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Effect of Orientation and Trace Crosslinking on the Properties of High Wet-Modulus Rayon*

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Synopsis

Technology is now available to produce superior quality rayon fibers with a wide range of tenacity, elongation, and modulus. In-process modification results in rayon fibers suitable for a great variety of end uses as continuous filament yarn or staple, either in 100% construction or blended with synthetics. In addition to versatility, such modified rayons have unique dimensional stability and chemical resistance. The developments leading to a method for preparation and the characteristics of such a highly oriented rayon, modified through trace crosslinking, are described here. The discovery of a triple modifier system utilizing poly(ethylene glycol)–dimethylamine in the viscose and small amounts of formaldehyde in a low zinc sulfate-containing acid spin bath, has made possible the production of rayon fibers with high strength (ca. 6 g./den.) and adequate elongation (ca. 10%) for good processability and which are highly resistant to caustic soda. Among the variables studied were spin bath composition, especially the relationship between formaldehyde and zinc sulfate concentrations, and bath temperature. Optimum modifier concentrations are defined with regard to particular fiber properties desired. The effects on orientation and fiber physical properties of spinning modified viscose into formaldehyde-free and formaldehyde-containing spinning systems are described. High orientation coupled with trace crosslinking provides greatly improved resistance to caustic soda over that resulting from orientation alone.

Introduction

There have been three major factors responsible for the development of new, high-performance rayons in the last 10 or 20 years. First, a review of the progressive change in purity for viscose-grade chemical cellulose reveals that long-chain cellulose content increased from less than 90% in 1930 to almost 99% by 1967. Second, the application of modifiers in the viscose or during spinning provided controls over the degree and type of crystallinity in the regenerated cellulose. This proved to be a vital tool in shaping both fiber morphology and fiber properties. Third, trading technology with synthetic polymers, cellulose took its place among the most functional polymers known to man.

Of the five general classes of rayon produced today, regular and polynosic rayons are generally made without modifiers, while the regeneration rate

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TABLE I
Characteristics of Various Rayon Fibers

	Regular	LWM (HT)[a]	IWM (HT)[a]	HWM (HT)[a]	Polynosic
Tenacity, g./den.					
Conditioned	1.5–2.8	3.0–5.0	3.5–5.0	4.0–7.5	3.6–5.0
Wet	0.7–1.6	1.9–3.8	3.0–3.8	3.0–6.0	2.5–4.0
Elongation, %					
Conditioned	15–30	14–25	12–17	5–10	7–11
Wet	20–35	17–30	14–20	6–11	8–15
Wet modulus, g./den.	0.12–0.25	0.12–0.25	0.5–0.7	1.8–2.5	0.9–1.1
Loop strength, g./den.	1.0–1.5	1.0–2.5	0.6–1.1	0.7–0.95	0.5–0.9
Knot strength, g./den.	0.7–1.6	1.7–2.5	0.6–1.8	1.2–2.8	1.2–2.9
Tensile strength, 1000 psi	29–46	58–90.5	60–100	80–156	60.5–120
Moisture regain, %	12–15	12.5–14.5	11–14	10–12	10–12
Fiber DP	300	300–500	350–600	600–800	550–650
Modifier	None	PEG + amine	PEG + amine	PEG, amine, HCHO	None
Stretch, %	60–120	100–120	140–150	200–400	200–300
Crystal size	Small	Small	Intermediate	Large	Large
Cross section	Skin-core	All-skin	All-skin	Layered	All-skin
Dimensional stability	Low	Low	Good	Excellent	Excellent
Caustic resistance	Low	Low	Good	Excellent	Excellent
Application	Versatile	Industrial, blends	Blends	100%, blends	100%, blends

[a] L is low, I, intermediate, and H, high wet-modulus (WM) rayons of high tenacity (HT).

of low, intermediate, and some high wet-modulus rayons is controlled by modifiers. One of the authors in a review of the past, present and prospects of viscose rayon[1] summarized the properties of these five types of rayon (Table I). Production of these fibers involves a wide range of specifications and conditions. Carbon disulfide content, aging, ripening, the number, temperature, and composition of spin baths, and the many other variables each have definite bearing on the type of product obtained. No factors are more important, however, than the cellulose source, preparation of the viscose, the type of modification, and the degree of orientation effected through stretch.

The 13 North American and 150 world rayon manufacturers produced about 7.5 billion pounds of fiber in 1966. Rayon yarn, the main outlets of which are tire cord and industrial yarn, is in a continuing battle with synthetics such as nylon and polyester. High-tenacity, high-modulus, low-elongation, rayon tire cord is ideally suited for the newly developed radial-ply automobile tires. The fibers used by some manufacturers to make these cords have conditioned tenacities of up to 7.5 g./den., elongation of 5–6%, and modulus, in terms of tenacity at 5% extension, of 5.5–6.0 g./den. However, conventional high-tenacity rayon cords are being effectively used in some components of the presently produced radial tires.

Developments in staple fiber, which represents almost three-quarters of the total rayon production were no less dramatic. Along with the number of regular rayons, low wet-modulus staple fibers like Durafil (Courtaulds), Avron (FMC-AVD), Airon TK (Chatillon); intermediate wet-modulus fibers, Airon PL (Chatillon), Fiber 24 (Industrial Rayon), Fiber-40 (FMC-AVD), Vincel (Courtaulds); and the polynosic fibers, Zantrel (Enka), Polycot (Teijin) are some of the better known staple fibers receiving wide commercial acceptance today.

Modifiers used in spinning low, intermediate, or high wet-modulus fibers act as regeneration retardants. The material being extruded through the spinneret holes is viscose, i.e., cellulose xanthate dissolved in caustic soda. Under the conditions of the acid primary spin bath, cellulose xanthate is first coagulated and then completely regenerated as cellulose, rayon. Cellulose xanthate in solution cannot be oriented, and only a very small degree of orientation, if any, can be introduced after regeneration. Coagulated cellulose xanthate, however, is fully accessible to accept orientation and modifiers help to maintain the state of coagulation by delaying regeneration. It is best to separate at this point catalytic modifiers, such as surface-active agents, from reactive modifiers, such as cross-linking agents.

During the course of investigations on high performance rayons at Rayonier's Research Laboratories, among the most important developments has been the discovery of the means to attain synergistic regeneration retardation of viscose based on a mixed modifier system consisting of dimethylamine and poly(ethylene glycol).[2] This modifier system has been used successfully for the production of tire yarns of high strength and good flex resistance. The same or variations of this mixed modifier system are also being used to produce high performance rayon staple.

A more recent development of Rayonier research has been the definition of balanced conditions under which utilization can be made of triple modifications, yielding a still stronger fiber of remarkably improved toughness, dimensional stability, and caustic soda resistance. This is accomplished by spinning a two-way modified viscose, containing dimethylamine and poly(ethylene glycol) (Carbowax) into an acid bath containing a third modifier, formaldehyde.

