Peroxide brightening of kraft pulp

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ABSTRACT: In response to increasing bleached market pulp prices and mounting environmental pressure, a totally chlorine free process to brighten kraft brown stock was developed at Longview Fibre Co. The brightening process was designed to use equipment from a decommissioned bleach plant. Process development began with a rigorous study at an outside laboratory. Laboratory data were then used to define the mill brightening process parameters. A process employing chelation with EDTA and brightening with hydrogen peroxide was tried to achieve a nominal 50 TAPPI brightness level. The trial was quite successful and the mill is currently investigating the feasibility of including the brightening process as a permanent part of production. The resulting medium brightness pulp can be used alone or as a base for colored grades. The time from initial laboratory study to mill operation was only four months.

KEYWORDS: Brightening, brightness, chelation, chlorine free bleaching, EDTA, hydrogen peroxide, kraft pulps, market pulps, mills (factories), peroxide bleaching, two stage process, unbleached pulps.

In March 1994, bleached market pulp (BMP) prices were low. Longview Fibre Co. had decommissioned both its No. 1 and No. 2 bleach plants and moved to the use of BMP to satisfy its bleached pulp needs. From March 1994 to early 1995, BMP prices rebounded and made it economically necessary to search for alternatives to satisfy bleached pulp demand.

At the outset, there were many challenges with finding a bleached pulp alternative. The U.S. EPA proposed Cluster Rule along with public and market perception of chlorine were two of the main issues. The cost and time involved with development of a process to bleach kraft brownstock to full brightness by reactivating a decommissioned bleach plant was another issue that needed to be addressed.

In light of the environmental pressure, it was decided no chlorine would be used in production of any bleached pulp alternative. Bleaching to full (80–90) TAPPI brightness without chlorine would be attainable only with significant capital equipment expenditures. As a result, a nominal 50 TAPPI brightness was targeted. The No. 2 bleach plant was already partially activated as part of the BMP distribution system, but equipment was available for four bleaching stages in the No. 1 bleach plant.

Given these considerations, the search for a process to produce economically viable, chlorine free, medium brightness pulp began. After a thorough literature search, eight bleaching sequences were proposed that would fit with existing No. 1 bleach plant equipment. These eight bleaching sequences were investigated at an outside laboratory. The eight sequences investigated ranged from a simple hydrogen peroxide treatment of brownstock in high density storage to an extensive sequence employing peracetic acid, chelant, and hydrogen peroxide. Based on the results of the study, it was determined a “brightening” sequence consisting of chelation with ethylenediaminetetraacetic acid (EDTA), Q, followed by brightening with alkaline hydrogen peroxide, P, would best suit the mill’s needs.

The QP brightening sequence has many benefits in light of the mill’s situation. The sequence does not employ chlorine or any chlorine derivatives. Although the chemical cost is greater than with previous mill bleaching sequences, the brightened pulp costs are still reasonable when compared to the current cost of BMP. Only two stages of the No. 1 bleach plant would need to be reac-

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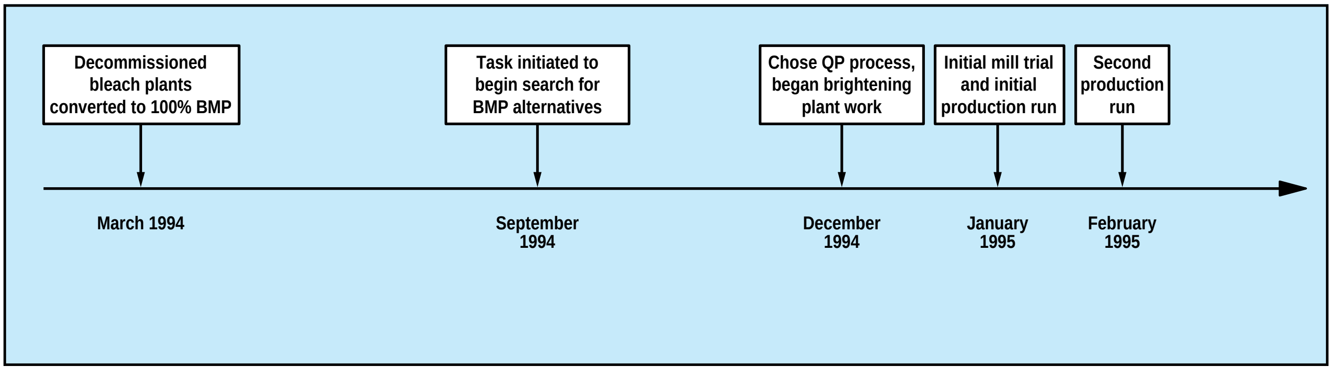
1. Timeline of events leading to the mill brightening trial



