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Ai, Tran Van
Laboratory of Wood Chemistry, Faculty of Agriculture, Kyushu University

Sakai, Kokki
Laboratory of Wood Chemistry, Faculty of Agriculture, Kyushu University | Laboratory of Wood Chemistry, Faculty of Agriculture, Kyushu University

Kondo, Tamio
Laboratory of Wood Chemistry, Faculty of Agriculture, Kyushu University

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Studies on the Holopulp
IV. Beating Behaviour of Woody Holocellulose Pulps

Tran Van Ai, Kokki Sakai and Tamio Kondo

Laboratory of wood Chemistry, Faculty of Agriculture,
Kyushu University 46-08, Fukuoka 812

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The beating behaviour of the chlorite and peracetic acid pulps prepared from beech (temperate hardwood), red pine (temperate softwood), and red lauan (tropical hardwood) was studied. The differences in the beatability of those pulps lie in the differences amongst fiber morphology of wood species and amongst holopulping conditions. An excess oxidative delignification or a sulfuric acid treatment can improve the pulp beatability. The removal of hemicelluloses and the structural modifications of the external and internal surfaces of the pulp fibers take place simultaneously in those chemical treatments. It is shown that the variation of pulp beatability depends on the structural modifications of pulp fibers rather than on the quantity of lignin *or* hemicelluloses or on the kind of hemicelluloses. A decrease in the degree of polymerization of the hemicelluloses can also affect the beatability of pulp fibers. It is inferred that the positive influence on pulp beatability should be attributed to the regions of structural modifications existing in the outside and inside of pulp fibers, which facilitate further their swelling and fibrillation. The presence of hemicelluloses in those regions is preferable for the amelioration of pulp beatability. The action of the excess oxidative delignification and the sulfuric acid treatment is like that of a prebeating process. A new method based on the rate of evaporation of acetone sorbed by pulp fibers has been developed to estimate the internal surface of pulp fibers.

INTRODUCTION

Up to now it is still believed as a general rule that the greater the amount of hemicellulosic materials in the pulp, the faster the beating response. This concept was resulted mainly from earlier works on the papermaking properties of chlorine-monoethanolamine and chlorite holocellulose pulps. Recently other results, as far as the beating behaviour of the holocellulose pulps is concerned, also showed that temperate hardwood chlorite pulps tended to beat more rapidly than the kraft pulps prepared from the same wood species (Nicholls et al., 1975). Consequently, the above rule seems to be more concreted because the former contained more hemicelluloses than the latter. It was found simultaneously, however, that the chlorite pulps from temperate hardwoods, aspen and red oak, were more resistant to beating than the counterpart kraft pulps although the alkali-chlorite pulps made from tropical hardwoods, *Cryptocarya* and *Schima*, required less beating than the corresponding kraft pulps to attain a given freeness (Silitonga and McGovern, 1975). No

reasons were given to account for such contradictory beating characteristics of those chlorite holocellulose pulps. Thus, it is not always a correct fact that the pulps having high hemicellulose content, i. e. holocellulose pulps, need less beating than the low ones. In the general rule mentioned above, the quantity of hemicellulosic materials is emphasized. It would aid in fiber swelling thereby facilitates pulp beatability. So far, no works relating to the beating behaviour of the peracetic acid pulp-another kind of holocellulose pulps-have been reported in the literatures.

In the investigation of papermaking properties of the chlorite and peracetic acid pulps (Ai *et al.*, 1977), it was noted that the chlorite pulps of beech, red pine, and red lauan were somewhat more or less difficult to beat than the corresponding kraft pulps. The beating behaviour of the peracetic acid pulps, on the other hand, responded differently to the kind of wood species. For beech, the peracetic acid pulp tended to beat more slowly than the bleached kraft pulp. For red pine and red lauan, however, the peracetic acid pulps required less energy as shown by revolutions in PFI mill (Fig. 1) to reach a freeness of 350ml CSf than the bleached kraft pulps prepared from the same wood species. An observation made for all the wood species examined indicated that the bleached sulfite pulp, compared with the other pulps, was the easiest-to-beat-pulp.

The purposes of this work were thus to find out factors other than the quantity of hemicelluloses, which governed the beatability of beech, red pine, and red lauan holocellulose pulps.

EXPERIMENTAL

1. Holopulping

General procedures were described previously (Ai *et al.*, 1977). The holopulping was carried out in a 5-liter-plastic beaker at 70°C for the chlorite method and at 80°C for the peracetic acid method. Liquor to wood ratio was 8. The holopulping conditions of the standard holocellulose pulps are given in Table 1. To prepare holocellulose pulps of higher and lower yields than those of the standard pulps, the pulping time and the dosage of the oxidative reagents were changed. Fiberization was done in a Rritish disintegrator for high-yield pulps and by hands for low ones. (In this study, high-yield and low-

Table 1. Standard holopulping conditions.

Species	Chlorite method		Peracetic acid method		
	Temp., ℃	Chloriting number	Temp., ℃	Peracetic acid dosage, %*	Time, hr
Beech	70	5	80	100	2
Red pine	70	7	80	200	4
Red *lauan*	70	6	80	125	2

* based on wood chips weight.

yield pulps were called the pulps of mild and drastic pulping conditions respectively). Accepts were separated from screen rejects by a B-cut flat screen, air-dried, and then stored in polyethylene bags for other experiments.

2. Beating

Beating process was carried out in a PFI mill using the following conditions: 22.5 g, o. d., pulp charge at 10 % consistency; 0.25 mm clearance between roll and housing; 1.8 kg/cm beating pressure: 6 m/sec relative speed between roll and housing. Beating was done until pulp freeness fell to 300-350 ml CSf, and the time required to refine a pulp to a freeness of 350 ml CSf was deduced as PFI mill revolutions.

3. Ballooning test

Swelling process was carried out with cupriethylene-diamine sodium hydroxide (Cuene) solutions of various concentrations (from 0. 05 to 0. 15 M Cu). Cuene was prepared according to ASTM Standard DI 795 method. When pulp fibers of a species were immersed in Cuene, balloons developed. If balloons could be maintained for a long period in one of the above concentrations, such a concentration was considered adequate for that species, although in some cases it was observed that some fibers might be dissolved, some without balloons, and some exhibited only a few balloons.

