Replacing Chemicals in Recycle Mills with Mechanical Alternatives

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By

Howard Corcoran, Dong-Jin Sung, Feroz Kazi, Sujit Banerjee
Institute of Paper Science & Technology
Atlanta, GA 30318

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Executive Summary

A high-intensity spark fired underwater decomposes a small amount of the water into hydroxyl radicals, which are strong oxidants. These are able to oxidize contaminants such as glue and wood pitch that enter paper recycling mills as a part of the incoming furnish and cost the industry several hundred million dollars. The sparking technique is safe, inexpensive, and is capable of treating large volumes of water, which makes it attractive for mill applications. Several mill trials were run. Sparking caused a decrease in the tack of the deposits in one case. Lower bleach use occurred in two other mills; sparking reduced the degree of ink reattachment to fiber. The payback for either application is attractive. Sparking induced deposition of contaminants in another mill, which is a positive development - if it can be controlled. The technique is also able to degas water and to oxidize odor-causing sulfur compounds. Although one unit has been purchased by a mill, second-order effects caused by the technology needs to be defined further before the technology can be broadly applied.

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1. Introduction

In pulsed power a series of short high-intensity sparks is fired underwater. The technology is currently used to keep water intake piper free of zebra mussels. The paper industry has had one unit operating at the Georgia-Pacific, Plattsburgh, NY, mill for several years. The initial objective of this project was to explore other potential applications such as fiber refining, disinfection, and stickies dispersion. It turned out that the most effective use of the device was in the detackification of stickies (1-15) and pitch (16), and this report will describe this and other applications from initial laboratory studies through full-scale mill trials.

2. The equipment

The first trial was run at Pulsed Power Technology Inc. in San Diego, California, as per our proposal. However, Pulsed Power declined to be involved in a long-term developmental project, and we were able to interest Sparktec Inc., a company that manufactures and sells very similar technology. The Sparktec unit is illustrated in Figure 1. The white unit is the submersible electrode; the darker pieces are capacitors. The cost of the unit is about $65K, and the electric power costs (assuming continuous use) is minimal at about $2,000 per annum. Figure 2 illustrates the sparker immersed in a 30-gallon tank where some of the experimental work was conducted. Experiments were also run in a smaller 2-gallon tank (with a smaller electrode assembly). This tank is constructed from a section of pipe, and is meant to simulate the effect of sparking in a flowing system. The two tanks are referred to in this report as the large and small tank, respectively.

The spark was characterized by Dr. C.R.Welch of the Army Corps of Engineers at Vicksburg, MS. It is of 50,000 amps, 6,000V, and of 5-300 µs duration. The pressure developed in open water at one foot from the source is 300-400 psi., and the speed of propagation is 5,000 fps. The spark converts the water between the electrodes into plasma, which generates a shock wave. Importantly for our application, oxidative species such as hydroxyl radicals are also created.

The pressure on the shock wave front was evaluated (17) from equation (1), where P_f is the pressure of the shock wave front, m is a dimensionless parameter (2.1 for water), ρ_o is the unperturbed density of water (0.997 g/cm^3), V is the velocity of water at the shock wave front, and V_o is the room temperature velocity of sound in water (1,460 m/s).

$$P_f = (1/m)\rho_o V (V-V_o) \qquad (1)$$

3. Stickie detackification

Two 316 stainless steel coupons (5.5 cm^2) were coated with 10 mL of an acrylate PSA and dried so that the stickie formed a thin surface film. The PSA used throughout this study was Carbotac latex from B.F.Goodrich (unless otherwise noted), which is widely used in the paper industry. One coupon was placed in the large tank at a distance of about 1 meter from the source and pulsed 30X with the stickie facing the spark. FTIR analysis of the stickie showed no changes before and after sparking. Microscopic examination revealed small cracks along the edges. However, the film was clearly less tacky to the touch, and the reduction in tack was supported by contact angle measurements, which were converted to surface energies to give the following results.

Figure 1: Illustration of the sparker.

Figure 2: Illustration of the sparker immersed in a 30-gallon reaction vessel.

before treatment:	15.7 dy/cm
after treatment:	22.9 dy/cm

A second trial was run with a larger set of coupons. Unless otherwise noted, the temperature was 15°C, and the pH was 7, with the coupon positioned at about 1.5 meters from the source, such that the stickie surface faced the spark. The results with the coupons in the large tank are listed in Table 1, and show that the surface energy increases, and the tack (as measured on an Instron instrument) decreases upon sparking. The surface energy results are similar for the samples positioned both facing and away from the spark, suggesting that the shock and the light associated with the spark are unlikely to be responsible. Hence, the oxidative species created by the spark probably cause the detackification. The effect seems to be insensitive to the distance of the sample from the spark, at least in the 10-50 cm. range. Sparking was also conducted in the presence of air bubbled through the system in two of the experiments, but the presence of air did not appear to affect the results. Tack reduction was especially high in whitewater or in the presence of hypochlorite. An experiment conducted with the stickie film prepared on blotting paper also showed an appreciable increase in surface energy, demonstrating that a solid support is not essential for detackification.

The effect of hypochlorite was further explored by immersing a PSA-coated steel coupon in 500 ppm sodium hypochlorite, and sparking 40 times in the small tank at pH 7 and at 45°C. A control without chlorite was also run. The results, shown in Figure 3, confirm that detackification improves in the presence of hypochlorite, further supporting a chemical basis for the process. A Polyken tack tester was used for this measurement and the others that follow from this point on. Hypochlorite should give rise to chlorine radicals, which are oxidative species. As will be discussed later, our present view of the mechanism is that detackification is caused by oxidation of the surface of the stickie by hydroxyl or other radicals. Measurements made in the smaller tank confirm the insensitivity of the results to distance from the electrodes, since the tack reduction in both the large and small tanks is roughly the same.

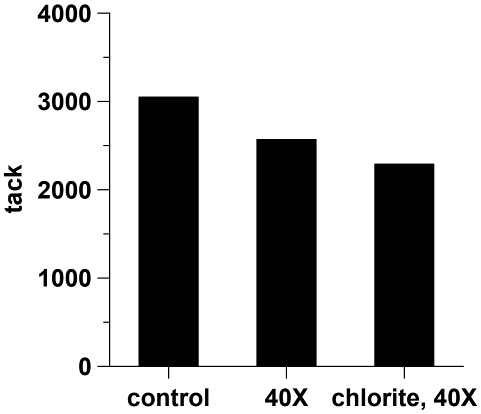

Figure 3: Effect of chlorite on tack (g/cm^2)

Table 1: Effect of sparking on PSA tack.			
conditions	**no of sparks**	**surface energy (dy/cm)**	**tack (psi)**
large tank, PSA on metal			
control		17.4	20.6
facing spark	30[1]	24.3	
control		18.5	17.5
facing away from spark	30[1]	27.8	9.41
air[3]	30[1]	27.4	7.76
close to spark	30[2]	26.5	8.64
close to spark	60[2]	22.7	12.2
air[3]	60[1]	30.2	5.8
large tank, PSA on fiber			
	30[1]	30	
small tank, PSA on metal			
	10[1]	28.8	11.7
	30[1]	26.7	9.03
	60[1]	27	9.78
whitewater[4]	30[1]	29.6	6.49
45°C	30[1]	24.4	6.27
45°C + hypochlorite[5]	30[1]	29.6	3.45
[1] 50 cm from spark; [2] 10 cm from spark; [3] air bubbled at about 3 lpm; [4] from Visy Paper, Conyers, GA; [5] a pinch of sodium hypochlorite was added in a preliminary experiment			

The effect of hypochlorite was further explored by immersing a PSA-coated steel coupon in 500 ppm sodium hypochlorite, and sparking 40 times in the small tank at pH 7 and at 45°C. A control without chlorite was also run. The results, shown in Figure 3, confirm that detackification improves in the presence of hypochlorite, further supporting a chemical basis for the process. A Polyken tack tester was used for this measurement and the others that follow from this

Table 2: Surface analysis of stickies.

		O:C ratio
polyacrylate	control, pH 7	0.28
polyacrylate	control, pH 7	0.28
polyacrylate	40X, pH 7	0.32
polyacrylate	40X, pH 7, 500 ppm hypochlorite	0.30
polyvinyl acetate	control	0.35
polyvinyl acetate	40X, pH 10	0.42

point on. Hypochlorite should give rise to chlorine radicals, which are oxidative species. As will be discussed later, our present view of the mechanism is that detackification is caused by oxidation of the surface of the stickie by hydroxyl or other radicals. Measurements made in the smaller tank confirm the insensitivity of the results to distance from the electrodes, since the tack reduction in both the large and small tanks is roughly the same.

3.1 Mechanism of detackification

Since the mechanism of detackification was believed to be chemical rather than physical in origin, a Fricke dosimeter (18), a $FeSO_4$ solution that responds to free radicals and other oxidants, was sparked in the small tank in three ways. The $Fe^{2+} \rightarrow Fe^{3+}$ transition was monitored spectrophotometrically at 350 nm. The small tank was first filled with the solution (0.175M), which was exposed directly to the sparks. The solution was then placed in 10 mL quartz or Pyrex tubes, which were then submerged in the tank and exposed to the sparks. The quartz tube contained a 0.175M solution, whereas a concentration of 0.1M was used in the Pyrex vessel. The absorbances of the resulting solutions measured after spark treatment are illustrated in Figure 4 and show that an absorbance increase was only realized for the open solution, indicating that it is the effect of chemical species and not the light that was responsible.

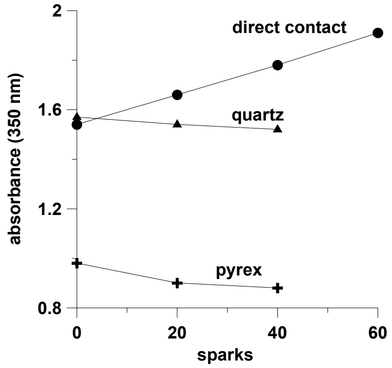

Figure 4: Effect of sparking on a Fricke dosimeter

In order to examine surface effects, the stickies listed in Table 2 were plated on metal coupons, sparked, and their surfaces examined by X-ray photoelectron spectroscopy, with an incident angle of 36°. As shown in Table 2, the O:C ratio increased in all cases. In order to determine the significance of the increase, *i.e.* the uncertainty in the O:C ratio, a metal surface was coated with a polyacrylate film, dried, and five different regions were analyzed by XPS. The results are presented in Table 3; the standard deviation is 0.01 units. Hence, the spark-induced differences in Table 2 are small, but significant.

Chlorine was detected at a level of 0.29% for the experiment run in the presence of hypochlorite; there was no chlorine found for the other cases. These measurements strongly suggest a free radical mechanism, with detackification caused by oxidation of the surface. This finding contrasts with previous work where chemical degradation caused by sparking was

Table 3: O:C ratios from five different areas of a PSA film.			
C	**O**	**Si**	**O:C**
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
average (sd)			
72 (1)	**23.1 (0.4)**	**5 (1)**	**0.32 (0.01)**

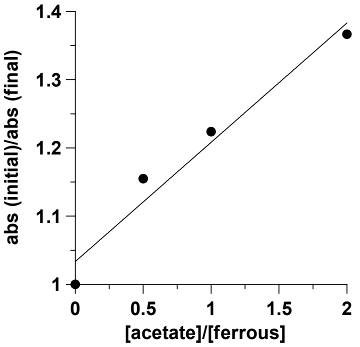

Figure 5: Oxidation of ferrous sulfate and sodium acetate with hydroxyl radicals.

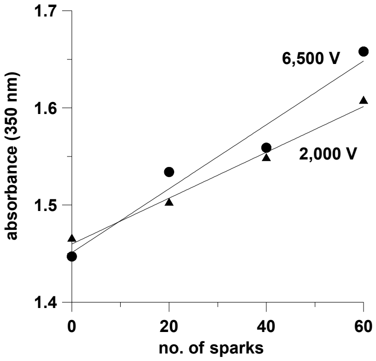

Figure 6: Effect of voltage on radical generation.

ascribed to photolysis (19). Finally, we reasoned that sparking in the presence of hydrogen peroxide might enhance the process by promoting radical generation. The presence of peroxide did increase the surface energy, but XPS analysis of the treated polymer showed that the O:C ratio remained unchanged at 0.30. This suggests that an increase in the O:C ratio is not an absolute requirement for detackification.

3.2 Generation of hydroxyl radicals through sparking

In order to establish that sparking produced hydroxyl radicals, the oxidation of Fe^{2+} (0.625 mM) was monitored in the presence of various amounts of sodium acetate by following the $Fe^{2+} \rightarrow Fe^{3+}$ conversion at 350 nm. Each mixture was sparked 100 times in a 10L tank; the results are provided in Figure 5. The rate of oxidation of Fe^{2+}, k_2, was found from the equation

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

where A and A_o are initial and instantaneous absorbances, and k_1 (0.085×10^9 L mol^{-1} s^{-1}) is the rate constant for acetate oxidation by hydroxyl radical (21). A rate constant of 4.86×10^8 was obtained for k_2, which compares well with the reported value of $3.2\text{-}4.3 \times 10^8$ (5) for the oxidation of Fe^{2+} with hydroxyl radicals.

