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Curing Property and Plywood Adhesive Performance of Resol-Type Phenol-Urea-Formaldehyde Cocondensed Resins

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Summary

The curing processes and thermal properties of resol-type phenol-urea-formaldehyde cocondensed resins, which were prepared by alkaline treatments of the cocondensed resins once synthesized from UF-concentrate and phenol, were investigated by torsional braid analysis. The resol-type cocondensed resins displayed almost the same curing behaviors and heat-resistance as a commercial resol. Their apparent activation energies determined by measuring temperature dependence of gel time were almost identical with that of resol, and quite different from that of UF resin. Their plywood adhesive performances were evaluated with a cyclic 4-hour boil test and a 72 hour boil test. The plywood test results passed the requirements for the JAS special grade structural plywood.

Introduction

The successful synthesis of cocondensed resins by reacting a mixture of methylolphenols and urea has been reported (Tomita and Hse 1992, 1993). These resins were named "Resin I". Further, a new method to synthesize phenol-urea-formaldehyde cocondensed resins (Resin II) has been developed (Tomita *et al.* 1995). The new method of Resin II was derived from reacting so-called UF-concentrate with phenol, and is quite different from that of Resin I. Moreover, it was found that this new cocondensed resin can be converted into a resol-type resin (Resin II-2) by a simple alkaline treatment. Since these cocondensed resins seem to cure like resols, an investigation on their curing behaviors and thermal properties were attempted by torsional braid analysis method (TBA). Further their practical performances as wood adhesives were evaluated by accelerated aging tests of plywood. The accelerating aging tests included plywood shear strength and estimated wood failure evaluations.

Experimental

Materials

Commercial urea-formaldehyde resin (UF resin, U-310) and resol (PL-266) were supplied from Mitsuitoatsu Chemical Co. A blended resin was prepared by mixing the UF resin with resol (50/50, w/w).

Preparation of cocondensed resins

The cocondensed resin (Resin I) was prepared with the molar ratio of F/U/P = 3.5/1/1 according to the previously published work (Tomita and Hse 1993). The UF-concentrate, cocondensed resins (Resin II) and resol-type resins (Resin II-2) were prepared according to the new method (Tomita *et al.* 1995). However, the UF-concentrates used in this study were synthesized only under acidic conditions. The final molar ratio (F/U/P) and pH of Resin II-2 were varied as noted in each figure and table.

Torsional braid analysis (TBA) of resin curing process

Torsional braid analysis was carried out with a free torsional pendulum apparatus (RESCA Co. Ltd.). The liquid samples of the cocondensed resins, resols, UF resin, and blended resin of resol and UF resin were separately brushed onto a glass braid after adding curing agent or adjusting pH at target levels, respectively. The amount of each dried resin on the braid was generally 60–90 mg. TBA measurements were started immediately after immersing the resins onto the glass braids. The rate of elevation of temperature was 3 °C/min. Results were plotted in the terms of logarithmic decrement, α_T, and relative rigidity, $Gt/Go = (Po/Pt)^2$, where Po is frequency interval at the starting of measurement (around 20 °C) and Pt is that at temperature of t °C. Samples and curing conditions for dynamic mechanical measurements of each curing process are cited in every figure.

Torsional braid analysis of thermal properties of cured resins

The resol-type cocondensed resins were cured on a glass braid at 150 °C for 30 min. The amounts of these resins on the glass braid were also 60–90 mg in dried weight. The measurements were performed under the same conditions as the previous section, and samples and curing conditions are shown in every figure.

Measurement of gelation time

Resin samples (about 20 g) were put into test tubes after adjusting pH and maintained in a constant temperature oil-bath with stirring. A glass rod was used as a probe, determining the resin viscosity by pulling straight upward from the resin mass. As the resin sample became viscous, a resin string line was formed when the glass rod moved upward. The gel time was determined as the time when the solidified resin string line was broken. Gel testings were done between 130 °C and 190 °C at 10 °C intervals.