I. Brightening trial metals profile (January 10, 1995)

Sample	*Time*	*Metal content, ppm*					
		Iron	*Manganese*	*Copper*	*Zinc*	*Magnesium*	*Calcium*
Brownstock	8:10 am	51.9	-	0.0	5.3	403	1620
Chelated, washed brownstock	8:56 am	29.2	-	0.0	3.4	197	709
Metals removal, %		43.7	-	-	35.8	51.1	56.2
Brown stock	12:22 pm	40.8	20.4	9.8	17.3	52	3550
Chelated, washed brownstock	12:56 pm	22.1	8.5	1.8	9.1	22	1240
Metals removal, %		45.8	58.3	81.6	47.4	57.7	65.1
Brownstock	6:55 pm	48.6	-	0.0	7.4	339	1381
Chelated, washed brownstock	7:07 pm	18.4	-	0.0	2.3	231	779
Metals removal, %		62.1	-	-	68.9	31.9	43.6

tivated, and the mill already had a modern hydrogen peroxide delivery system in place.

All of the engineering, pipe-fitting and instrument work to ready the No. 1 bleach plant was completed in three months. After the equipment modifications were complete, the No. 1 bleach plant was renamed the brightening plant. Interpretations and decisions based on the laboratory study of the QP brightening sequence were finalized, and coordination of chemical delivery for a trial in early January 1995 was completed.

A timeline of events leading up to the mill trial and beyond is illustrated in **Fig. 1.**

Mill trial/discussion

As planned, the mill trial took place in early January 1995.

The brightening plant fiberline is depicted in **Fig. 2.**

On the morning of the mill trial, hot water was pumped through the system to preheat it. Following the hot water, brownstock (batch kraft, kappa number 25–35) was started through the system.

Initial process parameters were as follows:

pH Adjustment

Lower the brownstock pH with dilute H_2SO_4 to pH 4.5–6.0 for the Q stage.

Chelation Q Stage

0.4% EDTA (as 100%) on pulp (moisture free)
3% stock consistency
60°C (140°F)
pH 4.5–6.0
30 min retention time

Wash Stabilization

1.0% Na_2SiO_3 (as 100%) on pulp (moisture free)

