

**Quarterly Progress Report For: Replacing Chemicals in Recycle Mills with Mechanical Alternatives****Covering Period:** January 1, 2000 to March 31, 2000**Date of Report:** April 14, 2000**Contractor:** Institute of Paper Science and Technology**Award Number:** DE-FC36-99GO10381**Contact:** Sujit Banerjee (404) 894-9709; s.banerjee@ipst.edu**Project Team:** DOE-HQ contact (Valri Robinson), AF&PA contact (Conni Kunzler), project mentors (Tom Friberg, Weyerhaeuser, Jim Ramp, Southeast Paper).

**Project Objective:** The objective of this project is to explore potential applications of underwater pulsed power technology to the paper industry. These included fiber refining, disinfection, stickies dispersion, and stickies control.

**Background:** In pulsed power a spark is discharged underwater. Present commercial applications of the technology include the detonation of land mines, zebra mussel control, and water disinfection. In preliminary work we have found that stickies are rapidly dispersed under the influence of pulsed power. The purpose of this project is to explore other applications of the technology in the recycle paper industry, especially in applications where the technology can replace potentially expensive chemical use.

**Status:** We have confirmed sparking does not affect the cationic charge demand of whitewater, nor does it change the zeta potential of solids suspended therein. It lowers the zeta potential of stickies, indicating the formation of acidic groups. Pitch deposition is reduced upon sparking. The particles are reduced in size and their zeta potential is decreased. The hydroxyl radical yield from sparking has been measured and has been found to be higher than that obtained from 80 kV X rays. The effective range of the spark is over 4.5 meters. The increase in surface oxygen upon sparking has been confirmed. A full-scale trial at Visy Paper, Conyers, GA, is being set up.

**Plans for the Next Quarter:**

- Run laboratory studies with furnish obtained from Visy Paper.
- Run a mill trial at Visy Paper.

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ID Number	Task/Milestone Description	Planned Completion	Percent Completion	Actual Completion	Comments
1.1	Laboratory studies on stickie detackification.	12.00	50	3.00	
1.2	Study of stickies attached to machine surfaces.	12.99	100		
1.3	Mechanism of stickie passivation.	12.00	50		
1.4	Application to stickies dispersion.	6.00			
1.5	Depth profiling of detackification.	3.00	20		
1.6	Comparative study of other means of inducing detackification.	12.00	10		
2	Studies on fiber refining.	12.99	100	6.99	
3	Laboratory studies on biocidal activity.	12.99	100	6.99	
4.1	Planning for field work.	12.99	10		
4.2	Field work for stickies detackification.	9.00			
4.3	Field work for biocidal activity.	12.00			
5	Economic analysis.	3.01	20		
6	Final report.	3.01			

**Budget Data (as of 3.30.00)**

Phase / Budget Period			Approved Spending Plan			Actual Spent to Date		
			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1		6.99	46,064			45,994		
Year 2	7.99	3.00	108,654			56,060		
Year 3								
Totals			154,718			102,054		

# Replacing Chemicals in Recycle Mills with Mechanical Alternatives

(DE-FC36-99GO10381)

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## *Accomplishments*

- Sparking does not affect the cationic charge demand of whitewater, nor does it change the zeta potential of solids suspended therein.
- Sparking lowers the zeta potential of stickies, indicating the formation of acidic groups.
- Pitch deposition is reduced upon sparking. The particles are reduced in size and their zeta potential is decreased.
- The screenability of an acrylate PSA increases upon sparking.
- The hydroxyl radical yield from sparking exceeds that from 80 kV X rays.
- The effective range of the spark is 4.5 meters as determined through measurements made in large tanks.
- The uncertainty of XPS analysis has been determined, and the increase in surface oxygen upon sparking has been confirmed.

