

Factors Affecting Viscose Ripening*

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A number of kinetic treatments of viscose ripening data are found in recent literature,¹⁻⁸ along with the newly developed analytical techniques which have made these studies possible. It was the purpose of this study to explore kinetic methods of treating ripening data; to evaluate effects of pulp type, variables in the concentration of the main components of viscose solutions, ripening temperature, and preparation variables on dextranation rates; and to correlate these effects with physical changes occurring in the viscose during ripening.

METHODS OF PREPARING VISCOSE

Except where the condition was a special factor under study, the viscose solutions were prepared from sulfate pine pulp by conventional methods. The sheets were steeped 1 hr. in 18.5% sodium hydroxide solution held at 26°C., shredded 1 hr. at room temperature with a Baker-Perkins shredder, aged 20 hr. at 29°C., and xanthated 2 hr. at 25°C. in small, sealed, glass jars which were rotated submerged in a water bath. The crumbs were transferred to a beaker also held in a 25°C. bath, and the contents stirred for 2 hr.

The composition of the viscose was calculated to give 7% cellulose, 2% sulfur, and 6% total alkalinity. This led to 4% free alkalinity and a xanthate sulfur content (XS) of at least 1.5%.

METHODS OF ANALYSIS AND RIPENING

The viscose solutions were ripened at full concentration at 15°C., over a period of two weeks. Xanthate sulfur and salt index determinations were made on aliquots daily; total sulfur, total alkalinity, cellulose, and free alkalinity were determined only on the green viscose. The analytical methods used were modifications of those reported by Treiber et al.¹

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The xanthate sulfur was determined iodimetrically by titrating a viscose solution which had been diluted 1 to 20 with water and subjected to ion exchange. To determine total alkalinity, a viscose solution was acidified, the volatile gases expelled by boiling, and the solution back titrated with sodium hydroxide. An alkaline peroxide oxidation of the sulfur compounds followed by a total alkalinity as before, gave a value for total sulfur by difference. The cellulose determination was the usual chromic acid oxidation in which the viscose was first acidified and boiled to expel the volatile gases.

The physical methods were empirical. Salt index was measured as concentration (in per cent) of sodium chloride in which 3 drops of viscose will barely coagulate after agitation for about 1½ min.

TREATMENT OF DATA

The xanthate sulfur values were converted to degree of substitution *DS* and plotted as a function of time. Figure 1 illustrates three runs with cotton linters. The curves show a rapid initial dextranation that gradually tapers off to a point of gelation after about 240 hr. The graph illustrates the close reproducibility that has been obtained between these separate runs, where almost the only difference appears to be the value of the initial *DS*.

Two methods have been used for further interpretation of this curve. The more interesting was proposed by Woodrow, Mackey, and Bachelott.² They reported that ripening could be expressed as the sum of two first-order reactions occurring simultaneously, one fast and virtually completed within the first portion of the ripening period, and the other about 1/10 as fast and continuing over the entire period. They attributed the difference in rates to dextranation from different positions in the anhydroglucose unit in the cellulose chain, secondary for the rapid reactions

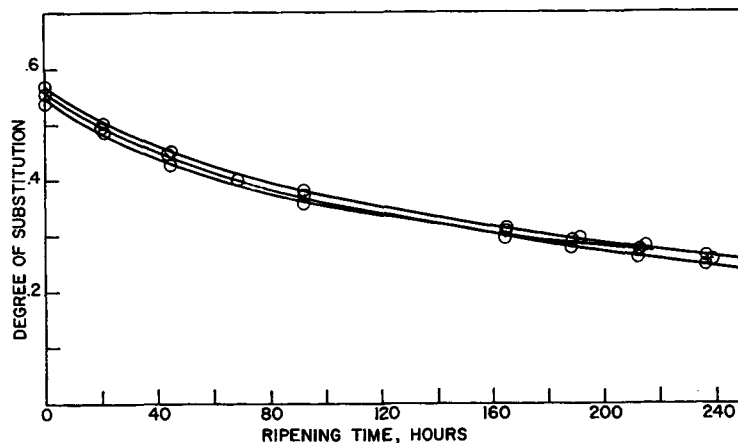


Fig. 1. Ripening curves for viscoses prepared from cotton linters.

and primary for the slow reaction. Thus, it seemed possible that the data on ripening might give information pertinent to the structure of cellulose xanthate which could not be obtained in any other way.