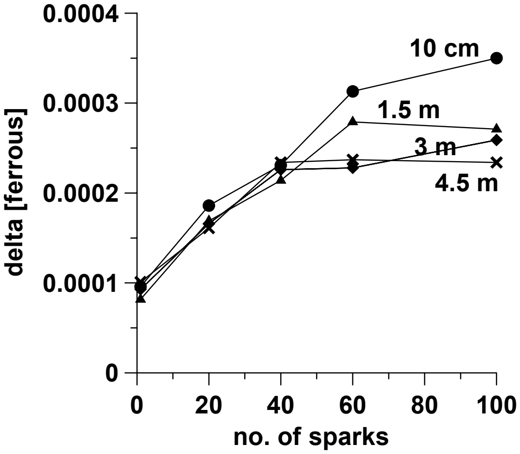

Figure 7: Change in Fe^{2+} concentration *vs.* sparks in 4,000 L of water.

3.3 Effect of voltage on hydroxyl radical yield

In order to determine how the applied voltage influenced the generation of hydroxyl radicals, a Fricke dosimeter, $FeSO_4$; 8.5×10^{-3} M (2) was sparked at 2,000 and 6,500 V. The results, presented in Figure 6, show that the two voltages lead to roughly similar increases in absorbance. Experiments with the dosimeter conducted in the 2.5 and 35-gallon tanks, showed that the resulting absorbance changes were very similar, suggesting that volume was not critical, at least over this range. Hence, the hydroxyl radicals are probably generated locally by the propagating shock wave, and not just in the plasma region.

3.4 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 7, show that the reactivity is independent of distance up to 40 sparks. Beyond this point, the oxidation decreased with increasing distance from the source.

3.5 Sparking PSA in the presence of other constituents

Our initial finding that sparking increased the surface energy of a PSA adhesive was confirmed and extended. The results of sparking PSA (cured as a film on a metal plate) under various conditions are reported in Table 4. Under most treatment conditions, the surface energy rose by 2 to 7 dynes/cm, which was smaller than that observed before. However, the surface energy of the control was also much higher, and we ascribe the lower tack reduction to the lower starting tack of the sample, caused possibly by differences in film thickness.

In an unrelated experiment with hydrogen peroxide, unbleached Kraft softwood pulp (kappa 75) was sparked 60X and 100X, in 3% hydrogen peroxide. Bleached fibers were seen after an hour in both the 60X and 100X sparked samples. Bleaching did not occur in the absence of sparking. Hence, sparking appears to enhance the oxidative ability of peroxide.

Table 4: Effect of sparking on the surface energy of PSA.[1]

	no. of sparks	surface energy (dynes/cm)	O:C ratio[2]
45°C	0	22.4	0.29, 0.30
45°C, towards spark	40	24.7	0.32
45°C, away from spark	40	25.4	0.32
45°C, 0.1% retention aid[3]	0	25.4	
45°C, 0.1% retention aid[3]	40	26.8	
45°C, 0.1% surfactant[4]	0	23.8	
45°C, 0.1% surfactant[4]	40	25.7	
22°C, 0.1% peroxide	0	22.3	
22°C, 3% H_2O_2	20	26	
22°C, 3% H_2O_2	40	27.5	0.30
22°C, 3% H_2O_2	60	26.6	
22°C	0	19.4	
22°C	40	25.7	
22°C	60	28.2	

[1] pH 7; [2] by XPS at an incident angle of 38°; [3] Tween 80, 1% in water; [4] Nalco 7655, 12.5% solids

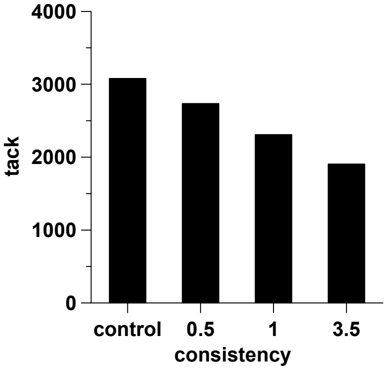

Figure 8: Effect of pulp consistency on tack

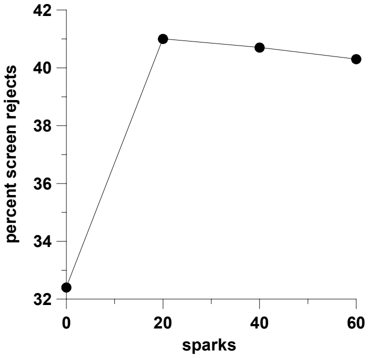

Figure 9: Effect of sparking on PSA screenability.

The presence of fiber did not interfere with tack reduction. Stainless steel coupons coated with acrylate as above were sparked 40X (45°C, pH 7) in the presence of a bleached softwood Kraft pulp suspension of different consistencies. The results, shown in Figure 8, demonstrate that the degree of detackification increases progressively with increasing consistency. However, since fiber was included on the surface of the film, the tack measurements could be compromised. Nevertheless, we can conclude that the presence of pulp does not detract from the efficiency of detackification.

3.6 Effect on stickie screenability

Since sparking appeared to modify the surface of the stickie, it seemed worthwhile to explore whether the screenability of a stickie would also be affected. Accordingly, we dried PSA, homogenized it, resuspended it in water to form a 1% suspension, and sparked it in the small tank. The results, shown in Figure 9, demonstrate that the rejects (as measured with a 0.006” screen) increased significantly after 20 sparks.

Next, a PSA emulsion was dried on glass plates and re-emulsified using a homogenizer with a small amount of sodium silicate surfactant. The emulsion was diluted to 0.5% by weight in water, and sparked. Samples were run through a Pulmac shive analyzer with a 0.006” (150 μ) screen. The rejection percent increased from 59.1 (control) to 61.4 (40X) and 70.5 (60X). The value for the control is higher than that in Figure 9 because of differences in the degree of homogenization. The above experiment was repeated in the presence of bleached kraft pulp of 1% consistency. The rejection percent was 59.1 (control), 61.3 (40X), and 63.4 (60X). Although the rejection efficiency dropped somewhat in the presence of pulp, the improvement in screenability was still significant.

In more detailed follow-up work, cured PSA was mechanically homogenized in acetone. Water was added to the suspension, which was allowed to equilibrate, and most of the solvent was removed. More water was added and the process was repeated several times to wash out the acetone. Mixtures of bleached softwood pulp (0.1, 1.0, and 2.0 % consistency) and stickie (0.1% by volume of water) were sparked 50 times in a 2.5-gallon tank, and the rejection percentage determined with a Pulmac analyzer fitted with a 0.006” (150 μ) screen. Prior to sparking the stickie suspension was filtered through a black filter paper and image-analyzed (with an ImagePro system) to determine the size distribution. A total of 1,300 particles were counted; the results are provided in Table 5.

The results of the screening experiments are provided in Table 6. The final column is the percentage reduction of stickies in the accepts stream after sparking. The initial screen rejects increase with consistency due to stickie-fiber agglomeration. Although the rejects increase after sparking, the improvement is *nominally* quite small. However, the actual improvement is much better as per the following analysis. It can be seen from Table 5 that half the stickies are less than 150 μ in size. The screening efficiency in the absence of pulp is also 50%, which indicates that stickies of < 150 μ in size pass through. Now, the largest stickies will be rejected, regardless of whether or not they are sparked. Unfortunately this fraction is not known. If we estimate that stickies of size greater or equal to 350 μ (twice the slot width) are always rejected, then only one-third of the stickies are potentially treatable. If so, then the final column in Table 6 should be multiplied by a factor of three.

In order to determine whether sparking altered the size of the stickies, a 0.3% suspension of dried homogenized PSA in water was sparked, processed through the Pulmac, and the size distribution measured. The results, listed in Table 7, 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

Table 5: Size distribution of stickies prior to sparking.	
size range (μ)	**percent**
0-50	24.3
50-70	13.2
70-80	6.83
80-90	4.86
90-100	4.94
100-200	25.7
200-300	7.37
300-400	3.87
400-500	2.81
500-1,000	6.07

Table 6: Screening efficiency of stickies in the presence of pulp.

pulp consistency (%)	percent screen rejects before sparking	percent screen rejects after sparking	percent reduction in accepts stickies
0	50.6	53.1	5.1
0.1	59.2	61.4	5.4
1.0	59.4	59.6	0.5
2.0	71.7	73.0	4.6

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 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 8), which is similar to the value obtained in Table 7. The size of the stickies appeared to decrease somewhat on sparking. This suggests that the better screenability does not derive from a growth in the size of the stickie particles, but through an increase in the rigidity of the stickie surface.

Finally, 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 9. Sparking induced a 2 percentage point increase in rejects for the Abitibi fine screen sample, but the other samples were unaffected. However, many of the stickies were associated with fiber, and would be screened out with or without sparking, and these 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 9. Not surprisingly, the distribution is unaffected by sparking.

Table 7: Size distribution (percent) and screening efficiency of stickies in the absence of pulp.

size range (μ)	**total sample**		**Pulmac accepts**		**Pulmac rejects**
no. of sparks:	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
cumulative percentile at 150 μ	**71.4**	**72.6**	**79.8**	**86.2**	**67.2**
total count	3,202	1,775	3,036	2,971	725
screen rejects (%)	44.0	50.2			

Table 8: Size distribution (percent) and screening efficiency of stickies in the presence of pulp.

	total sample		**Pulmac accepts**		**Pulmac rejects**
no. of sparks:	**0**	**80**	**0**	**80**	**0**
size range (μ)					
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
cumulative percentile at 150 μ	**44.1**	**64.4**	**74.2**	**62.6**	**30.2**
total counts	1,424	1,097	472	297	447
screen rejects (%)[1]	62.5	67.5			

[1] screen rejects were 57 percent in the absence of pulp

Table 9: 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**

Table 10: 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

3.7 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 μ 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 10.

Figure 10 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

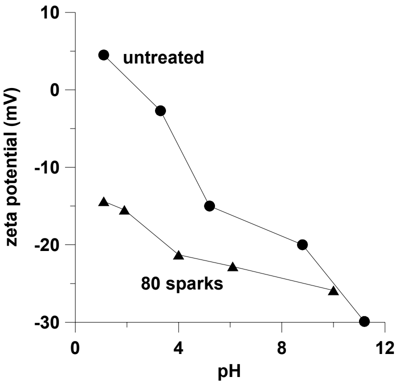

Figure 10: Zeta potential vs. pH plots for Carbotac.

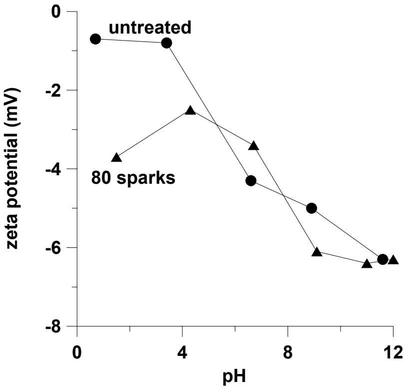

Figure 11: Zeta potential vs. pH plots for mill rejects.

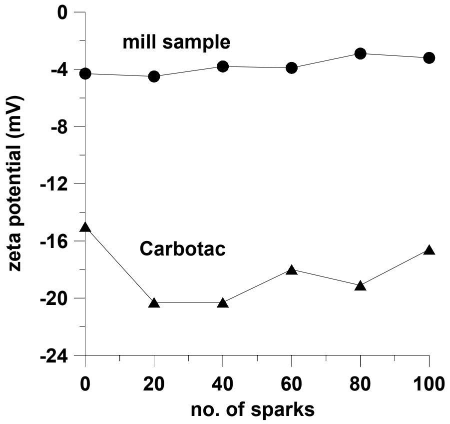

Figure 12: Zeta potential vs. no. of sparks plots for Carbotac PSA and mill stickies. The pH of the mill sample and Carbotac were 6.7 and 5.2-3.9, respectively.

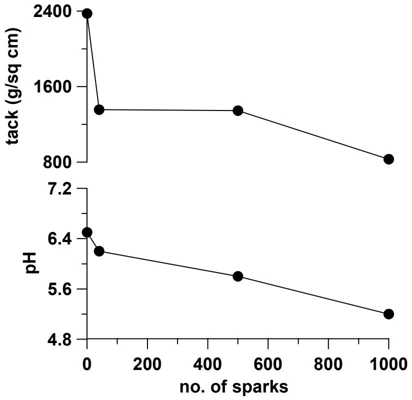

Figure 13: Tack and pH of sparked Carbotac films.

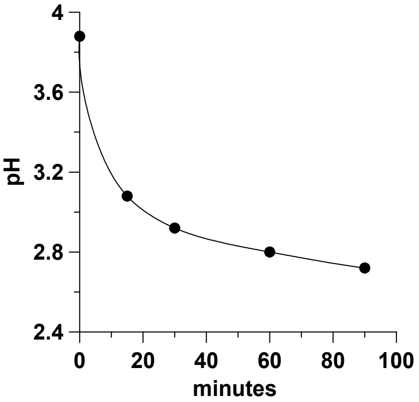

Figure 14: pH changes during sonication of a 1% Carbotac suspension.

groups at the surface, in keeping with our previous observations with methylene blue dye. Figure 11 shows corresponding plots for the mill rejects, 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 12 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 probably due to the increased dissociation of acidic surface groups.

