

Studies on the Mechanism of Fine-Structure Development during Industrial Cellulose Yarn Production

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Synopsis

A study has been made of the diffusion of zinc ions into alkaline solutions of sodium cellulose xanthate (viscose) when these are extruded into acidified salt solutions (spinbath). Under these conditions, which exist during the manufacture of regenerated cellulose industrial yarns, the zinc ions are diffusing into a continuously coagulating gel structure from which water is exuded as the structure is developed. It has been shown that the presence of certain additives (modifiers) in the viscose can slow down the diffusion of both zinc and hydrogen ions, thus retarding the coagulation and neutralization of the viscose. In the initial stages of coagulation, before the neutralization point is reached, the modifiers reduce the rapid filament shrinkage and pressure rise within the filament which would otherwise be caused by the presence of zinc ions in the spinbath. The mode of action of the modifiers is discussed in the light of current theories. A hypothesis is put forward that the modifiers act by preventing the initial rapid shrinking action of the outer cuticle of the filament. This permits the production of the desired fine structure inside the filament during a slower steady shrinkage which leads to a round cross-sectioned filament of good mechanical properties.

INTRODUCTION

Man-made cellulosic fibers have been made by the viscose process for about sixty years. Cross and Bevan¹ invented the process in which an alkaline solution of sodium cellulose xanthate was extruded through small holes (jets) into an acid bath containing salts. The cellulose was precipitated and drawn off onto a reel in fiber form. In 1935 Rose, Givens and Biddulph² invented the Tenasco tire yarn process which was based on the Cross and Bevan process but used 4% zinc sulfate in the spinbath in addition to acid and sodium sulfate. An acid hot stretch following coagulation was also introduced. Cox in 1946³ added amines to the viscose used for tire yarn spinning, and since then very many other substances have been suggested as viscose additives or modifiers. The process has made great strides technologically, but the exact role of the zinc and modifiers in the system is still in dispute.

It is not the intention of the authors to attempt a complete survey of all the literature on the subject of modifier and zinc interactions in the tire

yarn spinning process. This has already been done by various authors⁴⁻⁷ in the past. The work of Klare and Grobe repays careful study, although not all workers agree with all their conclusions. Some of the confusion in the literature has arisen because authors have not always stated exactly at what point in the spinning process they have taken their samples or made their observations. It is the opinion of the present authors that the region up to the neutralization point is the most important for studies of structure development, especially the initial part of this distance. Observation and sampling so near the jet face are of course difficult, but appropriate techniques have been devised to overcome these difficulties.

There are certain facts about the function of modifiers which have been established and are generally accepted. These are that the modifiers participate in the formation of a very thin membrane or cuticle on the filament surface soon after the viscose enters the spinbath solution.⁸ This cuticle decisively affects the diffusion of some or all of the spinbath components, and the point of complete neutralization of the filament is moved further from the jet. It is also generally accepted that the modifiers are at least partially responsible for the improved fine structure found in fibers spun from viscoses with modifiers present.⁹

It is also sometimes stated^{10,11} that the presence of modifiers enhances the effect of zinc and causes the filament to be more quickly shrunken and the gel swelling to be lower. These statements may be true of samples collected after the neutralization point, but it is shown in the present paper that such a view is an oversimplification of the facts. To do this it was necessary to find experimental techniques which would permit the examination of the effects of zinc-modifier interaction in the immediate vicinity of the jet face. Alternatively, techniques were required which would simulate at a much slower speed the very rapid changes which are so difficult to observe very near the jet face. To this end the following experimental techniques were devised.

A microanalysis technique was devised to study the transfer of zinc and hydrogen ions from a drop of spinbath placed for a few seconds on a thin viscose film. The effect of modifiers in the viscose film was observed. The rise of zinc concentration in the viscose could easily be observed by this technique. Most reported spinning techniques observe the later departure of the zinc from the spinning filament.

A photomicrographic technique to study the velocity and diameter of the spinning filament in the vicinity of the jet was developed. The effect of modifiers and zinc was again observed.