Figure 2 illustrates the treatment of the experimental data of one of the linter pulps shown in Figure 1. The raw data are replotted as curve #1. For a first-order reaction the DS values of the second week are replotted as the logarithm (curve #3), yielding a straight line with slope $K_1 = 1.08 \times 10^{-3}$. This represents the reaction rate constant for the primary dexanthation. It is extrapolated back to zero time and replotted as the antilog (curve #2). The difference between

curves #1 and #2 is plotted on curve #4 and represents the contribution due to the dexanthation from the secondary position. The logarithm of this value is plotted as a function of time in curve #5. This also results in a straight line with slope $K_2 = 1.19 \times 10^{-2}$. The ratio of the intercepts should represent the proportion of xanthate substituted in the two positions and has been expressed numerically as the ratio of the primary substitution DS_1 to the total substitution DS_t . Although this interpretation of the data is still open to question, it provides a method for resolving the ripening curves into numerical values. One minor disadvantage of this treatment is that a large number of precise data points is required in each section

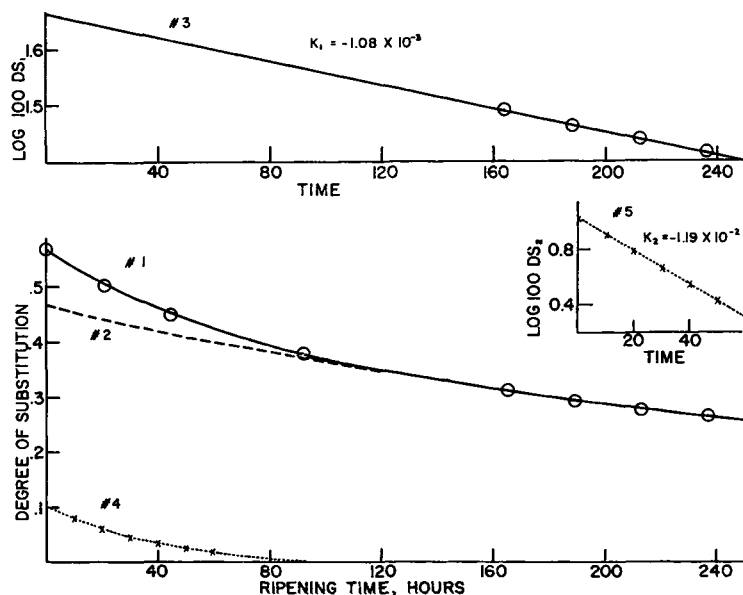


Fig. 2. Ripening curve treated as the sum of two first-order reactions.

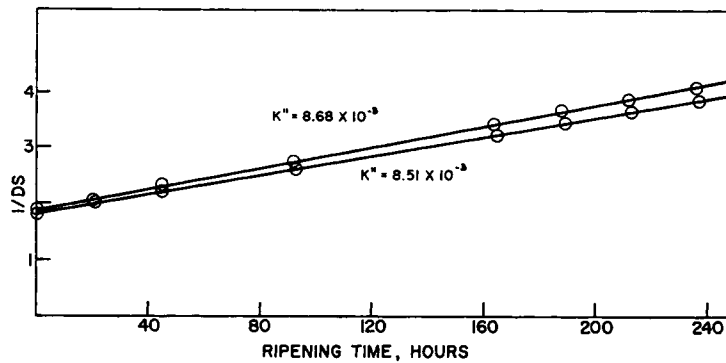


Fig. 3. Ripening curve treated as a single second-order reaction.

of the run, particularly in the second week to permit a long range extrapolation, and interpretation by difference.

While a number of other interpretations of ripening data have been made in recent years by Dux and O'Shaughnessy,³ Wronski,⁴ Vosters,⁵ Miller and Geerdes,⁶ and Philipp and Dautzenberg,⁷ as an alternate method, the simplest of these has been used, one originated by Kagawa and Kobayashi.⁸ They proposed that the reaction can be expressed as having second-order kinetics. Figure 3 illustrates their interpretation of the same data with cotton linters. The reciprocal of DS plotted against time also yields a straight line with slope $K'' = 8.51 \times 10^{-3}$. While this interpretation is easily the simplest, it ceases to hold as much physical significance; however, the data points need to be less frequent and less critical. Both interpretations of the data have been used. Each reduces the ripening curve into numerical coefficients which can be compared.