Because swelling and ballooning were diffffferent amongst fibers in a sample and between pulp types, the balloon index was used in the present work and defined as the average number of balloons per millimeter of fiber length. The balloon index was obtained by dividing the total number of counted balloons by the total length of observed fibers in millimeter. The variation of the ballon index was obtained with a certainty of about 1 % for most pulps by counting balloon number of a lot of fibers of 40 to 60 mm in total fiber length. Total number of counted balloons were all balloons observed including small, medium, and big ones. In measuring the balloon index it was assumed that the decrease in fiber length when ballooning occured had no effect at all because it was believed that the length of all balloon-bearing fibers decreased to the same extent.

4. Sulfuric acid hydrolysis of holocellulose pulps

Hydrolysis treatment of holocellulose pulps was carried out with dilute sulfuric acid solutions for two hours at 70°C for the chlorite pulps and at 80°C for the peracetic acid pulps. The concentrations of sulfuric acid solutions were varied for each kind of pulps in order to obtain hydrolized pulps having the same yields as those prepared under drastic holopulping conditions. Hydrolized pulps were washed with water until free of acid and then kept under that state for other experiments.

5. Extraction and determination of hemicelluloses

Holocellulose pulps were extracted with 24% KOH under N_2 atmosphere at room temperature for 24 hours. After filtering and washing the residue with water, the pH of the filtrate was adjusted to 5 with AcOH and the hemi-

celluloses precipitated by adding three volumes of 95 % EtOH. The precipitates were dried by solvent exchange through EtOH, Me_2CO, and Et_2O, and then in vacumn over P_2O_5.

The residue was washed further with water, then with AcOH and finally with water until free of acid. The residue was dried at 105°C, weighed and the content of the extracted hemicelluloses was calculated.

6. **Intrinsic viscosity of the extracted hemicelluloses**

Viscosity of the extracted hemicelluloses was measured with 0.5 N Cuene in a Ubbelohde viscometer. The intrinsic viscosity was then calculated as usual.

7. **Addition of the extracted hemicelluloses**

Hemicelluloses prepared from birch (*Betula platyphylla* var. *japonica*) holocelluloses by extraction with 24 % KOH as above (1 g) was dissolved in 200 ml of 20% NaOH solution and then neutralized with AcOH. The hemicelluloses-suspended solution was mixed with holocellulose pulps (22. 5 g) for about 24 hours prior to beating process.

8. **Measurements of fiber surface area of unbeaten holocellulose pulps**

Fiber surface area was determined by the following methods: water permeability (Hasuike, 1973), stearic acid and dye adsorptions (Browning, 1967).

9. **Evaporation rate of acetone sorbed by unbeaten holoccllulose pulps**

Air-dried holocellulose pulps (0. 6 g) were torn into small bunch of pulp fibers, immersed in acetone, and then evacuated for 30minutes. After that, excess acetone was carefully siphoned off. The weight of the acetone-pulp fibers mixture was measured at intervals until constant. All the measurements were made at 20°C. The average amount of acetone evaporated per minute was hence calculated.

RESULTS AND DISCUSSION

1. Morphological factors and holopulping conditions affecting the beating behaviour of holocellulose pulps

From Fig. 1 it may be assumed that within a wood species the changes of fiber structure during processes are responsible for the variations of the beatability of chlorite, peracetic acid, and conventional chemical pulps. Also, the morphological differences amongst wood species may relate to the beatability of various pulps prepared from beech, red pine, and red lauan. Attempts were first made to correlate the structural modifications of wood fibers by different pulping processes with the beatability of the resulting pulps.

Ballooning (Fig. 2) was used here as a measurement of the absence of the primary cell wall (P) because ballooning indicates the points of localized damages of fibers, namely the loss of P as well as the outer layer of the secondary cell wall (S_1) (Bolam, 1961; Kallmess, 1960). Since P is the sur-

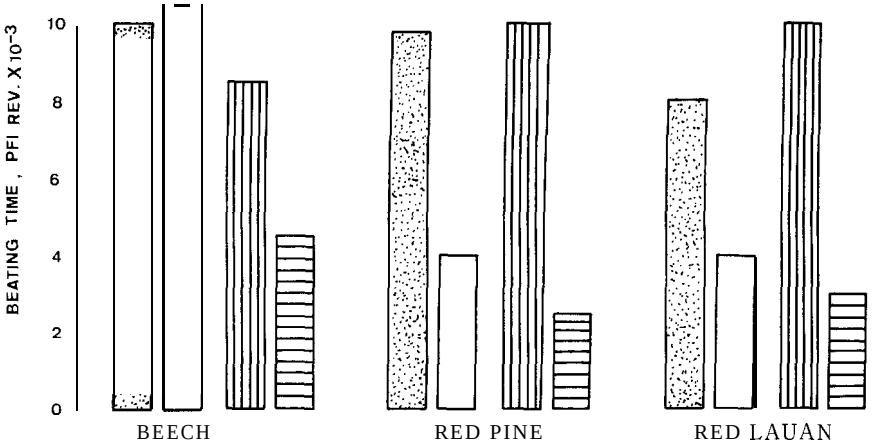

Fig. **1.** Times taken to beat woody holocellulose and conventional chemical pulps to 350 ml CSf. Spotted column: Chlorite pulps; Voided columns: Peracetic acid pulps; Vertically stripped columns: Bleached kraft pulps; Horizontally stripped columns: Bleached sulfite pulps.

rounding layer of the secondary cell wall and due to its mesh-like structure, it tends to prohibit the swelling of the cell wall and hence pulp fibers retaining P abundantly may beat slowly.

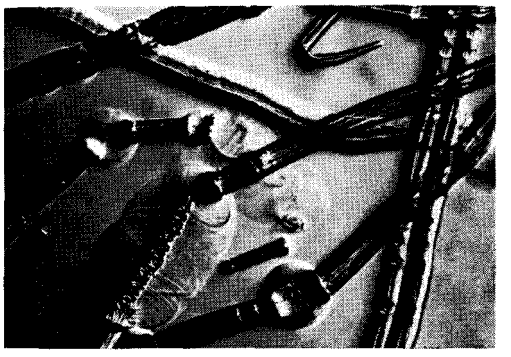

Fig. 2. Balloon swellings of red pine chlorite pulp.

Results of the ballooning tests are given in Fig. 3. For beech, the chlorite and peracetic acid holocellulose pulps retained P abundantly even when freeness fell to 350ml CSf. The bleached kraft pulp lost its P content to some extent, and the P of the bleached sulfite pulp was mostly removed during beating. For red pine, the outer surfaces of the peracetic acid and bleached sulfite pulps were greatly damaged in a short beating time. At freeness of 300 to 350ml CSf, the amount of P removed from both the peracetic acid and kraft pulps was nearly the same. The chlorite pulp, however, retained, after beating, more P than those three pulps. The red lauan wood pulps had the same trends as those of the red pine.

