Highly Reactive Wood Pulps for Cellulose Acetate Production

K. D. SEARS, J. F. HINCK, and C. G. SEWELL, *ITT Rayonier Inc.,*
Shelton, Washington 98584

Synopsis

Wood pulps highly reactive in both high- and low-catalyst cellulose acetate processes can be prepared by mercerization and then treatment with alkylene oxides; only trace levels of substitution are required. The fiber inactivating effects of mercerization after drying are overcome, and several acetate properties are improved by this process. The reactivity characteristics cannot be duplicated by similar modifications of nonmercerized fibers; in low catalyst processes such pulps actually show reduced reactivity.

INTRODUCTION

The goal of the study reported here was to develop highly reactive acetate pulps that might lead to significantly improved levels of production for cellulose acetate manufacturers. The strategy followed was to utilize mercerized cellulose stock (converted from cellulose I to cellulose II) because it is less crystalline and more readily accessible to reagents. Mercerized cellulose which has been acetylated without drying (with the removal of water by solvent exchange or other complex procedure) is known to show enhanced reactivity over native cellulose (cellulose I).[1] Unfortunately, when mercerized pulps are dried, they become relatively inert to acetylation as a consequence of structural collapse in the interfibrillar spaces upon drying. To overcome this inactivation, research efforts were directed at chemically modifying the internal pulp structure of never-dried stock so that instead of collapsing when dried, it would remain "wedged" open so that high reactivity might be maintained and good acetate properties attained as well. Our own studies and those of others[2] on hydroxyalkylation of nonmercerized cellulose fibers with alkylene oxides to improve acetate performance suggested that such reagents might adequately wedge mercerized fibers so that inactivation effects can be overcome.

RESULTS AND DISCUSSION

Initial small-scale studies with ethylene and propylene oxides were very encouraging. Treatment of two types of mercerized southern pine pulps with ethylene or propylene oxide (EO or PO) gave products with considerably improved properties in low catalyst (2.0% H_2SO_4) bottle-scale acetate evaluations[3] (Table I, A and B) compared to unmodified control stocks. The stocks were mercerized in a cold caustic bleach stage (X) prior to EO or PO treatment. The presence of undissolved fibers in the mercerized control stocks led to very cloudy acetate dopes. The ammonia-base sulfite (ABS) control pulp had the highest undissolved fiber content. Modification with EO or PO gave acetate gums with

TABLE I
Ethylene and Propylene Oxide Treatment of Southern Pine Pulps[a]

		DS	Bottle-scale acetate evaluations[b]	
			Haze (ppm)	Color (ppm)
A. *Ammonia-Base Sulfite (ABS) Pulp*				
		—OC$_2$H$_4$OH (%)		
EO-treated stock	9.5	0.27	65	200
		—OC$_3$H$_6$OH (%)		
PO-treated stock	4.22	0.09	60	350
Control stocks	0		Too cloudy to read (>150)	
B. *Steam Prehydrolyzed Kraft (SPK) Pulp*				
		—OC$_2$H$_4$OH (%)		
EO-treated stock	6.4	0.23	80	325
		—OC$_3$H$_6$OH (%)		
PO-treated stock	2.5	0.09	80	400
Control stocks	0		—	
			Too cloudy to read (>150)	

[a] Interstage bleached pulps mercerized in X bleach (10% NaOH, ~23°C) prior to treatment.
[b] Low catalyst, 1.9% H$_2$SO$_4$.

good clarity (haze) and nearly complete absence of unreacted fiber. Because the ABS stock was a highly purified fiber, it had better bottle-scale color than the steam prehydrolyzed kraft (SPK) stock. These studies also established that propylene oxide was considerably more effective than ethylene oxide at a given DS level (Table I, A, B) in overcoming the adverse effects of mercerization (i.e., it is probably a better "wedge" because of its larger molecular size). Since both reagents are of comparable cost, further efforts were focused on PO treatments since they would be the most economical.