EFFECT OF PULP TYPES

The behavior of pulp type with respect to dexanthation rates was of particular interest. Table I summarizes the results of 10 runs out of 25 examined under uniform conditions, changing only the pulp type.

Both methods for data interpretation were reasonably successful in the sense that straight lines were obtained in almost every case. The table shows only one instance of deviation, marked with an asterisk. Alpha values for the pulp type are also given. The results given here are experimental values for individual runs.

Data analysis was first attempted on the basis of duplicates, but it was soon evident that the ripening rates for sulfate pulps were essentially alike, and the data were given a replicate treatment. The last two lines give the standard deviation and confidence limits for all replicate runs. This was used as the yard-stick for future deviations. Deviations from these limits are italicized and

TABLE I
Effect of Pulp Type on Dexanthation

Pulp	Alpha value	XS/TS	DS_1/DS_t	$K_1 \times 10^3$	$K_2 \times 10^2$	$K'' \times 10^3$
Cotton linters 1	98.6	0.780	0.792	1.03	1.08	8.76
Cotton linters 2	—	0.757	0.816	1.08	1.19	8.51
Cotton linters 3	—	0.754	0.750	0.91*	0.92	8.68
Sulfate pine 1	97.3	0.752	0.823	1.08	1.08	8.88
Sulfate pine 2	96.5	0.773	0.760	0.96	0.81	9.24
Sulfate pine 3	94.2	0.753	0.738	1.03	0.92	9.54
Sulfate pine 4	93.8	0.780	0.765	0.99	1.00	8.33
Sulfate gum	96.2	0.774	0.817	1.03	1.32	8.40
Sulfite pine	94.8	0.746	0.795	1.19	1.42	10.1
Sulfite spruce	92.2	0.765	0.800	1.20	1.54	10.3
Reproducibility (based on 11 replicate runs)						
Standard deviation		0.01	0.06	0.07	0.16	0.49
95% Confidence limits		0.74–	0.65–	0.85–	0.68–	7.8–
		0.78	0.89	1.13	1.33	9.8

TABLE II
Effect of Composition on Dexanthation

Run	Viscose composition				Ripening data				
	Cellu-lose, %	Total sulfur, %	Total alkalin-ity, %	Free alkalin-ity, %	<i>XS/TS</i>	<i>DS₁/DS_t</i>	$K_1 \times 10^3$	$K_2 \times 10^2$	$K'' \times 10^3$
1	7.14	2.00	6.06	4.07	0.785	0.807	1.02	1.30	9.47
2	7.22	2.00	3.80	1.91	0.754	0.796	1.04	1.30	9.55
3	8.66	2.54	5.82	3.48	0.808	0.765	0.98	1.20	8.51
4	5.18	1.38	6.07	4.54	0.814	0.799	1.40	1.19	12.77
5	7.27	1.69	6.08	4.28	0.805	0.900	1.40	0.95	11.40
6	7.24	3.61	7.52	4.19	0.729	0.697	1.11	1.23	7.26
7	7.15	2.09	9.07	6.65	0.785	0.820	0.99	1.28	8.89
8	7.08	2.08	6.13	3.80	0.766	0.795	0.96	1.15	7.81
Range (from Table I)					0.74-	0.65-	0.85-	0.68-	7.8-
					0.78	0.89	1.13	1.33	9.8

suggest that ripening rates for sulfite pulps are slightly faster than those for sulfate pulps. There are no significant deviations in the other two columns, DS_1/DS_t , and reactivity, XS/TS (xanthate sulfur to total sulfur ratio).

The standard deviation of the replication seemed high, indicating randomness of composition as well as precision of results. Variations of the same magnitude were found for the concentrations of the major components of the viscose.