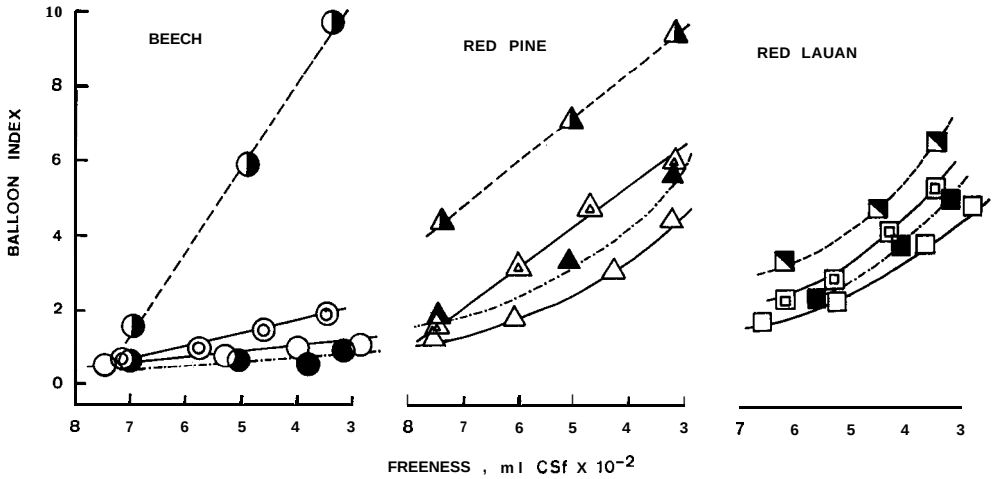

Fig. 3. Relationships between balloon index and pulp freeness.

Chlorite pulps
Peracetic acid pulps
Bleached kraft pulps
Bleached sulfite pulps

Circle : Beech
Triangle: Red pine
Square : Red lauan

In the previous work (Ai *et al.*, 1977), it was shown that for all species studied the chlorite and peracetic acid pulps were richer in the P amount than the bleached kraft and sulfite pulps. This fact was supported by larger amounts of arabinan and galactan in the former than in the latter. Arabinan and galactan exist dominantly in the P (Meier, 1961). Since the balloon indices of the chlorite, peracetic acid, and bleached kraft pulps of beech and red pine were very small at the unbeaten point, the differences in the P amounts of those pulps could not be proved by the balloon index measurements. However, the bleached sulfite pulps of theses two species evidently lost much of their P prior to beating. For all the three wood species, the chlorite and peracetic acid pulps still had more P than the bleached kraft and sulfite pulps even after freeness fell to 300–350 ml CSf.

The beatability of several pulps within a wood species can be predicted to some extent, from the balloon index measured at the unbeaten state (hereforth it is called the initial balloon index) (Fig. 4). For each species examined and to attain a given freeness, a pulp having small initial balloon index would require a long beating time. The reverse is true for those having large initial balloon index. Accordingly, it can be inferred that the damages caused by different pulping techniques to the P and S_1 layers of wood fibers are closely associated with the beatability of the resulting pulps. However,

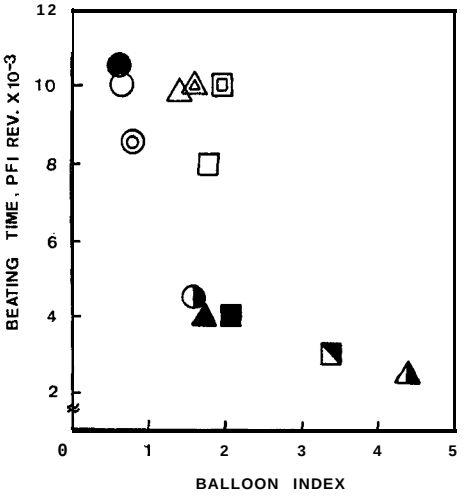

Fig. 4. Beating time as related to balloon index. Symbols as in Fig. 3.

the initial balloon index could not be used to account completely for the variations of the beatability of several holocellulose pulps produced from different wood species. For example, the chlorite pulps made from beech and red pine required almost the same beating time. Yet, the initial balloon index of the former was much lower than that of the latter. On the other hand, observations made for the peraceric acid pulps revealed that the red pine and red lauan peracetic acid pulps needed less beating than that of beech wood species. This is in agreement with the higher initial balloon index (Fig. 4) and the larger amounts of P removed during beating process (Fig. 3) of the formers. The variations amongst the beatabilities and amongst the initial balloon indices of various holocellulose pulps made from beech, red pine, and red lauan are probably due to the differences in the thickness of the outer cell wall layers (P and S_1) of these species and to the degrees of attack of pulping liquors on those layers, which are represented by different dosages of oxidative reagents used for each species (Table 1). It has been known that the thickness of P layer of beech and red pine was 0.07 and 0.06 μ respectively, and the S_1 layers, 0.51 and 0.31 μ respectively (Harada, 1965). The P and S_1 layers' thickness of red lauan wood fibers is unfortunately not available in the literatures so far. Owing to the thinner P and S_1 layers and to the larger dosages of oxidants required, the red pine holocellulose pulps, compared with those of beech wood, were damaged greater as revealed by their larger initial balloon index and accordingly they were easier to beat (Fig. 4).

As mentioned above, the balloon index could not elucidate completely the differences in the veriations of holocellulose pulps' beating behaviour of one species to another. For instance, the balloon index could not be employed to explain why the red pine and red lauan peracetic acid pulps were much easier

to beat than the corresponding chlorite pulp while the beech chlorite and peracetic acid pulps required almost the same beating time to reach 350ml CSf (Fig. 1) although within each species the balloon index of these two holocellulose pulps was approximately equal (Fig. 4). To clarify further the above facts, holocellulose pulps of birch (*Betula platyphylla* var. *japonica*), a temperate hardwood, and sawara cypress (*Chamaecyparis* ***pisifera),*** a temperate softwood, were prepared. Their holopulping conditions are given in Table 2, and the beating results in Fig. 5. It should be noted that the birch and sawara cypress holopulping conditions employed were those permitting the resulting pulps to be fiberized by hands.

Table 2. Holopulping conditions of birch and sawara cypress.

