{0.858}{10.858} \times 100 = 8.0\% \text{ 0-day aged}$$

In a similar manner, the compositions for the other batches were calculated, and are tabulated in Table 1.

Table 1

Compositions of Alkali-Cellulose Mixtures

F-1	4-day - 70.8%	F-6	5-day - 85.0%
	1-day - 29.2%		0-day - 15.0%
F-2	5-day - 16.4%	F-7	5-day - 47.4%
	2-day - 81.9%		2-day - 47.4%
	0-day - 1.7%		0-day - 5.2%
F-3	2-day - 100.0%	F-8	2-day - 100.0%
F-5	2-day - 18.4%	F-9	3-day - 46.8%
	5-day - 73.6%		2-day - 31.2%
	0-day - 8.0%		1-day - 22.0%

The mixtures of the variously aged alkali-cellulose were xanthated and dissolved in the usual manner. The time of ripening of the viscose was approximately 72 hours.

The spinning bath used was the same as that described in Part II. However, the spinneret used was different from that used previously. The spinneret used here had 50 holes of 0.003 inch diameter.

The tension devices previously described were used. Batches F-1 to F-3 were spun with medium tension using the hooked thread-guide. Batches F-5 to F-9 were spun with three different tensions, low, medium, and high. The low and high tensions were obtained as described in Part I.

## 2. Chain-length Distribution.

The methods of nitration and fractionation used are those described by I. Jurisch (13), with slight modifications.

Nitration. The nitrating mixture consisted of 28.2% phosphoric acid (85%), 32.2% phosphorus pentoxide, and 39.6% nitric acid (density 1.59 - 1.60). To prepare this mixture, the phosphorus pentoxide was slowly added to the phosphoric acid, with stirring and cooling. After all of the pentoxide was added, the mixture was heated and stirred until the particles of pentoxide were dissolved. After cooling, the fuming nitric acid was added while stirring. The mixture was placed in a glass-stoppered bottle and allowed to stand in a cool place. Before using, the mixture should be allowed to stand at least 12 hours, with frequent shaking.

A 1.5 gram sample of cellulose, dried over phosphorus pentoxide in a vacuum dessicator, was taken for nitration. The cellulose was placed in a 250 cc. glass-stoppered wide-mouth bottle, and 100 cc. of the nitrating mixture was added. The mixture was well stirred with a glass rod, and then allowed to



stand at room temperature for one hour, with frequent shaking. After the end of the nitrating period, the liquor was removed from the cellulose nitrate by suction on a fritted glass filter. The cellulose nitrate was dropped bit by bit into a one liter beaker containing about 300 cc. of saturated sodium carbonate solution. After thorough stirring, and allowing to stand for a while to insure complete neutralization of the acids, the cellulose nitrate was washed with distilled water. The excess water was sucked off on a filter funnel, and the cellulose nitrate was washed with methyl alcohol to remove the water, after which it was sucked dry on the filter funnel. The cellulose nitrate sample was then dried over phosphorus pentoxide in a vacuum desiccator.

Fractionation. Two and one-half grams of the cellulose nitrate were placed in a brown glass bottle containing 500 cc. of acetone. Glass beads were placed in the bottle to facilitate mixing, and the bottle was revolved end over end on a mechanical mixer until solution was complete.

The solution was filtered through a fritted glass filter to remove foreign particles, and 320 cc. were placed in a 1000 ml. Erlenmeyer flask stoppered with a cork.

An 80 cc. portion was placed in a 500 ml. Erlenmeyer flask, and methyl alcohol was added until the cellulose nitrate precipitated. This suspension was poured into 200 cc. of distilled water in a flask, upon which the gelatinous-appearing

precipitate flocculated and settled down. This precipitate was filtered on a weighed filter paper in a Bucher funnel. This portion, after drying, was used for the determination of the average degree of polymerization.

The 320 cc. portion was used for the fractionation. Distilled water was added slowly from a burette, with constant shaking of the flask. The particles which first precipitated out were redissolved on a continued shaking. After approximately 30 - 35 cc of water were added, a permanent turbidity set in. This was the first fraction, the portion of highest degree of polymerization.

The precipitate was removed from the liquor by centrifuging in pear-shaped centrifuge bulbs. The supernatant liquid was returned to the flask for further fractionation.

The precipitate in the bulb was removed and dissolved in a minimum amount of acetone. Methyl alcohol was added until precipitation occurred, and the precipitate was flocculated by pouring the suspension into water. The precipitated fraction was then filtered on a weighed filter paper. After drying in the vacuum dessicator and weighing, the weight of the fraction was found. All subsequent fractions were treated in this way.

To the flask containing the acetone solution a further small amount of water was added until a turbidity again appeared. This time only around 1 cc. was necessary for precipitation.



The precipitate was treated as before.

This process was continued until nine or ten fractions were collected. The last fraction, which took more water to precipitate, was not centrifuged, but the solvent was evaporated under vacuum, and then the liquid was filtered.

These fractions were used for viscosities in the determination of the degrees of polymerization.

Degree of Polymerization. The degree of polymerization was determined according to Staudinger's equation:

$$\frac{\eta_{sp}}{C} = K_m \cdot P$$

where  $\eta_{sp}$  = specific viscosity =  $(\eta_{rel} - 1)$   
C = concentration in grams per liter.  
 $K_m$  = a constant  
P = degree of polymerization.

The  $K_m$  constant for cellulose nitrate in butyl acetate is given by Staudinger and Sorokin (28a) as  $14 \times 10^{-4}$ . A one gram per liter solution of the cellulose nitrate in butyl acetate was used for the viscosity determinations.

An accurately weighed sample of cellulose nitrate of approximately 0.0500 grams was placed into an eight inch Pyrex test tube. 50 cc. of the butyl acetate was pipetted in, a few glass beads added, and the test tube was stoppered with a cork which had previously been extracted with butyl acetate. The



test tube was shaken until the cellulose nitrate was completely dissolved.

The solution was filtered through a fritted glass filter before being used for the viscosity determination. The viscosities were run in Ostwald viscometers, at 20.0° C. Five cc. of the solution were pipetted into the viscometer for the determination.

The viscometers used were calibrated by determining the viscosities of the pure butyl acetate in them. All viscosities were expressed in seconds, since the absolute viscosities were not necessary for the calculations.

A sample calculation will illustrate the method of measuring the degree of polymerization by Staudinger's method. Rearranging the equation given above,

$$P = \frac{\eta_{sp}}{C K_m}$$

If w is the weight of sample taken, then

$$P = \frac{\eta_{sp}}{\frac{w}{50} \times 1000 \times 14 \times 10^{-4}}$$
$$= \frac{\eta_{sp}}{a \times 0.0280}$$

Using the following data:

Weight of sample taken = 0.0515 grams

Viscosity of solution = 143.3 sec.

Viscosity of solvent = 56.3 sec.

$$\text{Specific viscosity} = 143.3/56.3 - 1 = 1.545$$

Then the degree of polymerization is

$$P = \frac{1.545}{0.0515 \times 0.0280} = 1072$$

### 3. Testing.

Crease-Angle. A file card approximately 0.006 inch thick was cut to a size of 3 inches by 1 5/16 inches. The card was divided in half along its length by a pencil mark. A rayon thread was wound around the narrow width of the card and the ends held in small cuts in the edges of the card. A wooden block weighing two pounds was placed on top of the wound thread and allowed to stand for twenty minutes. At the end of this period the block was removed, and the card was cut down the center line into two parts. The small angles of rayon were allowed to fall upon a smooth piece of cardboard and were arranged with a pair of tweezers so that they did not touch one another. The rayon was allowed to stand for thirty minutes, during which time the cardboard was gently tapped at intervals in order to free any angles adhering to the cardboard. The angles of recovery of the creased rayon were then measured with a protractor.

The crease-angle determinations were made in an atmosphere of 67% humidity.

Resiliency. The instrument used for making this test was a modification of the Saxl Stiffness Tester (26). Instead of using a beam balance, the chainomatic principle was used for applying the load which insured its more even application. The instrument was designed so that the force necessary to bend a prepared sample of rayon threads through a certain number of degrees could be measured. The angle of deflection could be read on an angular scale in degrees, and the force could be read in arbitrary scale units.

The resiliency of a body is its power to spring back, after deformation, to its original shape. The force necessary to bend the rayon fibers at successive angles of 10 degrees from 0 to 60 degrees was measured. Then the rayon was unbent through the same angles and the forces measured. Referring to Fig. 2, the curve AC is obtained by plotting the force against the deflection. If the fibers were perfectly resilient, upon deloading the force-deflection curve would come back along the line CA. If the fibers were perfectly plastic, they would be permanently deformed, and the deloading curve would follow the line CD.