EFFECT OF COMPOSITION VARIABLES

In order to determine how seriously a change in composition of the major constituents did affect the ripening, the study summarized in Table II was completed. Samples 1 and 8 represent control samples under normal conditions; 2 and 7 represent changes in caustic, with apparently no effect, though only over the limited range of the variation. In samples 3 and 4 the cellulose content was varied, but the ratio of sulfur to cellulose was kept constant, i.e., at the same DS , whereas in 5 and 6 the cellulose was held constant and only the sulfur changed. Increase in ripening rates occurred only when the concentration of xanthate groups was lowered, either with a change in the number of molecules of cellulose xanthate, or with the substitution along a molecule (DS).

The DS_1/DS_t values based on the dual first-order interpretation appear to be affected only in a random manner, but the range in the control runs is quite large, and it is difficult to find values beyond this range. The XS/TS column shows a number of deviations, as expected. Although no difference in reactivity for various pulps was

found, the differences in viscose preparation did show an effect.

EFFECT OF RIPENING TEMPERATURE

In order to estimate the molar activation energy coefficient, viscose solutions from a high alpha sulfate pulp were ripened at 15, 20, 25, 30, and 33°C. The results, Table III, show that the rate increases about 4-5 times for each 10°C. rise. The results are plotted in the Arrhenius format in Figure 4. The second-order K'' rate constants form a straight line leading to an activation energy of 23 kcal./mole. This is identical with the value reported by Philipp and Dautzenberg.⁷

TABLE III
Effect of Ripening Temperature on Dexanthation

Temperature, °C.	$K_1 \times 10^3$	$K_2 \times 10^2$	$K'' \times 10^3$
15	0.99	1.01	8.8
20	2.39	2.73	19.0
25	6.18	4.98	32
30	7.30	6.30	66
33	10.10	9.20	94

Plots of the first-order reactions do not seem to conform to a straight line. This presents a serious question to the physical significance of the dual first-order interpretation, which follows the essentially random distribution of the DS_1/DS_t ratios. However, these are not true kinetics experiments in the sense that the rate is a function of concentration, since the concentration is expressed in moles of substituent on a cellulose chain. Both kinetic interpretations are convenient for assem-

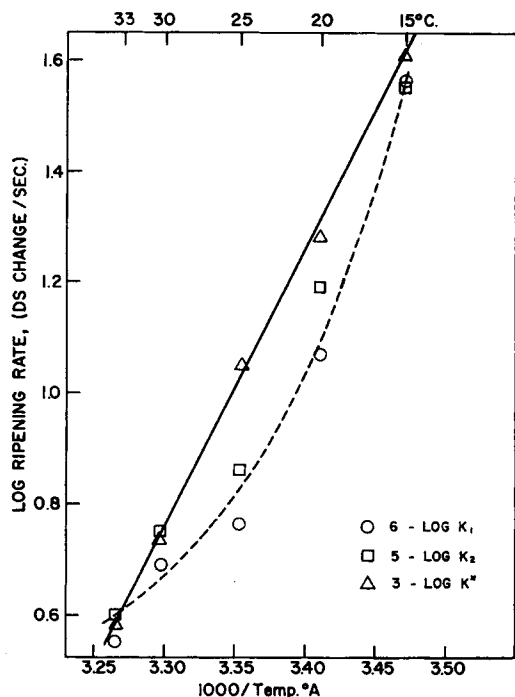


Fig. 4. Effect of ripening temperature on ripening rates.

bling the data in numerical form, and the use of both was continued.

EFFECT OF VISCOSE PREPARATION CONDITIONS

Salt indices have been collected and plotted against DS for all samples reported. Figure 5 illustrates these composite results for about a dozen samples, half wood and half lint, in which the salt index as per cent NaCl is plotted against the DS of the viscose measured at the same time. It was evident that for all pulps tested the salt index followed very closely the DS change, particularly at the end of the ripening period. At the beginning of the ripening there was a slight indica-

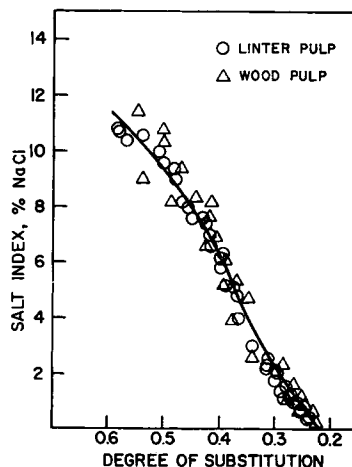


Fig. 5. Relationship between salt index and degree of substitution for viscoses made from linters and wood pulps xanthated and dissolved at 25°C.