Of the large number of modifiers considered for use in the viscose process, formaldehyde is particularly effective as a regeneration retardant. The reaction of various aldehydes with cellulose xanthate was patented 30 years ago, in 1938,[3] but without the benefits of modern viscose technology. It took over 20 years before formaldehyde could be applied successfully as a viscose modifier. In the first of two patents, Mitchell and his co-workers described the above-mentioned mixed-modifier system, the effectiveness of which may be increased when zinc salts are applied simultaneously in the spin bath.[2] Such modification permitted spinning under high tension at greatly increased speeds, while the fiber was stretched over 100%. All-skin type filaments were obtained. As described in a second patent, the incorporation of up to 1% formaldehyde into the viscose produced similarly all-skin type filaments of about 5 g./den. conditioned yarn tenacity; 0–3% $ZnSO_4$ was used in the primary bath.[4] Stretches of up to 120% were employed to impart orientation.

While Mitchell used 34–45% carbon disulfide to prepare viscose, some Courtaulds patents describe the manufacture of formaldehyde-modified, high-tenacity rayon filaments by using over 50% carbon disulfide in viscose making. These procedures employed 0–2% formaldehyde and 0–2% $ZnSO_4$.[5–7]

Formaldehyde reacts with cellulose xanthate, the product being similar in structure to cellulose double esters, I.

$$\text{Cell—OCSSR}$$

I

This school of thought was reinforced by Thurm and Tryon,[8] who proposed that the product in the reaction of formaldehyde with methyl and ethyl xanthates was ROCSSROH (II).

The reaction

$$\text{CHOH} + \text{RSH} \rightarrow \text{RSCH}_2\text{OH} \qquad (1)$$

was described by Posner in 1903,[9] over 60 years ago. The hydroxymethyl compound should react with a further mole of thiol,

$$\text{RSCH}_2\text{OH} + \text{RSH} \rightarrow \text{RSCH}_2\text{SR} \qquad (2)$$

which is a very plausible mechanism indeed for the crosslinking of sodium cellulose xanthate:

$$\text{Cell—OCSS}^- \xrightarrow{\text{CHOH}} \text{Cell—OCSSCH}_2\text{O}^- \xrightarrow{\text{Cell-OCSS}^-} \text{Cell—OCSSCH}_2\text{SSCO—Cell} \qquad (3)$$

Zinc also reacts with the xanthate group [eq. (4)]:

$$2\ \text{Cell—OCSS} \xrightarrow{Zn^{++}} \text{Cell—OCSSZnSSCO—Cell} \qquad (4)$$

The reaction with zinc is apparently preferred and, if there is sufficient quantity of zinc available, is the dominating reaction. Both zinc- and formaldehyde-crosslinked xanthates are more stable than the parent xanthate, thus modification or delayed regeneration is accomplished.

Formaldehyde reacts not only to form the thiomethylene link, but also through glycosidic hydroxyl groups to form a methylene crosslink,

$$2\ \text{Cell—OH} + \text{HCHO} \rightarrow \text{Cell—OCH}_2\text{O—Cell} \qquad (5)$$

Methylene links are much more stable than those formed between two xanthate groups. In this manner formaldehyde has a dual function in the viscose process. On the one hand, it delays regeneration by reacting with two xanthate groups; most of these bonds are eventually destroyed during the (delayed) regeneration step. On the other hand, it forms methylene crosslinks which remain in and influence the properties of the regenerated cellulose, rayon.

The purpose of this paper is to demonstrate the action of formaldehyde as a viscose modifier as well as a trace crosslinking agent. It shall have to be remembered that orientation can be introduced only while regeneration is being delayed and viscose is in the state of coagulation.

The literature on cellulose crosslinking in general is quite voluminous and is reviewed adequately in textbooks as well as in scientific publications; a treatment of this subject is quite beyond our present intent. Crosslinking of cellulose with formaldehyde dates back to 1904.[10] A comprehensive review of the literature relating to the interaction of cellulose and formaldehyde was published by Roff in 1963.[11] In general, crosslinking in cellulosic fibers reduces the ability of fibers to swell, decreases solubility, changes dye affinity, reduces extensibility, and increases strength, elastic recovery, and dimensional stability. The interaction between cellulose and formaldehyde is greatly dependent on the conditions, whether aqueous or nonaqueous.

Experimental

Because of the profound effects observed in earlier Rayonier research on viscose regeneration retardancy of formaldehyde used in a "triple" modification combination with dimethylamine and poly(ethylene glycol),[4] investigations were undertaken to develop this technology fully. By keeping as many conditions constant as possible and using DMA and Carbowax in the viscose, the concentration of zinc and formaldehyde in the primary spin bath were two of the variables first studied.

Relatively unripened, high (500–600) DP viscose modified with DMA/Carbowax-1540, was spun into an acid primary bath containing 0–6% zinc sulfate and 0–2% formaldehyde; the properties of the fibers so produced were evaluated on a contour plot (Fig. 1). Examination of this contour plot indicates an optimum tenacity area at 0.7–1.0% formaldehyde and 2–3% zinc sulfate concentration. A fiber having average conditioned tenacity of 6 g./den., elongation of 9%, and wet modulus of 1.8 g./den. was obtained in the preliminary experiments. This work gave the first indication of the effect that zinc and formaldehyde were competitive as

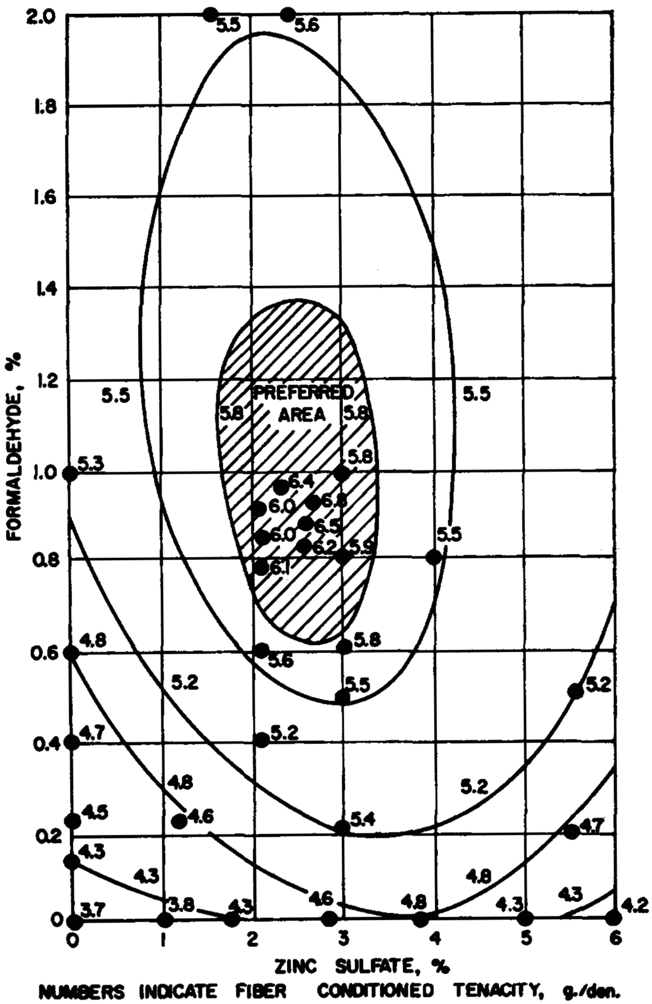

Fig. 1. Experimental Rayonier high wet modulus fiber. Grid experiment with optimum range of HCHO and Zn modification.

regeneration retardants. The investigation was subsequently extended to cover variables in the aging, xanthation, ripening, and other phases of viscose making, with particular emphasis on degree of polymerization and carbon disulfide requirements, to establish an optimum balance in the process.