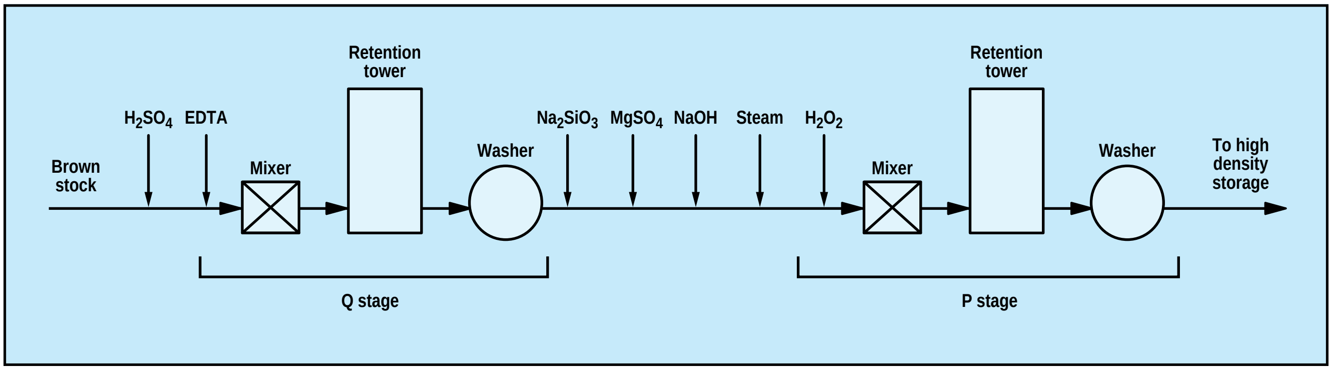
Protection

0.25% $MgSO_4$ (as 100%) on pulp (moisture free)

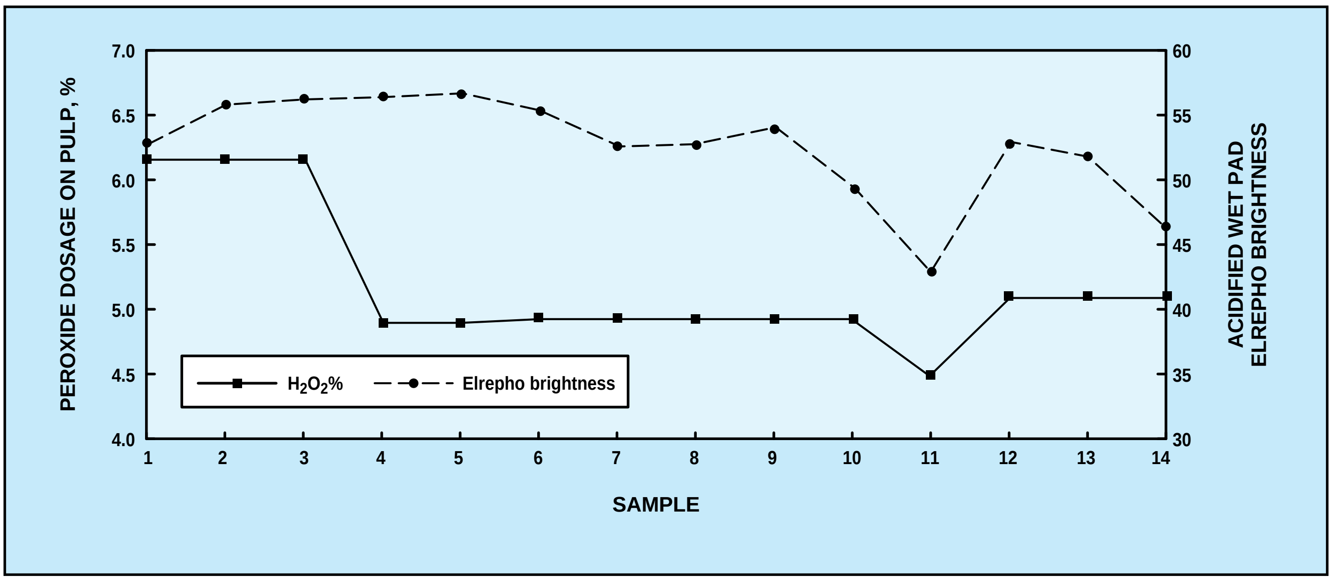
pH Adjustment

Raise the brownstock pH with dilute NaOH to pH 10.8–11.2 for the P stage.

2. The brightening plant fiberline



3. Brightness response to peroxide application. Included in the graph is a 2 h time delay between the peroxide dosage and the brightness response; i.e., 7:00 am H_2O_2 dosage with 9:00 am brightness.