## *Effect of sparking on whitewater*

Clarified whitewater obtained from Southeast Paper was sparked 80 times in our 8 L tank. The zeta potentials at the various pH values listed below show no significant change. The pH was adjusted by adding HCl or NaOH. The cationic charge demand was measured on filtered samples with colloid titration. The sample was diluted in half with deionized water, and excess DADMAC (5 mL) was added to 5 mL of the diluted sample. A part of the cationic polymer complexes with the anionic trash. Several drops of cationic dye (o-toluidine blue) were added, and the excess polymer was titrated with PVSK (polyvinylsulfate potassium salt). The results, shown below, show an apparent increase upon sparking, but the levels are too low for the difference to be meaningful.

zeta (pH)

control: -2.1(1.7), -12.7(3.3), -14.1(7.3), -15.6(9.4), -20.5(11.2)

80X: -3.2(1.5), -13.3(3.2), -13.0(7.1), -14.9(9.4), -19.6(11.2)

cationic charge demand

control: 26 meq/1000L

80X: 60 meq/1000L

A follow-up run was made with cloudy white water from Southeast Paper. The sample was sparked forty times in the 8 L tank and cationic charge demand and zeta potential were measured. The results, listed below, demonstrate that the whitewater is unaffected by sparking.

### cationic charge demand

0X: 120 meq/1000L

40X: 131 meq/1000L

### zeta (pH)

control: -3.1(1.7), -19.6(4.7), -20.9(6.7), -19.6(9.4), -21.6(11.5)

40X: -3.2(1.4), -19.3(4.7), -19.9(6.7), -19.8(8.6), -21.4(11.9)

### ***Effect of sparking on zeta potential***

The zeta potentials of stickie particles were measured as a function of pH and the number of sparks applied. The stickies used were Carbotac, and a sample from the tertiary fine screen rejects obtained from Lake Superior Paper Industries in Wisconsin. The Carbotac was prepared with acetone as described earlier, and was ground further to colloidal levels. The stickies in the mill sample were present at about 2.2%, and to remove the fibers, the sample was diluted five-fold and the fibers separated through a 3,000  $\mu$  mesh screen through gravity filtration. Both samples were sparked up to 100 times and samples were collected after every 20 sparks. Zeta potential was measured with a zetasizer (Malvern Instruments Ltd., UK). The pH of the solution was controlled by adding HCl or NaOH. The results are presented in Table 1.

Figure 1 presents plots of zeta potential vs. pH for untreated and spark-treated Carbotac. The plot for untreated Carbotac is typical of a non-polar polymer surface. The shift of the isoelectric point to lower pH for the spark-treated stickie suggests that sparking generates acidic groups at the surface, in keeping with our previous observations with methylene blue dye. Figure 2 shows corresponding plots for the mill stickie, whose surface is more weakly acidic in comparison to Carbotac. The complexity of the plots is probably due to other contaminants present in the sample. Figure 3 compares changes in zeta potential upon sparking for Carbotac and the mill sample. For the Carbotac PSA, twenty sparks decreases zeta potential from -15.0 to -20.3 mV. Beyond that, the zeta potential begins to increase to -16.6 mV at 100 sparks. This is due to a pH change; it was observed that the pH decreased after 100 sparks. The mill stickie showed a marginal change under similar conditions. The decrease in zeta potential with increasing pH is due to the increased dissociation of acidic surface groups.

**Table 1: Zeta potential changes upon sparking**

Carbotac, untreated		Carbotac, 80X		mill, un- treated		mill, 80X		no. of sparks	mill	Carbotac
pH	mV	pH	mV	pH	mV	pH	mV		mV	mV
1.1	4.5	1.1	-14.4	0.7	-0.7	1.5	-3.7	0	-4.3	-15.0
3.3	-2.7	1.9	-15.5	3.4	-0.8	4.3	-2.5	20	-4.5	-20.3
5.2	-15.0	4.0	-21.3	6.6	-4.3	6.7	-3.4	40	-3.8	-20.3
8.8	-20.0	6.1	-22.8	8.9	-5.0	9.1	-6.1	60	-3.9	-18.0
11.2	-29.9	10.0	-25.9	11.6	-6.3	11.0	-6.4	80	-2.9	-19.1
						12.0	-6.3	100	-3.2	-16.6

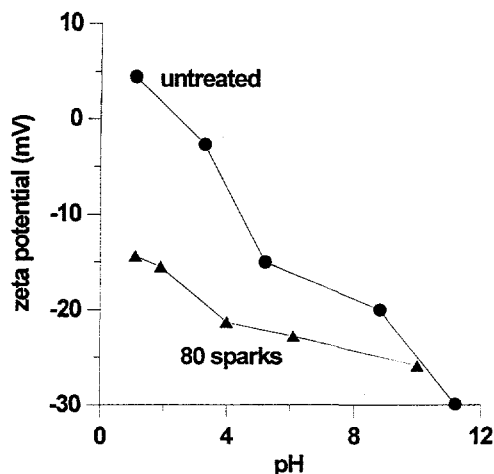


Figure 1. Zeta potential vs. pH plots for Carbotac.