An apparatus was specially constructed to permit the measurement of the pressure rise inside a cylindrical coagulating viscose skin supported on an elastic membrane. The initial rate of pressure rise was studied in the presence and absence of modifiers and zinc.

Full experimental details are given below.

EXPERIMENTAL

Throughout the various experiments a single viscose composition, where cellulose content lay in the range 6–8% and where the soda content lay in the range 5–7%, was used. The actual concentrations were controlled to $\pm 1.5\%$ of the nominal value. The salt index of the viscose was 9 ± 1 , and a modifier of the polyethoxylated type was used. Unless otherwise stated, the spinbaths were in the range 5–6% (w/w) sulfuric acid, 6–8% (w/w) zinc sulfate, 14–16% (w/w) sodium sulfate; or 5–6% (w/w) sulfuric acid, 14–16% (w/w) sodium sulfate. The actual concentrations were controlled to $\pm 2\%$ of the nominal value. The spinbath temperature was in the range 50–60°C and was controlled to within one degree of the nominal value, except for those experiments where it is mentioned that room temperature was used.

The Diffusion Experiment

Thin films were prepared in a standard manner from $\frac{1}{2}$ of viscose spread between two glass plates of fixed size. The viscose films were placed horizontally, below an Aglar micrometer syringe full of spinbath and fitted with a micrometer plunger drive. A droplet was formed slowly on the glass nipple of the syringe until it fell under its own weight onto the viscose film $1\frac{1}{2}$ in. below. By standardizing the weight of viscose, the area of the film, the shape of the syringe nipple, and the falling distance, it was possible to obtain drops of equal size covering a standard area of viscose film after their fall.

Each drop, after reaction on the viscose film for 5 sec, was removed with a second calibrated syringe. Ten or more drops were collected in this way until the syringe was nearly full.

At this point a needle was fitted, and 0.20 ml was ejected from the collection syringe into a 250-ml flask which was made up to the mark with distilled water. The experiment was repeated for reaction times of 10 and 15 sec, and a blank solution for zero contact time was also made up. These four solutions were then fed to an autoanalyzer which, after calibration, gave zinc concentrations directly. Once the drop technique had been standardized and the autoanalyzer calibrated it was possible to carry out a large number of experiments with and without modifiers in the viscose and with a range of spinbath compositions.

A series of acid, zinc sulfate, sodium sulfate baths was made at constant zinc and sodium sulfate concentrations and at 2.7, 4.0, 5.4, 6.7, and 8.0% (w/w) acid levels. The experiments were carried out twice at each acid level by different operators with modifiers present. The whole set of experiments was repeated in the absence of modifiers. These experiments were performed at ambient temperature ($18 \pm 1^\circ\text{C}$).

The whole series of experiments described in the previous section was repeated in the glove box at 55°C in an atmosphere of 95% RH to prevent

evaporation of the solutions used. Manipulation of the microsyringes inside a glove box while wearing rubber gauntlets was difficult. Condensation on the Perspex box walls obscured the apparatus from view. Forced draught heating was necessary inside the box to prevent temperature gradients.

In all experiments the autoanalyzer reading of zinc or acid concentration was compared with the initial concentration to indicate the amount of zinc or acid which had diffused into the viscose film.

The Spinning Experiment

A small-scale spinning machine was built to permit photography of the spinning filament. The viscose containing TiO_2 particles was metered by a variable-speed cylinder and piston-type extruder. Spinbath liquor was circulated by a peristaltic pump and electrically heated by a glass-enclosed Nichrome wire heater on the bottom of the Perspex spin bath. Jets with single holes were used. A microscope was mounted vertically above the spin bath and was attached to an optical bench which could traverse the