Brightening P stage

5.0% H_2O_2 (as 100%) on pulp (moisture free)
8% stock consistency
80°C (176°F)
pH 10.8–11.2
90 min retention time

Wash

Acceptable medium brightness pulp was produced approximately 3 h after the brownstock started through the system. Almost 1 h of off brightness pulp was produced before the pulp reached a 50 (acidified wet pad) Elrepho brightness level.

Throughout the trial, conditions varied slightly from the initially proposed process parameters. Incoming brownstock kappa number varied along with incoming stock pH and temperature. The acidification of the brownstock prior to the Q stage was controlled with manual adjustment of the acid flow and acid eductor water. This resulted in relatively slow response time to pH variations of incoming brownstock. The chelant dosage wandered slightly. This was probably due to the use of a gravity fed EDTA line using manual flow control with a rotometer along with hot chelant eductor water. Retention time in the Q stage retention tower (up flow, down flow) was 20–30 min. The magnesium sulfate dosage stayed fairly constant throughout the trial. The sodium silicate dosage was 30% lower than intended at 0.7% (as 100%) on pulp (moisture free). This was primarily due to the near freezing outside air temperature causing the sodium silicate solution to thicken, leaving the diaphragm pumps with insufficient excess capacity to deliver the intended dosage. The pH of stock going to the P stage retention tower drifted. Control of the stock pH to the P stage was done with manual adjustment of caustic flow to the steam mixer using a rotometer. As with pH control to the Q stage, manual control of pH to the P stage resulted in less than ideal response time to process pH variations. The peroxide dosage started out at 6.0% (as 100%) on pulp (moisture free). This dosage is 20% higher than originally intended. The high dosage resulted from the stock be-

II. Brightened pulp laboratory beater curve results[a]

Sample one / 12:55 pm					
CSF,[b] mL	TAPPI brightness	Burst index,[c] kPa·m²/g	Tear index,[d] mN·m²/g	Breaking length,[e] km	Folding endurance,[f] No.
602	-	-	-	-	-
554	54.6	5.91	7.61	8.47	907
458	53.3	6.56	7.59	9.73	1392
307	51.3	6.90	6.81	10.24	1754
225	50.1	7.00	6.83	10.19	1764
169	49.1	7.11	6.46	10.47	1711
Sample two / 4:10 pm					
CSF,[b] mL	TAPPI brightness	Burst index,[c] kPa·m²/g	Tear index,[d] mN·m²/g	Breaking length,[e] km	Folding endurance,[f] No.
640	-	-	-	-	-
550	50.2	5.88	8.16	8.69	1014
437	47.6	6.57	7.47	10.17	1501
281	46.1	7.07	6.74	10.40	1605
201	46.3	7.19	6.94	11.13	1712
152	45.5	7.21	6.80	10.78	1537

[a]TAPPI T 200
[b]TAPPI T 227
[c]TAPPI T 220 om-88 13.3.11
[d]TAPPI T 220 om-88 13.3.12
[e]TAPPI T 220 om-88 13.3.14
[f]TAPPI T 220 om-88 13.3.5

III. Brightening trial paper test results (January 10, 1995)

No. 2 Paper machine				
Grade	Burst index, kPa·m²/g	Tear index, mN·m²/g MD	CD	TAPPI brightness
Bag	3.57	8.09	7.66	57.0
OCC Bag	3.63	8.61	9.30	40.0
Colored	3.46	8.86	10.23	-
No. 3 Paper machine				
Grade	Burst index kPa·m²/g)	Tear index, mN·m²/g MD	CD	TAPPI brightness
Plotter	3.36	8.00	9.00	59.3
Stick	3.39	8.09	9.13	56.5
Giblet (wet strength)	3.95	8.13	8.44	57.7
Freezer (wet strength, filled)	3.38	8.41	9.91	63.0

ing wetter than expected coming from high density storage. When the stock consistency leveled, the peroxide dosage was lowered to just under 5.0% (as 100%) on pulp (moisture free). Retention time in the P stage retention tower (up flow, down flow) was 90-120 minutes. Due to the diameter of the P stage retention tower and stage stock consistency, there is a good chance there was some stock channeling in the tower. Despite process parameter fluctuations, the final brightness level re-