However, the actual fiber, upon deloading, gives a force-deflection curve which follows the line CB. There is thus formed a type of hysteresis loop. The smaller the area



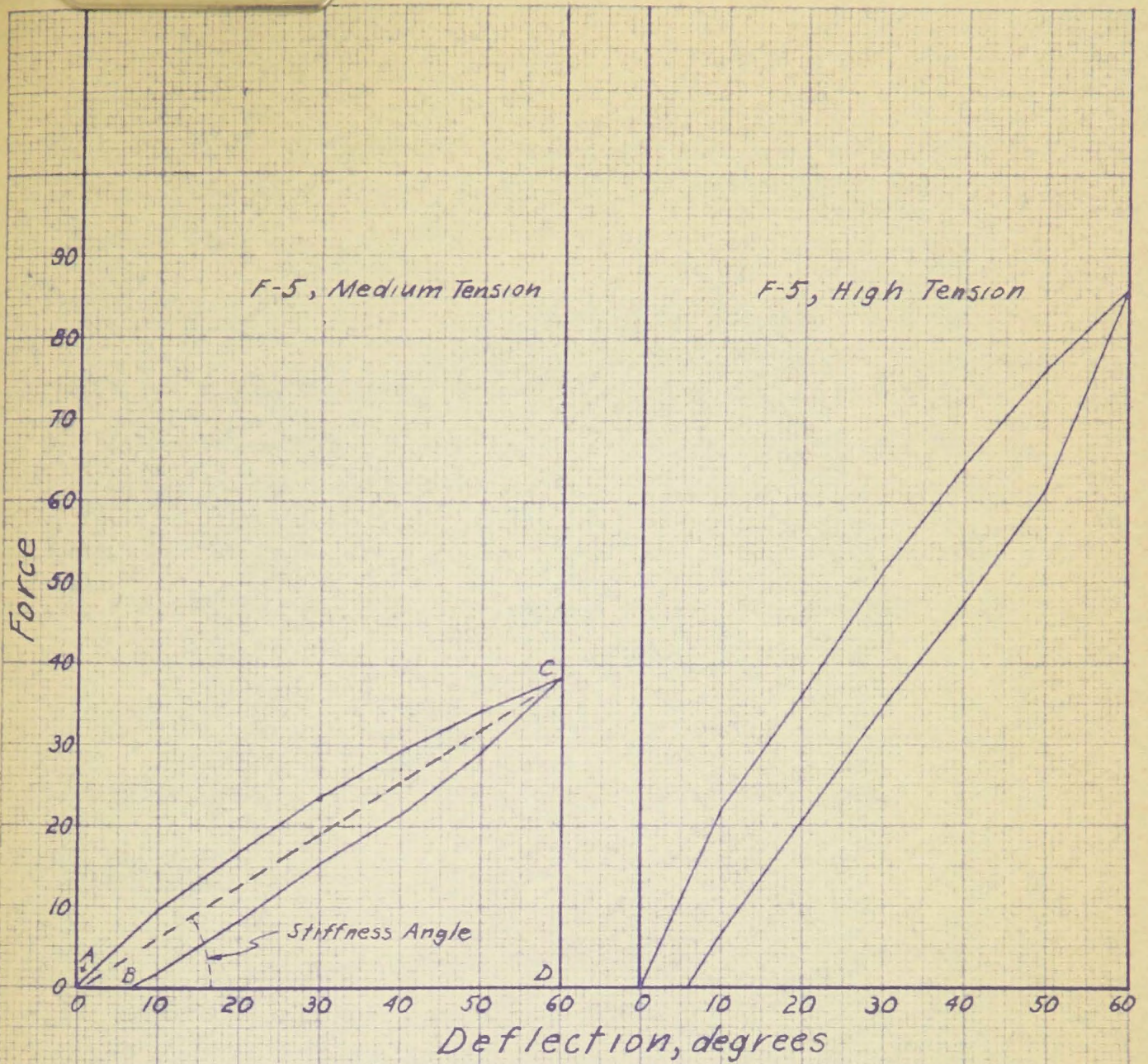


Fig. 2.  
Examples of Hysteresis Loops  
for  
Resiliency Determinations

ACB, the more resilient is the fiber. The degree of resiliency is thus the ratio of the area BCD to the area ACD. Thus as the area BCD approaches the area ACD, the fiber approaches perfect resiliency.

Stiffness. The stiffer a fiber is, the greater is the force necessary to deflect it. Referring again to Fig. 2, the slope of the hysteresis loop is a measure of the stiffness. Thus the angle the dotted line makes with the abscissa measures the stiffness. In the examples shown, the high tension fiber has a greater stiffness than the low tension one.

Tensile Properties. The dry and wet strengths and elongations were determined with the Suter serimeter.

### C. Results

Table 2 is a compilation of the tests connected with the deformation properties of the rayons. It will be noted that for each batch from F-5 to F-9, the crease-angle increases with increasing tension. This is in agreement with the Behr-Manning evaluation shown in the last column. The practical crush-resistance for all the rayons is low, but those spun with the highest tension have definitely the better crease-resistance. An inspection of the data for stiffness shows that the lowest stiffness occurs in fibers spun at medium tension. It also appears that a too high or a too low tension increases the stiffness, and that the rayons spun at the highest tension are

less stiff than those spun at the lowest tension.

In Table 3 are presented the tensile properties of the rayons. A comparison of the wet and dry elongations of the rayons spun at high tension shows that a maximum orientation of the fibers was reached, since there is very little difference, in most cases, between the two sets of values.

Table 4 presents the fractionation data for Batch , F-6, which will be used as the basis for illustrating the method of producing the distribution curves. The accumulative percent was plotted against the degree of polymerization to give the step-curve which is shown in Fig. 3. Each plotted point is the edge of a step. A smooth curve was drawn through the steps. This curve is the integral distribution curve, and a point on this curve gives the percent of material having chain lengths up to that represented by the point. This curve was differentiated graphically as shown in Fig. 3, in which the straight lines are the tangents to the correspondingly numbered points. Table 5 gives the slopes of these tangents. When the slope was plotted against  $\bar{x}$ , or D.P., the differential distribution curve was produced.

Figs. 4, 5, and 6 are the differential distribution curves of cellulose chain length in the viscose rayons under consideration. A point on one of these curves gives the percent of material having the chain length at that particular point. In Fig. 4, the curve for F-3 shows the distribution in



a normal rayon. The curves F-1 and F-2 exhibit two peaks, a result of the admixture of differently aged alkali-cellulose. Figs. 5 and 6 show similar curves for the other batches.

In order to obtain a correlation between the low molecular weight material, which was intentionally added, and the creasing properties, the distribution curves were integrated graphically between the limits 0 - 300 D.P., arbitrarily selected. This integration gave the percentages of low molecular weight material up to D.P. 300 contained in the rayon. Table 6 gives these values arranged in order of decreasing percentages. Also shown in Table 6 are the average degrees of polymerization of the batches.

In Fig. 7, the values for crease-angle, stiffness, and resiliency are plotted against the amounts of low D.P. material. For all three degrees of tension, the trend of the crease-angle curve is to decrease with increasing amounts of material of low D.P. In the case of stiffness, for low tension the trend seems to be one of constancy. For the medium and high tensions, the stiffness increases with increasing amounts of low D.P. material. In all cases, for the resiliency the tendency is to increase with increasing amounts of low molecular weight material.

Table 2

Deformation Properties of Rayons

Batch No.	Tension	Crease Angle, degrees	Stiffness, degrees	Degree of Resiliency	Behr-Manning Evaluation
F-1	Med.	105		0.632	P
F-2	Med.	101		0.614	P
F-3	Med.	108		0.529	V.P.
F-5	Low	107	49.9	0.646	V.P.
	Med.	109	34.2	0.690	V.P.
	High	110	55.7	0.720	P+
F-6	Low	97	57.2	0.656	P
	Med.	103	49.8	0.687	P
	High	115	52.6	0.683	P+
F-7	Low	99	49.2	0.646	V.P.
	Med.	107	49.4	0.665	P
	High	113	43.6	0.700	P
F-8	Low	101	54.9	0.598	P
	Med.	105	39.8	0.650	V.P.
	High	115	47.7	0.643	P+
F-9	Low	107	50.6	0.608	V.P.
	Med.	117	33.4	0.633	P
	High	125	45.6	0.656	P+

Behr-Manning Crease-Resistance Evaluation:

V.P. = Very Poor

P = Poor

P+ = Better than poor

Table 3

Tensile Properties of Rayons

Batch No.	Breaking Strength gm./den.		Elongation %	
	Dry	Wet	Dry	Wet
F-1 Med.	1.95	0.66	10.4	23.7
F-2 Med.	2.03	0.68	10.7	32.7
F-3 Med.	2.22	0.72	11.3	29.3
F-5 Low	1.46	0.30	19.4	18.9
F-5 Med.	1.45	0.30	10.4	12.4
F-5 High	2.18	0.60	5.7	5.4
F-6 Low	1.21	0.44	12.5	20.1
F-6 Med	1.51	0.49	10.0	14.1
F-6 High	2.11	0.94	5.1	5.0
F-7 Low	1.42	0.40	18.0	23.8
F-7 Med	1.57	0.48	10.1	16.1
F-7 High	2.18	0.71	5.7	5.3
F-8 Low	1.43	0.52	18.1	33.9
F-8 Med.	1.48	0.48	9.5	18.5
F-8 High	2.32	0.93	5.6	6.4
F-9 Low	1.44	0.58	15.0	31.8
F-9 Med.	1.57	0.50	8.7	17.0
F-9 High	2.42	1.24	5.6	7.1



Table 4

Fractionation Data

Batch F-6

Fraction No.	D.P.	Percent of Total	Accumulative Percent
1	1002	9.57	100.06
2	662	10.08	90.49
3	509	9.03	80.41
4	432	8.38	71.38
5	350	8.00	63.00
6	302	7.22	55.00
7	263	8.46	47.78
8	182	9.13	39.32
9	154	8.64	30.19
10	94	21.55	21.55
Average D.P.	328	---	---

Table 5

Differentiation of Integral Distribution Curve  
Batch F-6

Point No.	x	dy/dx	Slope
1	30	20/130	0.1538
2	95	18/110	0.1636
3	158	19/100	0.1900
4	188	21/110	0.1911
5	222	25/150	0.1665
6	252	17/140	0.1212
7	288	25/270	0.0926
8	315	25/190	0.1316
9	345	28/155	0.1805
10	395	24/210	0.1142
11	478	13/150	0.0866
12	610	13/230	0.0566
13	725	13/320	0.0406
14	820	11/345	0.0319
15	927	8/310	0.0258
16	1030	7/300	0.0234
17	1125	9/410	0.0220

Table 6

Proportion of Rayon Having Chain Lengths  
up to  
Degree of Polymerization of 300

