

Effects of By-products, Trace Components, and Similar Compounds in Viscose on Ripening

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INTRODUCTION

In a previous paper¹ methods of treating viscose ripening data were described which resulted in a set of numerical constants for each viscose. The constants were used to compare the effects of various factors on the rate of viscose ripening.

The work reported in this paper is a continuation of the study of factors affecting viscose ripening by means of the methods of data treatment of the previous paper and is concerned with the following classes of materials: (1) chemical by-products of xanthation and ripening; (2) materials chemically similar to these by-products; (3) oxidizing and reducing agents; (4) metallic salts which may be present in trace or greater than trace quantities in viscose, and other chemically similar salts which normally would not be expected in viscose.

PROCEDURE

The viscoses used in this study were of spinnable composition, containing 7% cellulose, 2% sulfur, and 6% alkali. The materials to be tested were added during the dissolving step in quantities ranging upward from 0.5% of the viscose. Test samples were removed for analysis as the viscose ripened at 15°C. during a two-week period. The results were compared with control samples treated similarly.

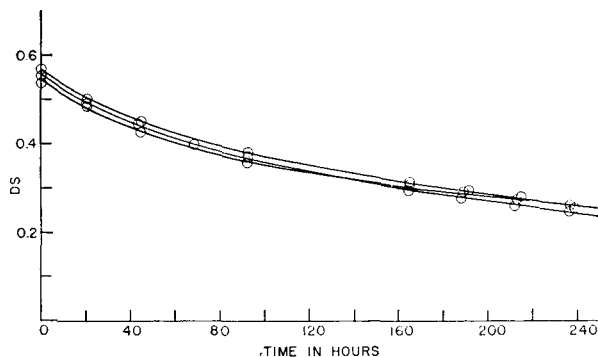


Fig. 1. Typical viscose ripening curve.

Figure 1 shows typical ripening curves, degree of substitution plotted as a function of time, for viscose made from cotton linters. The curve shows a rapid rate of decomposition initially, leveling off to a slower rate during the second week. This curve may be resolved into numerical constants by applying two kinetic treatments. The data were treated either as the sum of two first-order reactions or as a single second-order reaction.

Figure 2 illustrates the treatment as the sum of two first order reactions yielding three evaluation parameters. Curve No. 1 is the ripening curve with DS plotted as a function of time. The values obtained between 160 and 240 hr. were replotted as log DS versus time in curve No. 3 which is linear with a slope $K_{(1)}$. This is the rate constant of the slower reaction. The linear portion of the curve was extrapolated to zero time and the DS due to the slow decomposition determined and plotted as curve No. 2. The difference between curve No. 1 and curve No. 2, due to the initial rapid first-order reaction, is plotted in curve No. 4. The logarithm of the DS in curve No. 4 is

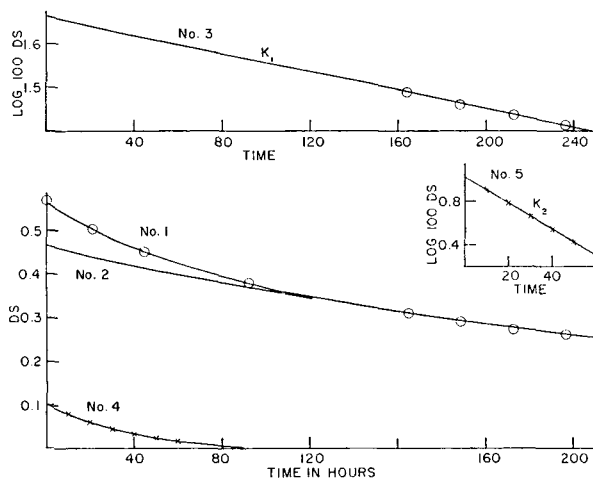


Fig. 2. Ripening curve treated as sum of two first-order reactions.

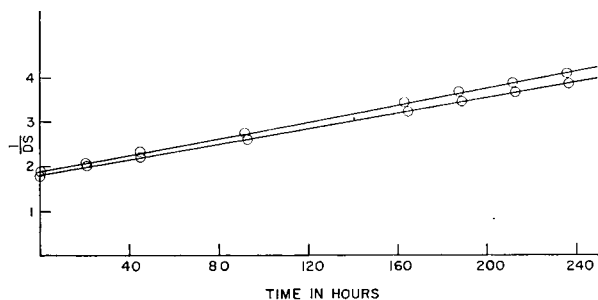


Fig. 3. Ripening curve treated as a single second-order reaction.

plotted as a function of time in curve No. 5, which is also linear with a slope $K_{(2)}$, the rate constant of the other first-order reaction. Such treatment of data yields the third evaluation parameter, the ratio of the degree of substitution of the slow reaction at zero time ($DS_{(1)}$) to the total degree of substitution, $DS_{(t)}$, or the $DS_{(1)}/DS_{(t)}$ ratio.

Figure 3 illustrates the data treatment as a single second-order reaction in which the reciprocal of the degree of substitution is plotted as a function of time, also resulting in a straight line with a slope K'' , the fourth parameter. A fifth parameter is the ratio of xanthate sulfur to CS_2 sulfur used in the viscose (the $XS/S_{(CS_2)}$ ratio). Although physical significance of these data treatments may be open to question, the ripening curve is resolved into numerical coefficients yielding five numbers which are indicative of, or related to, ripening rate.