Preparation and adhesive testing of plywood

Three-ply lauan plywoods (size 30 × 30 cm) were prepared using rotary veneers of 1.7 mm thickness. The preparation conditions were as follows unless otherwise stated in tables and figures: closed assembly time, 15–30 min; spread rate (double glue line), 30–34 g/(30 cm × 30 cm); press pressure, 10 kgf/cm^2 (0.98 MPa); press time, 5 min. Hot-press temperature was varied as noted in tables and figures. Coconut shell powder was added by 10 PHR (10 parts per hundred parts of resin) as a filler. Specimens were prepared according to JIS (Japan Industrial Standard) K 6802. Two types of accelerating tests were performed as well as a normal dry shear test. One accelerating aging test is a cyclic boil test (soaking in boiling water for 4 h; drying at 60 °C for 20 h; soaking in boiling water for 4 h; cooling and testing in the wet state) and the other test is a 72-hour boil test (soaking in boiling water for 72 h; cooling and testing in the wet state). The tensile shear strengths of the adhesive bondline were measured with a Tensilon testing machine (Toyo Baldwin Co. Ltd.) under a crosshead speed of 10 mm/min. Each value of bondline strength and wood failure in the figures and tables is an average of twelve test specimens.

Results and Discussion

Analysis of curing processes and thermal properties of resol-type cocondensed resins

The curing process of the cocondensed resin (Resin I) synthesized from methylolphenols and urea was compared with a commercial resol, a commercial UF resin, and a blended resin of resol and UF resin by the torsional braid analysis method (TBA). This method is well known for discriminating the dynamic mechanical variation of curing processes for thermo-setting resins as the function of time or temperature. The changes of relative rigidities (Gt/Go) of four resins are compared in Figure 1. The curing process of a commercial resol is well demonstrated by a remarkable increase of relative rigidity. Both gelation and curing process involving removal of water were completed until the relative rigidity began to drop slightly. This dropping was considered to be due to shrinkage of cured resins.

The curing process of UF resin catalyzed with ammonium chloride shows that the curing reaction began to take place at 80 °C and almost finished at 135 °C (Fig. 1). After completion of curing, it began to decompose at about 200 °C as indicated by the remarkable dropping of the relative rigidity.

The blended resin of resol and UF resin with ammonium chloride showed a quite different curing process from resol itself or UF resin itself (Fig. 1). On the other hand, the chemically cocondensed resin (Resin I) followed almost the same curing process as resol itself except for the curing beginning at the lower temperature of 80 °C. Also, the relative rigidity of the cocondensed resin did not decrease obviously after completing the curing reaction (Fig. 1). Therefore, it is concluded that the cocondensed resin has as high a heat-resistance as the resol.

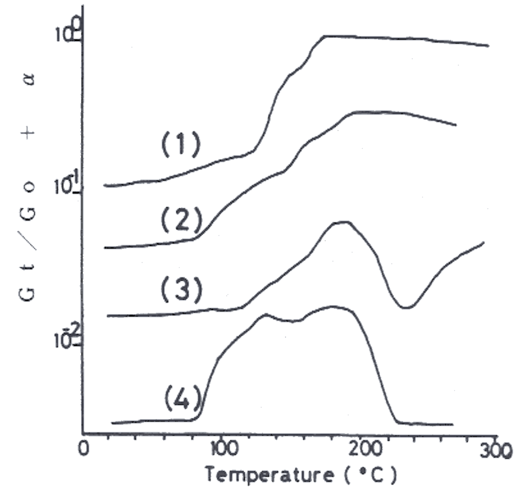

Fig. 1. Torsional braid analysis on curing reaction of various resins. (1) commercial resol; (2) cocondensed resins (Resin I) at pH 3.0; (3) blend of resol and UF resin with ammonium chloride; (4) commercial UF resin with ammonium chloride.

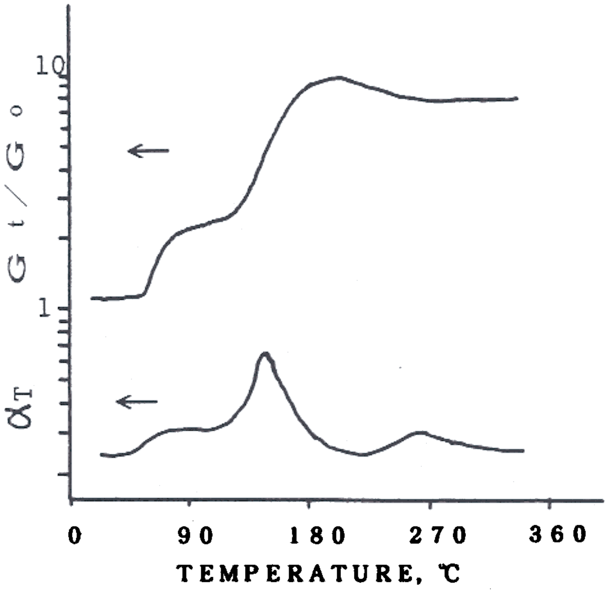

Fig. 2. Torsional braid analysis on the curing reaction of the resol-type cocondensed resin at pH 9.5 (Resin II-2, F/U/P = 3/1/1).