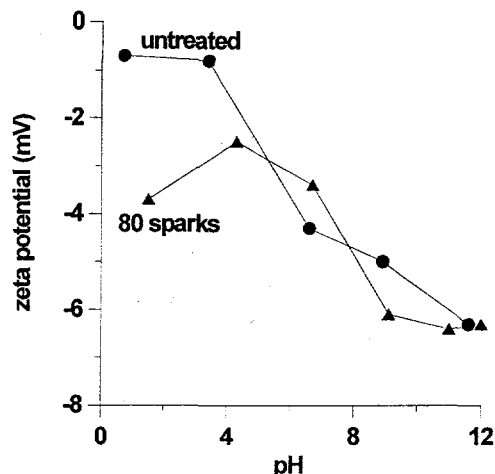


Figure 2. Zeta potential vs. pH plots for mill stickie.

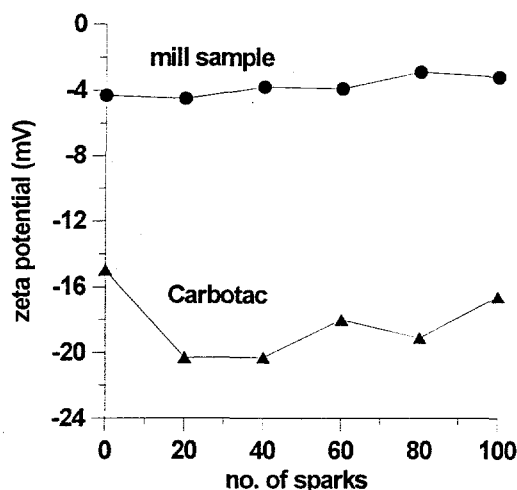
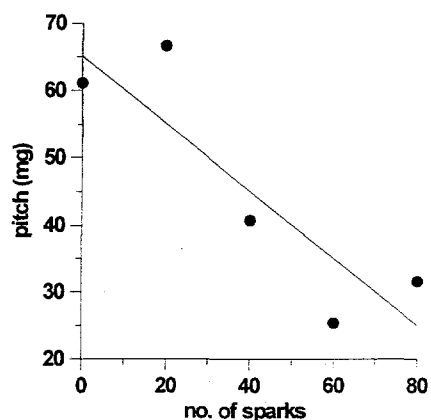


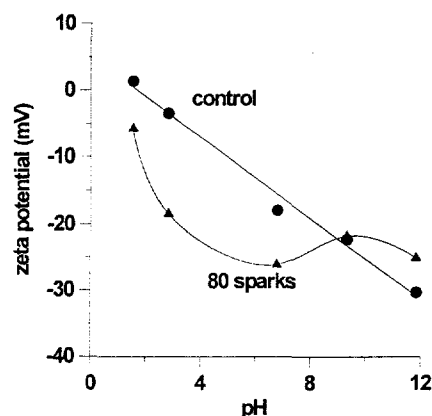
Figure 3. Zeta potential vs. no. of sparks plots for Carbotac PSA and mill stickise. The pH of the mill sample and Carbotac were 6.7 and 5.2-3.9, respectively.

### Pitch deposition

A BioFlo 3000 reactor (a mixing tank with a Rushton impeller) from New Brunswick Scientific, Edison, NJ, was used to monitor the rate of pitch deposition on metal surfaces. Pitch was collected from the Georgia-Pacific, Vienna, GA, particleboard mill just after the dryer. It was ground with a mortar and pestle, homogenized, and suspended at 0.3% consistency in 500 mL of 50°C water of pH 7.0. After 60 minutes of stirring at 300 ppm (including the initial 10 minutes of heat up), the impeller was removed, washed gently with water, oven-dried at 100°C for 15 minutes, and weighed. Replicate experiments conducted without sparking showed the uncertainty to be  $\pm 4.2\%$ . The results, shown in Figure 4, clearly demonstrate that sparking



**Figure 4: Effect of sparking on pitch deposition.**



**Figure 5: Effect of sparking on zeta potential.**

Table 2: Effect of sparking on the size distribution of pitch		
size range ( $\mu$ )	percent	
	control	80 sparks
0-50	25.6	0.2
50-70	11.8	21.5
70-80	6.1	13.2
80-90	5.1	10.5
90-100	4.7	9.2
100-200	28.1	37.5
200-300	10.0	6.0
300-400	4.0	1.6
400-500	1.6	0.1
500-1,000	3.0	0.2
$D_{50}$ , ( $\mu$ )	133	111

dramatically reduces the extent of deposition. Changes in zeta potential induced by sparking are illustrated in Figure 5. The particles are made more negative throughout the pH range, which should lead to an increase in colloidal stability. The size distribution of the particles before and after sparking is listed in Table 2. The particle size is reduced indicating that sparking has a dispersive effect.