RESULTS

Effect of By-Products and Other Sulfur-Containing Compounds

The effects on ripening by materials which are formed during viscose preparation and ripening were examined. Sulfides, polysulfides, and free sulfur are known to be present in viscose in small quantities; sodium trithiocarbonate and sodium

carbonate are present in increasingly larger concentrations as ripening progresses. Table I summarizes the effects on ripening of these materials when they are added during the dissolving step.

The sodium carbonate and trithiocarbonate appeared to have no effect on the ripening rates. Both were added in concentrations at least four times higher than those normally expected in a spinnable viscose.

The effects of sodium sulfide and the oxidized form, sodium polysulfide, were opposite. Addition of sodium sulfide resulted in a decrease in the ripening rate as indicated by K'' and complete elimination of the constant $K_{(2)}$. Thus the ratio $DS_{(1)}/DS_{(t)}$ was equal to 1.00. This was unexpected, because sodium sulfide is reported in the literature to accelerate ripening.² The most surprising fact, however, was that the xanthate sulfur to carbon disulfide ratio ($XS/S_{(CS_2)}$) was greater than 1.00, indicating that the value measured by the titration included some reducing material other than the xanthate sulfur. Tests showed that the ion exchange resin removed all the sulfide from a solution of sodium sulfide and sodium hydroxide and suggested the possibility that sodium sulfide actually bonded with some material in the complex mixture, possibly the cellulose xanthate, which prevented its complete removal by the ion exchange resin.

The same effect is suggested by the $XS/S_{(CS_2)}$ value for the sodium polysulfide sample which also is higher than that for normal viscose prepared under similar conditions. The dexanthation proceeded more rapidly than for a control viscose, as shown by the K'' constant—so rapidly, in fact, that the viscose gelled after only four days, preventing calculation of the $K_{(1)}$, $K_{(2)}$ and $DS_{(1)}/DS_{(t)}$ values.

Figure 4 compares the curves obtained for viscoses containing sodium sulfide and sodium poly-

TABLE I
Effect on Viscose Ripening of By-Products Normally Present in Viscose

| Additive | Additive level, % S | Initial DS | $\frac{XS}{S_{(CS_2)}}$ | $\frac{DS_{(1)}}{DS_{(t)}}$ | $K_{(1)}$ | $K_{(2)}$ | K'' |
|--|---------------------|------------|-------------------------|-----------------------------|-----------|-----------|----------|
| Na_2S | 2 | 0.78 | 1.10 | 1.00 | 1.00 | a | 5.45 |
| Na_2S_x | 4 | 0.74 | 0.95 | a | a | a | 18 |
| CS_2+S | 2 | 0.49 | 0.59 | 0.70 | 0.89 | 1.95 | 11 |
| Na_2CO_3 | 6 ^b | 0.61 | 0.86 | 0.79 | 0.95 | 1.15 | 7.70 |
| Na_2CS_3 | 2.5 | 0.59 | 0.82 | 0.76 | 0.97 | 1.32 | 7.60 |
| Control | — | 0.60 | 0.85 | 0.74 | 1.03 | 1.17 | 8.44 |
| 95% Confidence limits for normal viscose | | | | 0.68–0.88 | 0.86–1.14 | 0.75–1.39 | 7.4–10.1 |

a Values for these constants could not be determined.

b As % of total.

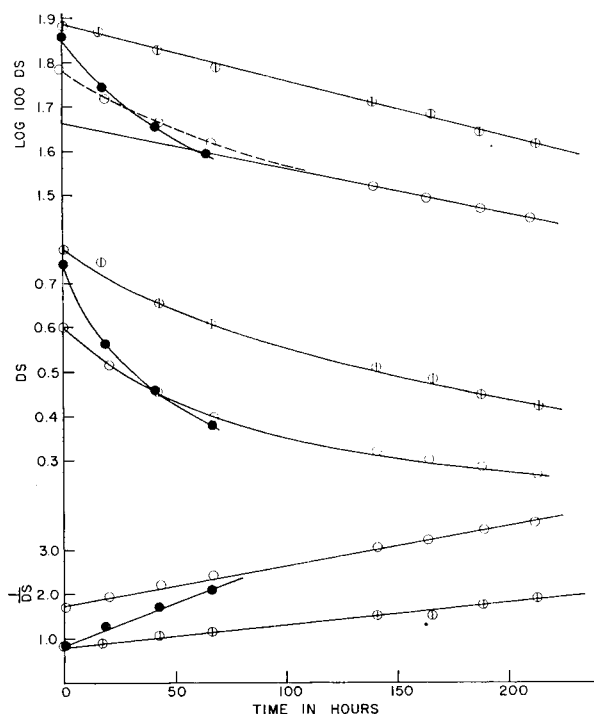


Fig. 4. Comparison of the effects on ripening of viscose of addition of sodium sulfide and sodium polysulfide: (○) normal viscose; (⊙) sodium sulfide added; (●) sodium polysulfide added.

sulfide with normal viscoses.

An observation to which little significance was attached at the time was the color of the viscose containing sodium sulfide. A thin film of the viscose appeared pink rather than orange, but no unusual color was observed upon examining a jar of the viscose.

The addition during xanthation of sulfur dissolved in carbon disulfide interfered with the formation of cellulose xanthate, and some of the dissolved sulfur crystallized from the solution. Nevertheless, the constants K'' and $K_{(2)}$ indicate that the small quantity of sulfur that remained in solution increased the ripening rates.