The resol-type cocondensed resin (Resin II-2) also exhibited quite similar curing process and heat-resistance to resol as shown in Figure 2. It should be noted that a great difference could be observed in the thermal properties between two kinds of cocondensed resins (Resin I and Resin II-2) and the blended resin of resol and UF resin with ammonium chloride.

Figure 3 shows the results of dynamic mechanical measurements of resol-type cocondensed resins synthesized with different molar ratio (F/U/P) after curing at the alkaline condition of pH 10.0. The resin prepared with F/U/P = 3/1/2 showed a remarkable drop of relative rigidity at about 160 °C, caused by a

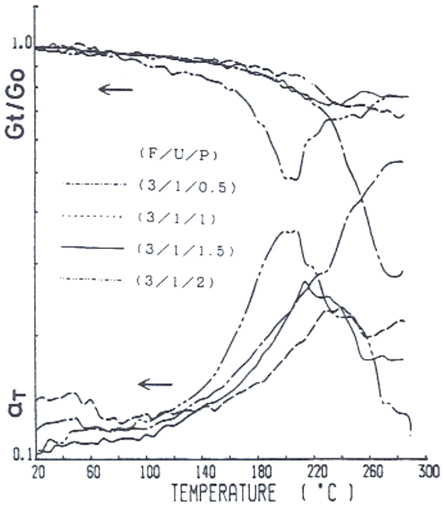

Fig. 3. Effects of the synthetic molar ratio (F/U/P) on dynamic mechanical property for resol-type cocondensed resins cured under pH 10.0 at 150 °C for 30 min.

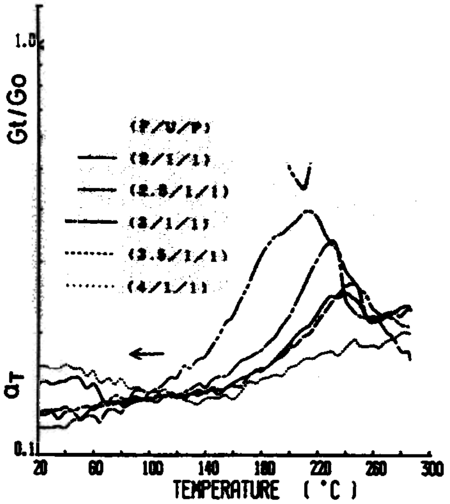

Fig. 4. Effects of the synthetic molar ratio (F/U/P) on dynamic mechanical property for resol-type cocondensed resin cured under pH 10.0 at 150 °C for 30 min.

lower cross-linking density due to a shortage of formaldehyde at preparation. A similar dropping of relative rigidity at about 200 °C was observed for the resin with F/U/P = 3/1/0.5. This phenomenon would result from a low heat-resistance due to the self-condensed networks of UF resin, because the amount of phenol incorporated into the cocondensed resin was low.

Figure 4 shows the effects of formaldehyde amount on thermal properties of cured resins, when the molar ratios of urea to phenol were kept constant at U/P = 1/1. It was observed that two resins having F/U/P = 2/1/1 and 2.5/1/1 displayed a low heat-resistance. On the other hand, the three resins of F/U/P = 3/1/1, 3.5/1/1, and 4/1/1 showed a high heat-resistance like resol. Therefore, these molar ratios were considered to be desirable to obtain the effects of cocondensation.

Table 1. Comparison of apparent activation energies of gelation among UF resin, PF resins, and reso-type cocondensed resin

Resin type	Reaction pH	Apparent activation energy, Ea (kcal/mol)
UF resin	11.1	32.9
PF resin	11.1	24.5
Cocondensed resin	9.6	24.1
	10.0	23.9
	11.1	22.8

Apparent activation energy of gelation

Arrhenius plots of gelation time were compared at various pHs for cocondensed resins with the molar ratio of F/U/P = 3.5/1/1, and those for UF resin and resol at pH 11.1. Apparent activation energies calculated for three kinds of resin are summarized in Table 1. A great difference between UF resin and resol due to the difference of reactivity between the two types of condensation was recognized. On the other hand, the resol-type cocondensed resin had similar values of apparent activation energy composed of the resol, and its pH dependency was quite low. Therefore, it can be concluded that the gelation or curing of the resol-type cocondensed resin was dominated by the self-condensations between phenolic nuclei through the formation of methylene linkages.