The shift of the isoelectric point to lower pH in Figure 10 suggests the formation of acidic groups at the surface. This was confirmed by measuring surface pH of an acrylate film coated on a metal coupon as a function of the number of sparks. The results, provided in Figure 13, show that sparking reduces both tack and pH. Sonication leads to similar results; treatment of a 1% suspension of Carbotac (uncured emulsion) decreased pH as shown in Figure 14. The similarity of the effects of sparking and sonication is discussed in Section 4.

3.8 Effect of sparking on the zeta potential of whitewater solids

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 potential, mV (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 potential, mV (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)

4. Comparison of sparking with ultrasonic treatment

The above experiments implicate the hydroxyl radical or other oxidant as responsible for detackification. Since these species can also be generated by ultrasonic treatment of water (20), studies were conducted to determine whether detackification could also be induced by ultrasound. Stickies were treated in 200 mL of water in a 80W Branson ultrasonic bath operating at 50 kHz. A Fricke dosimeter was used to monitor free radical generation. Sonication of a 0.179 M $FeSO_4$ solution leads to the spectrophotometric changes shown in Figure 15. Radical generation is not the only process that generates Fe^{3+}; the other oxidants are believed to be species such as hydrogen peroxide, which can oxidize ferrous ion (4).

These results demonstrate that both sparking and sonication generate hydroxyl radicals, which are probably responsible for the detackification. This is likely in light of our observation that oxygen is incorporated on the stickie surface. The spark creates a plasma channel between the electrode gap. The energy released upon collapse of the channel is dissipated as heat, light, and through an acoustic field. Thus, underwater sparking can induce the same chemical reactions achieved through sonochemistry. However, ultrasound heats the medium, which makes it expensive for industrial use. The range of the sparker is quite large, since hydroxyl radicals are generated locally by the moving sound wave.

Sparking attacks the stickies and leaves the other constituents unaffected, and on the surface, this suggests that sparking is selective for stickies. The opposite is true. Hydroxyl radicals are very reactive, and reactive species are not selective. However, the concentration of hydroxyl radicals needed to deactivate the surface of a stickie is small, since the “concentration” of a stickie surface is very small compared to the concentration of the other species present. These species must also react with the hydroxyl radical at rates comparable to those for the stickies, but the amount reacted is too small to be detectable. The proportional impact on the stickies is much greater since the stickies are present in such small quantities.

4.1 Detackification caused by sonication

A suspension of Carbotac acrylate latex was dried on stainless steel coupons and sonicated. Coupons were removed periodically, and the tack and the bath temperature were recorded. The results, presented in Figure 16, show a clear decrease in tack upon sonication. In order to verify that the decrease was not a consequence of the increasing bath temperature, acrylate-loaded coupons were exposed for 10 minutes to water at different temperatures. The results, shown in Figure 17, demonstrate that tack increases somewhat with temperature, as expected.

In order to determine whether sonication altered the screenability of acrylates, the acrylate was dried on a glass plate, peeled off, homogenized, and resuspended in water containing 1.6 weight percent of sodium silicate surfactant. The suspension was processed through a Pulmac shive analyzer with a 0.006 inch screen, before and after sonication for 40 minutes. The stickies retained in the collection basket were transferred to a pre-weighed filter paper, and dried. The effect of sonication on screenability was substantial; the amount rejected increased from 55 (56, 56, 53) to 80 (78, 83, 79) percent of the initial load. Given the parallel between sonication and

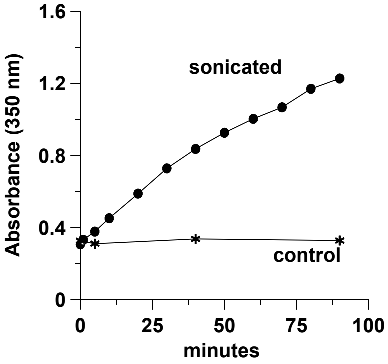

Figure 15: Absorbance changes upon sonication of $FeSO_4$.

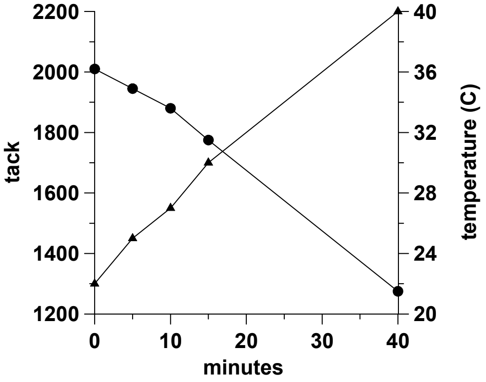

Figure 16: Effect of sonication time on tack (g/cm^2).

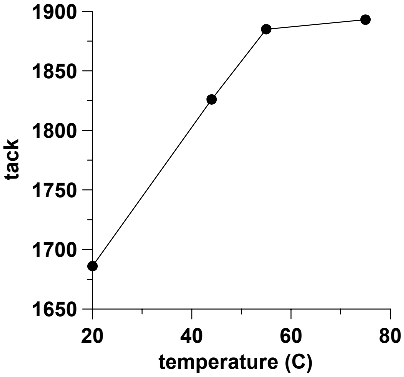

Figure 17. Effect of temperature on tack (g/cm^2).

sparking, our working hypothesis is that both processes create hydroxyl radicals through cavitation, which then oxidize the stickie surface.

4.2 Ultrasonic treatment of polyvinyl acetate

Sparking increases the surface energy of polyvinyl acetate (PVAc). In order to determine whether a similar effect could be induced by sonication, the stickie was dissolved in acetone (1:2 w/w), coated on a metal coupon to a thickness of about 0.1 mm., and sonicated for 40 minutes. No change in surface energy was observed for a PVAc of MW: 500,000. However, the room-temperature surface energy of a MW: 12,800 PVAc increased from 38.8 to 44.1 dyne/cm.

4.3 Effect of sparking and ultrasonic treatment on other acrylates

In order to explore the effect of sparking on other acrylates, four pure polymer films were formed on metal plates and sparked in a 2.5-gallon tank. Three samples showed a 5 dynes/cm increase in surface energy upon sparking (Table 11); the fourth was essentially unchanged. The O:C ratio was measured by XPS for two samples; both were unchanged. We interpret the results

Table 11: Effect of sparking on the surface energy of PSAs.			
	no. of sparks	**surface energy (dynes/cm)**	**O:C ratio**
poly(iso-butyl acrylate)	0X	10.1	0.31
poly(iso-butyl acrylate)	40X	15.9	0.31
poly (n-butyl acrylate)	0X	7.2	
poly(n-butyl acrylate)	40X	13.7	
poly(lauryl-acrylate)	0X	8.5	
poly(lauryl-acrylate)	40X	13.2	
poly(methyl styrene-co-indene)	0X	16.5	0.02
poly(methyl styrene-co-indene)	40X	15.5	0.02
[1]at 22°C, pH7; [2]run by XPS at an incident angle of 38°.			

Table 12: Effect of sonication on various acrylates.				
	surface energy (dynes/cm)		**tack (grams per 0.2 cm^2)**	
	control	**treated**	**control**	**treated**
poly(2-ethylhexyl acrylate)	8.5	8.8	514	503
poly(iso-butyl acrylate)	11.4	23.2	>2,000	1774
poly(lauryl acrylate)	7.4	17.1	660	512
poly(n-butyl acrylate)	7.0	12.2	908	643
poly(isoprene)	12.8	21.2	457	342
polymethyl styrene-co-indene	15.8	29.3	not tacky at room temp	

to indicate that the process applies to acrylates other than to just Carbotac, but not to all polymers. Again, an increase an increase in O:C ratio does not appear to be essential.

The results of experiments where the acrylates were sonicated for 40 minutes are provided in Table 12. Tack was measured with a Polyken tack tester on a 0.2 cm^2 surface at a 100 g/cm. contact pressure, 1 second contact time, and a 1 cm/sec withdrawal speed. The surface energy increased in all cases. A point of contrast is the behavior of poly(methyl styrene-co-indene) which is relatively unaffected by sparking, but is passivated by ultrasound. These measurements indicate that detackification is not universal, but depends upon the chemical structure for reasons that are presently unknown.

4.4 Sonication of stickies in the presence of pulp

Carbotac PSA was coated on 4.5 x 4.5 cm paper coupons (bleached softwood Kraft) at a level of 0.5 g/coupon. The coupons were sonicated in water and also in bleached pulp at 1.1% and 2.2% consistency. The tack decreased substantially from 365 (control) to 247 (in water),

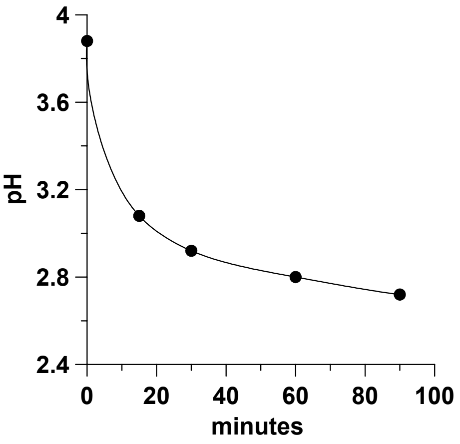

Figure 18: pH changes during sonication of 1% Carbotac.

290 (1.1%), and 240 (2.2%) grams/0.2cm^2. Hence, the presence of pulp does not significantly affect the decrease in tack induced by sonication.

In order to confirm that pulp did not inhibit radical generation, a 0.02M $FeSO_4$ solution was sonicated in the presence of 1.1% fiber. After 40 minutes, a handsheet (A) was made from the treated sample. Another handsheet (B) was made by sonicating the $FeSO_4$ (without fiber) and mixing it with untreated fiber, and a third (C) was prepared by mixing untreated chemical and fiber. There was a difference in color in the three handsheets. The color of handsheets A and B were a darker yellow as compared to that of handsheet C. Brightness measurements (TAPPI Test Method T-452) showed that handsheets A and B to be of 55 and 56 percent brightness, respectively, whereas the brightness of handsheet C was 60 percent.

4.5 Oxidation of aldehyde groups during sparking and sonication

Detackification of the polymer surface is probably caused by oxidation, and we thought it likely that the hydrocarbon groups would be converted to aldehyde functionalities. We treated 1 mL of a PSA emulsion (Carbotac) with Schiff's reagent (0.1 mL) before and after ultrasonic treatment. This reagent turns purple in the presence of aldehydes. The initial emulsion turned purple indicating that aldehydes were present in the original formulation. The emulsion was coated on metal coupons, dried and sparked 0, 40, and 60 times at 5,000 V, after which a drop of Schiff's reagent was added to the surface. No color change occurred over 2 hours, probably because the reagent was unable to diffuse through the stickie surface. However, purple spots appeared on the surface after 24 hours.

The PSA emulsion was then coated on 3 x 1 inch strips of bleached softwood pulp at a level of 0.3 g/strip and dried at 100°C for 12 hours. Some of the emulsion penetrated into the body of the paper. The strips were sonicated for 2 hours at 22°C, and re-dried at 100°C for 12 hours. They were then treated with Schiff's reagent for 30 minutes. While the initial strips contained aldehydes, the more highly sonicated strips did not, suggesting that the aldehydes initially present in the formulation were oxidized to carboxylic acids.

Table 13: Effect of sparking on contact angle and pitch detachment.

no. of sparks	contact angle	percent of pitch detached
0	73.3	0
10	70.6	0
20	69.5	10
50	69.2	20
100	70.6	30

Table 14: Effect of sparking on tack.

	tack (grams)				
temperature (^{o}C)	0 sparks	10 sparks	20 sparks	50 sparks	100 sparks
35	38	24	20	23	22
36.3	44	42	30	35	25
36.8	78	89	34	35	41
37.5	93	90	53	42	54
38.4	128	119	94	44	81
39.5	209	120	124	50	108
40	280	212	176	67	108
41	384	300	235	86	110
43	430	354	301	119	159
44	516	603	499	144	190
46	637	660	680	238	200
51	642	750	808	353	286
57	660	751	936	445	458
65	1315	1315	1070	1062	802

Sparking led to similar results. A Carbotac emulsion was coated on 3 x 1 inch strips of bleached softwood pulp at a level of 0.3 g/strip, and dried at 100^{o}C for 12 hours. The strips were sparked up to 150 times at 5,000 V, and dried at 100^{o}C for 12 hours. They were then treated with Schiff's reagent for 30 minutes. Aldehydes were initially present in Carbotac as indicated by the purple color, but the color faded as the samples were sparked.

In order to confirm that sonication led to oxidation, the pH of a Carbotac suspension was monitored during sonication. The results, presented in Figure 18 demonstrate the formation of acidic species, indicating that the aldehydes initially present in Carbotac are removed through sonication, probably through oxidation. Hence, both sparking and sonication appear to induce oxidation of the polymer surfaces.