Batch No.	Percent with D.P. to 300	Average D.P.
F-1	48.1	369
F-5	47.2	370
F-6	45.8	328
F-2	38.0	438
F-7	37.1	405
F-3	27.9	438
F-8	22.4	432
F-9	19.8	450



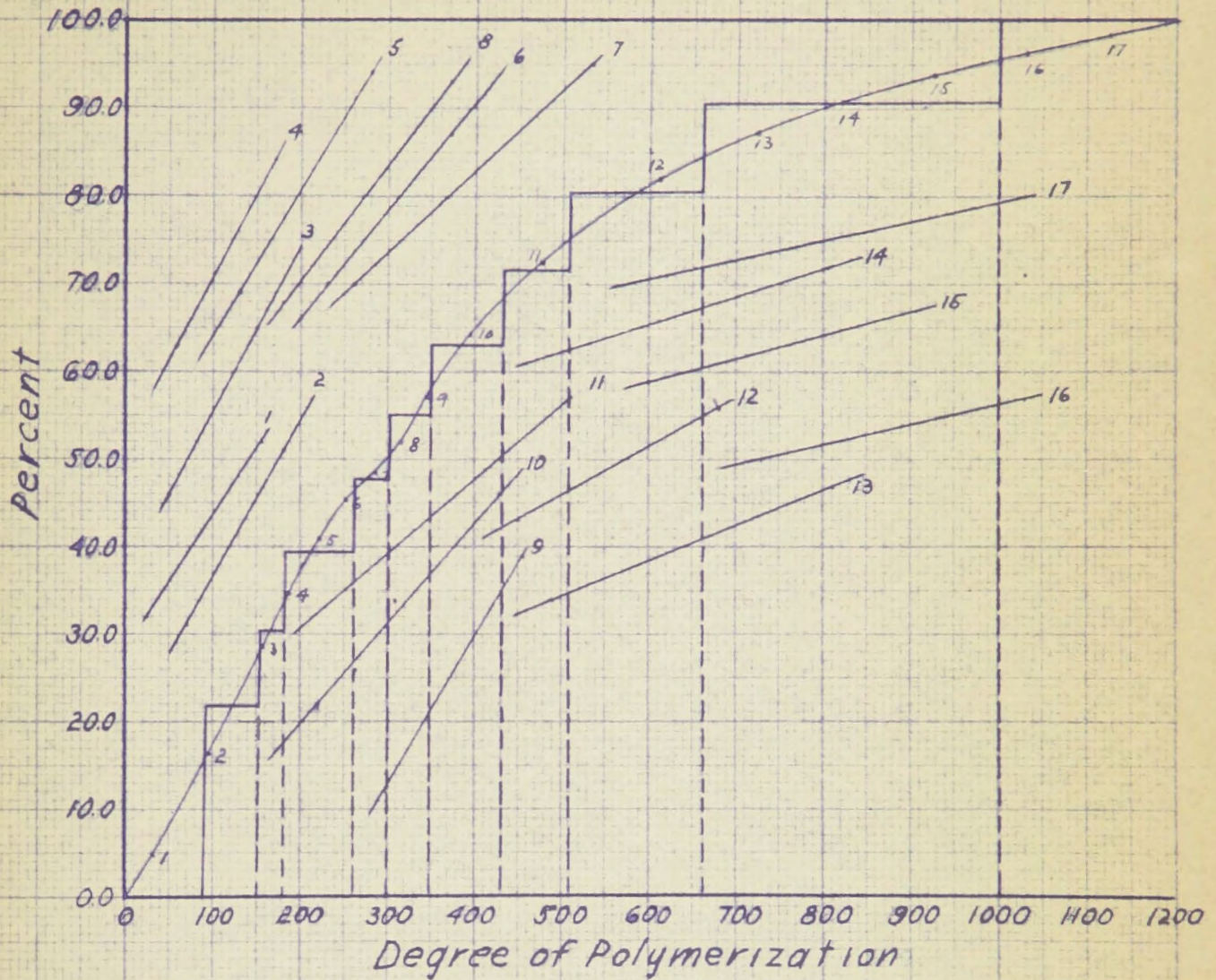


Fig. 3.

Integral Distribution Curve  
Showing  
Graphical Differentiation

F-6



Fig. 4.