tion of scatter; however, this was not the function expected. Lowering the temperature for dissolving the xanthate crumbs appeared to provide an answer. A factorial experiment was run in which the temperature of xanthation was varied over three levels (35, 25, and 15°C.) and the temperature of dissolving was also varied over three levels (25, 15, and 5°C.). A series of preliminary tests indicated that the xanthate sulfur content would be at a maximum after 90 min. at 35°C., 120 min. at 25°C., and 330 min. at 15°C. These were the xanthation periods chosen. The results are given in Table IV. Both the K'' and the K_1, K_2 ripening rates remained essentially constant. The DS_1/DS_t values are also statistically constant, but, as shown in Table V, there is an orderly arrangement that is interesting, provided the rate interpretation as a whole is significant. The ratio follows changes in the dissolution temperatures; this is readily explained on the basis that

TABLE IV
Effect of Xanthating and Dissolving Temperatures on Dexanthation

Run	Xanthation temp., °C.	Dissolution temp., °C.	XS/TS	DS_1/DS_t	$K_1 \times 10^3$	$K_2 \times 10^2$	$K'' \times 10^3$
A	35	25	0.727	0.765	1.04	1.21	9.00
B	35	15	0.794	0.718	0.99	1.08	9.05
C	35	5	0.805	0.676	0.86	1.01	9.20
D	25	25	0.768	0.763	0.98	1.19	8.54
E	25	15	0.830	0.766	1.02	1.08	9.20
F	25	5	0.860	0.770	1.07	0.85	9.18
G	15	25	0.823	0.833	0.99	1.29	8.76
H	15	15	0.842	0.824	1.03	1.30	7.63
J	15	5	0.879	0.809	1.08	1.29	7.61

dexanthation increases in rapidity with increasing temperature, as is the case with ordinary ripening; the component represented by DS_2 thus being eliminated. There is an even greater change with temperature of xanthation, which should mean, if this mechanism be accepted, that there may be an orienting influence during xanthation.

TABLE V
Effect of Xanthation and Dissolving Temperatures on the DS_1/DS_t Value

Xanthation		DS_1/DS_t for various dissolution temperatures		
Temperature, °C.	Time, min.	5°C.	15°C.	25°C.
15	330	0.809	0.824	0.833
25	120	0.770	0.766	0.763
35	90	0.676	0.718	0.765

The XS/TS ratios are arranged similarly in Table VI. The changes are statistically significant. The reaction is most efficient at the lowest temperature of xanthation and dissolving, and the contribution of each is about equal. The change with dissolving can be explained as before on the basis of increased dexanthation, but it is also indicated that the xanthation is more efficient at low temperatures in spite of the longer xanthating period.

TABLE VI
Effect of Xanthation and Dissolving Temperatures on the XS/TS Value

Xanthation		XS/TS for various dissolution temperatures		
Temperature, °C.	Time, min.	5°C.	15°C.	25°C.
15	330	0.879	0.842	0.823
25	120	0.860	0.830	0.768
35	90	0.805	0.794	0.727

Viscosity determination was included in this factorial as a regular test method. All viscosities were measured at a constant temperature of 15°C. as the time in seconds required for a $1/8$ -in. diameter stainless steel ball to fall 10 in. through the solution. Figure 6 illustrates typical viscosities. The samples appeared clearly grouped according to temperature of xanthation, suggesting that degradation can take place during this step. The viscosities passed through a minimum after about 3

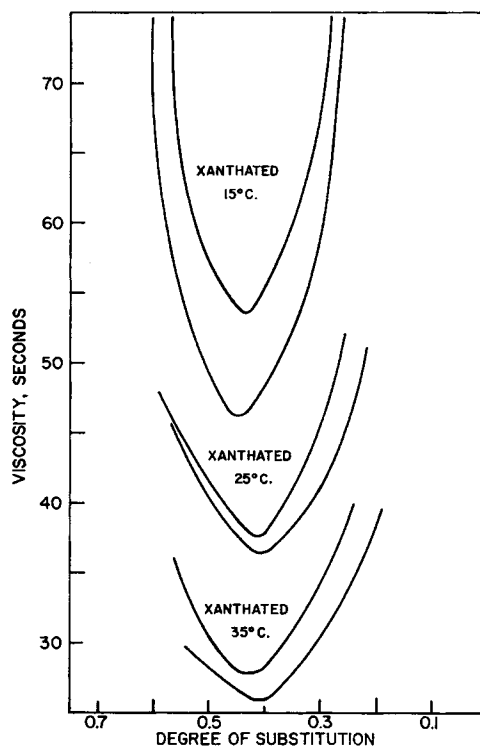


Fig. 6. Effect of temperature of xanthation on viscose viscosity curves during ripening.