IV. Brightening trial paper roll brightness and tear reversion[a]

Grade	TAPPI brightness		Change
	Off machine	*Roll reverted*	
Plotter	59.5	58.5	-1.0
Giblet (wet strength)	58.0	57.1	-0.9

Grade	Tear index, $mN \cdot m^2/g$				Change	
	Off machine		*Roll reverted*			
	MD	CD	MD	CD	MD	CD
Plotter	8.04	8.74	8.14	9.24	+0.10	+0.50
Giblet (wet strength)	8.14	8.44	8.14	8.52	0.00	+0.08

[a] Samples tested were taken from rolls one week after production

V. Brightening trial laboratory brightness reversion[a]

Grade	*Initial TAPPI brightness*	*Reverted TAPPI brightness*	*TAPPI brightness loss*
Bag	56.5	54.8	1.7
OCC bag	41.1	40.2	0.9
Plotter	58.4	56.7	1.7
Stick	56.6	54.5	2.1
Giblet (wet strength)	56.1	54.3	1.8
Freezer (wet strength, filled)	64.2	63.0	1.2

[a] Longview Fibre Co. Routine Method No. 104 based on TAPPI T 260

mained in the 50–60 (acidified wet pad) Elrepho brightness range.

Following production in the brightening plant, the brightened pulp was run on two of the mill's 12 paper machines. No. 2 paper machine trial ran the brightened pulp in two bag grades and a colored grade. No. 3 paper machine trial ran the brightened pulp in plotter paper, stick paper, wet strength giblet paper, and filled, wet strength freezer paper. A small amount of sodium sulfite was added at the machine beaters to quell any residual peroxide left with the pulp. No excess foaming or machine runnability problems occurred during the paper production runs on either paper machine.

Results

The chip furnish used to make the batch kraft brownstock pulp was 100% pine. The chips were light colored, good quality chips that were thickness screened to minimize shives. The chip furnish probably aided in the achievement of the brightness target.

The metals profile of three separate brownstock samples taken during the trial is included in **Table I**. Through chelation and washing, approximately half of all the tested metals were removed from the stock prior to the P stage. Of the metals remaining on or with the stock, some were probably chelated, thereby rendering them ineffective in decomposing hydrogen peroxide.

A graph illustrating brightness response to peroxide application is shown in **Fig. 3**. This graph shows the forgiveness of the brightness response to changes in the peroxide application. At the rate the brightening plant was running during the trial, the brightness response was fairly steady until the peroxide dosage dropped below a certain point (approximately 4.7%). This observation was further reinforced when the brightness rebounded upon raising the peroxide dosage back up beyond that crucial lower level.

The shive content of the brightened pulp was minimal. This was a result of well-screened chips and cooking the pulp to a low kappa. The shives in the brownstock that went to the brightening plant were effectively decolorized during the brightening P stage.

Laboratory beater curve results for two different medium brightness pulp samples taken during the trial are included in **Table II**. As expected, the brightness of both samples decreased with increased refining. The burst index, tear index, breaking length, and folding endurance response to increased refining was as expected.

The paper test results from both paper machine's trial production runs are included in **Table III**. The

TAPPI brightness with an inorganic filler in the paper was 4.5–6.5 points higher than without. The tear was marginal on the grades produced during the trial as judged by mill specifications.

Roll brightness and tear reversion results are included in **Table IV**. Although the reversion time in the roll was brief, the results are positive. The brightness reversion was minimal and the tear did not change significantly.