Distribution Curves  
of  
Cellulose Chain Length

Legend: F-1 -----  
F-2 - - - - -  
F-3 ————

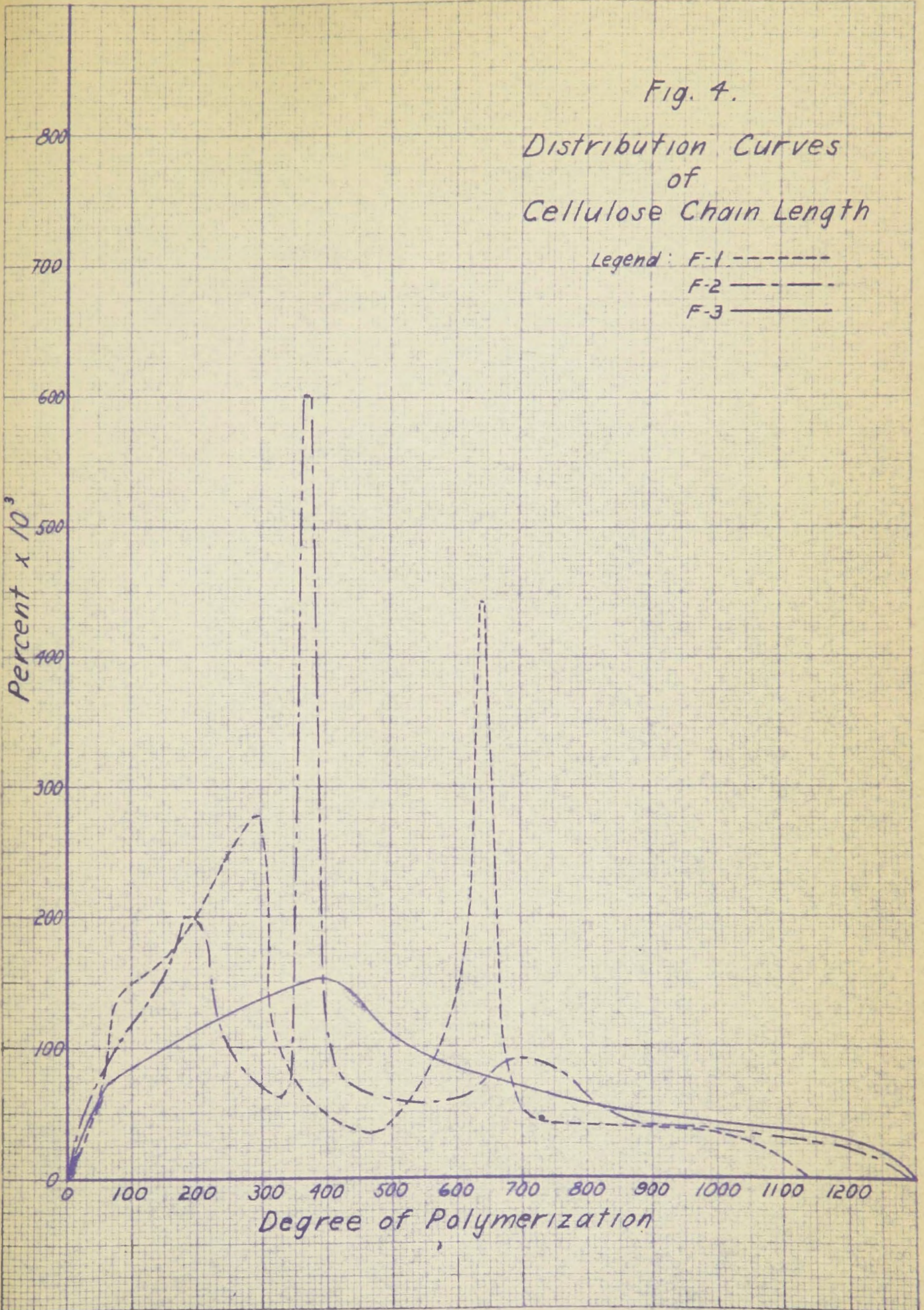




Fig. 5.  
Distribution Curves  
of  
Cellulose Chain Length

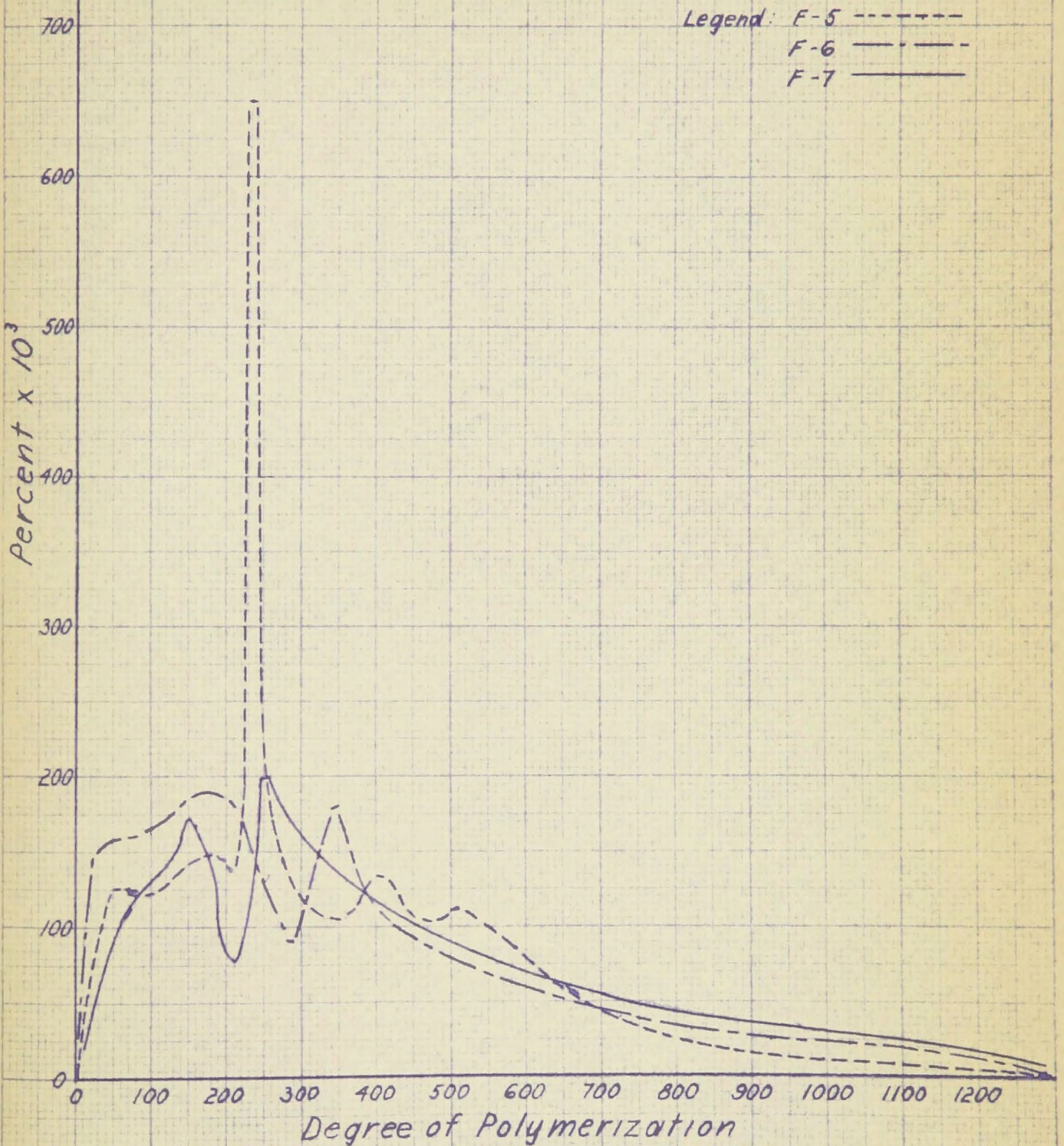
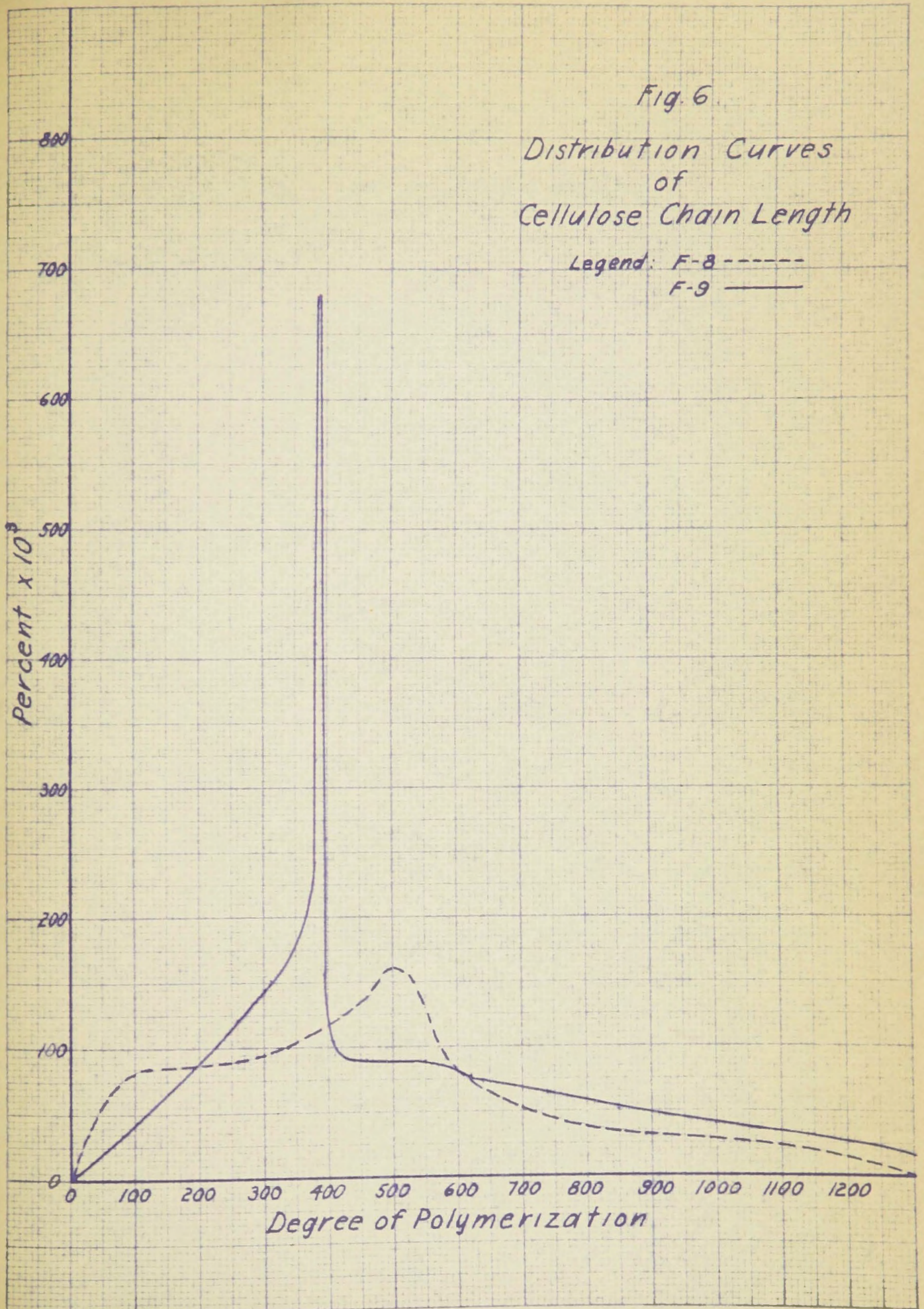




Fig. 6  
Distribution Curves  
of  
Cellulose Chain Length

Legend: F-8 -----  
F-9 —————





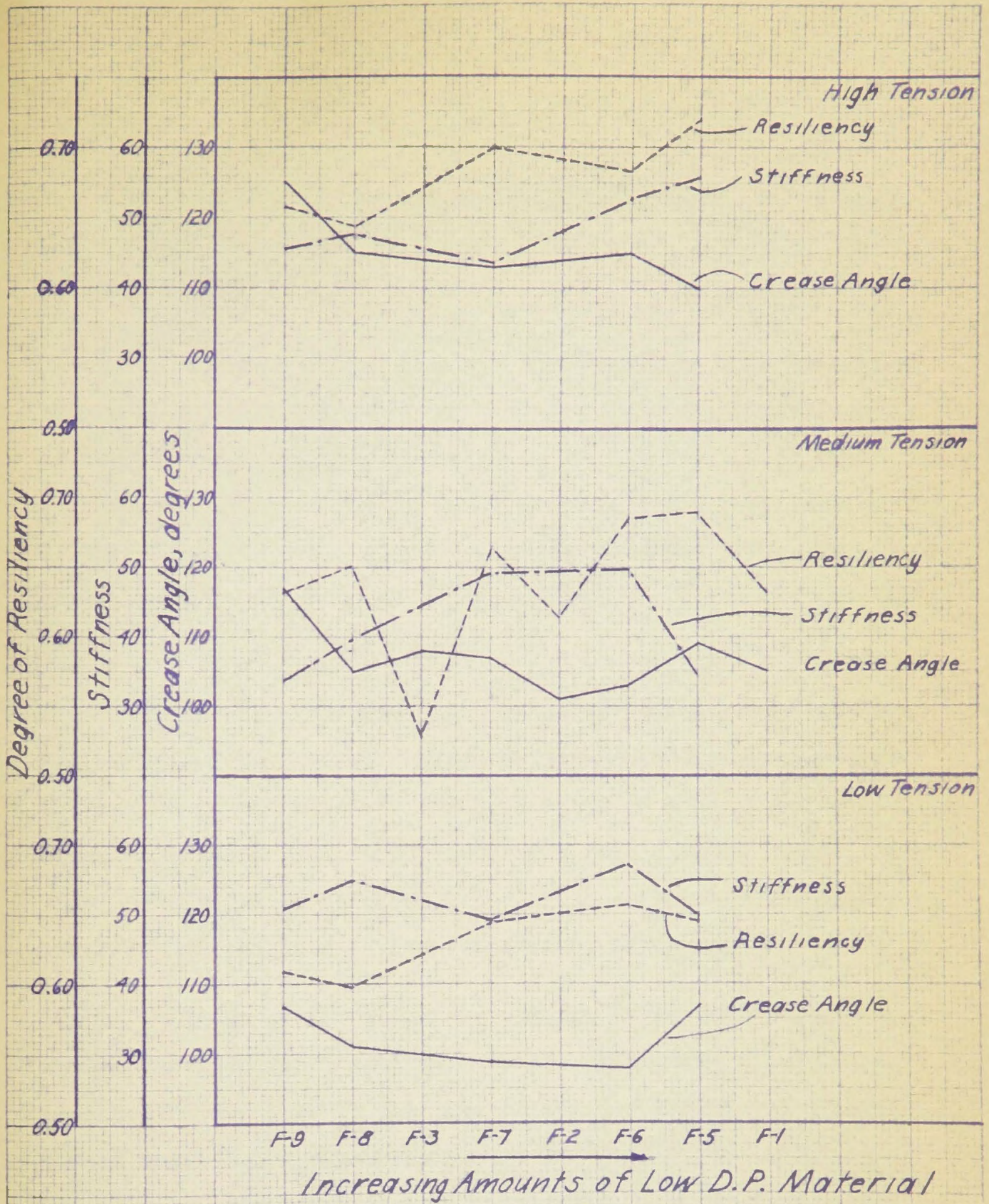


Fig. 7.  
Effect of Low D.P. Material  
upon  
Physical Properties

## DISCUSSION

The experiments in Part III on the effect of tension (or orientation) on crease-resistance can leave no doubt that in rayon a high orientation means a higher crease-resistance.