Species	Chlorite method		Peracetic acid method		
	Temp., ℃	Chlorite number	Temp., ℃	Peracetic acid dosage, %*	Time hr
Birch	70	5	80	100	2
Sawara cypress	70	7	80	150	2

* based on wood chips weight.

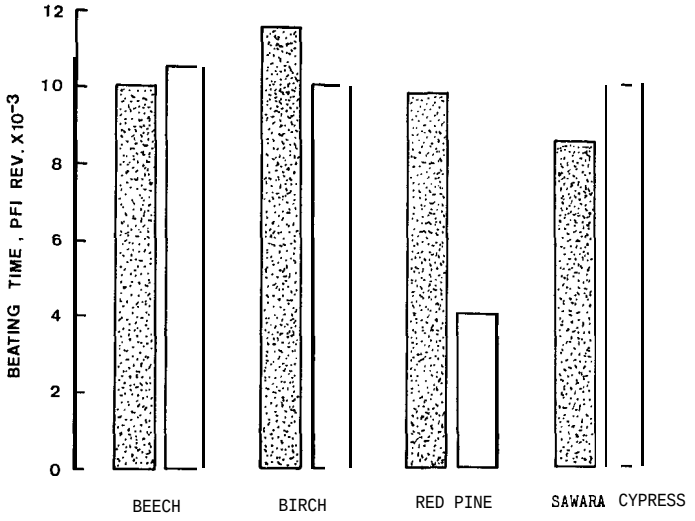

Fig. 5. Times taken to beat holocellulose pulps of various wood species to 350 ml CSf. Spotted columns: Chlorite pulps. Voided columns : Peracetic acid pulps.

As observed in Fig. 5, the beating times of the beech and birch holocellulose pulps were not different, therefore in accordance with their identical holopulping conditions (compared Tables 1 and 2). Similarly, to reach a freeness of 350ml CSf, the sawara cypress chlorite pulp needed a beating time approximately equal to that of red pine. However, the beating time of red pine peracetic acid pulp was surprisingly much shorter than that of sawara

cypress. The difference in the beating behaviour of these two peracetic acid pulps was in consistent with their different holopulping conditions (compared Tables 1 and 2). Accordingly, it can be assumed that the holopulping conditions have affected the beating behaviour of the resulting pulps. This assumption was supported by the fact that the saware cypress peracetic acid pulp of drastic pulping conditions was easier to beat than the same pulp prepared

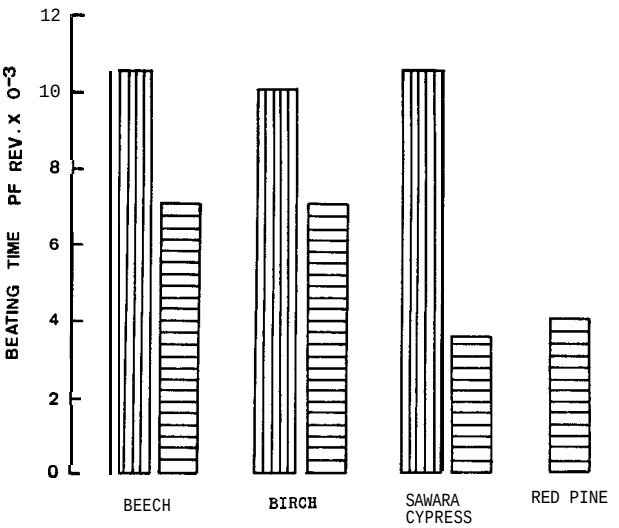

Fig. 6. Beating times of the peracetic acid pulps from various wood species. Vertically stripped columns : Pulps prepared under conditions given in Table 2; Horizontally stripped columns: Pulps prepared under conditions given in Table 1 for the red pine wood species.

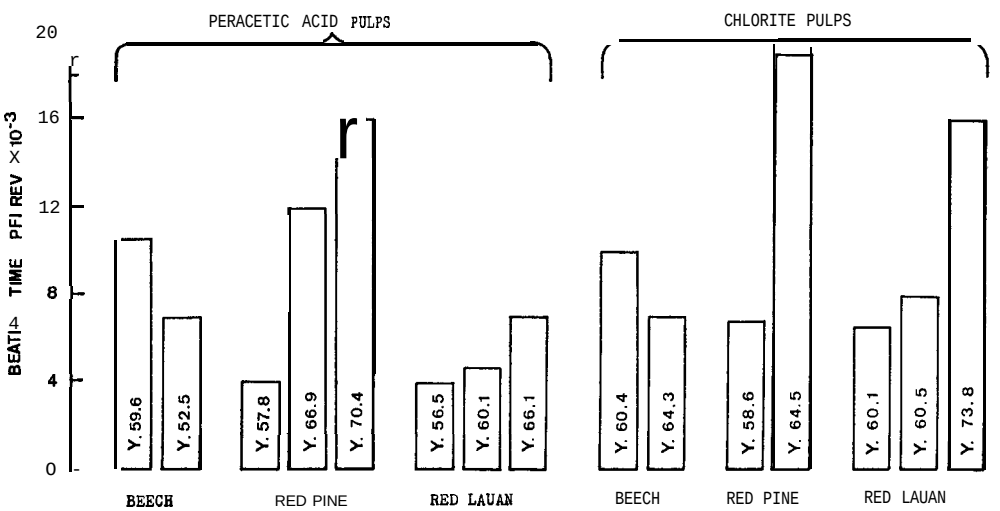

Fig. 1. Beating times of the holocellulose pulps of different yields.

under mild conditions (Fig. 6). Subjected to drastic holopulping conditions, the beating times of the resulting beech and birch peracetic acid pulps were much improved compared with those made under mild conditions, but still longer than those of red pine and sawara cypress (Fig. 6). This is probably owing to the morphological difference between hardwoods and softwoods as already discussed above. Based on these results, several peracetic acid and chlorite holocellulose pulps of red pine and red lauan were prepared by making their holopulping conditions milder or severer than those given in Table 1. The times required to beat those pulps to 350ml CSf are shown in Fig. 7. Evidently, pulps of mild conditions (high-yield pulps) responded slower to beating than those of drastic conditions (low-yield pulps). The above results indicated that the holopulping conditions influence greatly the beatability of the resulting pulps.