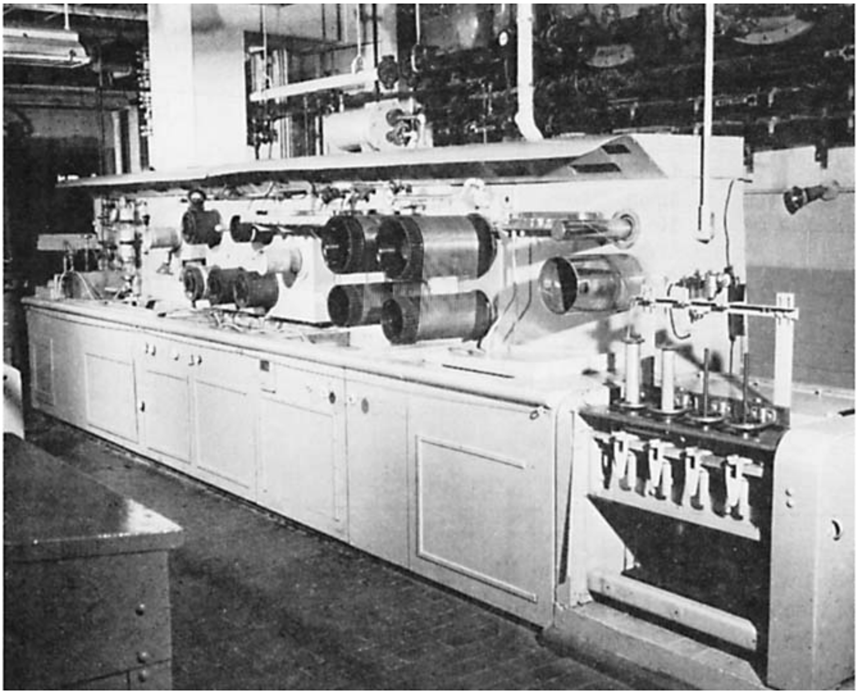

Fig. 2. Spinning machine used to produce experimental rayon fibers at Rayonier's Eastern Research Division.

Optimum spinning conditions were obtained by using a minimum ripened, relatively low-carbon disulfide (<40%), high DP viscose spun into a primary acid bath maintained at 20–25°C. The regeneration retarding effect of the triple modifier system, with dimethylamine and poly(ethylene glycol) added to the viscose during the dissolving step and formaldehyde in the primary bath, coupled with the action of zinc, also added to the primary bath as zinc sulfate, permitted maximum orientation of the filaments between the primary and secondary spin baths; stretch levels of 200% or higher could be attained. Orientation was indeed completed in a hot (88°C.) secondary acid bath, with partial dexanthation and some crosslinking taking place. The viscose contained 6% cellulose and 6% caustic soda and had a ball-fall viscosity of 40–50 measured at 20°C. It also contained 2.4% dimethylamine and 1.7% Carbowax-1540, calculated on the basis weight of the cellulose. Xanthate sulfur in the viscose was from 1.4 to 1.6%, and sodium chloride (salt) index from 12 to 13, both being measured at spin. The spinneret used had about 2900 holes of 0.0025 in. diameter each and produced fibers of 1.5 den./filament.

These experimental fibers were spun on a rayon spinning machine located at the Research Laboratories of Rayonier Incorporated. This spinning machine, shown in Figure 2, is versatile, allowing optimum coagulation and regeneration cycles. Thus, the maximum stretch obtainable

TABLE II
Average Properties of Experimental Rayonier High Wet Modulus Fiber

Property	
Denier	1.5
Tenacity, g./den.	
Conditioned	6.0
Loop	0.7
Knot	2.1
Wet	4.8
6.5% NaOH	2.8
Elongation, %	
Conditioned	9.0
Wet	10.0
6.5% NaOH	14.0
Wet tenacity at 5% extension, g./den.	1.8
Water retention, %	60
DP	550
Solubility in 6.5% NaOH at 20°C., %	3.5

with a given viscose and modification can be adjusted by setting the rate of viscose delivery, the speed of the godet roll and the speed of the wash reels.

The viscose was spun into a primary bath containing 6.4% sulfuric acid, 10.0% sodium sulfate, 2.3% zinc sulfate, 0.2% dimethylamine, and 0.9% formaldehyde at a temperature of 25°C. Leaving the primary bath, the acidic tow is stretched between the godet roll and first wash reel, through a secondary acid bath. Coagulation takes place in the primary bath and partial regeneration in the secondary. The secondary bath contained 3% sulfuric acid and was maintained at 88°C. The regenerated filaments were washed and cut while still in the acid state. Final washing, desulfurization, finishing, and drying were carried out in sequence.

Typical properties of the fiber so produced are shown in Table II while stress–strain curves of this fiber are depicted in Figure 3.

To obtain optimum fiber properties, the objective is to orient the filaments to the limit by applying maximum stretch. This limit is called maximum smooth stretch and is somewhat analogous to the plastoelastic–

TABLE IIIA
Viscose Conditions for Producing Rayonier Experimental High Wet-Modulus Fibers

Cellulose, %	6.0
NaOH, %	6.0
Modifiers (% on cellulose)	
Dimethylamine	2.4
Carbowax-1540	1.7
Xanthate sulfur at spin, %	1.5
Salt index at spin	12–13
Viscosity, bfs.	40–50
DP	550–650