### **Screenability of Carbotac**

A 0.3% suspension of dried homogenized Carbotac in water was sparked, processed through the Pulmac, and the size distribution measured. The results, listed in Table 3, show no change in size, even though the screen efficiency was increased from 44.0 to 50.2 percent. The experiment was repeated in the presence of pulp. A slurry of 0.5% bleached softwood kraft pulp was mixed with 0.1% of its weight of dried PSA. The initial size distribution of the stickies was measured by filtering an aliquot and subsequent staining and image-analysis. The mixture was



<b>Table 3: Size distribution (percent) and screening efficiency of stickies in the absence of pulp</b>					
<b>size range (<math>\mu</math>)</b>	<b>total sample</b>		<b>Pulmac accepts</b>		<b>Pulmac rejects</b>
<b>no. of sparks:</b>	0	80	0	80	0
0-50	28.5	35.2	44.2	51.2	10.1
50-70	11.3	5.9	8.9	12.9	21.7
70-80	5.3	4.2	3.9	4.7	5.8
80-90	4.9	5.2	4.0	4.1	4.7
90-100	4.3	5.0	4.3	2.8	5.5
100-200	27.5	27.4	24.2	16.7	30.8
200-300	9.2	9.3	7.3	5.2	11.7
300-400	4.1	3.4	2.2	2.3	4.7
400-500	2.3	2.6	0.6	0.1	3.6
500-1,000	2.7	1.9	0.3	0.0	1.5
<b>cumulative per-centile at 150 <math>\mu</math></b>	<b>71.4</b>	<b>72.6</b>	<b>79.8</b>	<b>86.2</b>	<b>67.2</b>
total count	3,202	1,775	3,036	2,971	725
screen rejects (%)	44.0	50.2			

<b>Table 4: Size distribution (percent) and screening efficiency of stickies in the presence of pulp</b>					
	<b>total sample</b>		<b>Pulmac accepts</b>		<b>Pulmac rejects</b>
<b>no. of sparks:</b>	<b>0</b>	<b>80</b>	<b>0</b>	<b>80</b>	<b>0</b>
<b>size range (<math>\mu</math>)</b>					
0-50	15.9	10.0	2.8	11.8	14.8
50-70	2.2	15.4	15.0	6.1	2.9
70-80	4.4	6.0	18.6	12.1	4.5
80-90	3.2	6.1	5.1	4.0	2.7
90-100	3.3	6.8	5.7	9.8	2.5
100-200	27.0	33.2	38.8	30.6	6.7
200-300	10.3	10.0	9.1	14.5	7.2
300-400	9.5	2.9	3.0	5.1	15.9
400-500	9.2	2.6	1.5	3.0	12.3
500-1,000	15.1	6.9	0.4	3.0	30.6
<b>cumulative per-centile at 150 <math>\mu</math></b>	<b>44.1</b>	<b>64.4</b>	<b>74.2</b>	<b>62.6</b>	<b>30.2</b>
total counts	1,424	1,097	472	297	447
screen rejects (%) <sup>1</sup>	62.5	67.5			
<sup>1</sup> screen rejects were 57 percent in the absence of pulp					

Table 5: Effect of sparking on stickie characteristics.								
	Abitibi				Westvaco		Superior Paper	
	fine screen rejects		coarse screen rejects					
consistency (%)	0.1		1.2		1.6		1.6	
control (rejects %)	2.5 ± 0.3		0.8 ± 0		0.4 ± 0		3.9 ± 0.1	
80 X (rejects %)	4.5 ± 0.6		0.8 ± 0.1		0.5 ± 0		3.6 ± 0	
	distribution (percent)							
size (μ)	control	80X	control	80X	control	80X	control	80X
150-200	13	15	14	14	8.1	7.7	15	11
200-300	33	41	37	36	28	29	28	26
300-400	24	15	16	17	22	20	13	16
400-500	8	10	8.9	12	14	13	8.1	9.2
500-1000	21	16	20	16	22	26	24	28
>1000	1	3.4	4.4	4.1	5.2	4.9	12	9.8
total stickie count	100	120	338	334	1,115	1,131	2,214	2,423

sparked, processed through a Pulmac, and the size distribution of the Pulmac accepts and rejects (> 150 μ) was measured. The screenability increased by 5% (Table 4), which is similar to the value obtained in Table 3. The size of the stickies appeared to decrease somewhat on sparking.