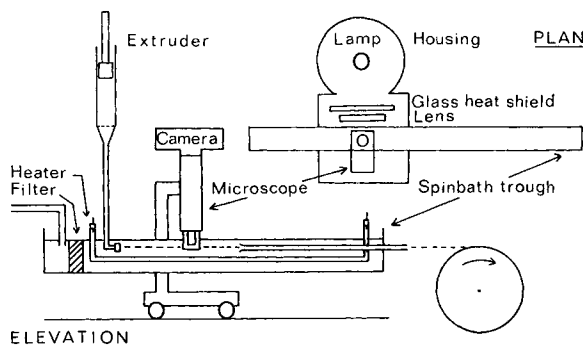


Fig. 1. The apparatus used for the spinning experiment. Spinning filament shown as a dotted line.

length of the bath (Fig. 1). Since the objective lens was either under the surface of the spinbath or so near the surface that it became steamed over, the lens was fitted with a glass cover. The end of this cover was always below the surface.

The camera used to photograph the spinning filament and the TiO_2 particles was an Edixa-mat reflex with a focal plane shutter. This gave the sharp cut-off necessary for accurate measurement of TiO_2 trace length. For photographing the spinning filament the fastest shutter speed was used, giving an exposure of 10^{-3} sec. The camera was attached to the top of the microscope. The light source was a Phillips CS500w compact source lamp with an output of 21,500 lumens and a high voltage starter unit. The lamp was mounted on the optical bench at the side of the spin bath so that the light was directed on to the filament at 90° to the microscope axis. The light was focused on to the filament by a movable lens mounted between

the lamp housing and the bath. This lens was protected from the heat of the lamp by a sheet of heat-resistant glass (Fig. 1).

Throughout the experiment, the eyepiece used was of magnification $\times 4$ and the objective $\times 5$. The distance between the eyepiece lens and the camera was 7.1 in. All the photographs were examined on an enlarger, which gave a further magnification of $\times 6$. The total magnification ($\times 120$) was checked by photographing a standard scale and measuring the enlarged image. The exposure times were checked against C. R. T. traces. Most work was done at 0.001 sec.

Samples of viscose (500 g) were obtained from the small-scale viscose mixers before and after the addition of modifiers. The weight of viscose required for spinning was 200 g, and TiO_2 (0.9 g) was added to each sample. The viscose was centrifuged in the extruder cylinder to remove air. The viscose pump rate was 0.13 g/min and the speed of the pull-off reel was 13.5 m/min. The jet hole size was 0.003 in. and the bath flow was 10 m/min.

Four spinning systems, with and without modifier and with and without zinc, were investigated, and graphs of filament velocity against distance from the jet were prepared from the photographs of the TiO_2 particle traces. Diameter measurements were also made and plotted against distance from the jet. Repeated experiments yielded consistent results. The shape of the graphs was not affected when, in further experiments, a larger jet hole size (0.008 in.) and zero bath flow were used.

The Shrinkage Pressure Experiment

A rubber finger-stall 0.75 in. in diameter was filled with water, coated with viscose, and immersed in spinbath solution. The viscose was regenerated by the spinbath solution and tended to contract. The resulting rise in pressure inside the finger-stall was recorded automatically. Changes in the shape and area of the film were eliminated by an electronic device which balanced out the pressure rise. The operation of this null method is explained below.

The automatic pressure measuring device was an electronic force-balance servo system of the type used as yarn tensometers. The equipment, much simplified, is shown in Figure 2. Movement of the balance beam altered the distance between the plates of the variable capacitor and so affected the balance of the capacitive bridge. This altered the grid potential of the thermionic valve. The anode of the valve was connected to earth via a variable resistance and a coil attached to the balance beam. As the beam moved, this coil moved between the poles of a permanent magnet. The coil current was linearly proportional to the applied load, and the induced force on the coil effectively prevented the beam from moving. Movement was less than 0.002 in. The voltage across the variable resistance in the circuit was recorded automatically by a Honeywell-Brown 10 mV potentiometric strip-chart recorder. The recorder pen deflection was therefore linearly

proportional to the applied load on the beam. The part of the apparatus to which the load to be measured was attached was called the tensometer head.