After X bleaching of never-dried interstage stocks, a series of PO reactions were carried out using more carefully controlled experimental conditions in order to prepare sufficient quantities of PO-treated, mercerized ABS and SPK pulps at varying levels of substitution that would enable a profile of acetate performance vs. PO substitution to be readily obtained.

Analyses and Acetate Evaluations on PO-Treated, Mercerized, Southern Pine Pulp

Analyses and Small-Scale, Low-Catalyst Evaluations

Analyses and bottle-scale acetate evaluation data are presented in Table II, A and B. The haze levels of triacetate gums decreased substantially as hydroxypropoxy content (—OC$_3$H$_6$OH) was increased. Since haze levels over ~90 ppm are unacceptably high, it was evident that —OC$_3$H$_6$OH levels in the range of the intermediate substituted ABS and SPK pulps (4.4–4.8%) would be required. At the lowest and highest levels of substitution in the two series, the SPK pulp had the best haze performance. Preparation of ABS and SPK stocks at identical levels of substitution (4.8%) also showed the SPK pulp to have the better haze levels (Tables II, A and B). The bottle-scale color values of triacetate gums from both types of PO-treated pulps are excellent compared to most commercial acetate pulps now sold (~350 ppm), and those from the ABS pulps

TABLE II
Analyses of Propylene-Oxide-Treated Southern Pine Pulps[a]

—OC_3H_6OH (%)	S_{10}, S_{18} (%)		Cuene IV (dL/g)	Limit IV (dL/g)	Bottle-scale acetate evaluations[b]	
					Haze (ppm)	Color (ppm)
A. Ammonia-Base Sulfite (ABS) Pulp						
3.6	23.9	1.4	5.27	0.57	135	237
4.4	33.6	2.1	5.33	0.54	65	237
5.3[c]	35.2	3.0	5.60	0.58	70	220
Treated control[d]	1.1	0.7	5.58	0.63	Much unreacted fiber	
X bleach only	0.8	0.7	7.92	0.65 (1.01)[e]	Much unreacted fiber	
4.8[c]	32.0	2.2	6.15	0.56	80	200
B. Steam Prehydrolyzed Kraft (SPK) Pulp						
3.4	21.3	1.6	5.14	0.60	110	300
4.6[c]	26.8	2.1	5.13	0.59	85	300
5.8	37.8	5.3	5.09	0.60	40	337
Treated control[d]	0.9	0.8	4.97	0.59	Much unreacted fiber	
X bleach only	0.6	0.6	6.03	0.63 (1.32)[e]	Much unreacted fiber	
4.8[c]	30.0	0.2	5.07	0.58	62	325

[a] Interstage bleached pulps treated with PO for 2 h at 50°C after X bleach.
[b] Low catalyst, 1.9% H_2SO_4; average of duplicate evaluations.
[c] Stocks prepared using same replicate procedures.
[d] X bleached stock (10% NaOH, ~23°C) treated for 2 h at 50°C in absence of PO.
[e] Limit IV values before X bleaching.

are highly superior (200–237 ppm). It was visually noted that the PO-treated pulps reacted very rapidly in the bottle-scale acetylation tests compared to standard acetate grades. The control stocks ("treated control" and "X bleached only"—Table II) had considerable amounts of unreacted fiber in their acetate gums, and no readings could be obtained.

As expected, the PO-treated stocks had significantly higher levels of alkaline solubility. The solubility in 10% sodium hydroxide (S_{10}, %) was highest for the most heavily substituted stocks. The cuene limit intrinsic viscosity (IV) data, which is a measure of cellulose accessability and cellulose crystallinity, show that all of the stocks were well mercerized (<0.70 dL/g) during X bleaching. (The expression "cuene limit IV" is similar to that referred to as "level off DP" as used in the literature.[4]) The cuene IV values indicate that there is some loss in cellulose DP during the PO treatment process itself (e.g., "treated control" ABS stock cuene IV level was 5.58 vs. 7.92 for the "X bleached only" stock). Shorter PO reaction times would probably diminish cellulose degradation. The cuene IV values for both ABS and SPK PO-treated pulps were quite similar (5.1–5.6 dL/g range).