In the previous theories on the effect of orientation, it was considered that disordered micelles in the outer layer of the creased fiber became oriented, but on removal of the stress, the micelles came back to their original positions. It was also considered that in a highly oriented fiber the micelles, under the bending stress, slipped away from one another and hence were unable to recover.

However, Hermans (12) has considered that the stretching of a cellulose fiber results in more contact points between the chains in the network. This increase in contact points means an increase in the forces between the chains. Hence, when the tension is released, the forces still hold the chains together and the orientation tends to be irreversible.

In agreement with this theory, it is believed that the explanation for the better crease-resistance of the highly oriented fibers lies in the greater van der Waals' and other forces between the chains which are in a state of high orientation. Upon stretching, a highly oriented fiber will not be able to undergo much elongation due to the high forces resulting from orientation, but it can stretch up to the limit of the



forces keeping the micelles, or chains, from slipping. Upon release of the tension, the van der Waals' forces would tend to draw the chains back to their original positions. As an analogy, the rungs of a ladder may be compared to the forces holding two chains together. If one rail of the ladder is fixed, and the other is moved, the rungs will tend to pull the rail back to its original position on release of the distorting force.

It has been noted in the results that the crease-angle (crease-resistance) tends to decrease with all the tensions with increasing amounts of material of low D.P. This may be due in part to a slightly decreasing orientation, which occurs owing to the fact that there is less probability for short chains to be oriented than long ones.

Elod and Hass-Wittmuss (9) have shown that the crease-resistance is directly connected with the swelling capacity of a fiber, and that the resistance against creasing decreases with increasing degree of swelling. The effect of high tension in giving the highest crease-resistance is probably connected with the swelling capacity of the fibers, in that the higher oriented fibers have a smaller swelling capacity, and have a better crease-resistance.

In this investigation, it was hoped that the addition of amorphous cellulosic material would significantly increase

the crease-resistance. On the contrary, the crease-resistance was lowered by the addition of the low molecular weight material.

It has also been brought out here that although spinning a rayon with higher tension increases the crease-resistance, this increase is too small to be of any practical value.

It has now become apparent that it is probably impossible to produce a rayon with better crease-resistance by simple modifications in the manufacturing process such as have been attempted here. In all likelihood, further improvement lies in a fundamental change in the chemical nature of the cellulose molecule.

The results obtained herein are strictly applicable only to the conditions of the experiments, but there is a strong possibility that an extension to other conditions might show that these results have a general applicability to viscose rayon.

### SUMMARY

Attempts were made to increase the crease-resistance of viscose rayon through an increase in spinning tension. Although the crease resistance is increased in this manner, the effect is too small to be of practical value.

Measurements of resiliency and stiffness were made on the rayon spun at three different tensions. The resiliency increases with increasing tension. The stiffness is lowest at the medium tension, while the low tension material shows a greater stiffness than the high.

Titanium dioxide pigment was incorporated in viscose rayon in amounts from 2% to 25% in order to mask the creasing marks in pile fabrics. At high loadings of pigment, there was less contrast between the crushed and uncrushed surfaces. There was no practical effect upon the crease-resistance.

Rayons of varying cellulose chain-length distributions were prepared by mixing alkali-celluloses of different aging periods. The distribution curves were determined by fractionation. The crease-angle, resiliency, and stiffness of these rayons were measured. It was found that increasing amounts of short chain lengths caused a decrease in the crease-resistance, but both the stiffness and resiliency increased.

The tensile properties of the rayons were measured.



No direct correlation was found with varying amounts of material of low D.P., but the strengths increased with increasing average D.P.

## CONCLUSIONS

1. (a) The crease-resistance of viscose rayon is increased by spinning with high tensions, but the increase is too small for practical purposes.

(b) The resiliency of the rayon increases with increasing tension.

(c) A medium tension produces a rayon of less stiffness than either a very high or a very low tension. The stiffness at the low tension is greater than at the high.

2. (a) The crease-resistance of viscose rayon decreases with increasing amounts of low molecular weight material.

(b) The resiliency of the rayon increases with increasing amounts of low molecular weight material.

(c) The stiffness increases with increasing amounts of low molecular weight material.

(d) The wet strengths of the rayons decrease with increasing low molecular weight constituents. No direct correlation could be found for dry strength or elongation.

The above conclusions are based on the particular experimental conditions used in this work (see pages 14, 15, 19 and 22).

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LITERATURE CITED

1. Carothers, W. H, and Van Watta, F. J. Studies of Polymerization and Ring Formation. J. A. C. S. 55, 4714 (1933).
2. Clark, G. L. Applied X-Rays. Third Edition. Pp. 617-626. McGraw - Hill Book Co. 1940.
3. Douglas, S. D. and Stoops, W. N. Polymer Distribution in Vinyl Ester Resins. Ind. Eng. Chem. 28, 1152-55 (1936).
4. Elod, E. and Etzkorn, P. The Crumpling Strength of Rayons. Angew. Chem. 51, 45-52 (1938).
5. Ibid.
6. Ibid.
7. Ibid.
8. Ibid.
9. Elod, E. and Hass-Wittmuss, H. The Resistance of Rayon to Creasing. Melliand Textilber. 21, 461-4 (1940).
10. Hall, A. J. The Fine Structure of Artificial Silks in Relation to Dyeing and Finishing Processes. J. Soc. Dyers Colourists 46, 257-62 (1930).
11. Hall, A. J. Effect of Swelling Agents on the Creasing Properties of Viscose Silk. J. Soc. Dyers Colourists 46, 293-4 (1930).
12. Hermans, P. H. and de Leeuw, A. J. The Deformation Mechanism and Fine Structure of Hydrate Cellulose. Kolloid-Z. 81, 300-26 (1937).
13. Jurisch, I. Fractionation of Cellulose and its Significance for the Artificial Fiber Industry. Chem. Ztg. 64, 269-72 (1940).
- 13a. Lottermoser, A. and Wultsch, F. Ripening of Viscose Solutions. Kolloid-Z. 83, 188 (1938).
14. Mark, H. Quoted by Hart, H. Creasing of Textiles. Kunstseide 14, 410 (1932).

LITERATURE CITED  
(Con't.)

15. Mark, H. Intermicellar Hole and Tube System in Fiber Structure. J. Phys. Chem. 44, 764-85 (1940).
16. Mark, H. Relation between Chain Length Distribution Curve and Tenacity. Paper Trade J. 113, 34-40 (1941).
17. Ibid.
18. Oglesby, N. E. and Hoogstoel, L. E. Electrocoated Pile Fabrics. Ind. Eng. Chem. 32, 1552-54 (1940).
19. Ohl, F. Melliand Textilber. 14, 485 (1933). Cited by K. Quehl, Ref. 25.
20. Ohl, F. Research Results on the Fractionated Precipitates of Cellulose Acetate with Particular Consideration of Rayon Production. Kunstseide 12, 468 (1930).
21. Patents: Brit. 291,473 and 291,474.  
U. S. 2,129,403.
22. Patents: Ger. 535,234 and 537,036.
23. Patents: Brit. 470,636, 466,015, 468,777, 471,666, 482,159, 493,938, 501,206, 482,254, 506,507, 495,645.  
  
U. S. 2,147,401, 2,231,458, 2,223,949, 2,223,349, 2,223,948, 2,224,011.  
  
Ger. 692,322.
24. Peters, H. Creaseless Finishing Without Resins. Textile Colorist 63, 515-16 (1941).
25. Quehl, K. A Theory of Wrinkling and of Rendering Wrinkle - Proof. Melliand Textilber. 20, 76-82 (1939).
26. Saxl, I., in Rayon Handbook. Third Edition. P. 555. Rayon Publishing Co. 1939.
27. Schwarzkopf, O. The Problem of the Crease-Resistance of Rayon. Kunstseide 14, 248 (1933).
28. Ibid.
- 28a. Staudinger, H. and Sorkin, M. Viscosity Investigations of Cellulose Nitrates. Ber. 70, 1993 (1937).
29. Spurlin, H. M. Homogeneity and Properties of Nitrocellulose. Ind. Eng. Chem. 30, 538-42 (1938).





A STUDY OF THE CREASE-RESISTANCE

OF

VISCOSE RAYON

by

NATHAN SUGARMAN

ABSTRACT OF THESIS

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## A STUDY OF THE CREASE-RESISTANCE OF VISCOSE RAYON

### INTRODUCTION

Present-day crease-resisting processes for viscose rayon generally require the addition of a foreign material to the fiber structure. From a study of the theories on the internal structure of the rayon fiber and its relation to crease-resistance, it seemed that it might be possible to improve the crease-resistance by simple modifications of the manufacturing process, without the introduction of any extraneous substances.

The creasing of rayon has been explained on the basis of the micellar theory of cellulose (2, 5). In creasing a fiber, a bending occurs in which the outer fiber layer is stretched, the middle hardly strained, and the inner layer is compressed. By stretching, an orientation of the micelles, heretofore disordered, occurs. When the strain is released, the micelles spring back to their unoriented position and the crease disappears. If, however, the micelles are already oriented originally, then by creasing, the micelles will not be able to resist the pull and will slide off from one another. In this case the stretch becomes plastic and the crease remains.