5. Effect of sparking on pitch

A pitch sample was collected from Georgia-Pacific’s Vienna, GA, particleboard mill as a deposit taken just after the dryer. The material was ground, heated, and then coated on 2 x 2 inch metal coupons. The coupons were sparked at room temperature up to 100 times at 5,000 V (50,000A) at a 1-inch distance from the spark gap. Since the pitch was not tacky at room temperature, changes in the surface properties were measured through contact angle at room temperature, and tack measurements at higher temperature. The contact angle results are presented

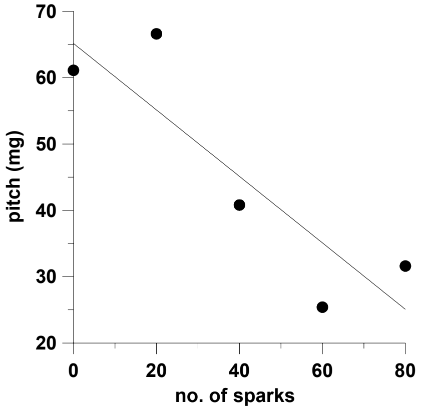

Figure 19: Effect of sparking on pitch deposition.

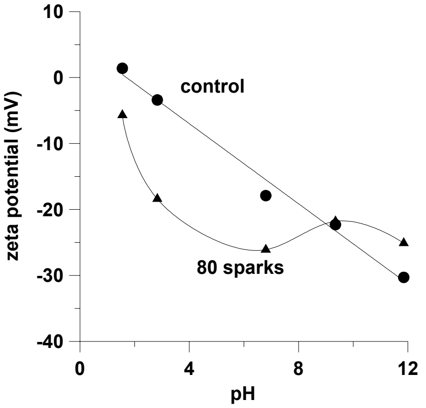

Figure 20: Effect of sparking on zeta potential.

in Table 13. The effect is marginal, probably because surface wettability is relatively unchanged. Some of the pitch detached from the coupon during sparking, and an estimate of the amount removed is included.

Tack measurements with a Polyken tack tester were made after the coupon was immersed in boiling water for 10 seconds to make it tacky. Readings were taken as the coupon cooled, with the surface temperature being monitored with a thermocouple. The results, listed in Table 14, demonstrate a substantial reduction in tack at the higher temperatures.

Pitch deposition measurements were then made to evaluate the extent of detackification. 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. The pitch was ground with a mortar and pestle, homogenized, and suspended at 0.3% consistency in 500 mL of 50^{o}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^{o}C for 15 minutes, and weighed. Replicate experiments conducted without sparking showed the uncertainty to be ± 4.2%. The results, shown in Figure 19, clearly demonstrate that sparking dramatically reduces the extent of deposition. Changes in zeta potential induced by sparking are illustrated in Figure 20. 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 15. The overall particle size is reduced indicating that sparking has a dispersive effect. However, the smallest size fraction appears to have agglomerated into larger particles upon sparking.

6. Mill trials and related studies

6.1 Trials at Visy Paper

A full-scale trial was run for five weeks during April/May 2000 at Visy Paper, Conyers, GA. The mill (850-1,000 tpd) makes liner (80% MOW, 20% OCC) and medium (25% MOW,

Table 15: Effect of sparking on the size distribution of pitch		
size range (μ)	**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}, (μ)	133	111

Table 16: Effect of sparking on brightness		
sparks	**Robond 90**	**Carbotac**
0	61.55	16.13
10	61.23	22.23
30	56.22	29.67
50	60.06	37.66
100	63.19	38.85
150	60.47	41.24

75% OCC). It pulps at pH 7.2 in a Black Clawson high density pulper, and it has primary through tertiary cleaners and coarse and fine screens. Kneading is used to disperse the stickies. No chemicals are used for stickies control. The major stickies-related problem is build-up on the dryer felts.

The sparker was submerged in the stuff box and run semi-continuously at 0.5 sparks per second. It was shut of when the machine went down. The noise of the sparker was negligible, since it was muffled by the pulp. The only maintenance required was an electrode change every 7-10 days which required 10 minutes. No effect was observed on the instrumentation and on product quality. We attempted to measure the stickies in the filtrate in the stuff box, but they were too few in number to allow quantitation. Over 99% passed through a 0.006” screen, and staining the rejects proved inconclusive. As a result, we developed a new tack test.

A sample was taken from the stuff box at Visy prior to the sparker unit being activated. A subsample was sparked 80 times, and both treated and control samples were filtered, and the filtrate (700 mL) dried to 5 mL over 4-5 hours. One or 5 mL of the concentrate was then coated on a metal coupon, and dried at room temperature overnight. These are referred to as the “thin” and “thick” film, respectively. The sample coating was a dark brown soft solid. The coupon was immersed in warm (60^{o}C) water for 10 seconds, and a tack measurement was made immediately with a Polyken tack tester. Warming the coupon was necessary, since the coupon was not very tacky at room temperature. The results are as follows:

thin film
control: tack (g): 107, 98, 102, 109, 114, 104, 112; **avg = 107 ± 6**
sparked: tack (g): 82, 75, 86, 80, 72, 57, 43; **avg = 71 ± 15**

thick film
control: tack (g): 238, 229, 200, 214, 268; **avg = 230 ± 30**
sparked: tack (g): 156, 157, 155, 156, 161, 159, 154; **avg = 157 ± 2**

Clearly, a significant decreases occurs upon sparking. The loss in tack of about 30% compares well with that obtained when a film of Carbotac is sparked. The results from the trial are provided in Table 17.

The overall results are summarized in Figure 21. The shaded region represents the time when the unit was on. The first downtime occurred when the sparker was shut off incorrectly, and the instrument had to be reset. The second occurred when the paper machine went down, the sparker unit was not shut off and sparking occurred in air, and some of the wires were burned. The third occurred accidentally. The tack values from Table 17 are included in Figure 21. No consistent trends can be identified because of the high value observed on day 19. The incoming furnish varied considerably, and the high value could represent a stickie surge. The asterisks represent the occasions when the felts were cleaned. Cleaning was difficult initially, but the first three cleanings were much easier since the sparker was running. The next cleaning was, again, difficult, since the sparker was only on briefly in the interim. The final two cleanings were, again, easier. Cleaning was consistently difficult after the end of the trial.

The mill subsequently rented a unit for a three-month trial. The sparker was installed on Oct 16, 2000 in a tank that was part of the whitewater system. The spark rate was once every 6 seconds. Once again, the deposits were easier to clean. However, since the felts are cleaned “opportunistically”, *i.e.* when the machine goes down for other reasons, a savings in downtime is not routinely realized. The mill reported a casual observation that the stickies in the calender stack increased. This suggests that more of the stickie was being removed with the paper, which would follow if the stickies were detackified. Only the stickies at the surface of the paper would deposit on the calender stack, which must mean that stickies in the interior of the sheet were being removed with the product.

The mill purchased the unit, but in the absence of quantitative measures, hard benefits were difficult to establish. A of this writing, the unit has been shipped to its parent company in Australia for further trials.

6.2 Trials at Augusta Newsprint

The fiberline used makes 850 tpd with a 35% recycle (83% ONP, 15% OMG) furnish. It has forward and reverse cleaners, and uses 0.005” slotted screens. On 9/11/00 the sparker was placed in silo tray water that dilutes thick stock feed to the fan pump. It was turned off on

Table 17: Tack values of the filtrate at Visy paper		
date	**tack (g)**	**avg tack (g)**
control (4.28)	332, 306, 290, 296	310 ± 20
4.30	250, 266, 320, 295	280 ± 30
5.8	209, 240, 257, 236	240 ± 20
5.12	199, 235, 240, 251	230 ± 20
5.15-5.18	off	
5.18	623, 783, 722, 752, 552, 772	700 ± 100
5.20-5.21	off	
5.27-5.29	off	
5.29	496, 361, 423, 497, 466, 342	430 ± 70

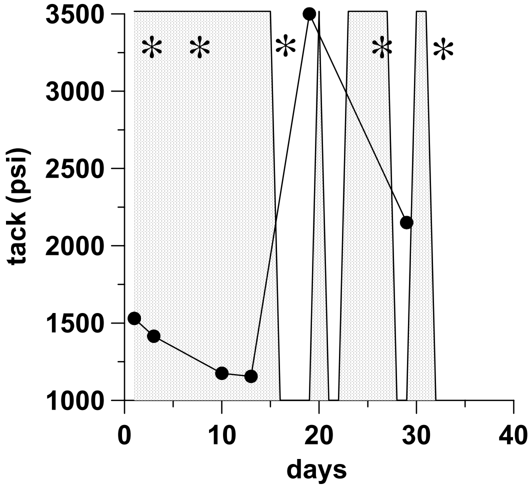

Figure 21: Overall results from the Visy mill trial.

9/14/00 because of a short, and was returned to service on 9/20/00 just after a boilout. It was then turned off on 9/24/00 because the #1 Paper Machine Crew reported atypical material at the Johnson screens (final stage vibrating screens). Material began to deposit in very small quantities on the previous day and then built up significantly. It was suspected that the material was plugging the primary stage cleaners. The substance was insoluble in sulfuric acid, caustic, acetone, boiling water, or kerosene. It was brown to gray in color and contained a significant clay component (12.5% ash). It crumbled under moderate pressure, and although it was denser than water, it was (inexplicably) accepted at the primary stage cleaners. FTIR analysis showed that it was composed primarily of ground wood fines with some kaolin clay and wood extractives that were probably pitch. The residue after ignition was identified by FTIR spectroscopy as a sodium silicoaluminate. No deposits were found at the #2 machine.

Table 18: Formation of hard aggregates from various mixtures.							
fines (OD %)	**PVAc (%)**	**Clay (%)**	**Pitch (%)**	Alum (%)	**DADMAC (ppm)**	**pH**	**hard aggregates**
0.1	0.05	0.26	1.16	0.26	44	4.2	yes
0.1	0.05	0.35	1.16	0.43	44	4.1	no

The sparker was moved to the RNP cloudy acid filtrate chest on 10/24/00. The spark rate had inadvertently dropped to one event every 20 seconds. The rate was increased to once every 6 seconds on November 11. On November 16 the secondary fine screens (0.006 slots) were plugged with a material of the same color and texture as that described above. The contamination in the screen basket could not be removed with high-pressure water. While the mill found the development to be "fascinating", and indicated that the device may eventually "revolutionize the way newsprint mills manage stickies and pitch" it could not afford further surprises and terminated the trial. It is open to additional trials, but only after we understand the process better.

An attempt was made to reproduce the deposition observed at Augusta in the laboratory. A 7 L sample from the silo was filtered and sparked 400 times. A deposit occurred which corresponded to a TSS value of 14 ppm, with an ash content of 64%. However, deposits (TSS 8.7 ppm, 95% ash) were also formed when distilled water was sparked; these were iron particles removed from the electrode. Hence, sparking leads to deposition of about 5 ppm of organic material. A similar experiment was run with a whitewater sample from Visy Paper, which was sparked 200 times. A deposit (TSS 18.5 ppm, ash 40%) was observed. This corresponds to about 11 ppm of solid organic matter. No agglomeration into larger particles were observed.

Several attempts were made to reproduce these deposits in the laboratory by mixing the mixture under shear before and after sparking. While deposits were occasionally obtained, they were soft and pliable. Finally, fines collected from the acid silo at Augusta were sparked (200 times), mixed with polyvinyl acetate (PVAc), clay, pitch, alum and DADMAC and the mixture agitated at 1,000 rpm for one hour. Hard aggregates were obtained on one occasion as shown in Table 18.

Since deposits only form in the presence of alum, it appeared that sparking makes the fines more negative and enhances the bonding between alum and fiber. In order to confirm this, the effect of sparking on the charge density of fines was measured. SSC pulp was refined in a valley beater for 45 minutes, and the fines 1.0 g (OD basis) dispersed in 10 L of DI water. An 8 L aliquot was sparked, and sample (10 mL) was drawn periodically and mixed with 20 mL of positively charged DADMAC (0.0001M). A drop of 0.1% toluidine blue-O was added. The mixture was back-titrated with PVSK (0.0001M), and the negative charge in each sample was calculated. The results are presented in Table 19. Surprisingly, sparking DI water alone also led to appreciable consumption of PVSK. This is probably a result of the iron released from the electrodes during sparking. The "charge" in DI water was subtracted from that of the fines. The results demonstrate that sparking induces a negative charge on fiber, probably through partial oxidation of the fiber surface.