Adhesive performance of resol-type cocondensed resin

The resol-type cocondensed resins seem to have practical application for wood adhesives since it can be cured like industrial resols. Their adhesive qualities were evaluated according to a JAS plywood test. The preliminary results of plywood tests are summarized and compared with a commercial resol as shown in Table 2, where the effects of the synthetic molar ratio and hot press temperature were mainly investigated as variables. The resins synthesized with the lower molar ratio of F/U/P = 3/1/1 generally had a poor water-resistance in both of a 4-hour cyclic boil test and a 72-hour boil test, but it had good adhesive strengths in a normal dry shear test. This result is likely caused by a low cross-linking density. On the other hand, the resin synthesized with F/U/P = 4/1/1 displayed a high water-resistance after soaking in boiling water for 72 hour and passed the JAS requirement (7 kgf/cm^2) for the special grade of structural plywood. However, the effect of hot-press temperature was obvious, and a low temperature of 130 °C did not give a high water-resistance

Table 2. Results of plywood shear tests for resol-type phenol-urea-formaldehyde cocondensed resins

Resin code	Molar ratio (F/U/P)	Solid content (%)	Viscosity (P)	Hot press temp. (°C)	Plywood shear strength kgf/cm^2(w.f., %)		
					Dry shear	Two 4-h boil	72-h boil
Resol		46.0	44.3	130	16.9 (35)	12.7 (50)	12.2 (55)
				150	18.2 (85)	12.4 (80)	14.3 (70)
3-	3/1/1	53.1	3.6	130	6.6 (5)	0	0
				150	13.0 (25)	1.6 (0)	0
3-1*				150	13.2 (25)	6.6 (0)	0
3-2	3/1/1	53.0	9.4	130	8.7 (0)	0	0
				150	12.9 (10)	5.3 (0)	0
4-1	4/1/1	49.2	2.4	130	5.3 (0)	0	0
				150	12.8 (20)	4.9 (5)	0
4-1*				150	15.5 (25)	9.6 (0)	8.6 (5)
4-2	4/1/1	55.0	110.3	130	11.4 (15)	0	0
				150	13.1 (85)	10.8 (35)	10.6 (10)

Note: All resins were added by 10 PHR (10 parts per hundred parts of resin) coconut shell powder except for the resin 3-1* and 4-1* by 20 PHR.

after soaking in boiling water. This result may be due to a low resin pH (below 10.0), compared to the resol pH of 10.6. It is well known for resol that a weak akaline condition requires a longer curing time to attain a satisfactory adhesive strength. Therefore, further investigation by changing the synthetic molar ratio and alkaline conditions may improve the adhesion properties.

Effects of molar ratio, curing temperature and pH on adhesive performance

Adhesive strengths of a normal dry shear test and a 72-hour boil test were investigated by changing the molar ratio and curing temperature while curing pH was maintained at 10.0. The results are shown in Table 3, where the effects of changes of the molar ratio on adhesive strengths were not obvious in a normal test. On the other hand, it was clearly observed that adhesive strengths in a 72-hour boil test were dependent on the molar ratio, and that the molar ratios between 3.5/1/1 and 4.5/1/1 were desirable to pass the JAS minimum shear strength value. Simultaneously, a higher plywood curing temperature than 150 °C was required to pass the standard value. These results were identical with those obtained in the preliminary test as shown in Table 2.

Table 3. Curing effects of various hot-press temperature and the synthetic molar ratio of resol-type cocondensed resin at pH 10 on plywood strength

Molar ratio (F/U/P)	Hot-press temp. °C	Plywood shear strength kgf/cm^2, (w.f., %)	
			72-h boil
3/1/1	130	10.2 (0)	0 (0)
	140	14.2 (5)	0 (0)
	150	16.4 (0)	4.6 (0)
	160	15.7 (70)	10.0 (45)
3.5/1/1	130	8.8 (0)	0 (0)
	140	13.9 (35)	0 (0)
	150	16.9 (20)	7.5 (0)
	160	18.2 (85)	11.4 (35)
4/1/1	130	12.2 (5)	0 (0)
	140	15.7 (60)	5.0 (0)
	150	15.4 (20)	7.7 (10)
	160	15.7 (40)	9.7 (20)
4.5/1/1	130	11.3 (0)	0 (0)
	140	13.0 (0)	0 (0)
	150	17.9 (30)	7.1 (0)
	160	19.0 (65)	10.4 (40)