Small-Scale, High-Catalyst Evaluations

In order to assess the reactivity and performance of the PO-treated products in high-catalyst processes (e.g., 14% H_2SO_4), the pulps were evaluated by two, small-scale fast acetylation characterization tests (FACT)—one an adiabatic method (results, Table III, A and B) in which the temperature was permitted to rise naturally during acetylation and the other (results, Table IV) in which

TABLE III
Adiabatic FACT[a] Analyses of Propylene-Oxide-Treated Pulps

—OC₃H₆OH (%)	Break point (min)	Transmittance (%) (670 nm)	Filterability (g/cm²)
A. Ammonia-Base Sulfite (ABS) Pulps[b]			
3.6	54.4	96.5	393
4.4	41.0	96.0	286
5.3	45.5	96.5	341
B. Steam Prehydrolyzed Kraft (SPK) Pulps[b]			
3.4	41.9	99	390
4.6	40.0	99	623
5.7	33.4	99	388
Treated control	84	92	297
Standard acetate pulp-1[c]	79.6	94	147
Standard acetate pulp-2[c]	87	94	125

[a] FACT = fast acetylation characterization test; high catalyst, 14% H_2SO_4; initial temperatures ~29°C, maximum temperatures reached: ~38°C.
[b] Average of duplicate evaluations.
[c] Hemlock sulfite pulps, cuene IV ~9.

temperature is kept constant (47°C). The latter is less time-consuming and is preferred for routine use; the adiabatic method, however, has the advantage of modeling commercial acetylation methods and is more sensitive to pulp reactivity.

The breakpoint values which are a measurement of acetylation time in these tests are found to be considerably better for the PO-treated pulps than for standard acetate pulp grades commercially available. In the adiabatic FACT tests, the best performing PO-treated stocks (Table III, A and B) are at least twice as reactive. In the case of the ABS pulp, it appears that the intermediate substituted pulp (4.4% —OC₃H₆OH) is most reactive; with the SPK pulps the product with the highest substitution is most reactive (Table III, B). Transmittance values of triacetate gums appear to indicate good clarity. The filterability values of these gums are considerably enhanced (the higher the better) for the PO-modified products compared to standard acetate grades. This is a significant observation because it indicates that increased production capacity

TABLE IV
Conventional FACT Analyses[a] of Propylene-Oxide-Treated SPK Pulps

—OC₃H₆OH (%)	Break point (min)	Transmittance (%) (670 nm)	Filterability (g/cm²)
3.4	12.5	98.5	882
4.6	12.7	99.0	1,075
5.8	9.7	98.0	1,084
Treated control	46.6	93.0	206
Standard acetate pulp-1	21.9	97.0	524
Standard acetate pulp-3[b]	27.5	93.5	190

[a] Conducted at 47°C.
[b] SPK pine pulp, cuene IV = 5.7.

realized by use of the more reactive PO-modified, mercerized pulps could be handled without additional capital expense for filtration equipment. The adiabatic FACT filterability results might indicate that 50–100% of additional acetate product can be processed through an acetate plant without additional changes in filter dressings.

In conventional FACT evaluations of PO-treated SPK pulps (Table IV), their high reactivity was also noted. Break-point values were again noted to be about twice as fast as for standard grades. A nonmercerized SPK acetate pulp grade (Standard Acetate Pulp-3) with a cuene IV (5.7 dL/g) near that of the PO-treated, mercerized products is a considerably slower reacting pulp (i.e., 27 vs. 12 min). Filterability values in the test were also found to be substantially enhanced for the PO-treated stocks.