Table 19: Effect of sparking on the charge density of fines.

sparks	fines		DI water		fines (net)
	charge (meq/10L)	pH	"charge" (meq/10L)	pH	charge (meq/g)
0	-0.098	5.33	-0.059	5.25	-0.039
50	-0.196	4.69			
60			-0.166	4.41	
100	-0.343	4.36	-0.235	4.35	-0.108
200	-0.588	4.21	-0.372	4.23	-0.215
400	-0.979	3.95	-0.646	3.90	-0.333

Table 20: Effect of sparking on the zeta potential of fines.

sparks	pH	zeta potential (mV)
0	6.27	-24.90
50	5.07	-21.83
100	4.52	-21.48
200	4.48	-21.43
400	4.10	-20.70
0	4.07	-21.00
50	4.08	-19.14
100	4.08	-18.27
200	3.98	-18.50
400	3.77	-18.60
0	10.07	-21.30
50	9.96	-22.86
100	8.82	-22.50
200	9.70	-23.35
400	9.55	-25.44

Zeta potential was also measured by first diluting NSSC fines with DI water to a consistency of 0.01%, and adjusting pH with 20% H_2SO_4 or 50% NaOH. An 8 L aliquot was sparked and samples were collected periodically, and analyzed for pH, particle size and zeta potential. The results are reported in Table 20. The results are ambiguous under acidic conditions since the pH changed to a greater-than-expected degree. Hence, any change in zeta potential caused by sparking is offset by a corresponding change induced by the decrease in pH. The zeta potential drops under alkaline conditions, which is consistent with oxidation at the particle surface.

The effect of sparking each of the several components that made up the aggregate was now determined. Fines collected from the paper machine #1 silo at Augusta were brought to 0.25% consistency with DI water. Calcined kaolin clay, alum, and resin (collected from the dryer section of a veneer mill) were added to the sample at a fiber (OD): clay: alum: resin ratio

Table 21: Effect of sparking and agitation on solids deposition.

	TSS (ppm)	impeller deposits (ppm)	zeta potential (mV)
control (no sparks, no agitation)	5,010		+14.03
agitated, no sparks	5,570	3.9	+10.73
400 sparks + agitation	5,080	19.6	+9.60

Table 22: Effect of sparking on clay at various pH values.

clay: 0.01%			clay: 0.05%		
sparks	**pH**	***zeta potential (mV)***	**sparks**	**pH**	***zeta potential (mV)***
0	6.93	-23.3	0	7.02	-23.7
50	6.77	-23.3	25	7.00	-23.3
100	6.62	-23.4	50	6.89	-23.6
200	6.44	-23.7	100	6.78	-24.1
400	5.93	-24.4	200	6.52	-24.1
			300	6.35	-24.8
			400	6.23	-25.6
0	4.88	-25.9	0	4.88	-25.9
50	4.59	-26.4	50	4.59	-26.4
100	4.54	-26.6	100	4.54	-26.6
200	4.35	-27.0	200	4.35	-27.0
400	4.23	-27.3	400	4.23	-27.3
0	9.35	-26.9	0	8.94	-25.5
50	8.96	-27.3	50	8.47	-25.9
100	6.96	-28.5	100	7.36	-25.6
200	5.56	-29.6	200	6.92	-25.6
400	5.00	-30.7	400	6.45	-26.2

of 2:1:1:1. The resin is meant to simulate pitch. The pH of the sample was adjusted to 4.4. A 7.2 L portion of the solution was sparked 400 times at 4.25 kV. A 2 L aliquot of sample was then agitated in a BioFlo reactor at 1,000 rpm for 1 hour at 50^{o}C. The agitation tends to agglomerate the stickies and deposit them on the impeller. The TSS (total suspended solids) was measured as was the quantity of the material deposited on the impeller. Agitation alone (without sparking) increased TSS and induced some deposition as shown in Table 21. This is because the larger particles are deposited through shear, and the remaining (smaller) particles have a lower zeta potential. Sparking increased the amount deposited on the impeller and further decreased the zeta potential slightly.

The increased deposition probably occurs because sparking made the pitch more negative and increased its association with the positive alum present in the system. By this logic the

Table 23: Effect of sparking on zeta potential of suspended pitch.

sparks	pH	zeta potential (mV)
0	5.51	-28.1
50	4.52	-32.9
100	4.38	-33.0
200	4.36	-34.6
400	4.28	-35.9
0	4.18	-19.9
50	4.09	-29.0
100	4.09	-33.2
200	4.05	-36.0
400	3.98	-38.3
0	9.52	-48.6
50	7.85	-52.7
100	6.55	-56.0
200	5.31	-58.5
400	5.07	-60.2

sparker should be placed before the screens and cleaners to increase the likelihood of removing agglomerated deposits.

Calcined kaolin clay obtained from Dry Branch Kaolin Company, was suspended in DI water at 0.01 and 0.05%. For each concentration, the pH was adjusted to 5, 7 and 9 by adding 20% H_2SO_4 or 50% NaOH solution. Samples were collected after subjecting a 7.2 L volume to 0, 25, 50, 100, 200, 300 and 400 sparks, and their zeta potential and pH determined. The results are shown in Table 22. The zeta potential drops at all pH values, but the drop is minimal, and for all practical purposes we can consider clay to be unaffected by sparking.

Pitch obtained from the Georgia-Pacific Madison, GA, veneer mill was ground in a mortar and suspended in DI water at 0.01% at pH levels of 4, 7, and 9, prepared by adding 20% H_2SO_4 or 50% NaOH. A 7.2 L aliquot was sparked and the resulting zeta potential and pH determined. The results, shown in Table 23, demonstrate that the zeta potential decreases and the pH increases, as they do when stickies are sparked. Further work will be conducted on sparking various combinations of these components.

None of these experiments gave rise to the hard aggregates seen at Augusta. Finally, we attempted to create the aggregates outside the pulper. A mixture of the above components was pressed (without suspending it in water) and dried at 105^{o}C. A hard “Augusta-type” aggregate was observed. A softer material resulted when alum was omitted. Work will be continued during the next phase of the project.

6.3 Trials at Bowater

A trial was run between February and May 2001 at the Bowater, Calhoun, TN, mill. Our initial objective was to evaluate the effect of sparking on stickies. The unit was placed just after the repulper, and we planned to move it progressively upstream. However, it was noted very early in the trial that the sparker appeared to increase yield and decrease bleach use, and the unit was kept downstream throughout the exercise so as to confirm these potential benefits.

A schematic of the recycle plant, which processes 400 tpd of newsprint and magazine stock is presented in Figure 22. The sparker was initially placed in the swell chest, but the high consistency impeded the movement of the electrodes. Although the pulp was at a nominal consistency of 3.5% there were regions near the surface where the consistency was much higher. Retrieving the unit against the drag of high consistency pulp was difficult and the sparker was moved to the coarse screen accepts chest in late March for the duration of the trial.

The effect of sparking (at 4 kV, 50 kA, spark interval: 4-8 seconds) on various parameters is shown in Figure 23 and is summarized in Table 24. The variability is quite high in the absence of sparking, which makes any spark-derived benefits difficult to establish. The reduction in (PM 5) hole counts is statistically solid; the effect on bleach use or yield is less definite because of the high variability. However, sparking *simultaneously* reduces bleach use and increases yield. While the effect on *either* parameter may be statistically marginal, the effect on *both* parameters taken together is much stronger. To arrive at a consolidated benefit, we assigned a value of $100/ton for the incoming furnish, and derived a dollar value for yield. That is, if the yield was 70%, then the pulp at that stage was assigned a value of $70/ton. We then subtracted 50¢/lb for the hydrosulfite bleach. The net cost of the bleached pulp is illustrated in the last panel of Figure 24. The benefit of sparking is now statistically valid and approximates $1.90 per ton, in addition to the product quality benefit derived from the reduced hole counts. There was also a statistically significant drop in primary polymer use from 6.4 to 5.8 lbs/ton, but since this benefit is small, it was not considered further.

The sparker had maintenance difficulties, which was not observed in other trials. One reason was that a spark rate of one spark/4-8 seconds was used, which was higher than the design rate of one spark/15 seconds. This was done since the spark rate necessary to induce an observable effect was not known at the outset, and the machine was pushed beyond its design limits. A new unit capable of sparking once every two seconds has now been constructed. More importantly, water was found inside the power supply in one instance, and this could have caused electrical problems. The machine was kept in an open area to allow easy movement from one location to another, which could have led to its exposure to water. In a permanent installation the unit would be located in an enclosed area and would be protected from contact with water.

The reduction in hole count is probably due to a reduction in the tack of stickie particles. A possible mechanism for the effect on yield and bleach consumption was brought up by David Flower of Bowater. He suggested that sparking could increase brightness by inhibiting ink reattachment to fiber. The resulting increase in brightness would be offset by clarifying less water (which would increase yield) and by a decrease in bleach use. However, this should have reduced freshwater use, which was not seen. The hypothesis that sparking reduces ink reattachment is supported by laboratory work (described below) where the zeta potential of ink and toner

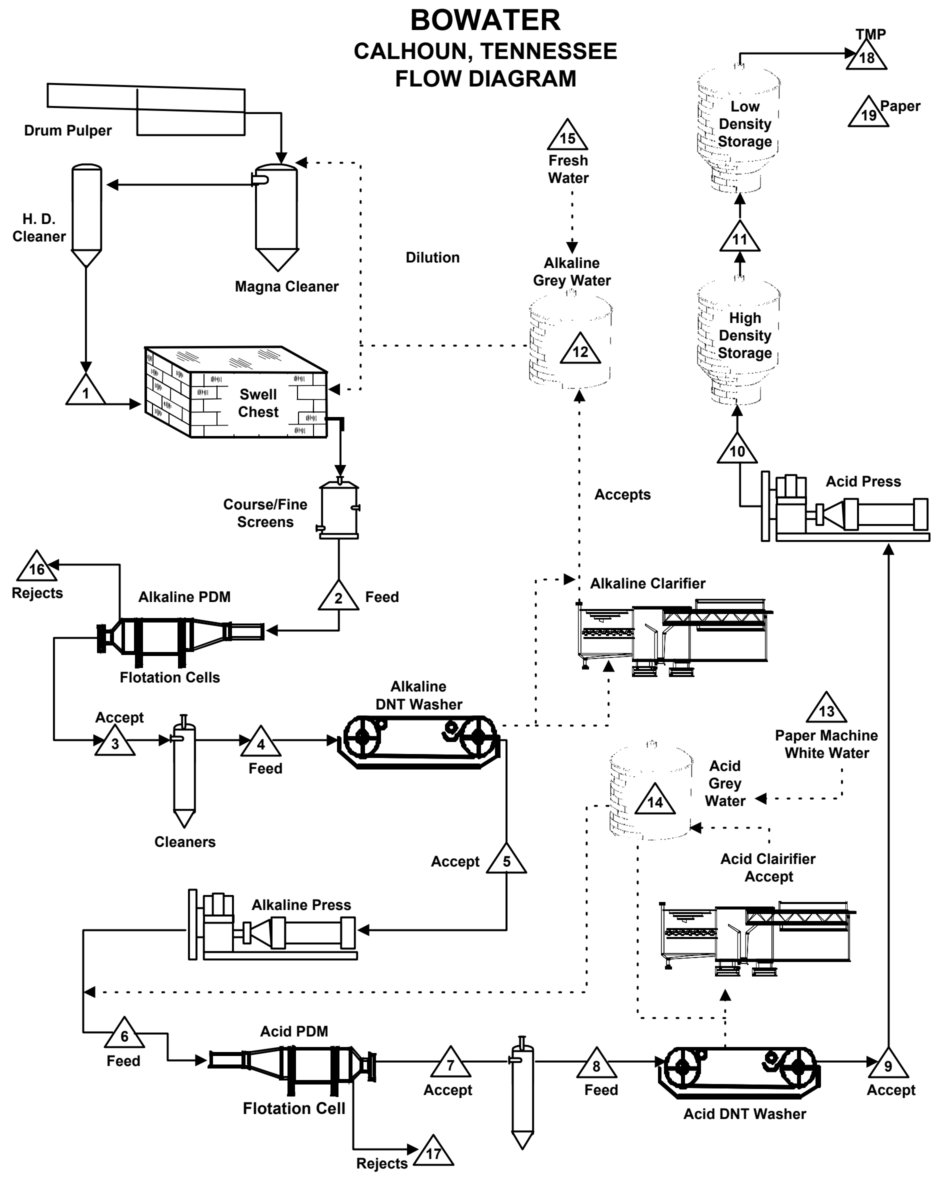

Figure 22: Schematic of the Bowater, Calhoun, TN, recycling facility.

particles was reduced through sparking. The (now) more negative particles would be repelled by the negative fiber. Hence, the Flower hypothesis is not fully supported (since freshwater use was apparently not reduced) but the other evidence points towards it.

Deposits of the type observed at Augusta were not seen at Bowater, and a brief laboratory study was done to determine the conditions that would favor deposition. One way to induce agglomeration of colloidal material is through the application of shear. To study this, samples from the feed to fine screen and the feed to the float cells (received on 2.20.01) were diluted fivefold with DI-water. The pH was adjusted to 5.0 with 20% H_2SO_4 and the solution subjected to 50 sparks. Both sparked and control solutions were stirred at 50°C for one hour at 1,000 rpm in a glass tank fitted with a Rushton impeller. The quantities of solids deposited on the impeller

Table 24: Results of sparking on various parameters.

	control	sparked	significance (F-test)
bleach use (lbs/ton)	13.9	11.1	86%
yield (%)	70.1	70.8	83%
benefit (bleach & yield)	$65.6	$67.5	96%
hole count	53	35	>99.9%

Table 25: Effect of sparking on solids deposition.

	deposits (mg/L)	
	initial	after 50 sparks
feed to fine screen	19	12
feed to float	13	10
feed to fine screen (with alum)	32	46

decreased after sparking, as listed in Table 25. Alum was added to the feed to fine screens to a final concentration of 0.033%, the suspension was sparked 50 times and stirred for one hour as above. Now, the deposition increased, as shown in Table 25.