As observed above, an improvement of the pulp beatability was accompanied with a reduction in the holocellulose pulp yield. Attempts were then made to equalize the yields of holocellulose pulps prepared under mild oxidative conditions to those of pulps of drastic conditions by a sulfuric acid hydrolysis treatment. The beating of the hydrolyzed pulps was, as expected, eventually facilitated (Fig. 8). It was observed that for beech, the beating time of the hydrolyzed peracetic acid pulp was about 80 % of that of the pulp resulting from mild pulping condition. For the chlorite pulp, it was about 50%. For red pine, the hydrolysis treatment could replace completely the excess oxidation in the amelioration of pulp beatability. And for red Iauan, it could replace about 10 %. As seen in Fig. 9, the balloon index of the hydrolyzed pulps

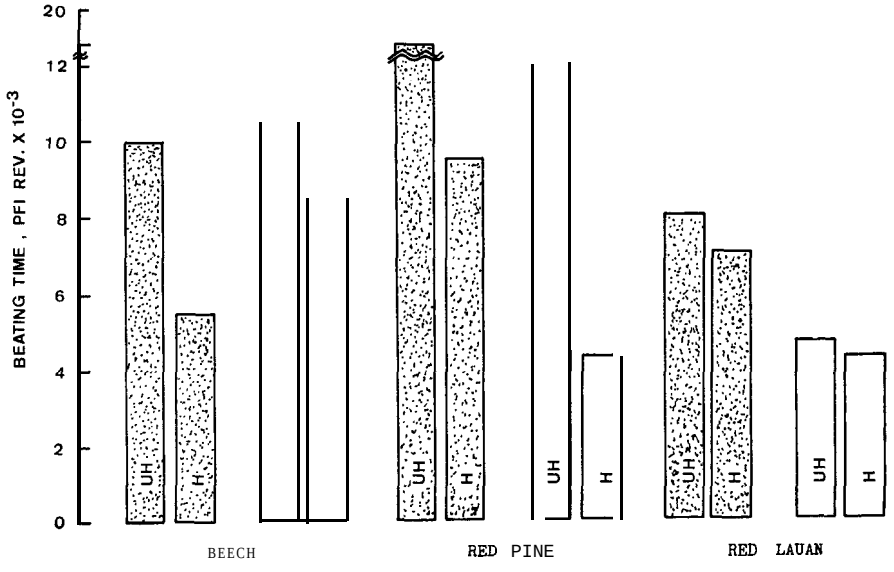

Fig. 8. Effect of the sulfuric acid treatment on the beatability of various holocellulose pulps. Spotted columns : Chlorite ; Voided columns :Peracetic acid pulps; UH: Unhydrolyzed; H: Hydrolyzed

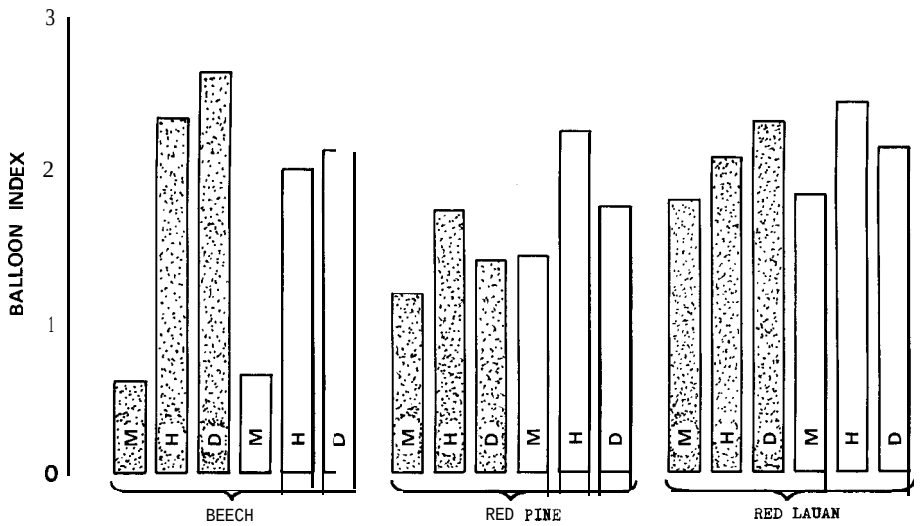

Fig. 9. A comparison of the balloon index of the holocellulose pulps prepared under various pulping conditions. Spotted columns : Chlorite pulps; Voided columns : Peracetic acid pulps. M: Mild holopulping conditions; H: Sulfuric acid treatment; D: Drastic pulping condition.

was much increased compared to that of the untreated ones. This result suggests that the hemicellulosic materials in the compound middle lamella and /or in the S_1 layer were at least partially degraded during the sulfuric acid treatment of the holocellulose pulp. Due to its hydrolytic effect, the sulfuric acid treatment might result simultaneously in lowering the degree of polymerization (Table 3) and creating more bulky and accessible fine structure of pulp fibers as observed for cotton cellulose (Abow-State and El-Megeid, 1977). These structural modifications are believed to be responsible for the increased ease of pulp beatability as will be demonstrated below. The structural modifications which we correlated to the beatability of pulp fibers may correspond to the wall dislocations and zones of dislocations as termed by Kibblewhite (Kibblewhite, 1976 and 1977). Those wall dislocations and zones of dislocations have been shown to be produced by the removal of lignin and hemicelluloses (Hoffmann and Parameswaran, 1976), the deformation of fibrils and the fibrillar contraction (Stöckmann, 1971), and the compressive stresses (Kibblewhite, 1976; DeGrace and Page, 1976), during pulping and chemical treatments.

It was shown above that the excess oxidation and the sulfuric acid treatment could ameliorate the pulp beatability. However such effects were accompanied with a loss in pulp yield which, in turn, implies that structural modifications such as the enlargement of fiber surface and the recrystallization of cellulose molecule in pulp flbers have occured in those chemical treatments. The relationship between fiber recrystallization and pulp beatability was obscure (Centola and Borruso, 1966). Hence the development of external and