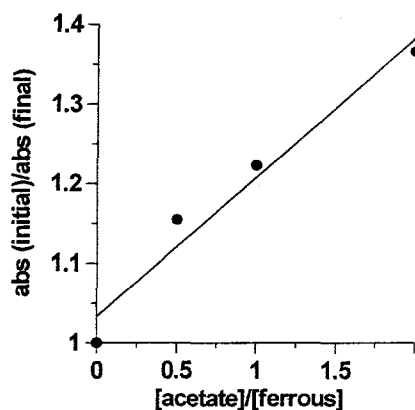
#### ***Screenability of mill stickies***

The screenability of stickies from Abitibi Consolidated, West Tacoma (fine screen and coarse screen rejects), Westvaco, Tyrone, PA, and Lake Superior Paper, Wisconsin, was tested. The samples were first screened through a 0.01" (250 μ) flat screen to remove large contaminants. They were then sparked 80 times in duplicate in the 14 L tank, and processed through the Pulmac (0.006"). The results are summarized in Table 5. Sparking induced a 2% increase in rejects for the Abitibi fine screen sample, but did not affect the quantity of the coarse screen rejects. For the Westvaco reject, only a 0.1% increase in rejects was obtained. The Superior samples did not show an increase in rejection. However, many of the stickies were associated with fiber, and would be screened out with or without sparking, and the results are inconclusive. The effect of sparking on the size distribution of stickies was measured by staining and image analyzing the rejects streams from the Pulmac. The results are included in Table 5. The distribution is relatively unaffected by sparking.

#### ***Generation of hydroxyl radicals through sparking***

In order to establish that hydroxyl radicals were generated from sparking, the oxidation of Fe<sup>2+</sup> (0.625mM) was monitored in the presence of various amounts of sodium acetate. Each mixture was sparked 100 times in a 10L tank, and the Fe<sup>2+</sup> → Fe<sup>3+</sup> oxidation was followed at 350 nm (1). The results are provided in Figure 6. The rate of reaction of oxidation of Fe<sup>2+</sup>, k<sub>2</sub>, was found from the equation

$$A^0/A = 1 + k_1 [\text{sodium acetate}] / k_2$$

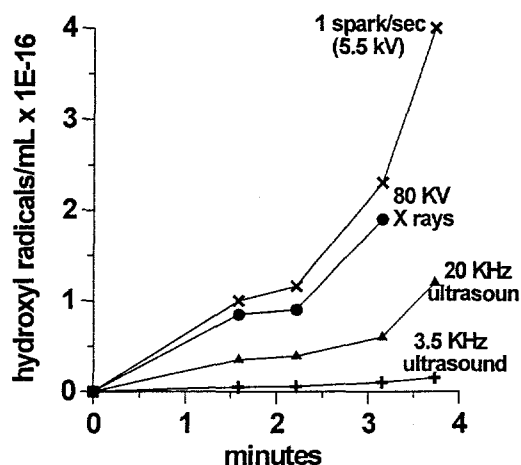


**Figure 6: Oxidation of ferrous sulfate and sodium acetate with hydroxyl radicals.**

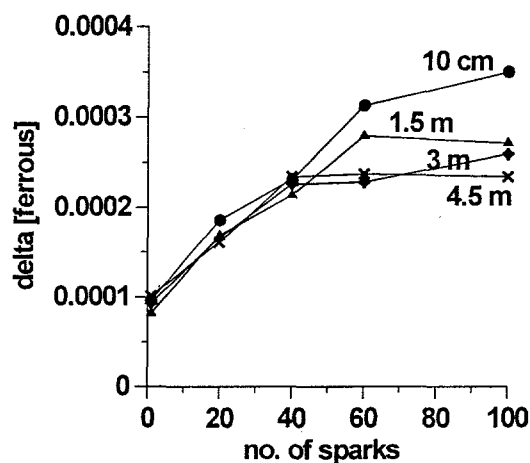
where  $A$  and  $A_0$  are initial and instantaneous absorbances, and  $k_1$  ( $0.085 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ ) is the rate constant for acetate oxidation by hydroxyl radical (2). A rate constant of  $4.86 \times 10^8$  was obtained for  $k_2$ , which compares well with the reported value of  $3.2\text{--}4.3 \times 10^8$  (3) for the oxidation of  $\text{Fe}^{2+}$  with hydroxyl radicals.