These findings are interpreted as follows. In the absence of alum, the particles that are already negative are made even more so through exposure to the sparks, and their tendency to agglomerate and deposit is reduced. When alum is added, the additional negative charge imparted to the particles makes them easier to complex with and deposit out with the positively charged alum. Hence, sparking shifts the charge distribution of the various ions in the system. This can either promote or retard deposition depending on the species present. Our working hypothesis is that sparking altered the charge distribution of the fines at Augusta, which then bonded to pitch through the agency of polymers or alum. It is possible that this did not occur at Bowater because the mix of chemicals was different. We will test this hypothesis over the next quarter.

6.4 Effect of sparking on the zeta potential of toner and ink

Laser printer toner, type PX Black (containing styreneacrylate copolymer, carbon black, polypropylen and charge control agents), supplied by Southern Cross Systems Corporation, was cured at 400^{o}C for 30 seconds. The toner fuses in less than one second at 400^{o}C in a printer. The fused toner (0.63 g) was ground to a fine powder and suspended in 7.2 L of DI water. The pH was adjusted to 6.6 with 50% NaOH. The suspension was subjected to sparking and samples were collected periodically during sparking. The results (Table 26) demonstrate that sparking decreases pH and zeta potential, suggesting that the particles are oxidized.

A similar experiment was done on (oil based) flexographic ink obtained from the *Atlanta Journal and Constitution*. A small quantity (0.34 g) of the ink paste was dispersed in 1% NaOH for 3 hours at 60^{o}C. The dispersed ink was added to 7 L of DI water, the pH was adjusted to either 6.0 or to <5 with 20% H_2SO_4. Both sets were sparked. The results, shown in Table 27, are similar to those in Table 26, in that sparking reduces zeta potential.

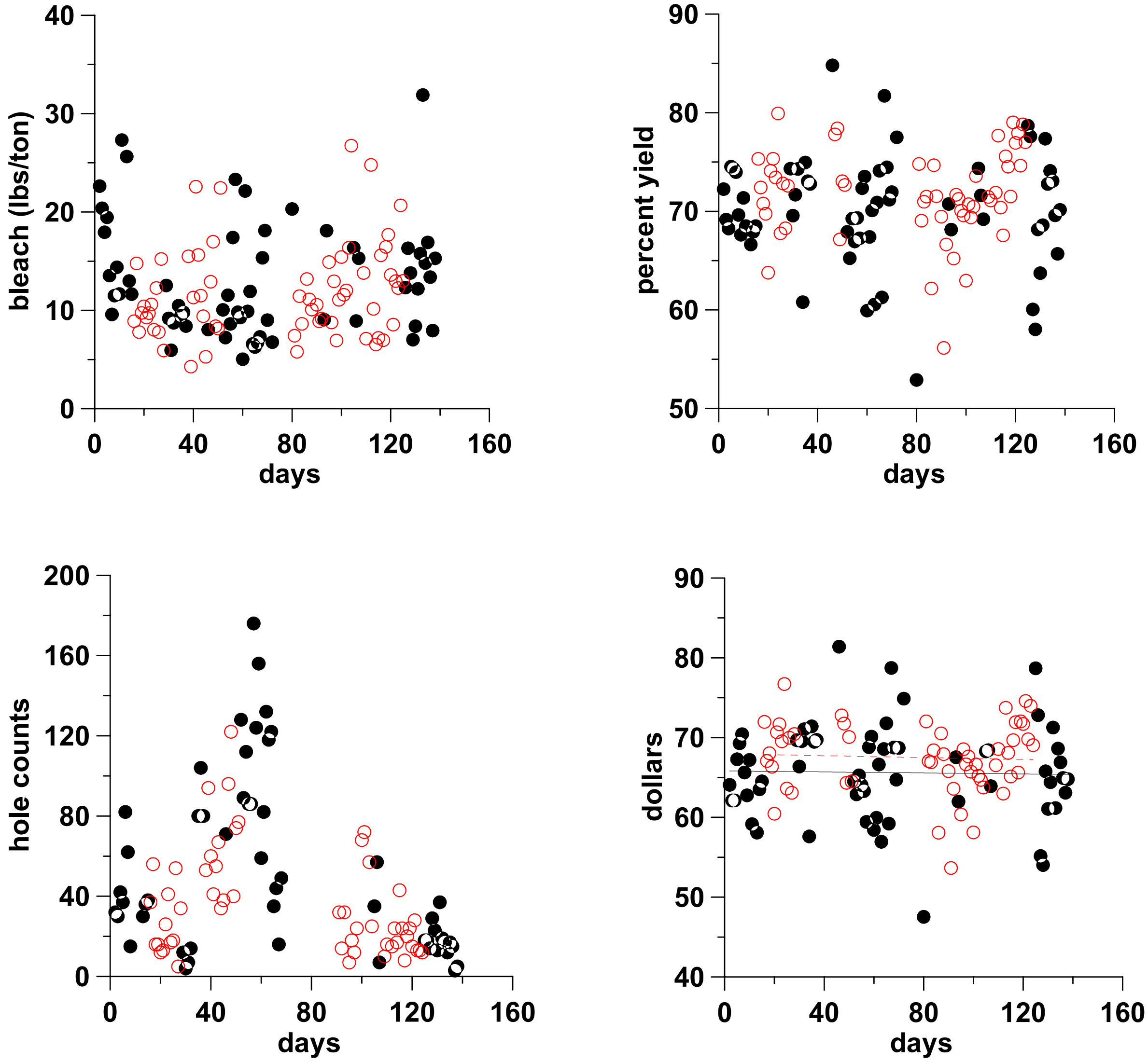

Figure 23: Effect of sparking on various parameters (sparker off: closed circles; sparker on: open circles).

Table 26: Effect of sparking on toner.			
no of sparks	pH	zeta potential (mV)	particle size (nm)
0	6.6	-3.8	636
25	6.4	-15.4	1,110
50	5.9	-16.0	271
100	5.1	-17.9	758
200	4.9	-19.6	834
300	4.8	-23.8	618
400	4.6	-21.6	853

Table 27: Effect of sparking on newsprint ink

no of sparks	pH	zeta potential (mV)	particle size (nm)
0	5.76	-32	450
25	5.94	-36	420
50	5.90	-36	440
100	5.82	-39	420
200	5.63	-39	400
300	5.45	-40	400
400	5.26	-41	400
0	4.64	-9.3	600
25	5.25	-20.5	438
50	5.05	-23.3	410
100	5.00	-24.9	403
225	4.72	-28.1	390
300	4.63	-29.5	408
400	4.51	-30.4	372

Table 28: Effect of 400 sparks on solids separation.

pH	TSS (mg/L)	ash (mg/L)
DI-water (control), pH 5.63	8.70	8.3
mill sample, pH 7.33	14.3	8.3
mill sample, pH 4.05	20.4	9.0

Table 29: Effect of sparking on TOC (ppm).

	pH	filtered	ultrafiltered
before sparking	4.00	513	397
after sparking	4.07	558	369

6.5 Trials at Abitibi, Sheldon

Preparatory work was undertaken to support a mill trial. A sample of deinked plant clarifier feed water (of pH 7.9) received on 12.21.00 was filtered. The pH of a second batch of filtrate was adjusted to 4.0, and both sets were exposed to 400 sparks, and the TSS and ash content determined. The TSS increase of 8.7 ppm (Table 28) when distilled water is sparked is from iron particles removed from the electrodes; as a result, the ash and TSS values are the same. Organic TSS deposited when the mill sample was sparked, especially at the lower pH. The pH 4 samples were centrifuged, and the deposits analyzed by FTIR. The spectra are illustrated in Figure 24. The 1700 cm^{-1} signal in the control decreases upon sparking. This signal could be related to pitch, which absorbs in this region. Also, the intensity of the signals located just above 1,000 cm^{-1} increases upon sparking. These correspond to groundwood, and it is likely that sparking deposits groundwood fines, similar to our experience at Augusta Newsprint.

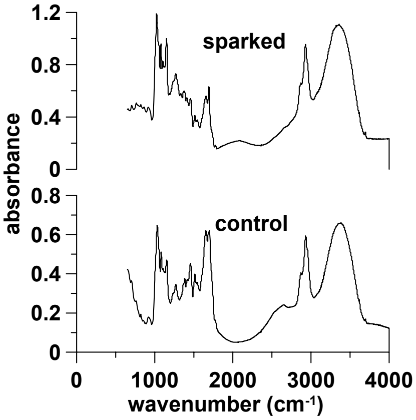

Figure 24: Spark-induced changes in the FTIR spectrum of deposits.

Table 30: Effect of sparking on tack (g force).

0 sparks		**50 sparks**	
temperature (°C)	**tack**	**temperature (°C)**	**tack**
31	69	30	18
34	63	33	123
34	79	33	56
34	50	34	107
35	79	35	98
36	81	36	22
36	74	36	39
38	69	37	88
38	80	37	104
40	83	37	64
42	87	37	32
43	68	37	76
46	117	38	59
		39	55
		39	101
		47	75
40 (interpolated)	**83**		**73**

The TOC (total organic carbon) was also measured before and after sparking for samples that were (a) filtered and (b) ultrafiltered through a 1,000 Da membrane. The difference in TOC represents dissolved material of molecular weight >1000. No significant differences are seen (Table 29), suggesting that the deposits observed constitute a small fraction of the dissolved material. Nevertheless, the potential for particle deposition is important, and we will site the sparker ahead of the cleaners and screens to avoid disrupting production. Laboratory work was also conducted to determine the effect of sparking on tack. A pulp slurry collected from the drum pulper stock vat on 9.14.01 was sparked 50 times at 4 kV. Filtrates from both sparked and control samples were boiled down from 1 L to 5 mL, and the concentrates analyzed for tack. Once again, high levels of clay were present and the high variability (Table 30) precluded a meaningful conclusion.

A trial was conducted at Abitibi, Sheldon, between late 2001 and early 2002. Two lines (B and C) lead from the coarse screens to the float cells. During the trial, lines B and C processed 250 and 750 tpd, respectively. The two lines then combine in the forward cleaner feed chest. Two sparker units were used: the "small" unit sparked once every 5 or 6 seconds, whereas the larger unit pulsed once every two seconds. The large sparker was initially placed just before the coarse screens, but the electrode assembly acted as a ragger and the attached debris physically impeded the movement of the electrodes. The large sparker was then moved to the C line flotation-deaeration chest, so that 75% of the stock was treated by the machine. The small unit was positioned at the forward cleaner feed chest where the two lines combine, and all the stock was exposed to it.

Some machine reliability issues surfaced. Initially, a board in the power supply blew; a new board had to be redesigned by Siemens-Westinghouse and this led to a delay. Also, the contacts to the electrode assembly blew on occasion and had to be soldered back. The mill also took some unanticipated downtime, and the machine switched to neutral papermaking towards the end of the trial. Our initial plan was to move the unit to the whitewater system, but this was shelved in light of these delays.

The results obtained are presented in Table 31. The production was constant over this period. The only stickies-related measure was the hole count, and this was unaffected by sparking. However, the unit was installed upstream of the acid-shocking operation where the stickies are agglomerated. The sparker increases the negative charge on the stickies, which may actually decrease the propensity of the stickies to agglomerate. The sparker should have been located after screening and cleaning to have an impact on stickies, and the absence of an observed effect is probably a consequence of its location rather than a measure of its effectiveness.

The only significant effect was on bleach use, which was reduced by 0.8 lbs/ton as shown in Figure 25. The values recorded for March 2002 represent the lowest bleach use since at least July 2001. Almost exactly the same reduction was realized at Bowater, Calhoun, so the effect is real. Operation of the smaller unit alone led to similar benefits, so the higher spark rate may not be necessary for this application. The mechanism behind this reduction is known. The ink particles are made more negative through sparking and their tendency to reattach to fiber is reduced. Less bleach is used as a result.

At 50¢/lb of bleach and a production of 1,000 tpd, payback for the sparker is 120 days. Given that one-third of the cost has already been paid through the trial, the payback for Sheldon is 80 days. However, this assumes that the machine is completely reliable, which is not presently the case. On the other hand, the improvements necessary should be relatively minor; *e.g.* the use of more robust connectors.