Laboratory brightness reversion results are included in **Table V**. This laboratory procedure attempts to accelerate natural brightness reversion with heat and moisture to gain an insight into how the paper will perform over time. The medium brightness stock did not revert any more than fully bleached stock produced at the mill before the bleach plants were decommissioned. The medium brightness stock has a fair amount of lignin left with it. A higher reversion might be expected, but the results of this particular study suggest paper produced from medium brightness stock will not revert more than two to three points of TAPPI brightness.

Mill secondary effluent BOD and COD levels were monitored before, during, and after the mill brightening trial. No significant difference was found between brightening plant operation times and "normal" mill operation times. This is quite positive in that any potential conflicts with BOD or COD emissions under the U.S. EPA proposed Cluster Rule are minimized. It is important to note the mill is quite large, and the amount of BOD and COD stemming from the brightening process was very small in comparison to other larger sources. A smaller mill might notice more significant changes in BOD and COD levels from the brightening process. The BOD and COD emissions from this particular QP process are much less than those from the fully bleached pulp process at the mill before the bleach plants were decommissioned.

Subsequent production

Following the initial mill trial, two medium brightness pulp production runs took place by the end of February 1995. During these two brightening plant runs, further insight was gained into the QP brightening process at the mill.

A chip mix of 70% pine and hemlock, 30% Douglas-fir, and a trace of hardwood was used to provide the batch kraft brownstock for use during a part of one of the production runs. No detrimental effects were observed in final brightness with this chip mix.

The retention time and temperature of the P stage proved to be pivotal in achieving desired brightness. When the production rate of the brightening plant was slowed, at least a 10% reduction in peroxide was achieved from the nominal 5% (as 100%) on pulp (moisture free). A drop in the stock level on the down flow of the P stage retention tower quickly resulted in off brightness pulp. Once the tower level was increased, the brightness returned to an acceptable level. A chance problem with the hot water supply to the brightening plant resulted in decreased P stage temperature and off brightness pulp. Once the temperature returned to the nominal 80°C (176°F) range, the brightness increased to an acceptable level.

Peroxide brightening theory suggests the pH of the P stage is important in achieving final brightness. The perhydroxyl anion (OOH^-) is best formed from hydrogen peroxide in a certain pH range. The perhydroxyl anion (OOH^-) is what does the brightening in the P stage. On the low side of the perhydroxyl anion formation pH range, the majority of the hydrogen peroxide is simply carried through with the pulp in the P stage. This results in the pulp not brightening and a large peroxide residual left on the pulp at the end of the stage. On the high side of the perhydroxyl anion formation pH range, the hydrogen peroxide converts to the perhydroxyl anion too quickly and completely. This does not give the brightening reaction sufficient time to happen and leaves no peroxide residual on the pulp at the end of the stage.

There is insufficient run time data to date to make any significant conclusions concerning P stage pH. Early indications suggest the final brightness decreases when the P stage initial pH is out of a nominal 10.5–11.5 range. When the P stage pH goes beyond 11.5, alkaline darkening may also occur.

The kappa number reduction through the QP brightening process averaged 13 points. This corresponded to an approximate 2% yield loss based on pulp coming to the brightening plant.

Subsequent paper machine production has been positive with the exception of tear test results. Tear continues to be something the paper machines are struggling to achieve.

There have been a variety of different grade trial runs with the medium brightness pulp. Numerous colored grades have been produced on machine and they have been well received by the customer. Another promising application of the medium brightness pulp is on the printed side of a corrugated box.

Conclusions

- Above a minimum dosage requirement to achieve a certain brightness level, the hydrogen peroxide dosage on pulp can vary slightly with little effect on final brightness.
- As with most bleaching or brightening applications, retention time, pH and temperature in the peroxide brightening stage are important to achieving brightness.
- Despite a drop in lignin content through the QP process as evidenced by the decrease in Kappa number, the QP process does not significantly impact BOD and COD levels in Longview's.

- Medium brightness pulp is an alternative to bleached market pulp that can help with the economics, environmental impact, and public perception of mill operation.