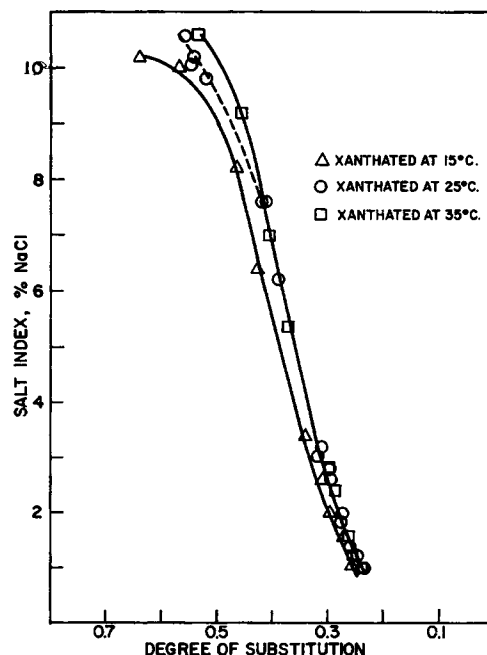


Fig. 7. Effect of xanthation temperature on the relationship of salt index to degree of substitution of viscoses dissolved at 25°C. and ripened at 15°C.

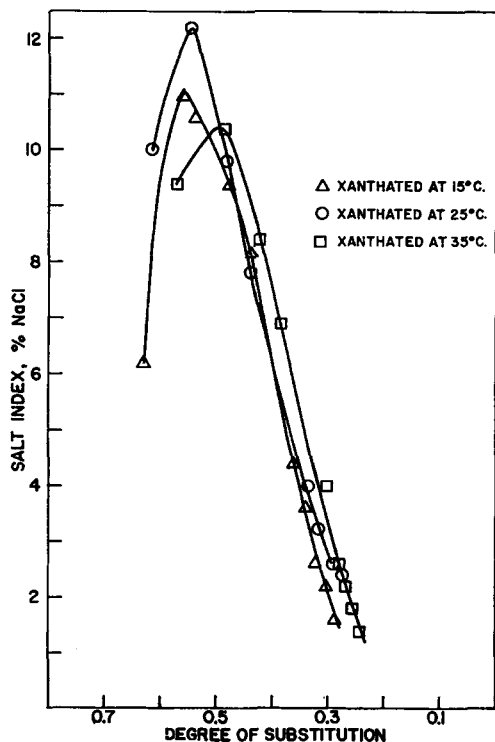


Fig. 8. Effect of xanthation temperature on the relationship of salt index to degree of substitution of viscoses dissolved at 5°C. and ripened at 15°C.

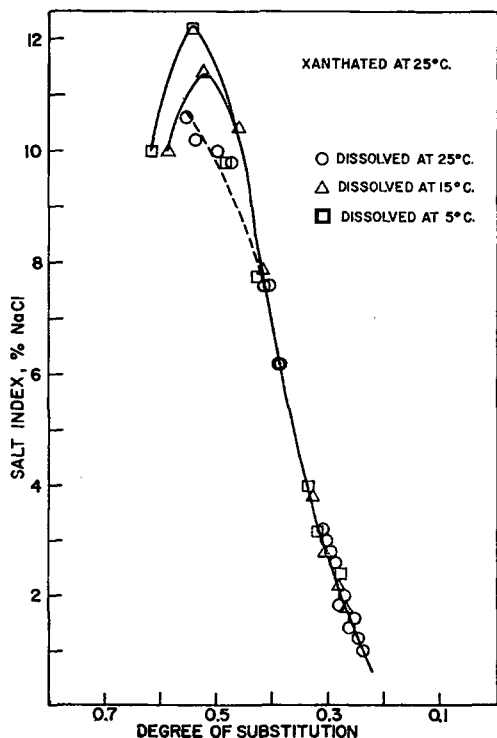


Fig. 9. Effect of dissolving temperature on the relationship of salt index to degree of substitution of viscoses xanthated at 25°C. and ripened at 15°C.

days at a *DS* of 0.45–0.40, but the changes in viscosity were relatively small.