Table 31: Effect of sparking on process parameters[1].

	dates	#5 holes	holes #7	ERIC	yield	bleach use (lbs/ton)
both units off	10.1-10.31	34 (18)	59 (22)	218 (212)	80 (83)	3.3 (3.0)
	1.23-1.28	26 (21)	20 (20)	210 (209)	85 (88)	3.8 (3.8)
small unit on	11.16-11.30	16 (11)	41 (35)	209 (209)	88 (88)	1.7 (1.6)
both units on	1.09-1.20	15 (11)	31 (25)	189 (190)	83 (84)	2.4 (2.3)
	1.29-1.30	7 (5)	-	229	82	2.1
	2.21-3.11	37 (21)	25 (20)	214 (212)	86 (84)	2.1 (1.8)
	11.06-11.13	33 (26)	35 (33)	220 (216)	81 (83)	1.9 (1.9)

[1] average values; the numbers in brackets are median values.

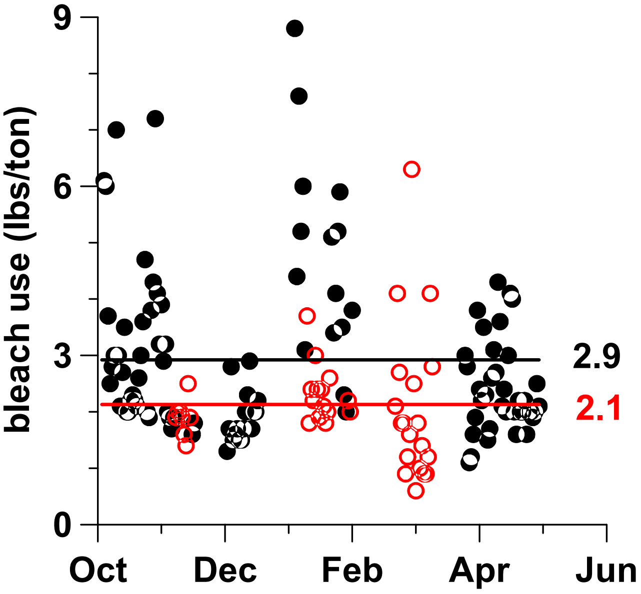

Figure 25: Effect of sparking on bleach use. The open circles represent values with the sparker on; the closed circles correspond to controls. The numbers on the graph are averages.

6.6 Attempted destruction of catalase through sparking

The mill reported that catalase from microorganisms was consuming peroxide. We ran a quick laboratory study to determine if the sparker would deactivate catalase. A sample from the coarse screen accepts (8 L) was sparked at 4.25 kV. Hydrogen peroxide was added to give a final nominal concentration of 0.5%. The solutions were back-titrated immediately with 0.1N sodium thiosulfate to determine the amount of residual peroxide. Concentrations of H_2O_2 are tabulated in Table 32. The results are ambiguous because the peroxide consumption in the control

Table 32: Effect of sparking on peroxide consumption.

no. of sparks	H_2O_2 (%)
0 (control)	0.48
25	0.47
50	0.48
100	0.49
200	0.48

Table 33: Consumption of peroxide over time.

minutes	H_2O_2 (%)
0	0.27
70	0.18
175	0.13

Table 34: Effect of sparking on peroxide consumption by catalase.

sparks	elapsed time (min)	peroxide (%)	
		sparked	control
catalase concentration: 4.3 ppm; peroxide added: 0.37 ppm			
0	0	0.33	0.33
50	30	0.36	0.36
100	60	0.35	0.33
300	120	0.33	0.35
catalase concentration: 50.4 ppm; peroxide added: 0.22 ppm			
0	0	0.22	0.22
50	30	0.22	0.22
200	60	0.22	0.21
400	120	0.22	0.22

was quite high, suggesting that the catalase concentration was low. Also, the peroxide concentration decreased over time even in the absence of sparking. One liter of sample was mixed with H_2O_2 (30%) solution to an approximate final concentration of 0.3%. The solution was periodically analyzed for H_2O_2. The results, provided in Table 33, show a steady decrease of peroxide.

Additional work was conducted with catalase obtained from ICN Biomedicals. Samples were sparked at 4.25 kV and samples were collected periodically. Control samples were also collected from the stock at corresponding intervals. Hydrogen peroxide was added, and the solutions back titrated with 0.1N sodium thiosulfate. The results, listed in Table 34, show that sparking does not change the amount of peroxide consumed. The sparker is not useful for this application.

Table 35: Tack results (g force) of thick stock feed (8.9.01).

0 sparks		**5 sparks**		**50 sparks**		**400 sparks**	
(^{o}C)	**tack**	**(^{o}C)**	**tack**	**(^{o}C)**	**tack**	**(^{o}C)**	**tack**
32.0	8	31.6	6	33.2	1	36.0	12
33.0	26	32.0	6	34.0	16	36.0	10
37.0	24	35.0	12	35.0	10	46.0	11
39.0	9	47.0	14	37.0	6	48.3	17
42.6	9			48.0	17		
40	**9**		**13**		**9**		**11**

Table 36: TOC values (ppm) of filtered and ultrafiltered thick stock feed.

sparks	**filtered**			**ultrafiltered**			**high MW TOC**
	TC	**IC**	**TOC**	**TC**	**IC**	**TOC**	
0	330	61.5	269	170	50.0	120	149
5	330	64.0	266	180	51.0	129	135
50	333	62.5	271	187	51.5	135	136
400	333	65.0	268	190	52.5	138	131

6.7 Effect of sparking on samples from a tissue mill

We ran some laboratory work to prepare for a confidential trial at a tissue mill and the results are reported here. A thick stock feed to PM sample (4% consistency) was sparked at different levels, 0 (control), 5, 50 and 400 times. Sparked and control samples were filtered, and the filtrate boiled down from 1 L to 2 mL. One mL of the residue was plated on a metal coupon, which was dried at 25-40^{o}C overnight. The coupon was warmed in warm water, the water was shaken loose, and the tack of the residue film measured with a Polyken tack tester as a function of temperature. The results, listed in Table 35, are highly variable; sparking does not significantly change the tack.

The TOC (filtered and ultrafiltered) of the sparked and control samples are tabulated in Table 36. The results show that sparking progressively reduces the high molecular weight TOC, which represent micro-stickies. Since the total quantity of stickies do not change (the filtered TOC is constant throughout), this must mean that sparking converts large stickies to small stickies, probably through mechanical action. This is an artifact since the reactor used was small and the shock wave from the spark was appreciable. This is not expected to occur in a large tank.

Another set of experiments was done on a similar sample received on 8/14/01. The filtrates of sparked and control samples were analyzed for tack following the procedure described as above. The results were too variable to be meaningful. Samples from the paper machine and in between the pulper and the DNT press for system 1 and 5 were received on 8/22/01. Again, the tack results were meaningless because of high variability. The samples were sparked and tested for TSS, TOC and zeta potential. Sparking slightly reduced the TSS values of the samples

Table 37: Effect of sparking on TSS.

	TSS (%)			
sparks:	**0**	**5**	**50**	**400**
Syst-1	0.78	0.78	0.79	0.80
Syst-5	3.03	2.72	2.70	2.70
PM	4.60	3.80	4.08	4.24

Table 38: Effect of sparking on zeta potential.

	sparks	**zeta potential (mV)**	***particle size (nM)***
Syst-1	0	-5.8	337
	5	-5.4	267
	50	-5.8	238
	400	-5.2	200
Syst-5	0	-7.1	555
	5	-7.5	525
	50	-7.5	532
	400	-7.4	585
PM	0	-14.5	641
	5	-14.6	662
	50	-14.2	619
	400	-14.3	656

collected from Syst-5 and paper machine, where the system-1 sample remained essentially unchanged (Table 37).

Sparking did not have any significant effect on zeta potential of all the three samples (Syst-1, Syst-5, and Pulp and Paper solution sample) as shown in Table 38. The particle size of Syst-1 sample decreased upon sparking, but the other samples did not show any significant change. The TOC results, shown in Table 39 are featureless.

Tack values were measured for samples from three different locations (paper machine, and at locations intermediate between the pulper and the DNT press for systems 1 and 5) collected on August 20, 2001. The samples were sparked and tested for tack, TSS, TOC and zeta potential. The filtrates were boiled down to a film, coated on a metal coupon and the tack measured. The results, listed in Tables 40-42, show that the Syst-5 sample was of higher tack. However, the variability in tack was high and obscured any effect that sparking might have had. High levels of clay were present in the sample, and it is likely that the stickies coat the clay. This could add to measurement variability, since the film coated on the metal coupon would tend to be less uniform because of the presence of clay.

Table 39: TOC (ppm) of 8/20/01 samples.

	sparks	filtered			ultrafiltered			high MW TOC
		TC	IC	TOC	TC	IC	TOC	
SYST-1	0	123	33	90	74	30	44	46
	5	119	33	86	61	31	30	56
	50	115	33	82	59	31	28	54
	400	112	34	78	59	32	27	51
SYST-5	0	389	96	293	303	87	216	77
	5	371	93	278	268	90	178	100
	50	364	89	275	272	91	181	94
	400	350	106	244	242	94	148	96
PM	0	201	79	122	156	71	85	37
	5	201	73	128	154	68	86	42
	50	200	69	131	151	66	85	46
	400	203	68	135	148	64	84	51

Table 40: Tack (g. force) from the Syst-1 sample.

0 sparks		5 sparks		50 sparks	
temperature (^{o}C)	tack	temperature (^{o}C)	tack	temperature (^{o}C)	tack
37	5	36	24	39	7
38	2	37	2	40	9
39	21	37	4	40	11
47	2	37	26	40	13
		39	7		
		44	22		
		45	24		
40 (interpolated)	**7**		**16**		**10**

Table 41: Tack (g. force) from the SYST-5 sample.

0 sparks		5 sparks		50 sparks		400 sparks	
temperature (^{o}C)	tack	temperature (^{o}C)	tack	temperature (^{o}C)	tack	temperature (^{o}C)	tack
34	34	36	24	35	30	37	67
37	36	37	27	36	46	39	22
38	18	38	54	37	12	38	20
39	25	38	66	37	31	40	18
39	33	39	41	38	35	42	113
41	44	42	78	40	72	43	90
42	49			41	32	44	46
43	34			42	29		
46	64			43	44		
40 (interpolated)	**38**		**51**		**38**		**54**

Table 42: Tack (g force) from the PM sample.

0 sparks		**5 sparks**		**50 sparks**		**400 sparks**	
temperature (^oC)	**tack**	**temperature (^oC)**	**tack**	**temperature (^oC)**	**tack**	**temperature (^oC)**	**tack**
35	19	35	24	36	10	35	6
38	26	36	20	36	12	36	11
38	26	37	32	39	62	37	32
39	11	38	17	40	20	38	11
40	16	41	39	41	30	40	12
		42	35			44	18
40 (interpolated)	**21**		**29**		**28**		**16**

Table 43: Effect of sparking on zeta potential.

sparks	**zeta potential (mV)**	**particle size (nM)**	**pH**
Syst-1			
0	-5.8	337	7.47
5	-5.4	267	7.51
50	-5.8	238	7.62
400	-5.2	200	7.61
Syst-5			
0	-7.1	555	7.36
5	-7.5	525	7.75
50	-7.5	532	7.82
400	-7.4	585	7.19
PM			
0	-14.5	641	7.65
5	-14.6	662	7.97
50	-14.2	619	7.67
400	-14.3	656	7.78

Sparking also did not have any significant effect on the zeta potential of any of the three samples. The particle size of Syst-1 sample decreased with sparking, but the other samples did not show any significant change (Table 43). The Total Organic Carbon (TOC) content of the sample was determined after coarse-filtration to remove fiber and then ultrafiltration through a 1,000 Da membrane to isolate the low-molecular weight fraction. The difference, the high-MW fraction, represents stickies. Interestingly, the TOC drops upon sparking for the Syst-1 and Syst-5 samples (Table 44), suggesting that sparking removes TOC, most probably by converting it to solids. Insufficient sample remained to confirm the hypothesis that dissolved material was being converted to TSS. Hence, what remained of the Syst-1 and Syst-5 samples was mixed at a ratio of 1:3, filtered, and sparked. Sparking increases TSS as shown in Table 45.

Table 44: Effect of sparking on TOC.

	filtered			ultrafiltered			high MW TOC
	TC	IC	TOC	TC	IC	TOC	
SYST-1							
control	123	33	90	74	30	44	46
5 sparks	119	33	86	61	31	30	56
50 sparks	115	33	82	59	31	28	54
400 sparks	112	34	78	59	32	27	51
SYST-5							
control	389	96	293	303	87	216	77
5 sparks	371	93	278	268	90	178	100
50 sparks	364	89	275	272	91	181	94
400 sparks	350	106	244	242	94	148	96
PM							
control	201	79	122	156	71	85	37
5 sparks	201	73	128	154	68	86	42
50 sparks	200	69	131	151	66	85	46
400 sparks	203	68	135	148	64	84	51

Table 45: Effect of sparking on TSS for the mixed sample.

sparks:	0	5	50	400
TSS (ppm):	0	5	16	30

Table 46: Effect of sparking on the zeta potential of coated broke.

control		treated	
pH	**mV**	**pH**	**mV**
1.7	-0.8	2.9	-1.7
3.9	-1.5	4.5	-3.7
7.5	-8.9	7.8	-2.4
9.5	-14.4	9.8	-16.2
10.7	-16.5	11.5	-20.7

In conclusion, sparking converts low-molecular weight TOC to suspended solids. While this has no bearing on stickies, it suggests that sparking cleans up the stream, and that the unit should be placed ahead of cleaning equipment to remove the deposited solids. The mill trial as run in early 2002and was deemed to be inconclusive because of high background variability.