High-Catalyst Semiworks Evaluations

These small-scale acetate evaluations were followed by a series of semiworks evaluations in order to better assess the potential of these pulps in a manufacturing operation. The performance of PO-treated stocks (600–800-g batches) were evaluated in both low- and high- catalyst processes. The results are summarized in Tables V and VI. In high-catalyst tests on PO-treated ABS samples (Table V, A) the product of intermediate substitution level was found to be the most reactive (50 min). This conforms to the observations made in the FACT tests. In these tests, such an esterification value represents a substantial improvement in reactivity compared to standard grades (~64–74 min). The di-

TABLE V
High Catalyst, Semiworks Acetate Evaluations[a] of Propylene-Oxide-Treated Pulps

	—OC$_3$H$_6$OH (%)			Standard acetate grade-4[b]
A. Ammonia-Base Sulfite (ABS) Pulps				
	3.6	4.4	5.3	
Esterification (min)	54	50	55	65
Triacetate haze	14.8	11.4	17.7	11.5
Diacetate haze	17.6	13.6	19.3	17.3
Diacetate dispersion color[c]	6.7	6.7	7.6	9.3
IV (dL/g)	1.66	1.65	1.60	1.57
False viscosity effect	10	0	0	50
Filterability (g/cm^2)	260	230	230	400
B. Steam Prehydrolyzed Kraft (SPK) Pulps				
	3.4	4.6	5.8	
Esterification time (min)	55	45	50	
Triacetate haze	14.4	14.4	9.8	
Diacetate haze	23.2	18.6	16.2	
Diacetate dispersion color	12.5	13.1	13.6	
IV (dL/g)	1.48	1.47	1.49	
False viscosity effect	20	30	0	
Filterability (g/cm^2)	550	340	390	

[a] 14% H$_2$SO$_4$; standard temperature profile rise (0–47°C) used.
[b] ABS pine pulp.
[c] 18% dispersion in methylene chloride–methanol.

TABLE VI
Low-Catalyst, Semiworks Acetate Evaluations[a] of Propylene-Oxide-Treated Pulps

	—OC$_3$H$_6$OH (%)			Standard acetate grade-4[b]
A. Ammonia-Base Sulfite (ABS) Pulps				
	3.6	4.4	5.3	
Temperature (°C)	23	19	22	37
Esterification time, min.	237	154	199	174
Triacetate haze	11.1	6.7	10.0	11.8
Diacetate haze	12.4	9.4	11.2	17.9
Diacetate dispersion color[c]	6.2	6.7	7.0	7.6
Diacetate IV (dL/g)	1.65	1.64	1.63	1.58
Plastics color	12.1	14.1	14.6	14.8

				Standard acetate grade-1[d]
B. Steam Prehydrolyzed Kraft (SPK) Pulps				
	3.4	4.6	5.8	
Temperature (°C)	27	21	24	39
Esterification time (min)	175	243	243	186
Triacetate haze	7.4	10.0	6.2	13.9
Diacetate haze	15.4	16.8	13.5	21.2
Diacetate IV (dL/g)	1.87	1.71	1.81	13.6
False viscosity effect (FVE)	45	20	0	150
Filterability (g/cm^2)	230	450	460	390
Plastics color	29.2	26.3	24.5	26.2

[a] 1.4% H$_2$SO$_4$; all values represent average of duplicate determinations except for FVE, filterability, and plastics color.
[b] ABS pine pulp.
[c] 18% dispersion in methylene chloride–methanol.
[d] Hemlock sulfite pulp.

and triacetate haze values of the intermediate substituted ABS pulp are really very good, as well as the diacetate dispersion color.

When the viscosity of 18% dispersions of the diacetates from PO-modified products are measured at low shear, the viscosities approximate those of cotton linters acetate dispersions of the same IV. This is in contrast to diacetates from regular wood pulps which show viscosities (the false viscosity effect) two to four times higher than cotton linters acetate. Normally, in the latter case this false viscosity is not present at the high shear rates present in extrusion. Rheological studies at high shear rates have not been performed with diacetates of PO- or EO-modified products to see if the low apparent viscosities could contribute processing advantages in extrusion.