The largest differences were found in the salt index. When the samples were dissolved at 25°C., after xanthation at various temperatures, the curves were very similar to the ones obtained previously (Fig. 7). There was a slight deviation for the samples xanthated at 15°C., and these were also the samples with the higher viscosities.

When the xanthate crumbs were dissolved at 5°C. (Fig. 8), the distinct peaking effect, indicated in the literature, appeared. The effect was most pronounced with samples xanthated at the lowest temperature, but appeared with all temperatures of xanthation. There seems to be an indication that the height of the peak is related to temperature of xanthation, but since only one test was made each day, the position of the maximum is uncertain.

Figure 9 reviews this effect with respect to dissolving temperature. It appears that with dissolution at 25°C., the ripening study is entered about 4½–5 hr. late, and the initial stages of ripening can have progressed through their peak values. This cannot be a complete explanation, however, because the peak occurs definitely later with respect to *DS* and time and at a high salt index value. It does not coincide with the minimum point for viscosity which occurs about 2 days and 0.10 *DS* later. After the initial period, all curves appear to be essentially coincident, indicating similar internal structure.

SPLIT XANTHATION

The peaking effect is believed to be an indication of two simultaneous reactions, the usual dexanthation leading to lower salt index and a randomizing of substitution yielding improved solubility. With xanthation as crumbs under heterogeneous conditions, there should be a high degree of substitution at accessible areas and relatively low substitution elsewhere. On dissolution at low temperature, the cellulose-bonding forces are active at the low or unsubstituted areas and tend to make precipitation relatively easy. As the distribution becomes more random with ripening, dissolution is improved, precipitation is less easy, and salt index is high. With further ripening, dexanthation becomes the prominent factor, and precipitation occurs more easily as the xanthate substitution decreases. It is interesting to note that, although, the various solutions may be different initially,

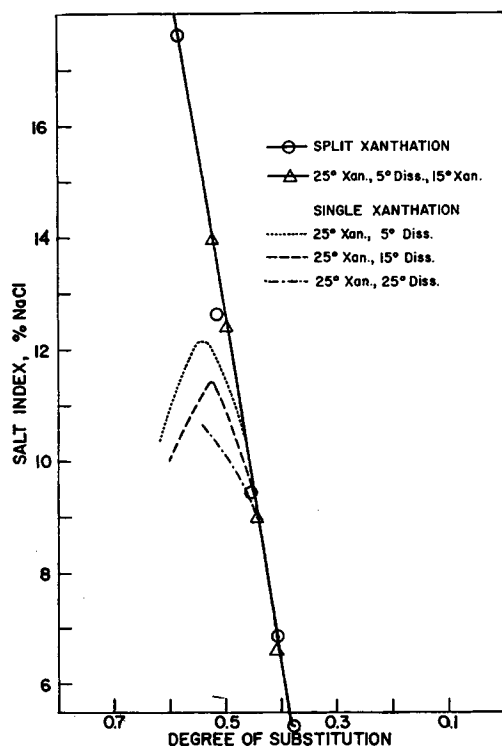


Fig. 10. Effect of split xanthation on the relationship of salt index to degree of substitution of viscoses ripened at 15°C.

all tend to possess the same final characteristics, indicating final internal structures to be identical.

This idea has been tested by xanthating under more homogeneous conditions. The alkali cellulose was xanthated at 25°C. with half the normal amount of CS_2 , then dissolved, and the remaining CS_2 added to the solution at 5°C. The results are illustrated in Figure 10, which shows two runs at different CS_2 levels. The green viscose had an unusually high salt index—above 20. Other samples have been measured at higher DS at a salt index above the measuring limit of 20 for at least 1 day. The change in salt index thereafter was almost linear, meeting the conventionally prepared viscose solutions after the second day, and then following the same ripening curve.