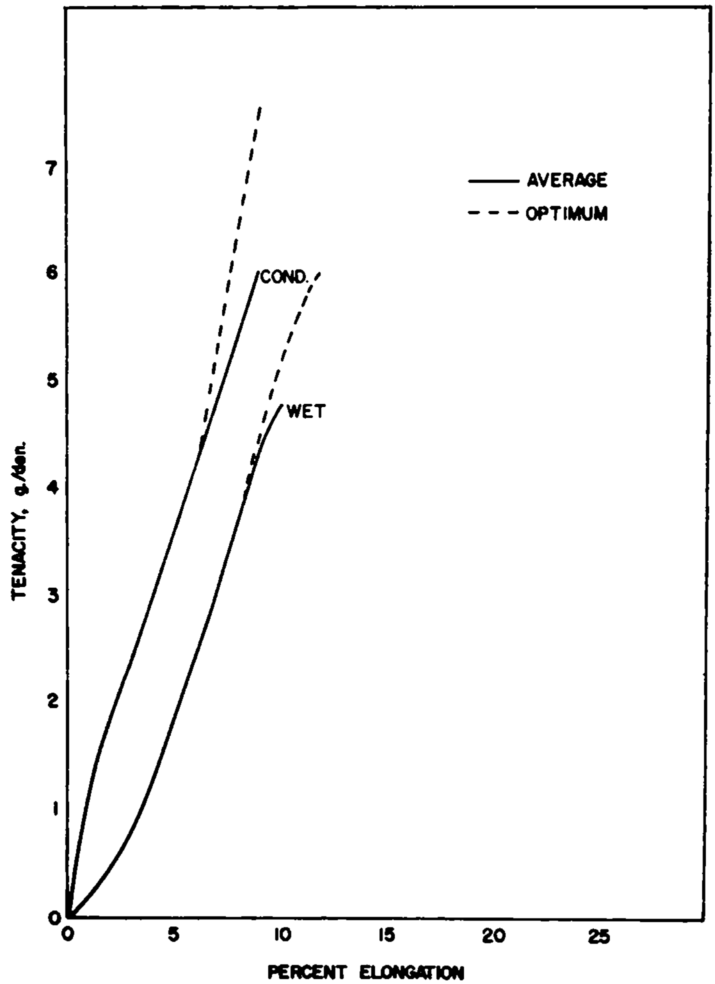

Fig. 3. Experimental high wet modulus fiber. Stress–strain curves.

permanent deformation interchange. Coagulated cellulose xanthate is stretched to the maximum, while avoiding filament breakage.

In subsequent experiments, fibers were spun at varying levels of stretch, up to and including maximum smooth stretch, under two distinctly different conditions. First, the above-described viscose with the mixed modifier system of dimethylamine and poly(ethylene glycol) was spun into a formaldehyde-free acid bath. Both the rate of viscose delivered through the spinneret holes and the speed of the washreels were kept constant, while the speed of the godet roll was varied to yield the desired levels of stretch. Second, an identical viscose also containing mixed modifiers was spun into the same primary acid bath which, in this case, contained 0.9% formaldehyde. Viscose and spin-bath conditions are shown in Tables IIIA and IIIB, respectively. Without formaldehyde modification, fibers

TABLE IIIB
Conditions for Spin Baths for Producing Rayonier Experimental High Wet Modulus Fibers

	Primary	Secondary
H_2SO_4, %	6.4	3.0
Na_2SO_4, %	10.0	—
$ZnSO_4$, %	2.3	—
Dimethylamine, %	0.25	—
HCHO, %	0 or 0.9	—
Temperature, °C.	25	88

were produced at four levels of orientation, employing 75, 125, 170 and the maximum smooth stretch obtainable of 190%. Beyond 190% stretch, the tow became rough, indicating filament damage.

With 0.9% formaldehyde in the primary bath, fibers were obtained similarly at 75, 125, and 170% stretch, but also at 200, 220, and 240 and at the maximum smooth stretch of 260%. Regeneration and processing were carried out in the normal manner.

Results and Discussion

It was shown in Table I that viscose containing the mixed modifier of poly(ethylene glycol) and dimethylamine spun under certain conditions yields an intermediate wet modulus type rayon. The wet modulus of this fiber is in the range of 0.5–0.7 g./den. Triple modification, with formaldehyde as the third modifier, results in a markedly different fiber with a higher wet modulus in the range of 1.8–2.5 g./den. Other properties are correspondingly different.

The primary purpose of this investigation was to study the properties of fibers spun at varying degrees of orientation with and without formaldehyde modification. Orientation is affected through stretch; the higher the stretch applied, the higher the degree of orientation. The viscose used was identical in both studies. Regeneration and post-regeneration treatments were also the same.

Without formaldehyde modification, the maximum level of stretch attainable was 190%. Fibers were spun at 75, 125, 170, and 190% stretch, respectively. The properties of the fibers spun at each of these four levels of orientation are shown in Table IV. Physical testing was carried out according to ASTM standard methods. Filament denier was measured on the SATEC vibrascope and tensile properties on the Instron; gauge length was fixed at 1 in., and an extension rate of 0.5 in./min. was applied. Wet breaks were made on completely immersed specimens, while denier and conditioned tenacity were measured in an atmosphere of 60% R.H. at 75°F. Conditioned loop and knot tenacities were measured in accordance with accepted methods.

Increasing stretch from 75 to 190%, fiber conditioned tenacity increased from 3.2 to 5.3 g./den. and wet tenacity from 2.0 to 3.8 g./den. Both

TABLE IV
Effect of Increasing Orientation on Fiber Properties Without Formaldehyde in the Spin Bath

								6.5% NaOH			
Stretch, %	Cond. tenacity, g./den.	Cond. elongation, %	Wet tenacity, g./den.	Wet elongation, %	Wet modulus, g./den.	Loop tenacity, g./den.	Knot tenacity, g./den.	Tenacity, g./den.	Elongation, %	Wet modulus, g./den.	Solubility, %[a]
75	3.2	14.1	2.0	18.6	0.5	1.2	2.6	0.1	8.7	0.1	20.3
125	4.2	10.8	2.9	14.8	0.8	1.1	2.1	0.2	11.7	0.1	15.9
170	5.0	12.6	3.3	11.7	1.0	0.9	1.6	0.6	16.8	0.1	14.6
190	5.3	12.6	3.8	11.1	1.1	1.1	1.6	1.0	23.5	0.1	13.2

[a] Solubility in 6.5% NaOH at 20°C.

TABLE V
Effect of Increasing Orientation on Fiber Properties with Formaldehyde in the Spin Bath

								6.5% NaOH			
Stretch, %	Cond. tenacity, g./den.	Cond. elongation, %	Wet tenacity, g./den.	Wet elongation, %	Wet modulus, g./den.	Loop tenacity, g./den.	Knot tenacity, g./den.	Tenacity, g./den.	Elongation, %	Wet modulus, g./den.	Solubility, %[a]
75	3.3	13.6	2.1	18.1	0.6	1.4	2.4	0.2	9.4	0.1	7.0
125	4.1	12.7	2.6	15.1	0.6	1.4	2.6	0.6	13.3	0.1	6.3
170	4.7	13.2	3.6	14.2	0.9	1.4	2.4	1.0	16.0	0.2	5.6
200	5.7	10.4	4.2	10.9	1.3	1.0	1.9	1.7	15.0	0.2	4.2
220	6.0	10.2	5.0	11.1	1.4	0.9	1.8	2.2	15.6	0.2	3.9
240	6.2	10.7	4.7	11.8	1.5	0.9	1.8	2.3	16.5	0.2	3.7
260	6.8	9.5	4.6	10.3	1.9	0.9	1.6	2.8	15.0	0.2	3.5

[a] Solubility in 6.5% NaOH at 20°C.