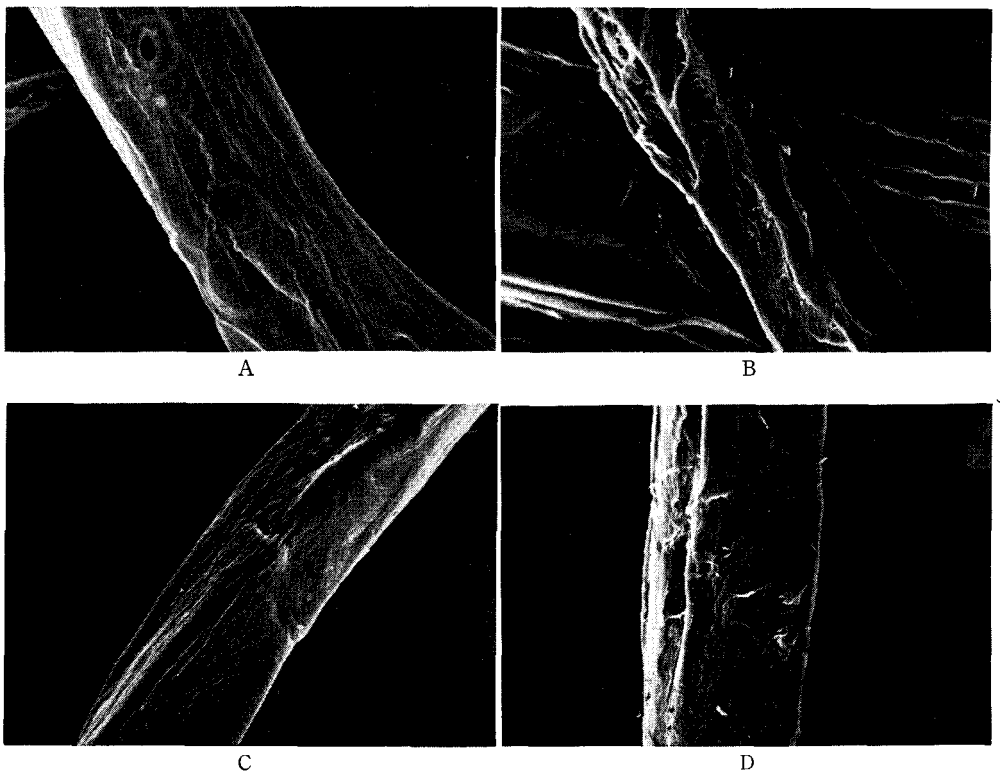

Fig. 10. Scanning electron micrographs of the red pine holocellulose pulp fibers. A: Chlorite fiber of mild holopulping conditions ; B: Chlorite fiber of drastic holopulping conditions; C: Peracetic acid fiber of mild holopulping conditions ; D: Peractic acid fiber of drastic holopulping conditions.

internal surfaces of the fibers would be focussed on. The external surface area was determined by various methods and all the results showed that the holocellulose pulps subjected to excess oxidative and hydrolysis treatments had larger external surface area than the untreated ones. Under scanning electron microscope, the difference in the external surface of the pulps of excess chemical treatments and the untreated ones could also be observed (Fig. 10). Good correlations between the external surface area with the beating time required to attain a freeness of 350ml CSf for each species were noted (Fig. 11). As indicated above, the subseqent oxidative and sulfuric acid treatments removed further lignin and hemicelluloses in the peripheral regions of the cell wall (Stockmann, 1971) and the hemicelluloses deposited in the middle lamella, S_1, and the outer regions of the middle layer of the secondary cell wall (S_2) (Hoffmann and Parameswaran, 1976). Those chemical treatment also split off the P and S_1 layers further (Fig. 9), thereby voids and pores were created in the fiber structure. The enlarged external surface area of those

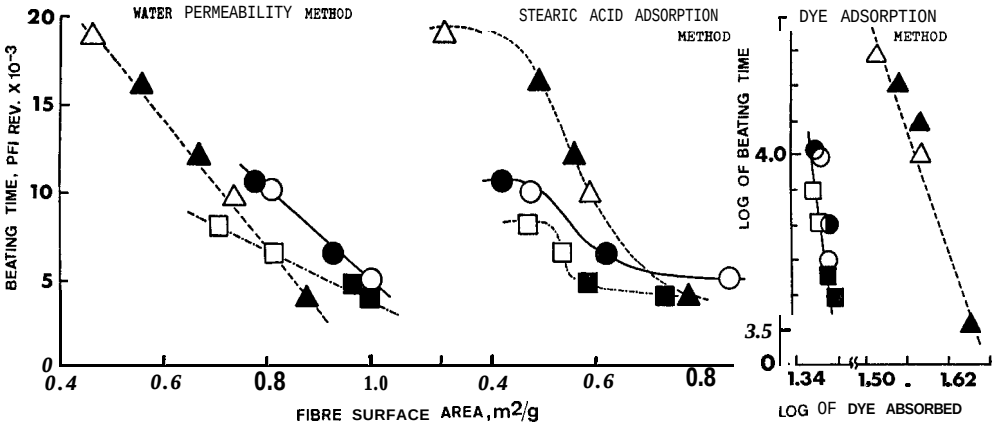

Fig. 11. Relationships between beating time and fiber surface area determined by several methods. Symbols as in Fig. 3.

pulps undergone further chemical treatments comes as a result. The pulp fibers of large external surface are understandable of having great swelling which, in turn. will facliltate their beatability. The differences in the relationships of beating time and external surface area of beech, red pine, and red lauan (Fig. 11) are perhaps due to their structural differences.

In general a pulp of large external surface area is expected to release its absorbed acetone faster than a small one. The results obtained here were rather contradictory, however. As seen in Fig. 12, acetone sorbed by a pulp of low beatability (high-yield pulp) had greater rate of evaporation than that of high beatability (low-yield pulp). In other words, a pulp having small external surface would release its absorbed acetone faster than a larger one

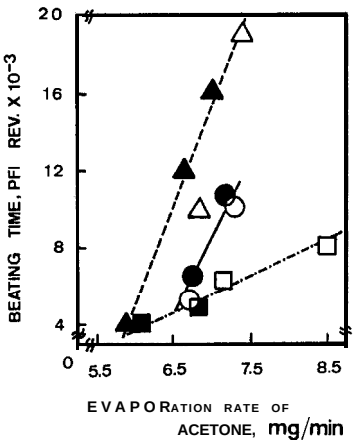

Fig. 12. Correlation between beating time and evaporation rate of acetone absorbed by pulps. Symbols as in Fig. 3.

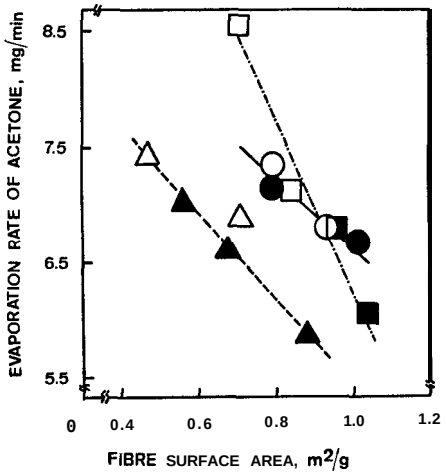

Fig. 13. Correlation between evaporation rate of acetone absorbed by pulps and fiber surface area determined by water permeability method. Symbols as in Fig. 3.