Filterability values of 18% diacetate acetone dispersions for both PO-substituted ABS and SPK products in the high-catalyst, semiworks test[5] (Table V, A and B) do not show enhanced filterability levels compared to standard grades. This observation is in contrast to the results observed in the small-scale FACT tests. More work will need to be carried out to further optimize the performance of these highly reactive pulps in semiworks, large-scale evaluations for filterability enhancement to be observed. Better cooling during the exothermic acetylation process is a factor that may be important to achieving this objective; such control

is important to promoting a good balance between esterification and cellulose hydrolysis processes which occur simultaneously during acetylation. Economic analysis indicates that the additional cooling costs would not significantly impact the overall manufacturing costs.

The PO-substituted SPK pulp at the intermediate level of substitution (4.6% —OC_3H_6OH) was found to be most reactive in the semiworks tests (45 min, Table V, B). To reach the target diacetate cuene IV level of 1.60 dL/g, even less time would have been required. Haze levels were found to be reduced as substitution increased. As mentioned above, the filterability levels were not enhanced compared to standard grades. They were, however, substantially improved compared to those for their PO-modified ABS counterparts. The mercerized control stocks ("treated control" and "X bleached only") were also evaluated in the high-catalyst semiworks tests. They performed very poorly because of high amounts of unreacted fibers that were present in their acetate gums.

Low-Catalyst Semiworks Evaluations

In the standard low catalyst (1.4% H_2SO_4) semiworks test used by Rayonier,[6] efforts are made to select conditions requiring an esterification time in the 170–190-min range. For highly reactive pulps it is necessary to use a lower activation temperature to slow the acetylation process down to conform with the desired time frame. The lower activation temperatures required in the low catalyst processes for the PO-substituted ABS and SPK pulps (Table VI) are therefore a measure of their greater reactivity. The reactivity of the intermediate stage ABS pulp was noted to be very high. Even at 19°C, compared to ~37–40°C for standard acetylation grade pulps, the reaction time was less than desired (154 min). The PO-substituted SPK pulps were less reactive than their ABS counterparts.

The very low diacetate haze values reached for the PO-modified ABS and SPK pulps, although the trends appear a bit inconsistent, indicate the potential of such highly reactive pulps to yield acetates of exceptional clarity, which could be important in such markets as specialty plastics. Undoubtedly, carrying out the acetylation in time frames presently used, but at lower temperatures, would be necessary to obtain this excellent enhanced performance. Conducting acetylations in shorter reaction times at normal temperatures would be expected to lead to more standard levels of haze performance.

Acetate plastic color values were obtained on the PO-modified ABS pulp to see how they compared with a standard southern pine ABS acetate pulp (grade 4—Table VI, A) which is a premium plastics grade product. The PO-modified stocks performed just as well in this test (12.1–14.6 vs. 14.8). The better PO-modified SPK products had values (26.3 and 24.5, Table VI, B) comparable to those of an intermediate grade plastics pulp (e.g., Standard Grade-1, Table VI, B).

Filterability values of 18% diacetate acetone dispersions obtained on the SPK pulps at the higher substitution levels were quite good (450–460 g/cm^2) and represented some enhancement over existing pulp grades (330–400 g/cm^2). It is still believed that more significant improvements in filterability can be realized by conducting further optimization studies as suggested above. False viscosity effect (FVE) values were noted to be very low for the PO-modified products in

low catalyst processes as well (Table VI, B). In low catalyst tests, the mercerized control stocks were again found to perform poorly because of unreacted fibers present in their acetate dopes.

Analyses and Acetate Evaluation of EO- and PO-Treated Nonmercerized Southern Pine Pulp

In studies by Riley,[2] who treated lower quality pulp with EO under nonmercerizing conditions to upgrade it to acetylation quality stock, it was found that the acetylation reactivity improved in high-catalyst systems with increasing levels of hydroxyethylation. In order to directly evaluate those observations on acetate reactivity and other properties, an ABS southern pine acetate grade stock was modified with either EO or PO under nonmercerizing conditions. The analyses and data from acetate evaluations of these treated products are summarized in Tables VII and VIII.