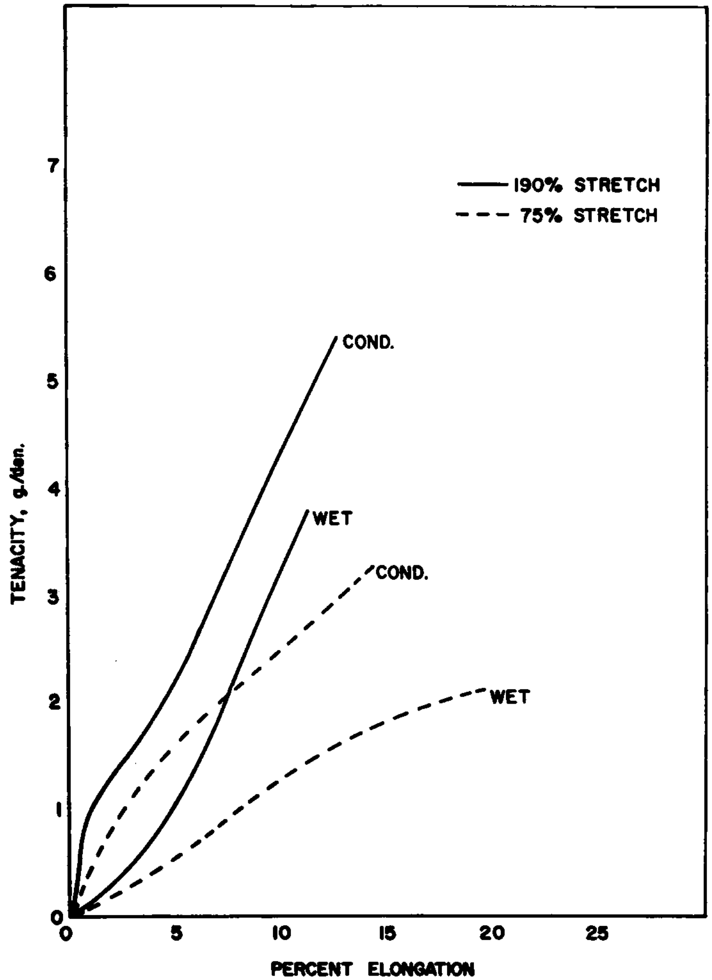

Fig. 4. Effect of stretch on stress–strain properties of fibers spun without formaldehyde.

conditioned and wet elongations decreased rapidly, from 14.1 to 12.6% and from 18.6 to 11.1%, respectively, reaching the lower levels even before maximum smooth stretch was applied. Both loop and knot tenacities decreased only slightly with increasing stretch. The wet modulus of the fiber produced at 75% stretch was 0.5 g./den. and increased to 1.1 g./den. when 190% stretch was applied. A fiber with such properties is indeed superior to fibers generally classified as intermediate wet-modulus type. The effect of stretch on the stress–strain properties of fiber produced without formaldehyde modification is shown in Figure 4.

By spinning the same viscose into an acid bath containing, in addition to the other components, 0.9% formaldehyde, it was possible to increase maximum attainable smooth stretch to 260%. Fibers were also collected at lower stretch levels of 75, 125, 170, 200, 220, and 240%, respectively.

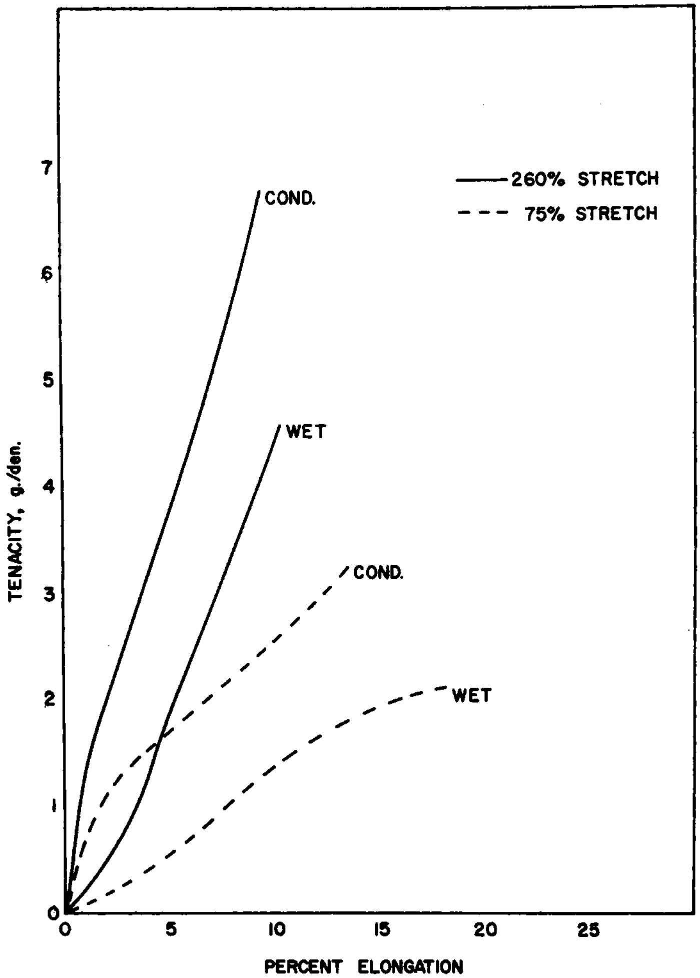

Fig. 5. Effect of stretch on stress-strain properties of fibers spun with formaldehyde.

The properties of fibers spun at each of these levels of orientation are shown in Table V. Conditioned tenacity ranged from 3.3 to 6.8 g./den.; wet tenacity from 2.1 to 4.6 g./den.; loop tenacity from 1.4 to 0.9 g./den.; and knot tenacity from 2.4 to 1.6 g./den. Conditioned elongation was from 13.6 to 9.5%, while wet elongation was from 18.1 to 10.3%. This is a superior high wet-modulus fiber with a wet modulus of up to 1.9 g./den.

The effect of stretch on the stress-strain properties of fiber produced with formaldehyde modification is shown in Figure 5.

The relationship between conditioned tenacity and stretch for both types of fibers is shown in Figure 6, and between wet tenacity and stretch in Figure 7. Wet modulus is shown as the function of stretch in Figure 8.