Effect of By-Product Removal on Ripening

Two methods of purification were attempted in

order to study the ripening characteristics of cellulose xanthate solutions free from normal by-products. First, the viscose solution was purified by treating with the hydroxide form of an ion-exchange resin (Amberlite IRA-400). This gave the so-called "white" viscose which was actually a very pale green. A second method, washing the xanthate crumbs with 80% aqueous methanol and subsequent vacuum drying, gave a pale yellow solid which dissolved to give a pale yellow viscose. The methanol treatment caused a very marked reduction in the degree of substitution of the viscose (see Table II). An indication of the efficiency of the purification method is shown in the XS/TS column of Table II. The xanthate sulfur content of the ion exchanged samples was 95 to 97% of the total sulfur present, while for the methanol-treated sample 11% of the sulfur was by-product sulfur, much of which could have been produced by dexanthation during dissolving.

Since ripening studies suggested a reduction in the factor estimated as $DS_{(2)}$, as shown by the $DS_{(1)}/DS_{(2)}$ ratio, the value $K_{(2)}$ could not be calculated. The $K_{(1)}$ values were normal, but the K'' indicated a slowing of ripening rates.

The purification step should remove all the divalent anions present: sulfide, polysulfide, trithiocarbonate, and others. However, there is the possibility that in the case of the ion exchange resin, the viscose could become contaminated with an amine-type side chain from the resin or with chloride not completely removed during the conversion of the resin from chloride to hydroxide form. In the case of the methanol-washed viscose there is the possibility of contamination with sodium-methyl xanthate which is readily formed by treating methanolic sodium hydroxide with carbon disulfide.

Effect of Miscellaneous Sulfur Compounds

The unexpected behavior of sodium sulfide on ripening led to an investigation of three other sulfur compounds: sodium sulfite, sodium sulfate, and dimethyl sulfoxide. They were added on the basis

TABLE II
Effect on Viscose Ripening of By-Product Removal

| Method of preparation | Initial DS | XS/TS ^a | $\frac{DS_{(1)}}{DS_{(2)}}$ | $K_{(1)}$ | $K_{(2)}$ | K'' |
|--|------------|--------------------|-----------------------------|-----------|-----------|----------|
| Ion exchange | 0.566 | 0.97 | 0.916 | 1.00 | | 6.64 |
| Ion exchange | 0.539 | 0.96 | 0.955 | 1.04 | | 6.04 |
| Methanol washing | 0.393 | 0.89 | | 0.95 | | 6.22 |
| 95% Confidence limits for normal viscose | | | 0.68-0.88 | 0.86-1.14 | 0.75-1.39 | 7.4-10.1 |

of the sulfur content, 2% added sulfur in the viscose. Sodium sulfite is among those compounds listed by Ott and Spurlin² as ripening retarders for viscose. Sodium sulfate is the oxidation product of sodium sulfite, and dimethyl sulfoxide is an interesting organic sulfur compound known for its unusual solvent characteristics. Sodium chloride was included in this set because it was a possible contaminant in the ion exchanged samples.

The results, summarized in Table III, show that sodium sulfate, sodium chloride, and dimethyl sulfoxide did not affect ripening rates.

Addition of sodium sulfite, however, showed some marked effects. The color of the viscose in the jar was pink rather than orange, the intensity of the pink color increasing until the second or third day of ripening, then remaining until the viscose gelled—some time between four and five weeks; in comparison, the gelation time of a normal viscose was about two weeks. The color effect was similar to but much more pronounced than that observed for the viscose containing sodium sulfide. The initial viscosity of the viscose containing sodium sulfite was higher than normal, the ball-fall time being 203 sec. compared with an initial viscosity of 68 sec. for the control made from the same alkali cellulose under the same conditions.

The ripening data in Table III show an $XS/S_{(CS_2)}$ ratio of 1.24, which indicates that some reducing material was not removed by the resin. This is similar to the effect found for sodium sulfide. The slope constant calculated as $K_{(1)}$ was very low; $K_{(2)}$ could not be calculated. The value for K'' was estimated from the curve obtained after the first week of ripening.

Figure 5 shows the ripening curve obtained for viscose containing sodium sulfite. The initial decrease in apparent DS followed by an increase in apparent DS, the change in color, and the very high viscosity of the solution were strong indications that some abnormal change in the chemistry had occurred.

A second set of samples was prepared by split

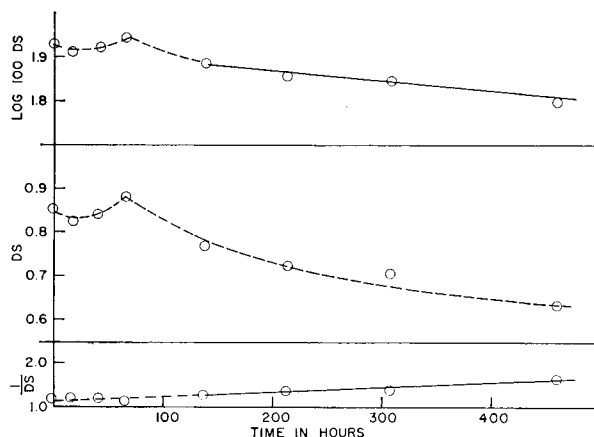


Fig. 5. Ripening curve for viscose containing sodium sulfite.

xanthation which, for a normal viscose, gives a linear salt index-DS relationship. One viscose was prepared and divided into two equal parts. To one part, sodium sulfite (equal in sulfur content to the CS_2 sulfur) dissolved in a minimum quantity of water was added. To the second part was added a quantity of water equal in weight to the sodium sulfite solution added to the first part. Both samples were mixed for 1 hr. at $5^\circ C$. and ripened for one week; during this period they were examined daily for xanthate sulfur and salt index. Each viscose was analyzed for xanthate sulfur by both the iodimetric titration method normally used and by the photometric method reported by Dux and Phifer³ based on the absorbance at $303 m\mu$ by the xanthate group. For the normal viscose the two methods were in excellent agreement; however, for the viscose containing sodium sulfite wide variations were observed. This is illustrated in Figure 6.