The top of a small brass bellows assembly was rigidly clamped to the body of the tensometer, as is shown in Figure 2B. The movable lower end of the bellows was linked to the tensometer head by the coupling shown in

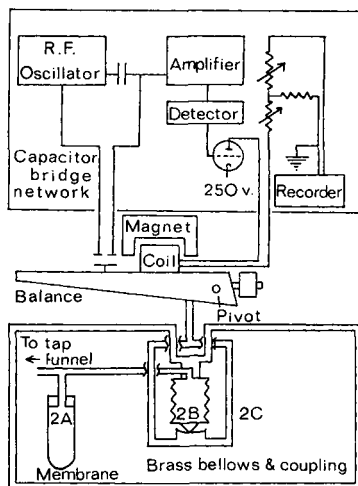


Fig. 2. The apparatus and pressure balancing circuit used for the shrinkage pressure experiment: (A) rubber membrane; (B) bellows; (C) coupling transmitting the bellows expansion force to the balance beam.

Figure 2 C, so that any expansion of the bellows caused a downward force to be applied to the head. A rubber finger-stall was fitted over a shaped PVC bung and held in place by rubber bands. The bung was joined to a T-piece, and this was connected to a tap funnel and to the bellows assembly (Fig. 2). The tap funnel was used to fill the membrane, the nylon tubing, and the bellows with water which had been boiled to remove dissolved air. The filling operation was helped by the addition of a few drops of detergent to the water. When the system was completely air-free, the funnel tap was closed. It was found that slight movement of the nylon tubing considerably affected the pressure in the system, and the membrane assembly was therefore clamped permanently to the supporting framework of the tensometer.

The same spinbath and viscose systems which were used for the spinning experiments were examined by the shrinkage pressure technique, so that the results could be compared directly. However, the spinbaths were used at room temperature (21°C), since hot spinbaths caused expansion of the water acting as the hydraulic fluid and correspondingly anomalous pressure readings were obtained.

The regenerated cellulose film could easily be removed from the rubber, and so a rapid series of repeated experiments was possible for each system. It was found that reproducible results were obtained. Whenever a dam-

aged rubber was replaced by a new one it was found that changes in the value of the recorded pressure at a given time were sometimes obtained. The relative values for the four systems were unaltered, however. Reproducible results could therefore be obtained by the use of a standard system in each series of experiments.

Because the radius of the envelope used was many orders larger than the radius of the spinning filament the pressures developed were correspondingly small ($P \propto 1/r$). This fact permitted the indirect study of the rapid pressure changes in a filament by providing the necessary reduction in the rate of pressure rise to be measured.

RESULTS

The Diffusion Experiment (Expt. 1)

The results (Figs. 3 and 4) show the effect of modifiers on the decrease in the zinc concentration in the droplets of spinbath solution. It is seen that

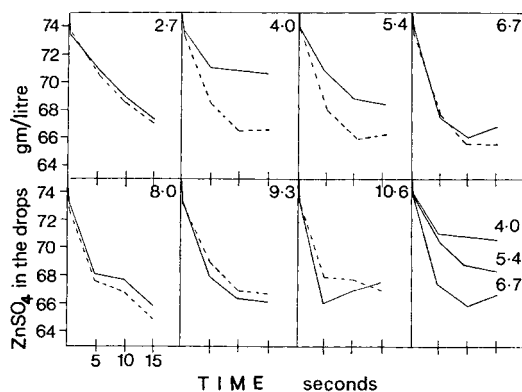


Fig. 3. Effect of modifiers on the movement of zinc from the droplets to the viscose film, at 18°C: (—) modified viscose; (---) unmodified viscose. The figures (top right) give the acid concentration in the spin bath solutions which all have the same zinc and sodium sulfate concentrations.