Formaldehyde used in the spin bath produced a drastic change in the caustic soda resistance of the fiber. Measured in 6.5% sodium hydroxide, when no formaldehyde modification was applied, tenacity ranged from 0.1 to 1.0 g./den., elongation from 8.7 to 23.5%, and wet modulus was 0.1 g./den. With formaldehyde modification, however, also in 6.5% sodium hydroxide, tenacity ranged from 0.2 to 2.8 g./den., elongation

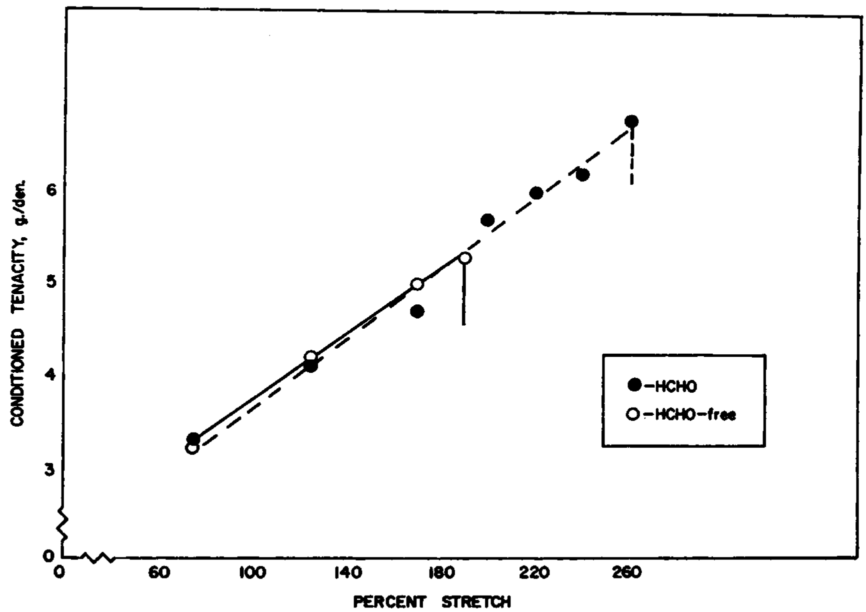

Fig. 6. Fiber conditioned tenacity vs. stretch.

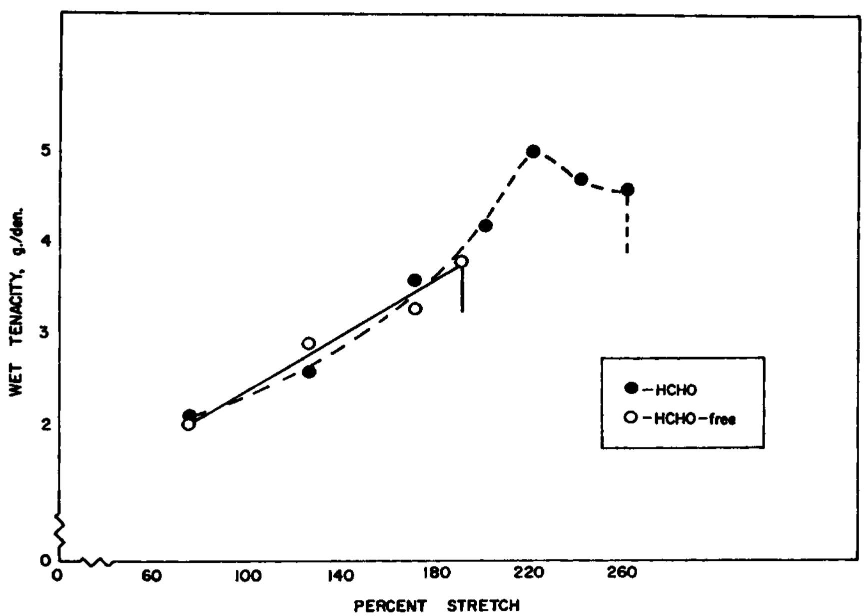

Fig. 7. Fiber wet tenacity vs. stretch.

from 9.4 to 15.0%, and wet modulus was 0.1–0.2 g./den. The relationship between tenacity in 6.5% sodium hydroxide and stretch is shown in Figure 9 for both types of fibers.

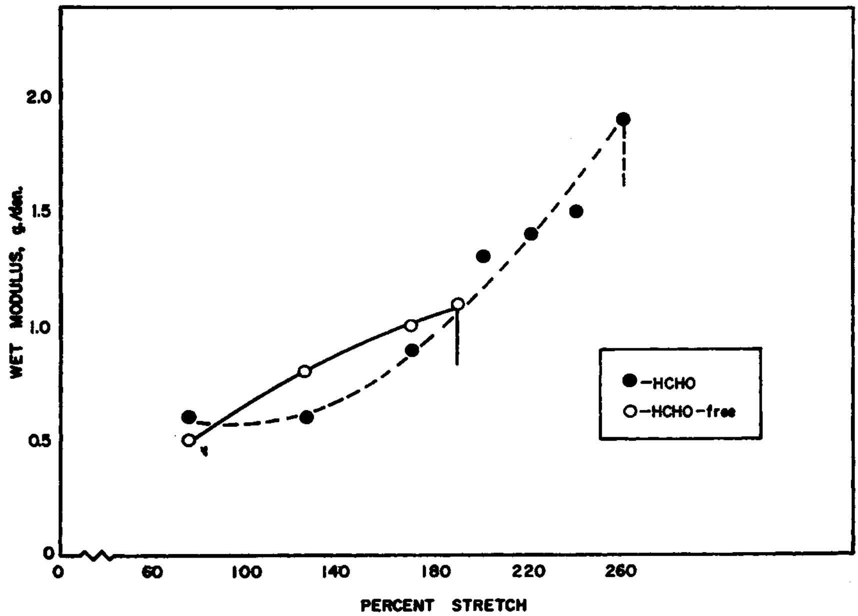

Fig. 8. Fiber wet modulus vs. stretch.

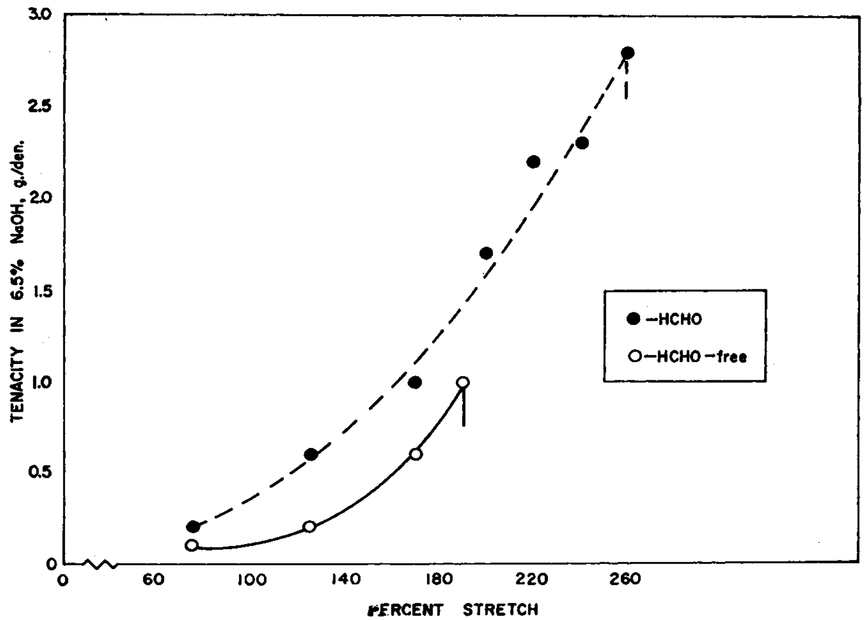

Fig. 9. Fiber tenacity in 6.5% NaOH vs. stretch.