In order to compare sparking with other method for generating hydroxyl radicals, 10 L of water containing 1 mM each of  $\text{FeSO}_4$  and  $\text{NaCl}$ , and 0.4 M  $\text{H}_2\text{SO}_4$ , were sparked at 1 spark per second with samples taken at 0, 10, 20, 40, 60, 100, 150, and 200 sparks. The  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  oxidation was followed at 350 nm (1). The number of hydroxyl radicals was estimated at 25% of the total number of oxidized ion molecules (3). The results are compared to hydroxyl radical generation by ultrasound and by X-rays in

Figure 7, and show that sparking is a very efficient means of producing hydroxyl radicals.



**Figure 7: Comparison of hydroxyl radical formation through sparking and other means.**



**Figure 8: Change in  $\text{Fe}^{2+}$  concentration vs. sparks in 4,000 L of water.**

#### *Determining the oxidative range of a spark*

Water (4,000 L) containing 2.5 kg of ferrous sulfate was sparked in a 1-meter deep tank with the submersible sparker placed flush against the wall at one end. Samples were collected after 1, 20, 40, 60, and 100 sparks at distances of 0.01, 1.5, 3, and 4.5 meters away from the source at a depth of 10 cm from the surface. Their absorbance at 350 nm was taken immediately. The results, illustrated in Figure 8, show that the reactivity is independent of distance up to 40 sparks. Beyond this point, the oxidation decreased with increasing distance from the source. These results contrast with earlier studies, where the change in  $\text{Fe}^{2+}$  was fourfold greater than

when sparking is conducted in a 10 L tank. The difference is likely related to shock wave reflection, which will be greater in a smaller volume.

### ***Reproducibility of XPS analyses***

We had previously shown by XPS that the O:C ratio of the surface of an acrylate increased slightly upon sparking. In order to place the increase in perspective, we established the experimental uncertainty by coating a metal surface with a film of Carbotac, drying it, and analyzing five different regions by XPS. The results are listed in Table 6; our previous data are provided in Table 7. The differences in the O:C ratio induced by sparking are well outside the experimental error.

<b>Table 6: XPS results of five different areas of a Carbotac film.</b>			
<b>C</b>	<b>O</b>	<b>Si</b>	<b>O:C</b>
69.7	23.7	6.6	0.340
72.6	23	4.4	0.317
72.3	23	4.7	0.318
71.2	22.6	6.2	0.317
72.7	23.3	3.9	0.320
<b>average (sd)</b>			
<b>72 (1)</b>	<b>23.1 (0.4)</b>	<b>5 (1)</b>	<b>0.32 (0.01)</b>

<b>Table 7: Previously reported XPS results.</b>				
	<b>C</b>	<b>O</b>	<b>Si</b>	<b>O:C</b>
control	77.2	21.9	0.92	0.284
control	77.8	21.5	0.78	0.276
40X	74.5	24.1	0.70	0.324

### ***Mill trials***

Mills that showed real interest in a trial were G-P, Plattsburgh, NY (for pitch), Abitibi, Augusta, GA, and Visy Paper, Conyers, GA, the last two for stickies. The first trial will start at Visy Paper on April 20. The mill is only 30 miles away from our facility. A trial plan is being drawn up.

### ***References***

1. Price, G; Lenz, E. The use of dosimeters to measure radical production in aqueous sonochemical systems. *Ultrasonics*. 31(6):451-456 (1993).
2. Buxton, G. Rate constants for reactions of radicals in aqueous solution. *Journal of Physical Chemistry Reference Data*. 17(2): 682 (1988).
3. Jana, A; Chatterjee, S. Estimation of hydroxyl free radicals produced by ultrasound in Fricke solution used as chemical dosimeter. *Ultrasonics Sonochemistry*. 2(2): S87-91 (1995).