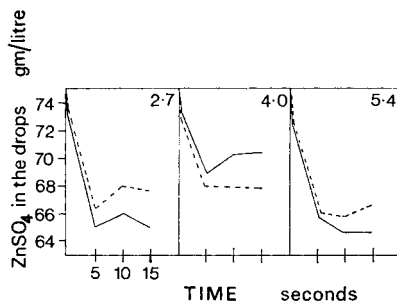


Fig. 4. Effect of modifiers on the movement of zinc from the droplets to the viscose film at 55°C: (—) modified viscose; (---) unmodified viscose. The figures (top right) as for Fig. 3.

the zinc concentration falls more slowly in the presence of modifiers. The delaying action of the modifiers is also seen to be dependent on the acid concentration in the spinbath solution.

Furthermore, it is evident that the effect of the modifier becomes more pronounced as the time increases until the zinc concentration remaining in the droplet reaches a minimum. The results at 18°C and 55°C both indicate that the modifier effect under the conditions used was most marked at the 4% acid level.

The results for the acid diffusion experiments showed that acid penetration into the viscose film was also reduced in the presence of modifiers.

The Spinning Experiment (Expt. 2)

The velocity data (Fig. 5) calculated from the length of the TiO₂ traces showed that after leaving the jet the viscose suffered a sharp fall in velocity, so that the extrusion velocity was quickly reduced to a velocity near that of

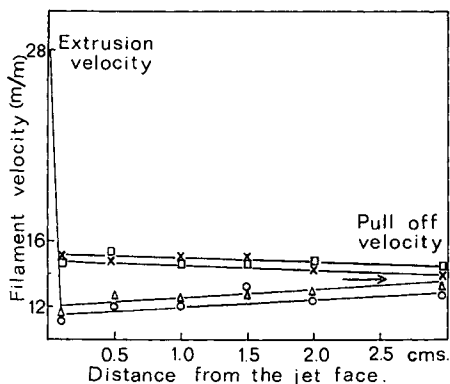


Fig. 5. Effect of zinc and modifiers on the filament velocity at distances from the jet face up to 3 cm.

the take-up reel. However, it was possible by repeating the comparison between modified and unmodified systems to show a distinct effect of modifier on filament velocity. Whether there was zinc in the spinbath or not the viscose containing modifier reached a minimum velocity below that of the take-up reel before accelerating up to the take-up velocity, whereas the unmodified viscose approached the take-up velocity from above and did not show a minimum. Again this was independent of the presence or absence of zinc in the spinbath solution.

The diameter data (Fig. 6) showed that the fastest percentage reduction in diameter occurred with the unmodified zinc system. With modifiers added to the zinc system the modifiers were so effective in the first 3 cm that the effect of the zinc was nullified. The modifier-zinc and modifier-no zinc curves were superimposable in this region. Thereafter the two systems

with zinc both showed faster diameter reductions than the two systems without zinc present.

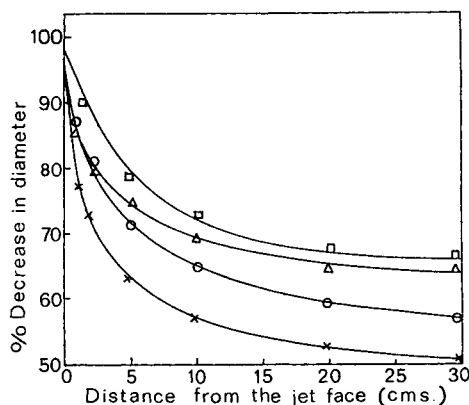


Fig. 6. Effect of zinc and modifiers on the filament diameter at distances from the jet up to 30 cm.