This theory was based upon experiments in which the crease-resistance of stretched rayon was shown to be less than that of unstretched. H. Mark (5) believed that the ideal fiber with regard to crease-resistance was one which had an unoriented

outer layer and a highly oriented core to give it strength. To prove this, a viscose thread of high orientation was dipped in viscose which was regenerated on the surface. This should give an oriented outer layer. It was found that the crease-resistance of a fiber so prepared was greater than that of the original. Further evidence of the effect of orientation was given in an experiment with a silkworm. Natural silk, which has a high crease-resistance, is known to have a highly oriented inner core with a less oriented outer layer. Mark made fibers of extremely oriented silk by forcing a silk-worm to spin its thread under tension. This was done by means of an electric motor, which wound up the silk while drawing it out of the worm. This procedure resulted in a silk which was very strong, but which was as creasable as ordinary rayon.

The theory has also been advanced (9) that the crease-resistance of the different fibers is bound up in the relative amounts of crystalline and amorphous material present in the fibers. According to this theory, the creasing becomes greater with increasing proportion of crystallites to amorphous material with increasing crystallite size, and with increasing degree of orientation of the crystallites in the fiber. These conclusions were based largely on a review of the micellar structure of various textile fibers.

It is now recognized that high polymeric systems, such as cellulose, are not homogeneous as regards molecular



weight, but consist of mixtures of chains of varying lengths. Different samples which show the same average degree of polymerization may have entirely different chain-length distributions. Little is known about the connection between the chain length distribution and the physical properties.

It has been pointed out (8) that cellulose acetates having the same average chain length but different distribution curves seemed to have different tenacity properties. Spurlin (511) prepared a series of fractions of nitro-cellulose, from which he cast films upon which he made tenacity and folding endurance tests. He found little difference in the stress-strain curves of the various fractions, but there was a superiority of the fractions over the original blends in the fold tests. Mixtures which contained a comparatively large amount of low molecular weight material proved inferior. Mark (6) prepared blends of equal average degree of polymerization of high and low molecular weight fractions of cellulose acetate and spun them into fibers. The fibers with the greater proportion of low chain lengths had the lowest tenacity.

Since the theories of crease-resistance seemed to emphasize the effects of orientation of the micelles and of the crystalline-amorphous relationship, the problem was attacked from these two points of view.

In order to attain the greatest possible disorienta-

tion, rayon was spun with a minimum possible tension. At the same time, medium and high tensions were also used in order to determine the effect of tension (or orientation) upon the crease-resistance.

According to the crystalline-amorphous theory, the crease-resistance increases with increasing amounts of amorphous material. It was sought to introduce this amorphous material in the form of cellulose of short chain length. If a viscose solution containing very long and very short chains in definite proportions were spun into rayon, it seemed reasonable to expect the very short chains to fill in the voids between the longer chains. It appeared probable, too, that shorter chains would have less chance of becoming oriented and adding to the crystallinity of the fibers. Thus rayon fibers with artificial chain-length distributions were prepared and the effect upon the crease-resistance and other properties was determined.

#### EXPERIMENTAL

The viscose solutions contained seven percent cellulose and six and one-half percent sodium hydroxide. They were prepared according to the following procedure:

Weight of pulp: 700 gms. per batch.

Dipping: 1 hr. at 20° C. in 18% NaOH soln.

Press Ratio: 3.33

Shredding: 3 hrs. with temp. rise to 21 - 23°

Aging of Alkali-cellulose: Variable time at 18° C.

Xanthation: 1 3/4 hrs. at 28° C. 37% CS<sub>2</sub>, based upon weight of cellulose, used.

Dissolving: 2 hrs. with temp. rise to 28 - 30° C.

Ripening of Viscose: 69 - 71 hrs. at 18° C.

Mixtures of alkali-celluloses of different aging periods were used to obtain the different chain-length distributions. The aging period for a normal (unmixed) batch was two days. The mixtures were made by using varying proportions of 0-day aged to 5-day aged, calculated to give approximately the same average degree of polymerization in the rayon. The compositions of the various batches are given in Table 1.

Table 1

Compositions of Alkali-Cellulose Mixtures

F-1	4-day - 70.8%	F-6	5-day - 85.0%
	1-day - 29.2%		0-day - 15.0%
F-2	5-day - 16.4%	F-7	5-day - 47.4%
	2-day - 81.9%		2-day - 47.4%
	0-day - 1.7%		0-day - 5.2%
F-3	2-day -100.0%	F-8	2-day -100.0%
F-5	2-day - 18.4%	F-9	3-day - 46.8%
	5-day - 73.6%		2-day - 31.2%
	0-day - 8.0%		1-day - 22.0%

The mixtures of the variously aged alkali-cellulose were xanthated and dissolved in the usual manner.

A single-jet bobbin-spinning machine was used. The spinning jet contained 50 holes.



The spinning bath composition was as follows:

$\text{H}_2\text{SO}_4$	-	10.0%
$\text{Na}_2\text{SO}_4$	-	16.0%
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	-	30.0%

In order to achieve minimum tension, a small grooved roller, similar to a small pulley, was used as the thread guide. The roller was very free-rolling, and the thread passed over it with very little friction.

The roller was mounted on a holder which had attached to it three parallel glass rods mounted horizontally. When the condition of maximum spinning tension was desired, the thread was allowed to pass over these rods in such a manner that a large amount of friction occurred. This, of course, resulted in a high tension between the thread-guide and the spinning bobbin.

Medium tension was secured by using an ordinary glass thread guide.

The chain length distribution curves were determined by methods of fractionation and treatment of results as described by Jurisch (4) and Mark (7).

The crease-angles were determined by winding the rayon thread around a card 3 inches by  $1 \frac{5}{16}$  inches. A two-pound weight was placed upon the winding and allowed to stay

for twenty minutes. At the end of this period, the block was removed, and the card was cut in two along its length. The small angles of rayon were allowed to fall upon a smooth piece of cardboard and were allowed a period of thirty minutes for recovery. The angles of recovery of the creased rayon were then measured with a protractor.

The resiliency and stiffness were determined with a modified stiffness tester based upon the Saxl Stiffness Tester (10).

## RESULTS

Table 2 is a compilation of the tests connected with the deformation properties of the rayons. It will be noted that for each batch from F-5 to F-9, the crease-angle increases with increasing tension. This is in agreement with the Behr-Manning evaluation shown in the last column. The practical crush-resistance for all the rayons is low, but those spun with the highest tension have definitely the better crease-resistance. An inspection of the data for stiffness shows that the lowest stiffness occurs in fibers spun at medium tension. It also appears that a too high or a too low tension increases the stiffness, and that the rayons spun at the highest tension are less stiff than those spun at the lowest tension.

Figs. 1, 2, and 3 are the differential distribution curves of cellulose chain length in the viscose rayons

Table 2

Deformation Properties of Rayons

Batch No.	Tension	Crease Angle, degrees	Stiffness, degrees	Degree of Resiliency	Behr-Manning Evaluation
F-1	Med.	105		0.632	P
F-2	Med.	101		0.614	P
F-3	Med.	108		0.529	V.P.
F-5	Low	107	49.9	0.646	V.P.
	Med.	109	34.2	0.690	V.P.
	High	110	55.7	0.720	P+
F-6	Low	97	57.2	0.656	P
	Med.	103	49.8	0.687	P
	High	115	52.6	0.683	P+
F-7	Low	99	49.2	0.646	V.P.
	Med.	107	49.4	0.665	P
	High	113	43.6	0.700	P
F-8	Low	101	54.9	0.598	P
	Med.	105	39.8	0.650	V.P.
	High	115	47.7	0.643	P+
F-9	Low	107	50.6	0.608	V.P.
	Med.	117	33.4	0.633	P
	High	125	45.6	0.656	P+

Behr-Manning Crease-Resistance Evaluation:

V.P. = Very Poor  
P = Poor  
P+ = Better than poor



**Table 3**  
**Proportion of Rayon Having Chain Lengths**  
**up to**  
**Degree of Polymerization of 300**

<b>Batch No.</b>	<b>Percent with D.P. to 300</b>	<b>Average D.P.</b>
F-1	48.1	369
F-5	47.2	370
F-6	45.8	328
F-2	38.0	438
F-7	37.1	405
F-3	27.9	438
F-8	22.4	432
F-9	19.8	450

Fig. 1..