Table 4. Effects of curing pH and hot-press temperature on plywood strength test of resol-type cocondensed resin of F/U/P = 3.5/1/1

Curing pH	Hot-press temp. °C	Plywood shear strength kgf/cm^2, (w.f., %)	
			72-h boil
10.2	130	10.5 (0)	0 (0)
	140	13.7 (0)	0 (0)
	150	15.8 (0)	4.2 (0)
10.5	130	12.6 (0)	0 (0)
	140	14.2 (0)	0 (0)
	150	16.7 (0)	7.1 (0)
11.2	130	14.6 (5)	1.6 (0)
	140	15.7 (10)	6.1 (0)
	150	17.6 (15)	7.6 (0)
11.5	130	14.9 (15)	5.1 (0)
	140	15.6 (30)	6.3 (0)
	150	17.4 (25)	7.5 (0)
11.9	130	16.8 (50)	6.8 (0)
	140	17.4 (45)	7.1 (0)
	150	19.6 (75)	8.7 (0)

The effects of curing pH on both adhesive strengths were determined at three levels of curing temperature while keeping a constant molar ratio of F/U/P = 3.5/1/1. The normal dry shear tests displayed the pH dependence on adhesive strength at every curing temperature as shown in Table 4. Further it was found that the pH dependence became obvious as the curing temperature was lowered. The 72-hours boil tests also displayed the same pH dependence in Table 4. It can be concluded that the curing temperature is the most important among these three factors to obtain a high adhesive strength in a 72-hours boil test.

Conclusion

The resol-type cocondensed resins displayed almost the same curing behaviors and heat-resistance as a commercial resol. It was found that a high heat-resistance can be attained by the resins synthesized with the molar ratio between F/U/P = 3.0/1/1 and 4.0/1/1. A great difference could be recognized in thermal properties between the cocondensed resins and the blended resin of resin and resol.

Apparent activation energies of gelation were determined as 23–24 kcal/mol for the pH between 9.6 and 11.1. These values were almost identical with that of resol, and quite different from that of UF resin.

The cocondensed resins synthesized with the molar ratio of above F/U/P = 3.5/1/1 have a high water-resistance after soaking in boiling water for 72 hour, and pass a JAS minimum shear strength value for the special grade structural plywood. However, it was concluded that the rather high curing temperature above 150 °C is necessary to pass the standard value.

The resol-type cocondensed resins used in this paper were synthesized only from the UF-concentrates which were prepared under strongly acidic conditions. In a previous work, Tomita *et al.* (1995) pointed out that the resins synthesized from the UF-concentrate prepared under alkaline conditions were abundant in the formation of cocondensed methylene linkages. Therefore, further investigations on the resol-type cocondensed resins synthesized from the UF-concentrates, which are prepared under alkaline conditions, will be encouraged to improve the practical performances.

Acknowledgement

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Literature Reports

Chemistry

B. B. Sitholé: A rapid spectrophotometric procedure for the determination of total resin and fatty acids in pulp and paper matrices. Tappi J. *76* (1993): 10, 123–127.

Current methods for the determination of fatty and resin acids in pulp and paper matrices are time consuming and require sophisticated instrumentation not available in most mills. The industry needs rapid techniques for monitoring these compounds. A rapid colorimetric procedure used for determining free fatty acids in vegetable oils has here been adapted for monitoring total free fatty and resin acids in acetone extractives from pulp and paper samples (including pitch deposits, wood chips, effluents etc.). The acids in the extracts form a complex with cupric ions which is extracted with hexane. The concentration is determined colorimetrically at 680 nm. A disadvantage of this simple and rapid technique is that it does not detect trace quantities and that it requires large samples.

Treiber/1267

U. Westermark and B. Samuelsson: A spectrophotometric method for the determination of sulfonic acids in wood material. Nordic Pulp Paper Res. J. *8* (1993): 4, 358–359, 398.

A spectrophotometric method to determine sulfonic acids in wood material (wood samples after passing a ground mill and a 40 mesh sieve; pulp samples directly) was worked out. Quinoline hydrochloride is ionically bound specifically to the sulfo group by treatment of the sample with a quinoline solution at pH 2.5. After removal of the excess of quinoline the ionically bound quinoline is eluated with hydrochloric acid and determinated by UV-spectrophotometry. The highly selective and sensitive method analyzes a sulfonic acid content of about 5 μekv/g and higher.

Treiber/1273

D. Fengel: Neuere Erkenntnisse über die Feinstruktur der Cellulose. (New findings on the fine structure of cellulose.) Das Papier *47* (1993): 12, 695–702.