(Fig. 13). It is therefore inferred that this fact was due to the contribution of larger capillaries and submicroscopic cavities, i. e. the internal surface, of the latter. These new capillaries and submicroscopic cavities are created at the expence of the volume of solid material removed and the expense of the micro-porous system. The latter might be visualized as small pores combining to form larger pores as the solid material separating them is eroded away. Since the newly created internal surface are inside of the pulp fibers, an amount of time is need to transport to outside the acetone filled up those capillaries and submicroscopic cavities before it can evaporate. Consequently the rate of evaporation of acetone absorbed by pulp fibers having large external surface was lower than that of small one. Such internal surface was not detected by water permeability, stearic acid adsorption, and dye adsorption techniques which are usually employed for the determination of the external surface area of the pulp fibers. The evaporation rate of acetone absorbed by pulp fibers which is rather a new and simple method can therefore be used to estimate the internal surface area of a given pulp.

Besides the effects mentioned above, the excess oxidative pulping and the sulfuric acid hydrolysis treatment also reduced the initial freeness of the treated pulps, compared with the untreated ones (Fig. 14). In other words, the excess oxidative pulping and the hydrolysis treatment have affected pulp fibers like a prebeating process. Those chemical treatments decreased pulp yields. So the low-yield pulp would have larger number of fibers per unit weight than a high-yield one. Moreover, the former developed external and internal surfaces more than the latter. Accordingly, the swellability of the post-chemical treated pulps are higher than the untreated ones. It is therefore understandable that the pulps of the drastic holopulping conditions and of the sulfuric acid treatment had lower initial freeness than those from the

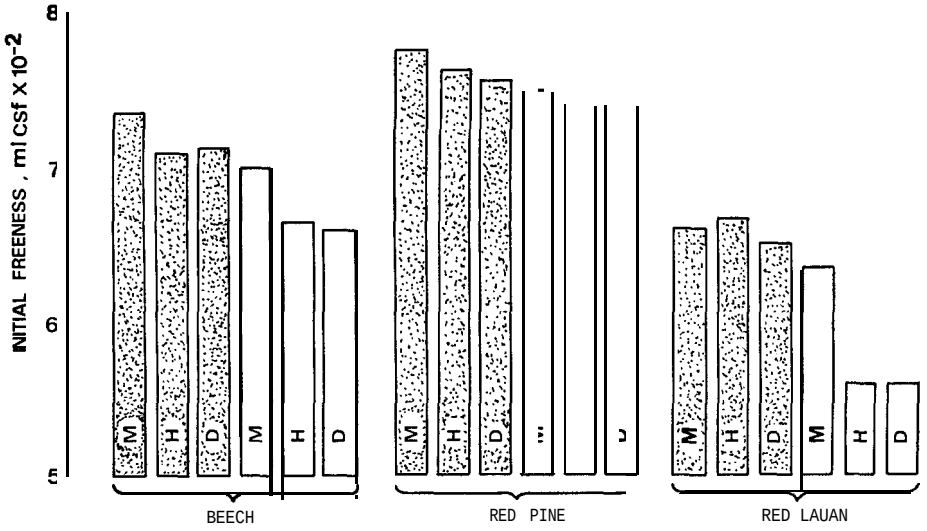

Fig. 14. Initial freeness of the holocellulose pulps prepared under various pulping conditions. Symbols as in Fig. 9.

mild holopulping conditions.

2. **Chemical factors affecting the beatability of holocellulose pulps**

By plotting hemicellulose content versus beating time in Table 3, relation-

Table 3. Analytical data of the holocellulose pulps prepared.

Species	Pulp types	Pulp yield, %	Residual lignin, %	Hemicellulose content, %	Intrinsic**** viscosity, dl/g	Beating time, PFI rev. x 10^{-3}
Beech	Chlorite	64.3*	0.90	18.15	0.57	10.0
		60.5**		15.07	0.54	5.5
		60.4***	**0.45**	14.32	0.50	5.0
	Peracetic acid	59.6*	0.42	17.33	0.a2	10.5
		52.5**		15.25	0.56	8.5
		52.5***	0.32	14.34	0.54	6.5
Red pine	Chlorite	64.5*	1.48	14.13	0.52	19.0
		60.2**	—	10.64	0.43	9.5
		58.6***	0.44	9.77	0.45	9.8
	Peracetic acid	66.9*	1.38	13.15	0.51	12.0
		58.4**		9.54	0.39	4.3
		57.8***	0.32	9.04	0.47	4.0
Red lauan	Chlorite	60.5*	1.03	13.46	0.48	8.0
		59.3**	—	12.25	0.46	7.0
		60.1***	0.84	12.22	0.45	6.5
	Peracetic acid	60.1*	1.12	10.82	0.72	4.7
		56.2**		9.74	0.66	4.3
		56.5***	0.94	9.72	0.63	4.0

—: not determined; * pulps of mild holnpulping conditions; ** pulps subjected to sulfuric acid treatment; *** pulps of drastic holopulping conditions; **** intrinsic viscosity of extracted hemicelluloses.

ships for each species examined would be observed. The results indicate that a hemicellulose-rich pulp (high-yield pulp) would need more beating than a hemicellulose-poor one (low-yield pulp) to reach 350ml CSf. Though the hemicellulose-rich pulp mentioned here is a high-yield one, its residual lignin was not higher than 1.5%, and thus the prohibiting effect of lignin on the pulp beatability, as will be shown later, may be negligible. Also, the results obtained are rather contradictory to the general rule that high hemicellulose content is a determining factor for the development of pulp beatability. Thus, an evaluation of the beatability of a given pulp based only on its hemicellulose content may be misleading.

Table 4. Beating time of beech holocellulose pulps with and without additions of hemicelluloses.