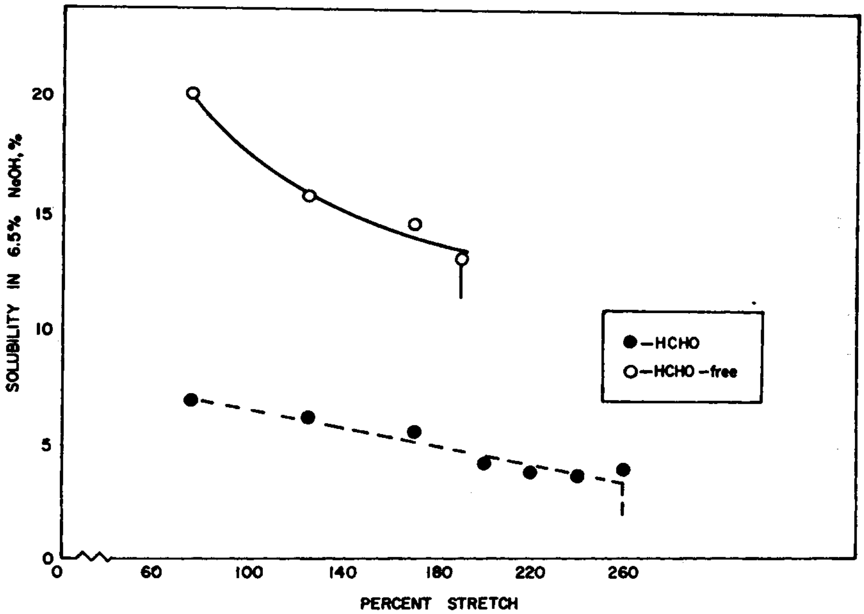

Fig. 10. Fiber solubility in 6.5% NaOH vs. stretch.

Caustic soda resistance of rayon can be improved by imparting orientation. Modification through trace crosslinking, however, has an even more pronounced effect on the caustic soda resistance. Without formaldehyde modification, when stretch was increased from 75 to 190%, fiber solubility in 6.5% sodium hydroxide at 20°C. decreased from 20.3 to 13.2%. In the case of the formaldehyde-modified fiber, however, fiber solubility was 7.5% even at the lowest (75%) stretch level and only 3.5% at the maximum smooth stretch of 260%.

Orientation alone improved caustic soda resistance by 35% in the case of fiber made without formaldehyde modification going from 75 to 190% in stretch and by 43% when formaldehyde modification was applied going from 75 to 260% in stretch. The improvement owing to formaldehyde modification only, however, was 291% at 75% stretch, 253% at 125% stretch, 262% at 170% stretch, and 314% at 190–200% stretch. Decrease in caustic soda solubility with both orientation and trace formaldehyde crosslinking is shown in Figure 10.

To avoid regeneration prior to stretching, both types of fiber were spun into a relatively cold primary acid bath. Once stretching and a high degree of orientation have been accomplished, regeneration was completed in a hot dilute acid secondary treatment. This was initially carried out under tension but completed in a relaxed state to give sufficient elongation, flexibility, and resistance to the finished fiber for good processability and conversion of strength in yarns and fabrics.

The presence of formaldehyde in the primary bath allowed higher stretches and thus higher orientation. This is demonstrated by differences

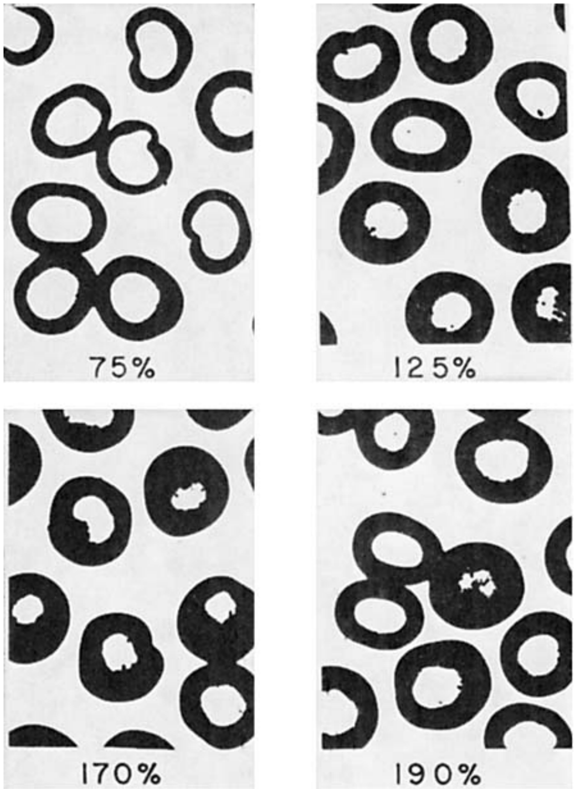

Fig. 11. Photomicrograph of cross section of fiber made at 75, 125, 170, and 190% stretch with no formaldehyde in the spin bath. Stained, 615×.

in fiber cross-sections. Without formaldehyde modification, cross section shape tends towards the circular, with skin thickness increasing with increasing orientation. Not much change in cross section shape is noted with increasing stretch (Fig. 11).

Formaldehyde-modified filaments also have increased skin thickness with increasing stretch (Fig. 12). Filaments spun at lower stretch levels have cross sections similar to those of regular rayon, i.e., crenulated, with skin and core sharply defined. The filaments tend to flatten at intermediate levels of stretch. At high levels of orientation, filaments become essentially circular (Fig. 13) with usually a rather sharp protuberance in one segment of the fiber. This is characteristic of this type of formaldehyde modification. The filaments have a layered skin structure.

It was mentioned earlier that formaldehyde reacts with glycosidic cellulose hydroxyls to form methylene crosslinks. The fact that this was one of the reactions involved when viscose was spun under the conditions of triple modification is demonstrated by an apparent increase in the degree of polymerization. The presence or absence of zinc salts has a profound effect on this apparent DP. Table VI illustrates this point.