The control viscose ripened normally, as indicated by the lower curve, and followed approximate second-order kinetics through the first week, as shown by the upper straight line. However, two curves were obtained for the viscose containing sodium sulfite. The open circles, DS determined

TABLE III
Effect on Viscose Ripening of Miscellaneous Sulfur Compounds and Sodium Chloride

| Additive | Additive level, % S | Initial DS | $\frac{XS}{S_{(CS_2)}}$ | $\frac{DS_{(1)}}{DS_{(t)}}$ | $K_{(1)}$ | $K_{(2)}$ | K'' |
|--|---------------------|------------|-------------------------|-----------------------------|-----------|-----------|----------|
| Na_2SO_4 | 2 | 0.558 | 0.820 | 0.835 | 0.97 | 1.22 | 7.58 |
| $(CH_3)_2SO$ | 2 | 0.605 | 0.775 | 0.809 | 1.07 | 1.00 | 7.62 |
| Na_2SO_3 | 2 | 0.850 | 1.24 | | 0.24 | | 1.0 |
| NaCl | 3.4* | 0.592 | 0.814 | 0.751 | 1.01 | 0.82 | 8.89 |
| 95% Confidence limits for normal viscose | | | | 0.68-0.88 | 0.86-1.14 | 0.75-1.39 | 7.4-10.1 |

* As % of total.

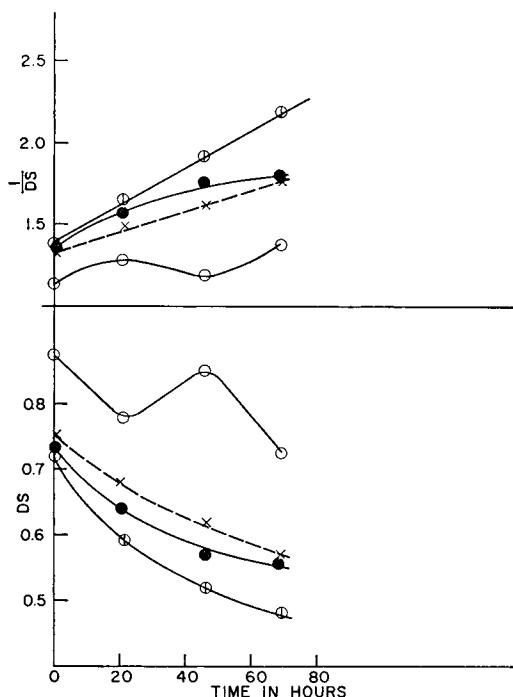


Fig. 6. Comparison of ripening curves determined by different analytical methods for normal viscose and viscose containing sodium sulfide: (O) Na_2SO_3 , iodimetric determination; (●) Na_2SO_3 , photometric determination; (X) Na_2SO_3 , DS from salt index-DS relationship; (⊙) control, iodimetric and photometric determinations.

iodimetrically, show the up-and-down pattern previously shown, with the 46-hr. peak corresponding to the development of the maximum pink color in the viscose. The values obtained by the photometric method for DS are shown by the filled circles. Neither set of data approximates second-order kinetics. The ion-exchanged solution from the sodium sulfite viscose retained the pink color, but upon dilution prior to reading the absorbance, the color changed first to yellow and then disappeared with further dilution. The salt index values indicated that the DS for the sodium sulfite samples should be higher than that found photometrically but lower than found by the iodine titration. The broken curve is a plot of the DS, indicated by

the salt index, as a function of time. It is the only curve obtained for the sulfite sample which approximates second-order kinetics during the first week of ripening. This appears to support the possibility of the formation of a chemical bond between the sulfite and the cellulose xanthate.

Effect of Oxidizing and Reducing Agents

Both sodium sulfide and sodium sulfite are mild reducing agents, which may, in part, account for their retarding effect on ripening. The accelerating effect of the sodium polysulfide may have been brought about by its action as a mild oxidizing agent.

Table IV shows the effects on ripening of two oxidizing agents and two reducing agents. Potassium chlorate showed no effect and probably does not act as an oxidizing agent in this system. The sodium borohydride reacted preferentially with water and was thus removed from the system in a few hours. These materials were added at 0.5% levels, lower concentrations than in the previous samples.

The sodium arsenite caused a slowing of the rate of ripening, less so than did sodium sulfite; however, the latter was present in a concentration about ten times that of the arsenite. The arsenite contributed a pink color to the viscose, whose viscosity was about double that of its companion viscose which contained the sodium borohydride; however, the significance of this is doubtful.

Hydrogen peroxide had an effect similar to though slightly greater than that of sodium polysulfide. Figure 7 compares the two ripening curves which are almost parallel. Since alkaline peroxide reacts readily with xanthate sulfur, converting it to sulfate, it is possible that polysulfides act in much the same way, forming oxidized thio compounds.