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Synopsis

Ripening of spinnable viscoses has shown dexanthation rates to be constant for sulfate pulps; however, sulfite pulps appeared to ripen slightly faster than the sulfate pulps. The rate of dexanthation was unaffected by changes in alkalinity over relatively narrow ranges, and slightly affected by sulfur and cellulose content. Dilution of the viscose increased the dexanthation rate. A molar activation energy of 23 kcal. was calculated from a study of temperature effects on dexanthation of a high alpha sulfate pine pulp. Changes in salt index with respect to degree of substitution for all viscoses xanthated and dissolved at 25°C. followed the same linear function. For viscoses prepared at lower xanthation and/or dissolving temperatures, the ripening curves exhibited an initial rise suggesting two simultaneous changes: dexanthation and a randomizing of substitution. Split xanthation (the final xanthation step under essentially homogeneous conditions) yielded viscose having random substitution and exceptionally high salt index. As this solution ripened the salt index decreased linearly with respect to degree of substitution and eventually followed the same function as normally xanthated viscose, indicating that the final internal structures of the two solutions are similar.

Résumé

Le mûrissement des viscoses filables a montré que les vitesses de dexanthogénéation sont constantes pour les pulpes au sulfate alors que les pulpes à sulfite semblent mûrir un peu plus rapidement que les précitées. La vitesse de dexanthogénéation n'est pas affectée par des variations d'alcalinité dans un domaine relativement étroit et légèrement affectée par le contenu en soufre et cellulose. La dilution de la viscose augmente la vitesse de dexanthogénéation. Une énergie d'activation molaire de 23 kcal a été calculée par l'étude de l'influence de la température sur la dexanthogénéation d'une pulpe de pin alpha au sulfate. Les variations d'indice de sel par rapport au degré de substitution de toutes les viscoses xanthogénées et dissoutes à 25°C suivent la même relation linéaire. Pour des viscoses préparées avec dex taux de xanthogénéation et/ou des températures de dissolution inférieures, les courbes de mûrissement montrent un accroissement initial suggérant deux changements simultanés: une dexanthogénéation et une substitution statistique. La xanthogénéation directe (l'étape de xanthogénéation finale dans des conditions essentiellement homogènes) produit de la viscose possédant une substitution statistique et un indice de sel exceptionnellement élevé. Lors du mûrissement de cette solution l'indice de sel décroît linéairement en fonction du degré de substitution et suit éventuellement une fonction identique à celle des viscoses xanthogénées normales, ce qui indique que les structures internes finales des deux solutions sont semblables.

Zusammenfassung

Die Reifung spinnbarer Viskose zeigte für Sulfatpulpas konstante Dexanthogenierungsgeschwindigkeiten, jedoch scheinen Sulfitpulpas etwas schneller zu reifen als die Sulfatpulpas. Die Geschwindigkeit der Dexanthogenierung blieb durch Änderung der Alkalität in verhältnismässig engen Grenzen unbeeinflusst und wurde durch Schwefel- und Cellulosegehalt etwas beeinflusst. Verdünnung der Viskose erhöhte die Dexanthogenierungsgeschwindigkeit. Aus der Untersuchung des Temperatureinflusses auf die Dexanthogenierung eines Alpha-Sulfat-Föhrenpulpas wurde eine Aktivierungsenergie von 23 Kilocalorien/Mol berechnet. Die Abhängigkeit des Salzindex vom Substitutionsgrad folgte für alle bei 25° xanthogenierten und gelösten Viskosen der gleichen linearen Funktion. Für Viskosen, die bei

niedrigeren Xanthogenierungs- oder Lösungstemperaturen dargestellt wurden, zeigten die Reifungskurven einen anfänglichen Anstieg, was für zwei gleichzeitige Vorgänge spricht: Dexanthogenierung und statistischer Ausgleich der Substitution. "Split"-Xanthogenierung (der letzte Xanthogenierungsschritt unter im wesentlichen homogenen Bedingungen) lieferte eine Viskose mit statistischer Substitution und einem ausnehmend hohen Salzindex. Beim Reifen dieser Lösung nahm der Salzindex linear mit bezug auf den Substitutionsgrad ab und folgte praktisch der gleichen Funktion wie normal xanthogenierte Viskose, was beweist, dass die schliesslich erreichte innere Struktur beider Lösungen ähnlich ist.

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