The Shrinkage Pressure Experiment (Expt. 3)

Results are shown in Figure 7. The time to neutralization (or D value) is marked on each curve to connect the time scale with the normal spinning immersions. The zinc present in the spinbath was clearly responsible for the rapid rise in shrinkage obtained in the absence of modifiers. When modifiers were added to the zinc system, the rapid shrinkage effect was nullified. In fact the curves show that the pressure rise for the modifier-zinc system was initially the slowest of the four systems studied. However, at longer time intervals the position was reversed and the modifier-zinc system emerged as the most highly shrunken of the four. This is in agree-

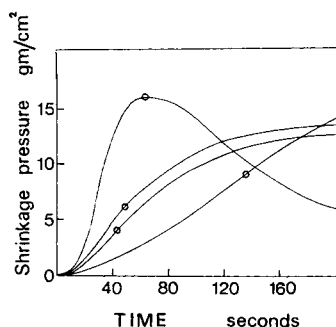


Fig. 7. Effect of zinc and modifiers on the shrinkage pressure: (m; z) modifiers in the viscose and zinc sulfate in the spin bath solution; (m; 0) modifiers in the viscose and no zinc present; (0; Z) no modifiers present but zinc sulfate present in the spinbath solution; (0; 0) neither present. The circles on the curves indicate the time to neutralization of the viscose.

ment with the low "gel swelling" data normally observed for tire yarn systems containing both modifier in the viscose and zinc in the spinbath. The gel swellings are always measured on the completely regenerated cellulose, i.e., after long time intervals. It is clear that the position at short time intervals is quite different.

The relevance of the results obtained from the shrinkage pressure apparatus was investigated by observing the response of the apparatus to all the obvious spinning variables and to modifiers of high and low power. In all cases the rate of pressure rise was as expected and the apparatus was therefore considered a useful tool for the present investigations.

DISCUSSION

The experiments described provide the following information about the sequence of zinc-modifier-viscose interactions during the early stages of the life of the viscose filament.

After the viscose stream emerges into the spinbath solution the acid and zinc begin to pass into the viscose (expt. 1).

Both acid and zinc pass into the viscose at a slower rate in the presence of modifiers (expt. 1). This could be either (a) a direct effect of the modifiers on the diffusion of ions into the viscose, or (b) an indirect effect resulting from the fact that with modifiers the filament shrinkage is less (expt. 3) and so less water is exuded into the spinbath. The measured ionic concentrations would then not fall as rapidly as they would in the absence of modifiers. Russian workers¹² have shown similar results.

The above effect of modifiers is small at first but increases steadily (expts. 1 and 3). It is stated by Kalafut and Fogeltanc¹³ that there is always a slight time delay before modifier action is evident.

The modifier effectiveness depends on the spinbath acid concentration and is a maximum at 4% for the system studied (expt. 1). Vroom and van de Ven^{14,15} studied the effect of acid concentration on the coagulation-regeneration point and found a similar maximum effect at 4% acid for a comparable system.

The protection against both zinc and acid attack afforded by the modifier to the viscose is consistent with a slower shrinkage rate (expt. 3) and presumably a weaker gel structure. Van de Ven¹⁵ came to the same conclusion from different evidence. He concluded that a deposit (of $ZnCS_2$) on the surface of the filament was capable, in the presence of modifiers, of protecting the filament from too rapid a decomposition by a spinbath acid. The coagulation and neutralization were therefore retarded.

The time to neutralization is increased by modifiers (expt. 3). This is generally accepted.^{4-7,15}

The gel structure found in the presence of modifiers is less capable of transmitting the pull-off force, and so lower viscose thread velocities are observed near the jet in the presence of modifiers than in their absence (expt. 2). This supports the concept of weaker gels in the presence of

modifiers. In the absence of modifiers coagulation in salt baths generally produces crenulated filament cross sections which may even strain "all skin." This is consistent with the faster rise of the shrinkage pressure in the absence of modifiers. "All skin" structures with round cross sections can only be produced in the presence of modifiers.

In the absence of modifiers the zinc would normally penetrate the viscose and cause a more rapid reduction in diameter and also a more rapid rise in shrinkage pressure inside the filament (expts. 2 and 3). Canadian workers¹⁶ have shown that initially the rate of decomposition of xanthate in the presence of modifiers is reduced.

In the presence of modifiers the shrinkage pressure rise and diameter reduction due to the zinc are nullified to some extent, especially in the period preceding complete neutralization of the thread (expts. 2 and 3). Mitchel et al.¹⁶ state that, in the presence of modifiers, after the initially slow rate of decomposition of xanthate, the rate is increased. Furthermore, at the moment of stretch they found the xanthate content of the modified fiber was lower than that of the unmodified fiber.