Pulp types	Yield, %	Pentosan, %		Beating time, PFI rev. x 10^{-3}		
		with addition	without addition	with addition	without addition	gain. %
Chlorite	64.3	24.25	23.90	6.0	10.0	**40**
	60.4	23.76	23.58	2.5	5.0	**50**
Peracetic acid	52.5	21.70	21.45	4.0	6.5	40

As seen in Table 4, although the amount of sorbed hemicelluloses onto the beech holocellulose pulps was very small, the pulp containing additive hemicelluloses was much easier to beat than the original pulp. Similar effects were observed with the additions to pulps of benzidine dyes (Centola and Borruso, 1966), dichloro-s-triazine (Allan et *al.*, 1968 and 1969), and arabinose-contatining hemicellulose fraction of rice straw (Mobarak et al., 1977), or by sulfonation and sulfomethylation (Nakano *et al.*, 1970; Ri and Nakano, 1974), carboxymethylation (Fahmy and ElSaied, 1974), and ammonium ion exchange (Nedeltschewa, 1972) of wood pulps. The additions of benzidine dyes and arabinose-containing hemicellulose of rice straw were considered as to increase the swelling of the pulp fibers in water and thereby to improve pulp beatability, and that of dichloro-s-triazine as attaching functional groups to pulp surfaces which would generate additional pulp swelling. Partial substitution of the hydroxyl groups in cellulose molecule by more hydrophilic groups such as sulfonic, sulfomethly, and carboxymethyl groups increased pulp affinity for water and thereby those processes were called chemical beating. Though the effect of ammonium ion exchange of wood pulps was not accounted for, it might be related to the enlargement of interfibrillar regions, thereby increasing the water uptake of pulp and facilitating pulp beatability. In spite of these explanations, the mechanism of the effect of additive hemicellulose on the beatability of holocellulose pulps is regarded rather different. As discussed above, the removal of lignin and hemicelloloese during pulping created outer and inner voids in the pulp fibers. It can not be known whether the additive hemicelluloses would penetrate into inner voids of pulp fibers, they at least bind preferentially onto the outer voids and bond through hydrogen

bridges to the surfaces of the fihrillar elements. Due to their hydrophilic characteristics, they introduce water into the zone located between these elements. The newly created swellability generates internal as well as external fibrillations of the modified fibers, which are arised from the insertion of bulky molecules between the cellulose chains. The increased ease of beating, then, comes as a result. It can hence be inferred that the positive influence on fiber beatability should not be attributed to the quantity of the hemicelluloses but rather to their location in particular regions which indicate the existence of structural modifications that facilitate further the swelling and fibrillation of the pulp fibers.

From the gas chromatographic analysis of the sugars obtained by total hydrolysis of pulp fibers prepared under mild and drastic pulping conditions and of pulps subjected to the sulfuric acid treatment, it was noted a decrease in the amounts of arabinan and galactan, an increase in mannan content, and an unchange in the amounts of xylan and glucan. However, no relationships between the variations of arabinan, mannan, and galactan contents and the beating time were found. It is inferred that the individual hemicelluloses had no positive effect on the beatability of pulp fibers as still believed. Though the quantity of hemicelluloses and the individual hemicelluloses did not affect the beatability of holocellulose pulps, their quality at least did (Table 3). As the holocellulose pulps prepared under mild conditions were subjected to further oxidation (drastic holopulping conditions) or sulfuric acid hydrolysis treatment, a removal of the hemicelluloses occured. This removal took place simultaneously with the decrease in intrinsic viscosity of hemicelluloses and with the structural modifications of pulp fibers as revealed by the enlargement of the external and internal surfaces of the fibers. However, it can not be known whether the former effect or the latter effect has greater influence on the beatability of pulp fibers. Another problem is that it is difficult to separate the effects that should be attributed to the removal of hemicelluloses from those associated with the structural modifications.

In the high-yield and low-yield holocellulose pulps, residual lignin contents were not excess than 1.5% (Table 3). Accordingly, the outer surfaces of the pulp fibers, composing of P and S_1 layers, may still contain lignin. A high-yield pulp would have more lignins deposited on the outer surfaces than a low one. The former is understandable to respond slower to beating than the latter, owing to the hydrophobic characteristics of lignin. On the other hand, the sulfuric acid treatment did not remove further the lignins deposited on the outer surfaces of pulp fibers but degraded and/or removed hemicelluloses instead (Browning, 1963 ; Hoffmann and Parameswaran, 1976). Such a removal and/or degradation of hemicelluloses, and an unchange of pulp lignin during the hydrolysis corresponded to an amelioration of the beatability of the hydrolyzed pulp fibers (Table 3). These results demonstrate that at low lignin content, the degradation of hemicelluloses and the structural modifications rather than the lignin content affect radically the beatahility of pulp fibers.

CONCLUSIONS

As having been known, a hemicellulose-rich pulp would tend to beat rapidly. This is not the cases, however, for the chlorite and peracetic acid pulp prepared from beech, red pine, and red lauan wood species. In spite of their higher hemicellulose content, all the chlorite pulps examined responded more slowly to beating than the bleached kraft pulps. The beech peracetic acid pulp was also slower to beat than the corresponding chemical pulps. The red pine and red lauan peracetic acid pulps, on the other hand, responded more rapidly than the bleached kraft pulps but still slower than the bleached sulfite pulps.

It was found that the nature and the degree of holopulping conditions as well as the structural modifications of wood fibers during pulping and beating processes influenced greatly the beatability of the resulting pulps.

High-yield holocellulose pulps contained more hemicelluloses than low-yield ones. The former were, however, slower to beat than the latter although the effect of residual lignin ought to be negligible. An evaluation of the pulp beatability based on the hemicellulose content alone is hence misleading.

An excess oxidative pulping or a sulfuric acid treatment could improve the beatability of the holocellulose pulps. These chemical treatments resulted simultaneously in the removal of hemicelluloses, the enlargement of the fiber surfaces, and the decrease in the degree of polymerization of hemicelluloses. The quality rather than the quantity and composition of hemicelluloses affected positively the pulp beatability.

An enlargement of the external and internal surfaces of the pulp fibers resulted from the post-chemical treatments showed that the fiber structure has been opened up and became more bulky. Structural modifications hence existed. Such structural modifications promoted further swelling and fibrillation of the pulp fibers. An increased ease of pulp beating came as a result. The presence of hemicelluloses in the regions of structural modifications is of valuable for the amelioration of pulp beatability.

The post-chemical treatments have affected the pulp fibers as a chemical prebeating process because they decreased initial freeness of the treated pulps.

The structural modifications of the fibers took place on the outer surface and in the inside of the fibers as well. The outer surface modification could be detected by the methods usually employed for the determination of the specific surface area. Those methods, however, failed to show the existence of the internal modifications. A new and simple method based on the rate of evaporation of acetone absorbed by the pulp fibers has been developed to estimate the internal surface area of the fibers.

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