### Distribution Curves of Cellulose Chain Length

Legend: F-1 - - - - -  
F-2 - - - - -  
F-3 - - - - -

Percent  $\times 10^3$

800  
700  
600  
500  
400  
300  
200  
100  
0

Degree of Polymerization

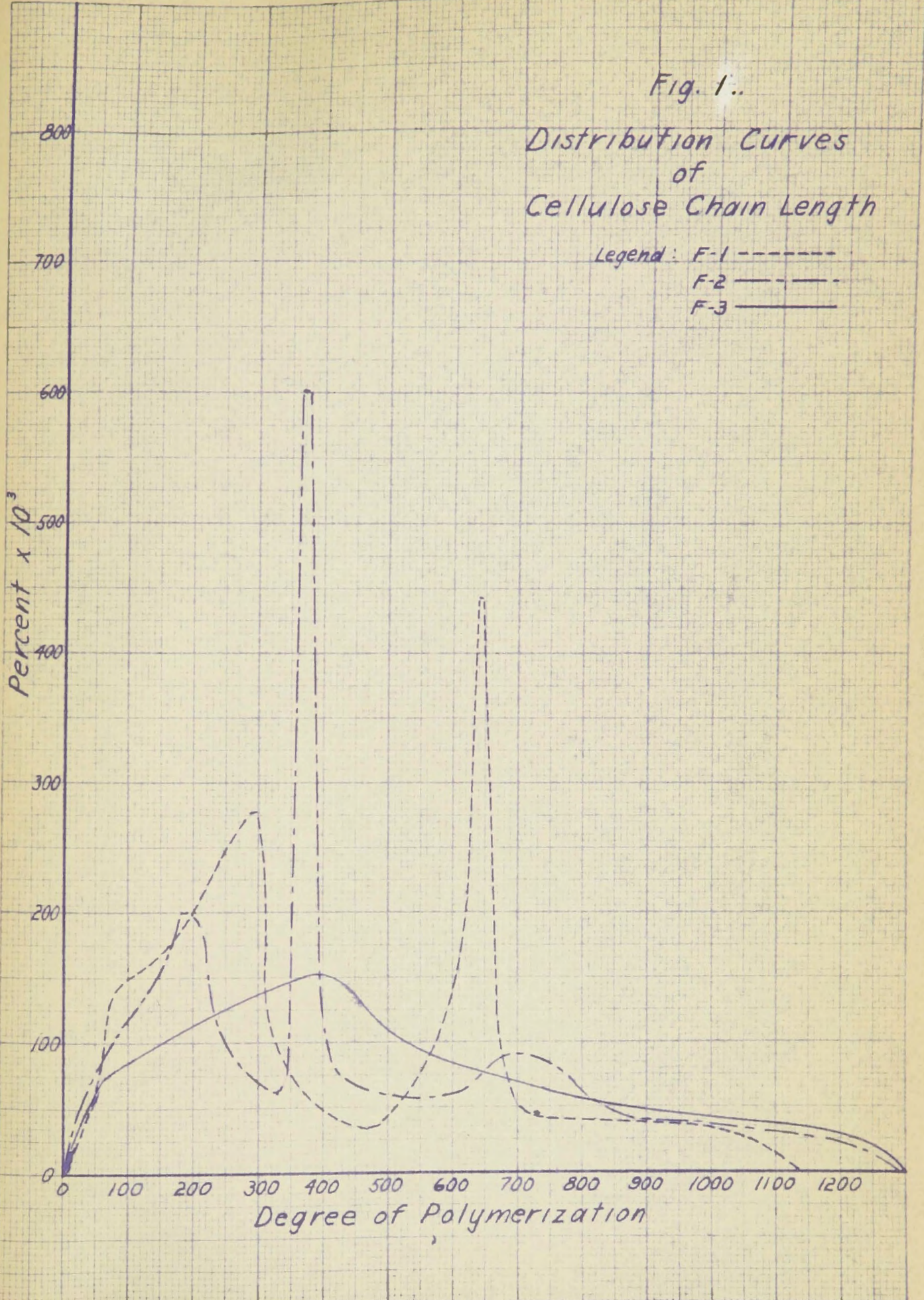




Fig. 2.

Distribution Curves  
of  
Cellulose Chain Length

Legend: F-5 -----  
F-6 - - - - -  
F-7 ————

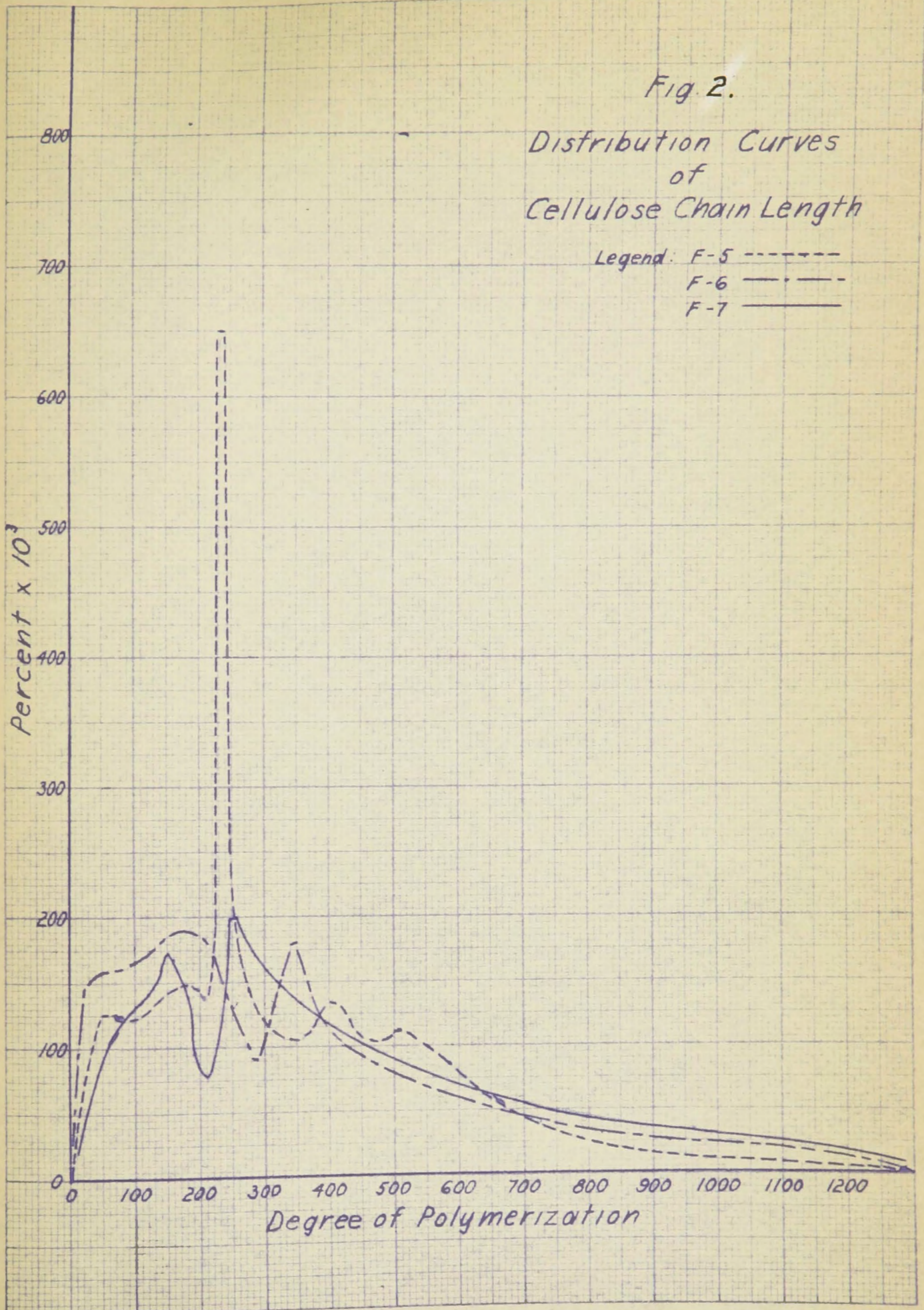
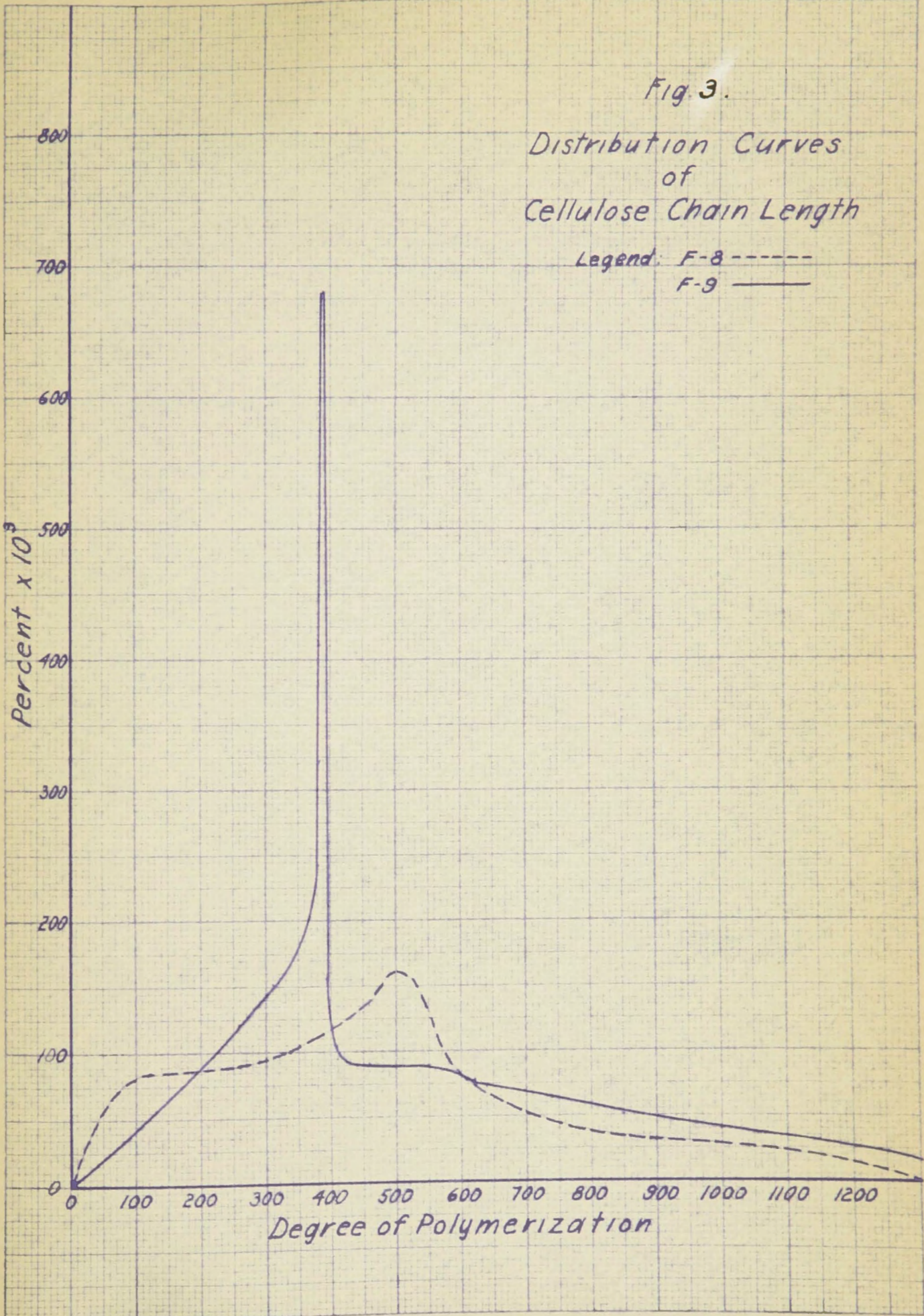




Fig. 3.