In the presence of modifiers in the viscose the effect of zinc from the spinbath is reduced for a while but predominates eventually (expt. 3). Schmiedeknecht and Klare¹⁷ show a plot of gel swelling against distance along the spinbath. Although the final gel swelling is lower in the presence of modifiers, the position is reversed for the gels near the jet.

This results in a final high shrinkage pressure and is consistent with a low gel swelling figure for the completely regenerated structure (expt. 3).

From the present work it therefore appears that the function of the modifier is temporarily to delay the effect of the zinc ions and the hydrogen ions. During this delay the zinc content of the thread is less, the neutralization of the viscose is retarded, the viscose gel is protected, is less coagulated, and weaker, the pressure rise within the filament is suppressed, and the diameter shrinkage is no greater than it would have been in the absence of zinc.

Combining the present work with that of other workers it is apparent that, after this temporary delay in zinc activity, the gel structure consolidates, and xanthate decomposition proceeds to give a final structure which is more compact (lower gel swelling) and has better physical properties than would otherwise have been the case.

Whether the zinc penetrates to the center of the filament or participates with the modifier and byproducts in the formation of a shrinking cuticle is not evident from the present work. However, it is clear that the zinc activity is very dependent on acid concentration and is responsible for the tendency of the structure to shrink as well as the production of "skin" cellulose. It is therefore possible that the function of the delay period is to provide a weak, unshrunk gel of the correct pH into which the zinc ions can penetrate slowly to crosslink the structure in a regular manner before the gel is too rigid and before the pH conditions become too extreme and the zinc is washed out of the system. Thiele¹⁸ has reported considerable evidence for the ordered coagulation of xanthate gels by zinc ions. Such a

structure would be more resistant to stretch because of the formation of "junction points" or zinc bridges. These will prevent the formation of large areas of order, and smaller crystalline regions, as actually found in tire yarns,⁹ would result. The idea that modifiers act by ensuring a time delay during which zinc cellulose xanthate exists was put forward speculatively by Vermass.

The present work seems to support his general hypothesis although until zinc cellulose xanthate has been detected across the entire cross section, the above mechanism can only remain hypothetical. It is conceivable that the steady regular shrinkage alone could be responsible for the "all-skin" round cross-sectional filaments of super tire yarn. In this case the modifier action in extending the period of shrinkage would be the same but the zinc activity would be restricted to the outer cuticle of the filament.

CONCLUSIONS

The function of modifiers in tire yarn spinning is to slow down the passage of both zinc and hydrogen ions from the spinbath solution into the viscose filament. This effect can be optimized by adjustment of the zinc to acid balance in the system. The result is a temporary delay period during which the effect of the zinc ions in the viscose stream is partially nullified by the presence of modifier. The rapid filament diameter decrease and the marked pressure rise inside the filament which would otherwise occur in the presence of zinc in the spinbath solution are considerably reduced by the presence of modifier in the viscose. This delay period occurs well before the neutralization point of the filament.

When the delay period is over, the evidence indicates that a more highly shrunken structure develops from the normal zinc-modifier system than from systems without modifier. The fact that the shrinkage pressure rises steadily for the modified system is consistent with the fact that round uncrenulated cross sections are normally produced. In other words the modifier allows the zinc ions to give the filament the desired "all-skin" structure but prevents the zinc from causing the crenulated cross section.

The results do not indicate whether the zinc assists the production of an all-skin structure, merely by participating in the formation of a shrinking cuticle or by penetrating into the center of the filament.

If the former is accepted, then the modifier can be considered as assisting the effect of the zinc by causing the shrinkage to take place more slowly over an extended period of time.

If the latter mechanism of zinc penetration across the entire cross section is accepted, then the modifier could be considered as an agent providing a delay period for the penetration to occur.

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