Future work

As of early 1995, the mill is investigating the process of making the brightening plant and the QP brightening process a permanent part of production. As QP brightening process development continues, pulp strength and yield will be studied further and optimized through the brightening plant. Automatic control of various process parameters such as pH control of incoming stock to the Q stage and chelated stock to the P stage will decrease upset response times and give tighter control of the process.

Future grade applications and development will stem from further market response to medium brightness pulp. Further development of medium brightness pulp should serve to give the pulp and paper industry one more choice to deal with changing economic and environmental climates.

I would like to thank Longview Fibre Co. for the resources, support, and initiative to make this work possible. Review and critique of this paper by mill personnel were invaluable.

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Appendix

Tables IIe, IIIe, and IVe are appended to show basis weight and paper test results in common mill testing units. The test results shown in Tables II, III, and IV are normalized for basis weight according to TAPPI test methods.

IIe. Brightened pulp laboratory beater curve results in common mill units[a]

Sample one / 12:55 pm

CSF [b], mL	*Basis weight, lb/3000 ft ^{2}*	*TAPPI brightness*	*Burst, psi*	*Tear, g*	*Tensile (lb on a 0.59 in. strip)*	*Folding endurance No.*
602	-	-	-	-	-	-
554	39.3	54.6	54.8	49.6	17.89	892
458	39.4	53.3	61.0	49.6	20.62	1373
307	39.6	51.3	64.6	44.8	21.84	1741
225	38.8	50.1	64.2	44.0	21.29	1715
169	39.6	49.1	66.5	42.4	22.30	1695

Sample two / 4:10 pm

CSF [b], mL	*Basis weight, lb/3000 ft ^{2}*	*TAPPI brightness*	*Burst, psi*	*Tear, g*	*Tensile (lb on a 0.59 in. strip)*	*Folding endurance No.*
640	-	-	-	-	-	-
550	39.6	50.2	55.0	53.6	18.50	1005
437	39.4	47.6	61.1	48.8	21.55	1480
281	38.6	46.1	64.5	43.2	21.64	1553
201	39.6	46.3	67.2	45.6	23.71	1696
152	39.7	45.5	67.6	44.8	23.03	1528

[a] TAPPI T 200
[b] TAPPI T 227

IIIe. Brightening trial paper test results in common mill units (January 10, 1995)

No. 2 Paper machine

Grade	*Basis weight, lb/3000 ft ^{2}*	*Burst, psi*	*Tear, g*		*TAPPI brightness*
			MD	*CD*	
Bag	35	29.5	47.0	44.5	57.0
OCC bag	35	30.0	50.0	54.0	40.0
Colored	44	36.0	64.7	74.7	-

No. 3 Paper machine

Grade	*Basis weight, lb/3000 ft ^{2}*	*Burst, psi*	*Tear, g*		*TAPPI brightness*
			MD	*CD*	
Plotter	30	23.8	39.8	44.8	59.3
Stick	35	28.0	47.0	53.0	56.5
Giblet (wet strength)	40	37.3	54.0	56.0	57.7
Freezer (wet strength), filled	38	30.3	53.0	62.5	63.0

IVe. Brightening trial paper roll brightness and tear reversion in common mill units[a]

Grade	*TAPPI brightness*		*Change*
	Off machine	*Roll reverted*	
Plotter	59.5	58.5	-1.0
Giblet (wet strength)	58.0	57.1	-0.9

Grade	*Basis weight, lb/3000 ft ^{2}*	*Tear, g* *Off machine*		*Roll reverted*		*Change*	
		MD	*CD*	*MD*	*CD*	*MD*	*CD*
Plotter	30	40.0	43.5	40.5	46.0	+0.5	+2.5
Giblet (wet strength)	40	54.0	56.0	54.0	56.5	0.0	+0.5

[a] Samples tested were taken from rolls one week after production