Distribution Curves  
of  
Cellulose Chain Length

Legend: F-8 -----  
F-9 —————





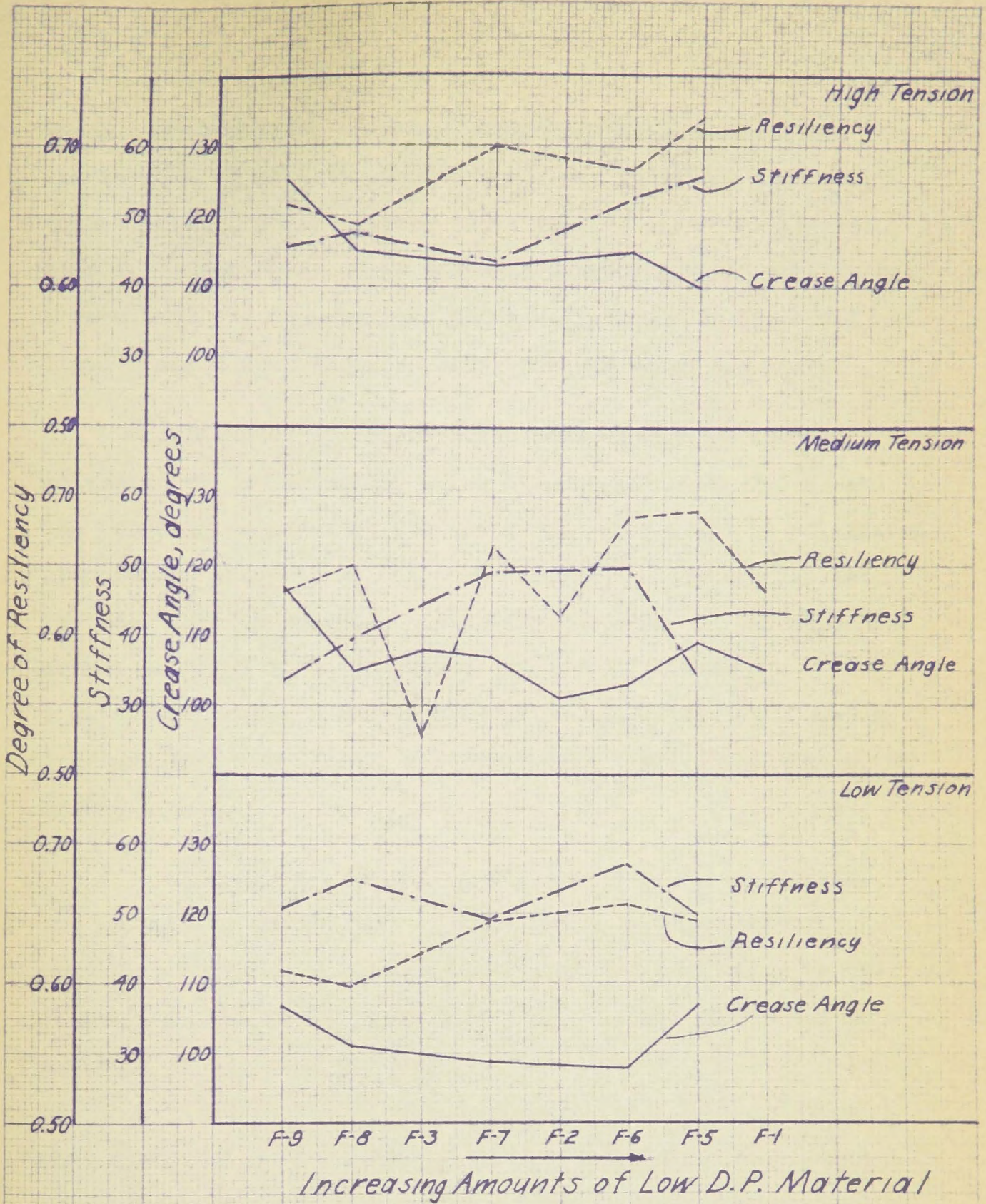


Fig. 4.  
Effect of Low D.P. Material  
upon  
Physical Properties



under consideration. A point on one of these curves gives the percent of material having the chain length at that particular point. In Fig. 1, the curve for F-3 shows the distribution in normal rayon. The curves F-1 and F-2 exhibit two peaks, a result of the admixture of differently aged alkali-cellulose. Figs. 2 and 3 show similar curves for the other batches.

In order to obtain a correlation between the low molecular weight material, which was intentionally added, and the creasing properties, the distribution curves were integrated graphically between the limits 0 - 300 D.P., arbitrarily selected. This integration gave the percentages of low molecular weight material up to D.P. 300 contained in the rayon. Table 3 gives these values arranged order of decreasing percentages. Also shown in Table 3 are the average degrees of polymerization of the batches.

In Fig. 4, the values for crease-angle, stiffness, and resiliency are plotted against the amounts of low D.P. material. For all three degrees of tension, the trend of the crease-angle curve is to decrease with increasing amounts of material of low D.P. In the case of stiffness, for low tension the trend seems to be one of constancy. For the medium and high tensions, the stiffness increases with increasing amounts of low D.P. material. In all cases, for the resiliency the tendency is to increase with increasing amounts of low molecular weight material.



## DISCUSSION

The results of these experiments show that in viscose rayon the crease-resistance increases with increasing orientation.

In the previous theories on the effect of orientation, it was considered that disordered micelles in the outer layer of the creased fiber became oriented, but on removal of the stress, the micelles came back to their original positions. It was also considered that in a highly oriented fiber the micelles, under the bending stress, slipped away from one another and hence were unable to recover.

However, Hermans (3) has considered that the stretching of a cellulose fiber results in more contact points between the chains in the network. This increase in contact points means an increase in the forces between the chains. Hence, when the tension is released, the forces still hold the chains together and the orientation tends to be irreversible.

In agreement with this theory, it is believed that the explanation for the better crease-resistance of the highly oriented fibers lies in the greater van der Waals' and other forces between the chains which are in a state of high orientation. Upon stretching, a highly oriented fiber will not be able to undergo much elongation due to the high forces resulting from orientation, but it can stretch up to the limit of

the forces keeping the micelles, or chains, from slipping. Upon release of the tension, the van der Waals' forces would tend to draw the chains back to their original positions.

It has been noted in the results that the crease-angle (crease-resistance) tends to decrease with all the tensions with increasing amounts of material of low D.P. This may be due in part to a slightly decreasing orientation, which occurs owing to the fact that there is less probability for short chains to be oriented than long ones.

Elod and Hass-Wittmuss (1) have shown that the crease-resistance is directly connected with the swelling capacity of a fiber, and that the resistance against creasing decreases with increasing degree of swelling. The effect of high tension in giving the highest crease-resistance is probably connected with the swelling capacity of the fibers, in that the higher oriented fibers have a smaller swelling capacity, and have a better crease-resistance.

In this investigation, it was hoped that the addition of amorphous cellulosic material would significantly increase the crease-resistance. On the contrary, the crease-resistance was lowered by the addition of the low molecular weight material.

It has also been brought out here that although spinning a rayon with higher tension increases the crease-resistance, this increase is too small to be of any practical value.



It has now become apparent that it is probably impossible to produce a rayon with better crease-resistance by simple modifications in the manufacturing process such as have been attempted here. In all likelihood, further improvement lies in a fundamental change in the chemical nature of the cellulose molecule.

The results obtained herein are strictly applicable only to the conditions of the experiments, but there is a strong possibility that an extension to other conditions might show that these results have a general applicability to viscose rayon.

#### CONCLUSIONS

The following conclusions are based upon the particular experimental conditions used in this work:

1. (a) The crease-resistance of viscose rayon is increased by spinning with high tensions, but the increase is too small for practical purposes.

(b) The resiliency of the rayon increases with increasing tension.

(c) A medium tension produces a rayon of less stiffness than either a very high or a very low tension. The stiffness at the low tension is greater than at the high.

2. (a) The crease-resistance of viscose rayon decreases with increasing amounts of low molecular weight material.



(b) The resiliency of the rayon increases with increasing amounts of low molecular weight material.

(c) The stiffness increases with increasing amounts of low molecular weight material.

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#### LITERATURE CITED

1. Elod, E. and Hass-Wittmuss, H. *Melliand Textilber.* 21, 461-4 (1940).
2. Hall, A. J. *J. Soc. Dyers Colourists* 46, 257-62; 293-4 (1930).
3. Hermans, P. H. and de Leeuw, A. J. *Kolloid-Z.* 81, 300-26 (1937).
4. Jurisch, I. *Chem. Ztg.* 64, 269-72 (1940).
5. Mark, H. Quoted by Hart, H. *Kunstseide* 14, 410 (1932).
6. Mark, H. *Paper Trade J.* 113, 34-40 (1941).
7. *Ibid.*
8. Ohl, F. *Kunstseide* 12, 468 (1930).
9. Quehl, K. *Melliand Textilber.* 20, 76-82 (1939).
10. Saxl, I., in *Rayon Handbook*. Third Edition. P. 555. Rayon Publishing Co. 1939.
11. Spurlin, H. M. *Ind. Eng. Chem.* 30, 538-42 (1938).