Effect of Sodium Cyanide on Ripening

Sodium cyanide, another salt reported to be a ripening decelerator,² was also examined. Here again the viscose was pink, and the ripening rates

TABLE IV
Effect on Viscose Ripening of Oxidizing and Reducing Agents

| Additive | Additive level, % | Initial DS | $\frac{XS}{\bar{S}_{(CS_2)}}$ | $\frac{DS_{(t)}}{DS_{(0)}}$ | $K_{(1)}$ | $K_{(2)}$ | K'' |
|--|-------------------|------------|-------------------------------|-----------------------------|-----------|-----------|----------|
| H_2O_2 | 0.5 | 0.645 | | | | | 21.0 |
| KClO_3 | 0.5 | 0.586 | 0.815 | 0.755 | 1.00 | 1.20 | 8.34 |
| NaBH_4 | 0.5 | 0.627 | 0.865 | 0.768 | 1.01 | 1.24 | 7.51 |
| Na_3AsO_3 | 0.5 | 0.623 | 0.855 | 0.790 | 0.70 | 1.25 | 5.85 |
| 95% Confidence limits for normal viscose | | | | 0.68-0.88 | 0.86-1.14 | 0.75-1.39 | 7.4-10.1 |

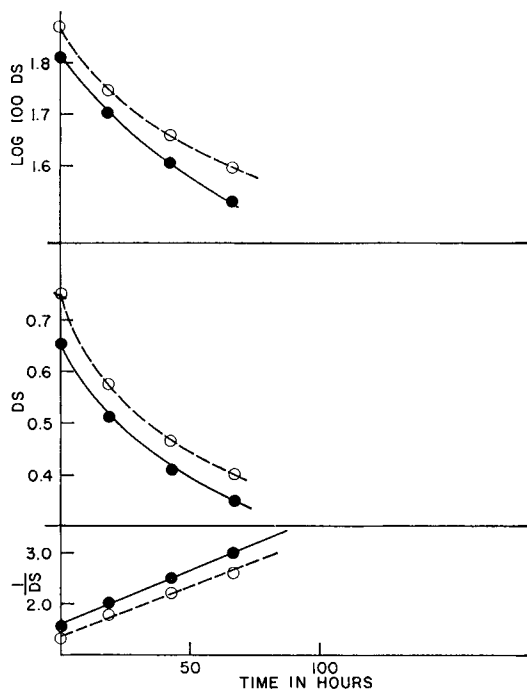


Fig. 7. Comparison of the effect on viscose ripening of addition of (O) sodium polysulfide and (●) hydrogen peroxide.

were retarded significantly as shown in Table V. No effect on viscosity was observed.

Effects of Trace Elements Which May Be Present in Viscose

A number of metallic ions which are normally present in trace or larger than trace quantities in viscose were examined. Their source may be the pulp, water, caustic or equipment used in manufacturing.

Table VI lists salts of typical trace contaminants which do not appear to affect ripening. Most of these materials are precipitated in alkaline solution as hydroxides or carbonates. The exception, sodium molybdate, is a stable salt and is not readily oxidized or reduced.

Table VII lists a series of metallic salts which form insoluble sulfides. Addition of these salts resulted in an initial increase in the rate of ripening as shown by the high $K_{(2)}$ values, but in the latter

stages, ripening proceeded normally, as indicated by the $K_{(1)}$ values. The curves for the second-order kinetic treatment were not linear during the first week of ripening, also indicating an initial acceleration of ripening.

These data suggest that the effect may possibly be caused by the reaction of the cation with sulfide to upset the xanthate-sulfide equilibrium. Apparently, after all the cation was precipitated as the sulfide, ripening proceeded normally. It is also possible that metallic xanthates were formed, although this appears unlikely, as the initial DS was normal.

Although iron and bismuth can form insoluble sulfides, they also form insoluble oxides. Iron is of particular importance since it is present as a contaminant of both pulp and caustic, and since iron and steel equipment is often used in viscose manufacture.

Iron was added at two levels, 0.1% and 0.5%. Table VIII shows a slight retarding effect for the lower level, and a significant retarding effect for the 0.5% level. A similar result was noted for bismuth. Both iron and bismuth caused a darkening of the viscose. Bismuth, however, was only slightly soluble in the dissolving caustic, and much of the bismuth settled out on the bottom of the ripening flask. Sodium arsenite was included for comparison with bismuth.

Values for $K_{(2)}$ could not be computed for viscoses containing iron or bismuth at the 0.5% level. In the case of iron there was an increase in the $DS_{(1)}/DS_{(t)}$ ratio. At the lower level of iron all values could be computed, but the overall rate was slow.

Linear relationships were not found when ripening data from viscose containing bismuth were analyzed according to the sum of two first-order reactions.