The article reviews results from FTIR spectroscopic and electron microscopic studies of cellulose. A mathematical processing of the FTIR spectra in the range of the OH/CH_2 valency vibrations results in a high band resolution. Thus, the cellulose modifications I, II, III, and IV can be differentiated. Also the action of alkali concentration and temperature during the transformation of Cell. I into Cell. II were studied. Furthermore, the dissolving process of cellulose was followed in the electron microscope. Differences in the behaviour of the fiber surfaces during treatments with a non-aqueous (LiCl/DMAc) and an aqueous solvent (EWNN) were observed. The dissolving process was made visible by freeze-etching technique in TFA. Finally, strongly degraded cellulose was labelled at the reducing end groups which verified an unidirectional orientation of the cellulose chains both in Cell. I and II.

Treiber/1279

K. Bachner, K. Fischer and E. Bäucker: Zusammenhang zwischen Aufbau der Zellwand und Festigkeitseigenschaften bei Faserstoffen von konventionellen und neuen Aufschlußverfahren. (Connections between structure of the cell wall and strength properties of fiber materials defibrated by conventional and novel pulping methods.) Das Papier *47* (1993): 10 A, V 30–V 40.

Pulps produced by the ASAM and Organocell methods have excellent strength properties. The reason for this lies in the distribution of hemicelluloses and DP-value across the fiber walls. With the aid of gradually peeling of layers and a combination of sugar analysis and SEM microscopy the assignment of mannan and xylan to the different wall layers was possible. In ASAM, Organocell and pine pulps the largest portion of hemicelluloses is located in the outer part of the primary wall. In spruce pulps the distribution of mannan and xylan is relatively uniform across the fiber wall. The highest DP was found in the outer part of the S_1, especially in ASAM pulp.

Treiber/1284

Technology

H. Leopold: Technologische Eigenschaften des Organocell-Zellstoffs. Neueste Erkenntnisse nach der Inbetriebnahme der Anlage in Kelheim. (Technological properties of "Organocell" pulp. Latest experiences after the start up of the pulp mill in Kelheim (Germany).) Das Papier *47* (1993): 10 A, V 1–V 5.

Fluff pulp produced according to the "Organocell" process was chosen as the first product of the mill "Bayerische Zellstoff GmbH" in Kelheim, Germany. It was possible to produce a very long fibered pulp of good quality parameters for fluff from saw mill residuals. Quality data are given. With the production of high-quality fluff pulps, a solid basis for the sale (better price than paper pulp) is given. After this phase of fluff pulp production the making of paper pulps is worked out. Further field for the use of "organocell" pulps such as dissolving pulps or other specialty pulps will be elaborated in cooperation with the consumer industries.

Treiber/1268

H. L. Schubert, K. Fuchs, R. Patt, O. Kordsachia and M. Bobik: Der ASAM-Prozess – eine industriereife Zellstofftechnologie. (The ASAM-process – a pulping technology ready for industrial use.) Das Papier *47* (1993): 10 A, V 6–V 15.

The ASAM-process makes it possible to produce pulps of high strength and brightness from usual varieties of pulpwood without the use of chlorine and chlorine containing bleaching agents. Delignification of spruce chips can be carried out up to Kappa numbers of 16. No troubles are observed during bleaching by a O-Z-P sequence to a brightness >88% ISO. The strength properties correspond to those of conventional kraft pulps. The methanol recovery system used for over 3 years in the pilot plant has achieved recovery rates of >99%. Thickening of the spent liquor is possible to a high solid content at low viscosity. Small water consumption and low burden in the effluent are assured by an almost complete system closure.

Treiber/1269

N. Neumann and K. Balser: Acetocell – ein innovatives Verfahren zur absolut schwefel- und chlorfreien Zellstoffproduktion. (Acetocell – an innovative process for pulping totally free from sulphur and chlorine.) Das Papier *47* (1993): 10 A, V 16–V 24.

This process has been developed by VEBA ÖL from the concept of Nimz *et al.* The delignification of soft- and hardwoods is made by acetic acid at high temperature (about 190 °C) without catalysts. The delignification hereby achieved can go to Kappa numbers of 16–20 at high yield. Subsequent ozone bleaching in a residual acetic acid environment leads to a further reduction of the Kappa number down to <2. Combined with an extraction stage followed by peroxide bleaching permits the production of pulps of high brightness (>80–85% ISO) with good mechanical properties. Laboratory experiments have shown that pulps of dissolving