It is clear (Table VII) that the haze values in bottle-scale acetate evaluations are considerably improved by treatment with EO or PO; again PO is observed to be more effective than EO in haze reduction. Color values are also seen to be substantially reduced. Clearly, marginally performing acetate quality pulp can be upgraded by alkylene oxide treatment under nonmercerizing conditions. Interestingly, the limit IV levels increased upon modification suggesting that a more "organized" cellulosic structure has resulted.

The high catalyst FACT data show that treated, nonmercerized fibers are very reactive compared to the control stock. The reactivity levels are in absolute terms just about as high as those obtained from modified, mercerized fibers (e.g., Table IV). This enhanced reactivity in high-catalyst processes was also observed in the semiworks evaluations (Table VIII, A). The reduced esterification times for the modified, nonmercerized ABS stock are comparable to those found for the modified, mercerized ABS pulps (compare values in Table VIII, A, with those in Table V, A).

In low-catalyst processes the effects on reactivity are remarkably different. From Table VIII, B, it can be concluded that the modified, nonmercerized ABS stocks are less reactive than the control stock. Even at higher temperatures

TABLE VII
Analyses of Alkylene-Oxide-Treated Nonmercerized[a] ABS Southern Pine Pulp

	—OC$_2$H$_4$OH (%)	S$_{10}$, S$_{18}$ (%)	Cuene IV	Limit IV	Bottle-scale Haze (ppm)	Bottle-scale Color (ppm)	FACT test Break point (min)	FACT test Filter-ability (g/cm^2)
EO-treated stock	6.8	18.8, 4.3	7.75	1.27	18	245	10.2	629
	—OC$_3$H$_6$OH (%)							
PO-treated stock	3.9	12.1, 3.0	7.77	1.28	20	285	12.8	637
Untreated ABS control	—	3.4, 1.9	8.42	1.05	80	360	20.0	206

[a] Fully bleached pulp pretreated with 5% NaOH at ~23°C before reaction with EO or PO.

TABLE VIII
Alkylene-Oxide-Treated, Nonmercerized ABS Southern Pine Pulp

	6.8% —OC$_2$H$_4$OH	4.6% —OC$_3$H$_6$OH	ABS untreated control
A. High Catalyst Semiworks Acetate Evaluations			
Esterification (min)	51	56	70
Triacetate haze	6.4	9.5	14.3
Diacetate haze	10.0	13.6	21.0
Diacetate dispersion color	6.5	7.5	10.9
False viscosity effect	15	15	65
Filterability (g/cm^2)	370	230	320
B. Low Catalyst Semiworks Acetate Evaluations^a			
Temperature (°C)	41	39	38
Esterification time (min)	217	226	192
Triacetate haze	6.2	5.2	17.9
Diacetate haze	5.8	13.3	29.1
Diacetate dispersion color	9.0	7.0	9.0
Diacetate IV	1.73	1.81	1.56
False viscosity effect	72.5	65	200
Filterability (g/cm^2)	395	350	380
Plastics color	11.8	13.0	15.8

^{a} Average value of several evaluations.

(39–41°C), the esterification process was slower (217–226 min) than for untreated control stock. These reactivity levels are significantly poorer than those observed for PO-modified, mercerized fibers of ABS stock noted in Table VI, A, where, for example, a substitution level of 4.6% —OC$_3$H$_6$OH gives a product which esterified in 154 min at 19°C. The obvious conclusion from these comparative data is that, for low-catalyst processes, the fibers definitely need to be mercerized prior to alkylene oxide modification to obtain products with significantly enhanced reactivity. This is not, however, true in high-catalyst processes.

The described reactivity in low-catalyst processes of alkylene-oxide-treated nonmercerized fibers may be related to morphological factors; substantially increased interfiber bonding was observed (using a scanning electron microscope) for the modified fibers. With the higher-catalyst processes perhaps the adverse effects of such bonding are overcome so that the benefits of "wedging" to increase reagent accessibility are observed. Clearly, this does not occur in the low-catalyst processes.