Comparison of Elements in Periodic Group V

A comparison of the ripening data of viscoses containing arsenite and bismuth suggested an interesting trend, especially when the insolubility of the bismuth salt was noted. An attempt to recover the bismuth from the bottom of the flask

TABLE V
Effect on Viscose Ripening Rates of Sodium Cyanide

| Additive | Additive level, % | Initial DS | $\frac{XS}{S_{(CS_2)}}$ | $\frac{DS_{(1)}}{DS_{(t)}}$ | $K_{(1)}$ | $K_{(2)}$ | K'' |
|--|-------------------|------------|-------------------------|-----------------------------|-----------|-----------|----------|
| NaCN | 2.9 | 0.589 | 0.843 | 0.815 | 0.42 | 0.86 | 4.0 |
| 95% Confidence limits for normal viscose | | | | 0.68-0.88 | 0.86-1.14 | 0.75-1.39 | 7.4-10.1 |

TABLE VI
Salts of Trace Elements in Viscose Which Did Not Affect Ripening

| Salt | Additive level, % | Initial DS | $\frac{XS}{S_{(CS_2)}}$ | $\frac{DS_{(1)}}{DS_{(t)}}$ | $K_{(1)}$ | $K_{(2)}$ | K'' |
|--|-------------------|------------|-------------------------|-----------------------------|-----------|-----------|----------|
| MgCl ₂ | 0.5 | 0.581 | 0.836 | 0.810 | 1.05 | 1.24 | 8.15 |
| CaCl ₂ | 0.5 | 0.568 | 0.813 | 0.792 | 1.07 | 1.24 | 9.00 |
| MnCl ₂ | 0.5 | 0.542 | 0.770 | 0.743 | 0.91 | 1.13 | 8.43 |
| AlCl ₃ | 0.5 | 0.598 | 0.834 | 0.730 | 0.93 | 0.99 | 8.72 |
| CeCl ₃ | 0.5 | 0.549 | 0.820 | 0.751 | 0.99 | 1.26 | 9.20 |
| Na ₂ SiO ₃ | 0.5 | 0.544 | 0.786 | 0.737 | 1.00 | 0.92 | 10.20 |
| Na ₂ MoO ₄ | 0.5 | 0.559 | 0.805 | 0.789 | 1.06 | 1.20 | 8.96 |
| 95% Confidence limits for normal viscose | | | | 0.68-0.88 | 0.86-1.14 | 0.75-1.39 | 7.4-10.1 |

TABLE VII
Effect on Viscose Ripening of Metallic Salts Which Form Insoluble Sulfides

| Salt | Additive level, % | Initial DS | $\frac{DS_{(1)}}{DS_{(t)}}$ | $K_{(1)}$ | $K_{(2)}$ | K'' |
|--|-------------------|------------|-----------------------------|-----------|-----------|-------|
| CoCl ₂ | 0.5 | 0.550 | 0.810 | 0.92 | 1.62 | a |
| CuSO ₄ | 0.5 | 0.615 | 0.730 | 0.90 | 1.71 | a |
| NiCl ₂ | 0.5 | 0.580 | 0.745 | 0.95 | 1.53 | a |
| PbCl ₂ | 0.5 | 0.591 | 0.761 | 0.92 | 2.07 | a |
| CdCl ₂ | 0.5 | 0.721 | 0.805 | 0.90 | 2.01 | a |
| 95% Confidence limits for normal viscose | | | 0.68-0.88 | 0.86-1.14 | 0.75-1.39 | — |

a Relationship not linear.

indicated that an estimated 0.1% of the bismuth salt remained in solution, probably as the BiOCl, yet its effect was almost as great as that of the sodium arsenite.

Other elements in Periodic Group V were added in the trivalent state at 0.5% levels to viscose. The pentavalent sodium arsenate was also used.

The data are given in Table IX for the series ranging from definitely nonmetallic sodium nitrite through the amphoteric arsenite to antimony and bismuth, which are definitely metals.

Only traces, if any, of the antimony went into solution, the oxide and the oxy salts of antimony are reported insoluble in alkali, and no effect on

ripening was observed. Sodium arsenate also had no effect; however, the arsenic is in the most highly oxidized form and has no electrons available for bonding.

For the other elements in Group V, however, a gradation in the evaluating parameters was observed. As the atomic numbers increase and the oxidation potentials decrease, there is an increase in the $XS/S_{(CS_2)}$ values from 0.800 for the nitrogen compound to 0.910 for bismuth. Thus, it follows that the initial DS also increased. The same trend was observed for the $DS_{(1)}/DS_{(t)}$ values for nitrogen, phosphorus, and arsenic. The $K_{(1)}$ decreased showing that the rate slowed as the oxidation potential of the test element decreased. The same was true for $K_{(2)}$ and K'' . The close K'' values for arsenic and bismuth are particularly note-worthy when the insolubility of bismuth is considered.

Effect of Zinc on Ripening

Zinc is normally used in viscose spinning to retard decomposition of cellulose xanthate and to control gel swelling. Although it is usually added in the spinning bath, it has been reported as being added to the viscose before spinning.⁴

The addition of 0.5% zinc chloride in the form of the soluble sodium zincate to the dissolving caustic resulted in a viscose having an apparent DS higher than normal; this continued to increase until the

TABLE VIII
Metallic Salts Which Retarded Viscose Ripening

| Salt | Additive level, % | Initial DS | $\frac{XS}{S_{(CS_2)}}$ | $\frac{DS_{(1)}}{DS_{(t)}}$ | $K_{(1)}$ | $K_{(2)}$ | K'' |
|--|-------------------|------------|-------------------------|-----------------------------|-----------|-----------|----------|
| FeCl ₃ | 0.1 | 0.601 | 0.843 | 0.853 | 1.00 | 1.12 | 6.97 |
| FeCl ₃ | 0.5 | 0.602 | 0.838 | 0.945 | 0.72 | | 3.88 |
| BiCl ₃ | 0.5 | 0.626 | 0.910 | | | | 6.00 |
| Na ₃ AsO ₃ | 0.5 | 0.623 | 0.855 | 0.790 | 0.70 | 1.25 | 5.85 |
| 95% Confidence limits for normal viscose | | | | 0.68-0.88 | 0.86-1.14 | 0.75-1.39 | 7.4-10.1 |