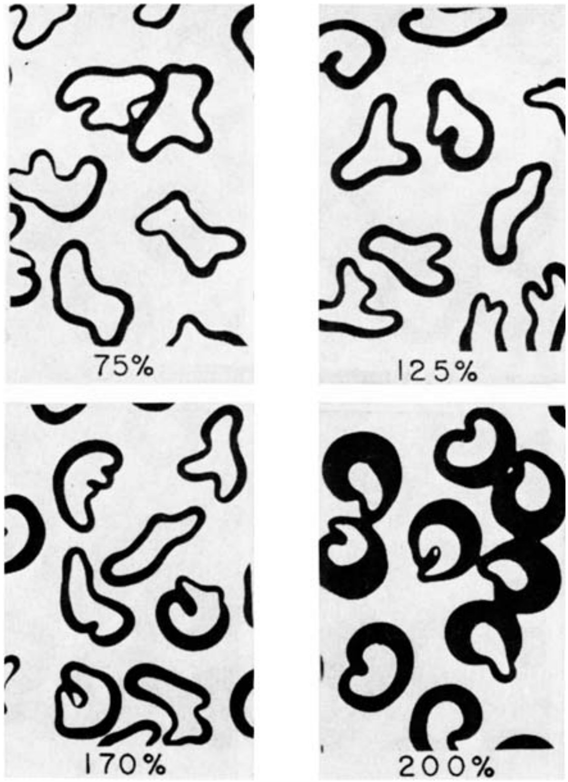

Fig. 12. Photomicrograph of cross section of fiber made at 75, 125, 170, and 200% stretch with formaldehyde in the spin bath. Stained, 985×.

In all five sample pairs, the fibers spun into a zinc-free, formaldehyde-containing bath had higher apparent DP values as determined by Cuene viscosity than those spun into a zinc-containing bath. This suggests

TABLE VI
Effect of Formaldehyde and Zinc in the Spin Bath on Apparent Cellulose DP

Sample	Concentration in spin bath		DP from Cuene IV
	$ZnSO_4$, %	HCHO, %	
1A	0	0.3	590
1B	3.0	0.2	560
2A	0	0.4	640
2B	3.0	0.2	560
3A	0	0.6	620
3B	3.0	0.2	570
4A	0	0.7	630
4B	3.0	0.2	570
5A	0	1.1	600
5B	3.0	0.2	570

Fig. 13. Photomicrograph of cross section of fiber made at 260% stretch with formaldehyde in the spin bath. Stained, 880×.

that zinc competes with formaldehyde in reacting with the cellulose. The point is further illustrated on a different set of samples, at higher DP levels, involving a set of four samples, using two levels of formaldehyde (0 and 0.9%) and two levels of zinc sulfate (0 and 5%) concentration (Table VII). The control without formaldehyde modification had a DP of 650. Using no zinc and 0.9% formaldehyde in the primary spin bath raised the apparent DP level of the regenerated cellulose to 680, or by about 4.5%. No corresponding change in apparent DP was found when zinc was added to a formaldehyde-free bath. The combined effect of

TABLE VII
Effect of Formaldehyde and Zinc in the Spin Bath on Apparent Cellulose DP

Sample	Concentration in spin bath: HCHO, %	Concentration in spin bath: $ZnSO_4$, %	DP from Cuene IV
1	0	0	650
2	0.9	0	680
3	0	5	650
4	0.9	5	670

0.9% formaldehyde and 5% zinc was less effective in increasing the apparent DP of the regenerated cellulose than the effect of 0.9% formaldehyde alone.

Formaldehyde modification was found to reduce the degree of swelling in solutions of cupriethylene diamine (Cuene) as well as to delay the onset of swelling as compared to that of fiber produced in formaldehyde-free spinning. This can be explained by the existence of crosslinks primarily in the skin area of the formaldehyde-modified fiber. Dissolution of this fiber started by internal swelling until the skin was split, followed by rapid removal of the inner layers. Fiber made without formaldehyde crosslinking dissolved by a continuous swelling and peptidization mechanism, involving the entire cross-section simultaneously.

Formaldehyde-modified fiber exhibited an inherently greater swelling capacity than regular rayon in 70% nitric acid. This can be attributed to its highly oriented fibrillar structure. Acid swelling severs the bonds responsible for linking the fibrils. Cuene, on the other hand, has a very limited bond-cleaving action.

The resistance of a formaldehyde-crosslinked skin to swelling was not unexpected; formaldehyde crosslinks with the cellulose are presumed to form very rapidly in the hot secondary acid bath. This bath is 30 in. long, allowing for a residence time of only about 1.5 sec. In addition, the tow is under high tension at this point making it extremely difficult to penetrate. While residual formaldehyde is only about 0.1% of the total regenerated fiber, its concentration in the skin area is expected to be relatively high.

Summary

It has been demonstrated that intermediate wet modulus rayon fibers are obtained when viscose of a specified composition, containing the mixed modifier system of dimethylamine–poly(ethylene glycol) is spun into a primary acid bath composed of sulfuric acid, zinc- and sodium-salts. This fiber can be stretched up to 190% during spinning while it is in a state of coagulation. Quite a different kind of fiber is obtained, however, when the same viscose is spun into an identical bath containing, in addition to the other components, a small amount of formaldehyde. The maximum attainable stretch under the conditions of triple modification is increased to 260%. Since higher stretch results in increased orientation, this formaldehyde-modified, highly oriented fiber has physical properties characteristic of high wet modulus rayon.

Increased orientation as well as formaldehyde crosslinking are responsible for the improved physical properties of this fiber. This rayon has higher conditioned and wet tenacities, somewhat lower elongation, and much improved resistance to caustic soda. Tenacity and modulus are greatly improved as measured in 6.5% sodium hydroxide; solubility in 6.5% caustic soda is reduced by 320% by trace crosslinking under conditions of maximum orientation. The fact that orientation as well as crosslinking are respon-

sible for the results obtained is evidenced by photomicroscopic and other means, such as the apparent increase in cellulose DP. The competitive nature of zinc and formaldehyde modification has also been demonstrated.

The textile industry must have rayons that show resistance to caustic soda during alkaline processing: mercerizing, dyeing, finishing. Such resistance has traditionally been achieved by post-regeneration treatment, e.g., crosslinking in the dry state with formaldehyde, reactants, or resins. The effect of crosslinking with up to 1.2% bound formaldehyde in the dry state on the caustic solubility of rayon has been previously described.[12] Crosslinking under such conditions reduced the solubility of rayon in 9% sodium hydroxide from over 30% to 4% by crosslinking. A similar increase in the caustic soda resistance of viscose rayon was accomplished in the work presented here during the spinning process owing to the combined effect of maximum orientation and trace crosslinking.

Such a fiber may be used to make fabrics in 100% construction as well as in blends with cotton, where it can be mercerized together with cotton, and with polyesters or other synthetics. Fabrics made from this rayon have high breaking strength, tear strength and flexabrasion resistance as well as firmer hand than most modified rayons. Low progressive shrinkage during laundering shows good potential for stabilization by Sanforizing.

Since it is realized that formaldehyde presents a problem in acid spin bath recovery systems, work is currently under way to reduce the amount of formaldehyde used in the spin bath still further.

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