Alkylene oxide treatment of nonmercerized fibers also led to significant improvements in haze, FVE, and plastic color values compared to untreated control stock (Table VIII).

SUMMARY

Highly reactive acetate pulps can be prepared by mercerization, followed by modification with EO or PO. Low levels of substitution (DS of 0.1–0.3) are required to obtain good performing pulps, with PO being more effective than EO. The hydroxyalkyl substituents appear to act as "wedges" which improve the accessibility of the reagents within the cellulose matrix, and also overcome the inactivation of mercerized fibers to acetylation which normally occurs upon

drying. Mercerized pulps inadequately wedged give acetate gums containing undissolved fibers, resulting in high acetate haze. The modifications are ideally conducted on never-dried fiber in conjunction with a cold caustic bleach stage.

Small-scale, high-catalyst acetate evaluations indicate these products have reactivities about twice as great as standard, nonmercerized acetate pulp grades in such processes; acetate filterabilities as well as acetate color were also found to be considerably enhanced. Small-scale, low-catalyst acetate tests showed high reactivity and gave acetate gums of superior color. Evaluation in acetate semiworks equipment in both high- and low-catalyst processes also showed the pulps to be highly reactive and to have better clarity (lower haze) as well as much lower false viscosity than conventional pulp grades. Notable filterability benefits were not observed in semiworks equipment, probably because testing conditions were not optimized for these pulps.

While alkylene oxide modifications of nonmercerized standard acetate grades can be employed to upgrade acetate performance (haze and color), reactivity characteristics of these pulps are quite different from those prepared by treatment of mercerized fibers. These pulps showed high reactivity in high catalyst evaluations but no reactivity improvement in low catalyst evaluations; actually reactivity was found to be impaired. This may be related to morphological factors.

The highly reactive, mercerized, alkylene oxide-modified products prepared in this study can result in a marked improvement in production throughput for acetate manufacturers.

EXPERIMENTAL

Preparation of PO-Treated, Mercerized Southern Pine Pulps

A representative procedure is as follows: Never-dried interstage ABS stock (1955 g, 780 g o.d.) was cold caustic extracted in a 10% NaOH solution (containing 0.005% H_2O_2) at 23–24°C for 10 min (2.6% consistency). After recovery in a centrifuge, the stock (2,870 g) was shredded in an alkali cellulose shredder (30 min). The alkali shredded stock (2646 g, corresponding to 720 g o.d. based on weight of starting pulp) was next treated with propylene oxide (144 g) for 2 h in a roller cabinet at 50°C using heavy duty, sealed plastic vessels (nitrogen atmosphere). The stock was removed, rinsed in water (10 min, 24°C), and then recovered with rinsing in a centrifuge. The stock was reslurried in SO_2 water (15 L at pH 2.7) for 10 min, and recovered in a centrifuge with rinsing. This product, after air drying, analyzed for 3.6% —OC_3H_6OH (Table III, A), which indicates that the PO conversion efficiency in the substitution reaction is low. Use of higher-consistency alkali-treated stock would be expected to improve the conversion efficiency. The other two products in Table II were prepared similarly, only PO dosages were higher: 216 g and 288 g, respectively. The SPK products in Table III, B, were prepared by analogous procedures. EO reactions (Table VII) used similar procedures, only reactions were carried out at room temperature (25°C).

Treated Control Pulps

These stocks were prepared by processing pulp in a manner identical to that above with the exception that no PO was added to the plastic reaction vessels. These pulps have been through the complete process (cold caustic extraction, then 50°C for 2 h) but in absence of PO.

Cold Caustic Extracted, Mercerized Stocks (X-Bleached Only)

These stocks were prepared by processing pulp through the 23–24°C cold caustic sequence described above. After cold caustic extraction, the pulp was rinsed free of caustic in 23°C water, and then SO_2-treated, after which it was recovered and rinsed in the centrifuge.