TABLE IX
Comparison of Effect on Viscose Ripening of Elements in Periodic Group V

| Additive | Additive level, % | Initial DS | XS $\overline{S_{(CS_2)}}$ | $\frac{DS_{(1)}}{DS_{(2)}}$ | $K_{(1)}$ | $K_{(2)}$ | K'' |
|---|-------------------|------------|-------------------------------|-----------------------------|-----------|-----------|-------|
| NaNO ₂ | 0.5 | 0.556 | 0.800 | 0.780 | 1.12 | 1.51 | 9.05 |
| Na ₂ HPO ₃ | 0.5 | 0.589 | 0.840 | 0.760 | 0.95 | 1.28 | 8.14 |
| Na ₃ AsO ₃ | 0.5 | 0.623 | 0.855 | 0.790 | 0.70 | 1.25 | 5.85 |
| BiCl ₃ ^a | 0.5 | 0.626 | 0.910 | | | | 6.00 |
| Sb ₂ O ₃ ^b | 0.5 | 0.592 | 0.841 | 0.692 | 0.90 | 1.13 | 7.65 |
| Na ₃ AsO ₄ | 0.5 | 0.600 | 0.832 | 0.800 | 1.10 | 1.40 | 8.00 |

^a Very slightly soluble; soluble portion probably BiOCl, estimated 0.1% or less in solution.

^b Insoluble.

second day when the per cent xanthate sulfur was equal to the total per cent sulfur, then decreased slowly during ripening. Sample data are given in Table X.

The effect of zinc could not be evaluated according to the sum of two first order reactions. The initial increase in the apparent xanthate sulfur prevented any estimation of $K_{(2)}$ and, in the later portion of the ripening, the plot of log DS versus time was not linear, although a $K_{(1)}$ value of about 0.5 was approximated. A second-order decomposition pattern was followed after the maximum DS was reached; this gave a slope constant about $\frac{1}{4}$ the normal value.

The increase in viscosity observed during the first four days of ripening suggested the possibility of formation of addition products or crosslinking.

The normal green viscoses had xanthate sulfur values of approximately 1.7%, leaving 0.3% by-product sulfur, which is equivalent to 3.1 mmoles of trithiocarbonate/100 g. viscose. A concentration of 0.5% zinc chloride, equivalent to 3.7 mmoles zinc/100 g. viscose, is in excess of the zinc required to crosslink the trithiocarbonate to xanthate sulfur, leaving zinc available to crosslink adjacent xanthate groups. The former may explain the very high xanthate sulfur value; the latter, the increase in viscosity. A reaction of this type may possibly account for the retarding effect of zinc.

Effect of Tin and Chromium on Viscose

The addition of stannous chloride at the 0.5% level in the dissolving caustic resulted in solidification of the viscose in less than $\frac{1}{2}$ hr.—long before the dissolving step was finished. A repetition, with addition of 0.5% sodium stannite, resulted in the same effect. Addition of sodium stannite at the 0.05% level, however, gave a viscose with a slightly higher viscosity, but the ripening data were normal. The addition of sodium stannate at the 0.5% level also resulted in gelled viscose in about $\frac{1}{2}$ hr. The effect was apparently independent of the oxidation state of the tin.

TABLE X
Effect of Zinc on Viscose Ripening

| | |
|-------------------------------------|-------|
| Initial DS | 0.652 |
| Maximum DS | 0.709 |
| Initial XS/ $\overline{S_{(CS_2)}}$ | 0.916 |
| Maximum XS/ $\overline{S_{(CS_2)}}$ | 0.995 |
| K'' | 2.64 |

The same gelling effect was observed upon addition of chromium chloride at the 0.5% level to viscose.

In the case of both tin and chromium the viscoses appeared to be solidified "green" viscoses, rather than dexanthated gels. The gels could be dispersed by adding large quantities of water (10–20 volumes) and mixing.

SUMMARY

The effects on ripening of the materials studied may be summarized as follows.

(1) Normal constituents in viscose, Na₂CO₃, Na₂CS₃, NaCl, did not appear to affect ripening. Sodium sulfide, however, retarded ripening. Removal of by-products appeared to retard ripening.

(2) Ripening was accelerated by oxidizing agents (H₂O₂, Na₂S₂) and retarded by reducing agent (Na₂SO₃). The latter gave some indication of possible formation of addition products.

(3) No effects were observed on addition of Na₂SO₄, (CH₃)₂SO, KClO₃, and Na₂BH₄.

(4) The addition of salts which are precipitated as hydroxides or carbonates or salts which are stable to mild oxidation and reduction had no apparent effect on ripening rates.

(5) Addition of salts which form insoluble sulfides resulted in an initial increase in ripening rates, but ripening proceeded normally in later stages, probably after the salts were removed by precipitation as the sulfides.

(6) Addition of FeCl₃, BiCl₃, and Na₃AsO₃ resulted in a retarding of ripening.

(7) A comparison of the ripening characteristics of viscoses containing elements in Group V of the periodic table in the trivalent state showed a gradation of effect. As the oxidation potential of the element decreased, $XS/S_{(CS_2)}$ and the initial DS increased and $K_{(1)}$, $K_{(2)}$, and K'' decreased, showing a retarding of ripening.

(8) The addition of the zinc resulted in a retarding of ripening and suggested the occurrence of possible crosslinking of xanthate and by-product sulfur and/or two xanthates.

(9) Addition of tin and chromium salts at the 0.5% level resulted in gelation of the viscose even before solution was complete.

References

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Synopsis

The effects on viscose ripening of a variety of materials are reported. (1) Normal constituents (Na_2CO_3 , Na_2CS_3 , $NaCl$) appeared not to affect ripening; however, Na_2S retarded ripening. By-product removal appeared to retard ripening. (2) Oxidizing agents (H_2O_2 , Na_2S_x) accelerated ripening; reducing agent (Na_2SO_3) retarded ripening; this is suggestive of possible addition product formation. (3) Na_2SO_4 , $(CH_3)_2SO$, $KClO_3$, Na_2BH_4 showed no effect on ripening. (4) Salts which precipitated as hydroxides or carbonates did not appear to affect ripening. (5) Salts which formed insoluble sulfides resulted in an initial increase in ripening rates. In later stages, ripening proceeded normally, probably after the salts were removed from solution as insoluble sulfides. (6) $FeCl_3$, $BiCl_3$ and Na_3AsO_3 appeared to retard ripening. (7) A comparison of the effect on ripening of the trivalent state of elements in group V of the periodic table showed that the rate of ripening decreased with the oxidation potential of the element. (8) The addition of sodium zincate retarded ripening and suggested possible cross-linking of xanthate and by-product sulfur, or of two xanthate groups. (9) Addition of tin and chromium salts at the 0.5% level resulted in gelation of the viscose within 30 min. after the addition.

Résumé

Les effets d'une série de matériaux sur le mûrissement de la viscose ont été rapportés. (1) Des constituants nor-

maux (Na_2CO_3 , Na_2CS_3 , $NaCl$) ne semblent pas affecter ce mûrissement; cependant Na_2S le retarde. L'élimination d'un produit secondaire retarde le mûrissement. (2) Des substances oxydantes (H_2O_2 , Na_2S_x) accélèrent le mûrissement, des substances réductrices (Na_2SO_3) le retardent; c'est possible qu'il y a ici la formation d'un produit d'addition. (3) Na_2SO_4 , $(CH_3)_2SO$, $KClO_3$, Na_2BH_4 n'influencent pas le mûrissement. (4) Des sels qui précipitent comme des hydroxydes en carbonates ne semblent pas l'affecter. (5) Des sels qui forment des sulfures insolubles donnent une augmentation initiale de la vitesse de mûrissement. Dans les étapes ultérieures le mûrissement continue normalement, probablement après que les sels sont éliminés de la solution comme sulfures insolubles. (6) $FeCl_3$, $BiCl_3$ et Na_3AsO_3 semblent retarder le mûrissement. (7) La comparaison de l'effet sur le mûrissement des éléments à l'état trivalent du groupe périodique V montre que la vitesse de mûrissement décroît lorsque le potentiel d'oxydation de l'élément diminue. (8) L'addition de zincate de sodium retarde le mûrissement et suggère un pontage possible du xanthate et d'un produit sulfuré secondaire ou de deux groupes xanthates. (9) L'addition des sels d'étain et de chrome à un pourcentage de 0,5 entraîne la gélification de la viscose endéans les 30 minutes après l'addition.

Zusammenfassung

Über den Einfluss einer Reihe von Stoffen auf die Viskosereifung wird berichtet: (1) Normale Bestandteile, Na_2CO_3 , Na_2CS_3 , $NaCl$, scheinen keinen Einfluss auf die Reifung zu haben; Na_2S verzögert jedoch die Reifung. Entfernen von Nebenprodukten scheint die Reifung zu verzögern. (2) Oxydationsmittel, H_2O_2 , Na_2S_x , beschleunigen die Reifung; ein Reduktionsmittel, Na_2SO_3 , verzögert die Reifung, was für eine mögliche Bildung von Additionsprodukten spricht. (3) Na_2SO_4 , $(CH_3)_2SO$, $KClO_3$, Na_2BH_4 zeigen keinen Einfluss auf die Reifung. (4) Salze, die als Hydroxyde oder Karbonate ausfallen, scheinen die Reifung nicht zu beeinflussen. (5) Salze, die unlösliche Sulfide bilden, ergeben eine anfängliche Erhöhung der Reifungsgeschwindigkeit. Im späteren Verlauf geht die Reifung normal vor sich, möglicherweise nach der Entfernung der Salze aus der Lösung als unlösliche Sulfide. (6) $FeCl_3$, $BiCl_3$ und Na_3AsO_3 scheinen die Reifung zu verzögern. (7) Ein Vergleich des Einflusses der Elemente in Gruppe V des periodischen Systems im dreiwertigen Zustand auf die Reifung zeigt, dass die Reifungsgeschwindigkeit mit steigendem Oxydationspotential des Elements abnimmt. (8) Der Zusatz von Natriumzinkat verzögert die Reifung und lässt eine mögliche Vernetzung von Xanthogenat und dem Nebenprodukt Schwefel oder von zwei Xanthogenatgruppen erkennen. (9) Zusatz von Zinn- und Chromsalzen in der Grössenordnung von 0,5% führt innerhalb 30 Minuten nach dem Zusatz zu einer Gelierung der Viskose.

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