Preparation of Alkylene-Oxide-Treated, Nonmercerized ABS Southern Pine Pulp

These pulps were prepared in a manner similar to that described above, except that the initial caustic extraction was carried out in 5% NaOH solution rather than the 10% NaOH (mercerizing strength) solution used to prepare the PO or EO-treated, mercerized products.

Analyses and Evaluation of Products

The —OC_2H_4OH and —OC_3H_6OH substitution levels were determined by a method adapted from a recently published procedure by Hodges.[7] The 10% and 18% sodium hydroxide solubility (S_{10} and S_{18}) determinations at 20°C were made by a technique similar to TAPPI (Technical Association of the Pulp and Paper Industry) Method T-235. Cuene IV data were determined by a procedure similar to TAPPI Method T-230. Cuene limit IV values, which are a measure of crystallinity, were carried out by hydrolyzing the cellulose sample (0.3 g) in $2N$ hydrochloric acid (75 mL) for 35 min. The residue was filtered off, washed, and dried. A cuene IV was run on the residue.

Low-catalyst bottle-scale tests were made by adaptation of a method described by Mitchell.[3] The high catalyst semiworks acetylation evaluations were conducted using a method published by Kent.[5] The low-catalyst semiworks acetylation evaluations were conducted using a method published by Malm et al.[6] Haze and diacetate dispersion color values in semiworks evaluations were determined by ASTM D 1003 and ASTM D 1925, respectively.

The adiabatic FACT tests were carried out as follows: Fluffed pulp (6 g, 93–94% o.d.), pretreated 1.5 h by tumbling with acetic acid (acetic acid/pulp ratio of 0.34), was added to a preheated (30°C) acetylation solution in a Dewar flask; the acetylation solution contained acetic acid (292 g), sulfuric acid (14% based on o.d. weight of pulp), and acetic anhydride (17.8 g + 42% excess for water in system). The mixture was stirred (600 rpm) with reaction temperature and transmission (670 nm) being simultaneously recorded. The time to reach break point was recorded. The break point is defined as the intersection of the two significantly straight portions of the transmission curve. Upon completion of acetylation, the reaction was quenched with acetic acid solution (75 mL of 3:1, acetic acid: water by volume). The triacetate was filtered under constant N_2

pressure (10 psi) through a Millipore filter (10 μ). The filterability value was calculated on a weight of filtered triacetate for a given time interval using as a basis the standard law of filtration.[8]

The conventional FACT method differs only in that, after pretreatment, the pulp is added to the acetylation mixture in a flask contained in a waterbath (47°C). There is no temperature rise—transmission only is recorded.

References

1. (a) H. Staudinger, et al., *Makromol. Chem.*, **9**, 148 (1953); (b) H. Staudinger, et al., *Makromol. Chem.*, **9**, 188 (1953).

2. (a) J. L. Riley, *Solvent Spun Rayon, Modified Cellulose Fibers and Derivatives*, edited by A. F. Turbak, ACS Symposium Series 58, American Chemical Society, Washington, D.C., 1977, p. 149; (b) N. I. Nikitin and T. I. Rudneva, *J. Applied Chem.* (U.S.S.R.) **8**, 1105 (1935). (c) N. I. Nikitin, *The Chemistry of Cellulose and Wood*, Israel Program for Scientific Translations, Jerusalem, 1966, p. 285.

3. J. A. Mitchell, *Tappi*, **40**(9), 713 (1957).

4. O. A. Battista, *Ind. Eng. Chem.*, **42**, 502 (1950).

5. Adaptation of method published by J. A. Kent, in *Riegel's Handbook of Industrial Chemistry*, 7th ed., Van Nostrand Reinhold New York, 1974.

6. Adaptation of method by Carl J. Malm, et al., *Ind. Eng. Chem.*, **38**, 77 (1946).

7. K. L. Hodges, W. E. Kester, D. L. Wiederrich, and J. A. Grover, *Anal. Chem.*, **51**, 2172 (1979).

8. P. H. Hermans and H. L. Bredee, *J. Soc. Chem. Ind.*, **55**, 26 (1936).