6.8 Effect of spark treatment on coated broke

Zeta potentials of samples (at 5% consistency) from Westvaco's Luke, MD, mill were measured after 100 sparks at various pH values. The results, shown in Table 46, indicate that the effect of sparking on zeta potential was small in comparison to the much larger reduction observed for stickies.

Table 47: TOC values of filtered and ultrafiltered samples[1]

	after agitation		before agitation	
	filtered	**ultrafiltered**	**filtered**	**ultrafiltered**
initial	957	353	935	337
after 50 sparks	936	375	980	335
after 400 sparks	510	560	1,000	396
[1] the inorganic carbon content was negligible				

6.9 Experiments with samples from the Weyerhaeuser Valiant mill

The mill has three paper machines. Two produce 2,400 tpd of linerboard and the third makes 700 tpd of medium. A washer filtrate sample (received on 2.2.01) was diluted tenfold with DI-water; the results reported here are for the diluted sample. Alum (5%) was added to the diluted sample at 15 lb of alum per ton of diluted filtrate as per the mill's instructions. The pH of the solution was adjusted to 5.0 by adding 20% H_2SO_4. A part of this sample was taken as control (2.5 L); the rest (7.2 L) was subjected to 400 sparks. The sparked sample and the control were stirred at 1,000 rpm and 50^{o}C in a glass tank fitted with a Rushton impeller for 1 hour. The pH of the solution was maintained by occasional addition of H_2SO_4.

Sparking followed by agitation greatly increased the TSS from 231 ppm (control) to 412 ppm (50 sparks) and 1,510 ppm (400 sparks). Sparking alone (*i.e.* in the absence of agitation) did not increase agglomeration, and the TSS values remained unchanged at 105 ppm. In order to determine whether low or high molecular weight material was being agglomerated, the total organic content (TOC) of the samples was measured before and after ultrafiltration through a 1,000 Da cut-off membrane, which isolates the low molecular fraction. The results are presented in Table 47. Note that the TOC of the X400 sample followed by agitation is reduced from 957 to 510 ppm, with the difference being converted to TSS. The ultrafiltered values (which represent low-MW compounds) increases slightly, which means that the TSS created must derive from high-MW material. These changes are not seen for the un-agitated sample. The reduction in TSS was 1,280 ppm. This is consistent with the TOC measurement since carbon only represents a fraction of the deposited material. In sum, sparking followed by shear removes much of the dissolved high molecular weight material in the sample and reduces its color.

*7 **Other applications of the sparker***

7.1 Potential disinfection of whitewater

Whitewater collected from Visy Paper (a 100% OCC mill), Conyers, GA, was stored cold until use. It was diluted fourfold to 10L, pulsed in the 2 L vessel, and samples were withdrawn for plate count analysis after 1, 10, and 30 pulses, respectively. The results, shown in Table 48, show that there is no disinfection.

7.2 Cleaning of wires and felts

Several used wire samples obtained from Albany International and from Donohue, Sheldon, TX, were immersed in the large tank and pulsed for varying periods. No effect was ob

Table 48: Effect of pulsing on viable biomass	
no. of sparks	**cfu/mL**
0	4.5E6
1	3.8E6, 3.8E6
10	4.9E6, 4.1E6
30	3.7E6, 3.9E6

served for wires plugged with small particles such as ink. Possibly, the ink was shaken loose, but was unable to escape the wire. Fiber or other larger debris was debonded after only a few pulses, and could be gently brushed off. However, the effect was not considered to be dramatic enough to justify the logistics of placing sparkers in a configuration where it would affect felts and wires, and this line of study will be abandoned.

7.3 Fiber refining

Northern bleached Softwood Kraft of 1.8% consistency was pulsed 100 and 400 times in the small reactor. Microscopic examination of the fibers by Derek Page showed no differences in fiber structure vis-à-vis a control. Accordingly, this line of investigation will be abandoned.

7.4 Oxidation of sulfides through sparking

Since sparking induces oxidation, a preliminary study was conducted to determine if sulfides could be removed through sparking. If so, this would lead to an easy means of odor control. Aqueous sodium sulfide solutions were sparked in a 10L reactor at 4.2 kV at two sparks/minute. Sulfide was monitored with a sulfide–specific electrode. The response curve for the electrode (mV *vs* [S]) was linear between 200 and 100,000 ppm. Sodium sulfide solutions of <1 ppm were sparked, and the sulfide content was monitored periodically. The results, presented in Table 49, demonstrate that the sulfide concentration decreases with time. The stability of a 0.3 ppm control sample is shown in Table 50. While some decrease occurs in the absence of sparking, the rate is much lower than that measured under sparking conditions. The pK_a of H_2S is 7.00.

Solutions of sodium sulfide or water with added black liquor (from hardwood obtained from the IP Cantonment, FL, mill) were sparked, and analyzed over time by a sulfide ion specific electrode. The initial concentrations were too high to be determined by the electrode, and titration with 0.1M lead perchlorate was used instead. The end point was monitored with the electrode. As expected, sodium sulfide had a sharp endpoint. However two end points were observed for black liquor; the second was used to calculate the total sulfide. For each experiment, a control where an equivalent sample was left open to the atmosphere was also run. The products and the total sulfur content were determined by capillary ion electrophoresis, and ICP, respectively.

Results from sparking aqueous sodium sulfide and black liquor are presented in Figures 26 and 27, respectively. The starting pH for the sodium sulfide was 10.68. It dropped to 6.37 and 10.1 for the sparked and control samples, respectively, showing that the oxidation product is acidic. The pH of the liquor sample dropped slightly from 11.71 to 11.22 and 11.60 for the sparked and control samples, respectively. The spark rate was slow, since our booster power

Table 49: Effect of sparking on sulfide oxidation.	
no. of sparks	**sulfide (ppb)**
set 1 (run no. 100500)	
0	678
50	240
100	92.5
150	33.6
200	8.6
set 2 (run no. 100600)	
0	332
25	226
75	59.2
125	25.7
175	7.4
225	5.5
set 3 (run no. 100900)	
0	941
7	720
32	173
82	20.3
132	5.8
182	4.2
232	3.5
282	2.9
332	2.3

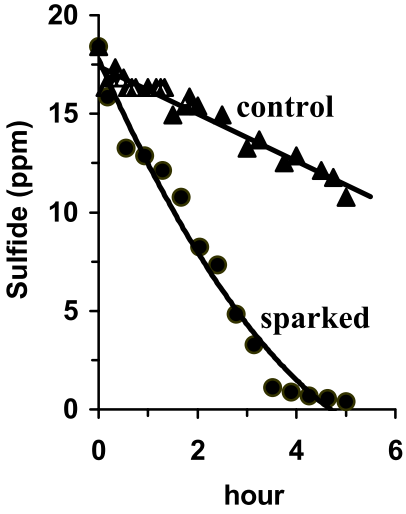

Figure 26: Oxidation of aqueous sodium sulfide.

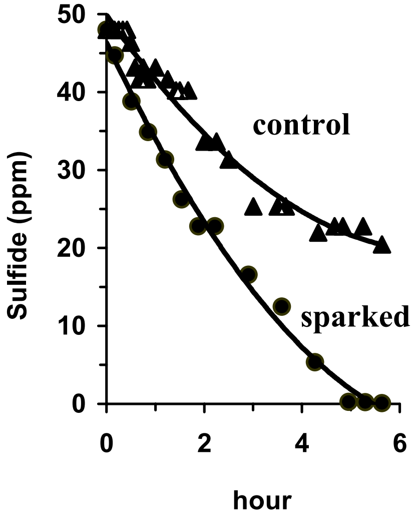

Figure 27: Oxidation of sulfide in black liquor.

Table 50: Stability of a sulfide control[1]	
minutes	**sulfide (ppb)**
0	342
5	286
10	332
17	353
18	363
27	353
39	313
51	313
62	313
72	286
75	313
82	286
93	286
104	278
110	278
120	270
132	233
140	247
150	233
[1] pH=7.1	

supply was being used in a mill trial, and we were only sparking once every 30 seconds. Loss from the control occurred through volatilization over this long period. At the faster spark rate the process would have been complete in less than 30 minutes, and loss from the control would have been negligible. Sparking sodium sulfide as well as black liquor (BL) leads principally to thiosulfate as shown in Table 51. The product distribution from sparking thiosulfate is shown in Table 52. It seems that sulfide is first oxidized to thiosulfate, which then coverts to sulfate.

The sulfide work was undertaken because there seemed to be interest in this in the Agenda 2020 Recycle Advisory Committee. However, this was outside the scope of the project and this work was discontinued. The State of Georgia has funded follow-on work in 2001-2003.

7.5 Effect of sparking on color removal

Washer filtrate from Weyerhaeuser (diluted tenfold) and clarifier samples from Rayonier were sparked at 4.25kV and then agitated for 1 hour at 1,000 rpm in a BioFlo reactor at 50°C. As mentioned before, agitation tends to agglomerate suspended particles. The samples were then analyzed spectrophotometrically. As shown in Table 53, color removal (brightness increase) was significant for the Weyerhaeuser sample when sparking was followed by agitation. Alum was added as recommended by Weyerhaeuser. We believe that sparking oxidizes the dissolved lignin, increase its affinity for alum, and removes it from solution. We expect similar results with other cations. Sparking made no difference to the Rayonier sample.

Table 51: Products from sparking sodium sulfide.

ID	sulfide (ppm)[1]		thiosulfate[2]	sulfite[2]	sulfate[2]
	initial	final	ppm	ppm	ppm
Na_2S 101600 (sparked x 675 over 5h)	18.4	0.27	22.5	<0.5	10.2
Na_2S 101600-control (exposed for 5 h)	18.4	10.78	14.0	6.66	12.1
BL 110100-1 (sparked x 825 over 5.6h)	48.0	0.05	78.4	42.0	54.0
BL 110100-2 control (exposed for 5.6h)	48.0	20.5	85.0	56.4	45.0

[1] estimated by titration using an ion selective electrode.

[2] determined by capillary ion electrophoresis.

Table 52: Oxidation of sodium thiosulfate.

no. of sparks	thiosulfate (ppm)[1]		sulfate (ppm)
	initial	final	
500 (over 2.87 h)	29.2	3.32	14.9
control (exposed for 2.87 h)	29.2	29.2	<1

[1] initial pH=5.25; final pH=3.87 (sparked) and 5.25 (control)

Table 53: Effect of sparking on the color of various filtrates

	dominant wavelength (nm)	purity	relative brightness (%)	pH
Weyerhaeuser				
no alum, no spark, no agitation, no pH control	585	90%	**25.4**	11.45
no alum, no spark, no agitation, pH-controlled	579	74%	**12.1**	6.70
alum (0.034%), no spark, no agitation	580	72%	**39.8**	6.67
alum (0.034%), no spark, agitated	600	3%	**37.7**	6.28
alum (0.034%), 400 sparks, agitated	572	8%	**76.6**	6.52
Rayonier				
alum (0.0067%), no spark, no agitation	593	97%	**2.92**	5.53
alum (0.0067%), no spark, agitated	597	99%	**0.56**	5.83
alum (0.0067%), sparked 400x	601	100%	**0.47**	6.59
no spark, no agitation	578	67%	**57.6**	5.30
no spark, agitated	578	66%	**57.8**	5.02
400 sparks, agitated	579	70%	**51.2**	5.48

Table 54: Effect of sparking on degassing water.

sparks	tap water			deionized water	
	DO (ppm)	Temperature (°C)	pH	DO (ppm)	temperature (°C)
0	5.20	20.5	6.45	8.15	20.8
50	5.00	20.3	6.32	6.66	20.9
100	4.78	20.7	6.05	5.33	21.1
200	4.55	20.8	5.99	5.66	21.3
300	4.49	20.9	5.84	5.70	21.6
400	4.01	21.1	5.27	5.25	21.8

7.6 Effect of sparking on degassing water

The sparker creates a sound wave, and since sonication is a well-known method for degassing, it was felt that sparking could also lead to degassing, which could be potentially beneficial in the clarifier and in the deculator. Deionized and tap water (8L) were sparked and dissolved oxygen (DO) measured concurrently. The results, shown in Table 54, demonstrate that sparking reduces DO by degassing the system. The results are better than they appear, because a spark was fired every 6-8 seconds, and the system partially re-aerated during the intervals.

7.7 Effect of clay-stickie interaction on centrifugal cleaner efficiency

In previous work we found that small clay particles can agglomerate with stickies to form neutral-buoyancy aggregates. In an effort to determine whether sparking interrupted the agglomeration process, we measured the effect of particle size and zeta potential on these agglomerates. As it turns out, sparking has no effect. Nevertheless, the baseline work provides insight into how clay carries stickies through centrifugal cleaners.

The efficiency of centrifugal cleaners depends principally on the size and specific gravity of the particles to be removed (22). Cleaners are used extensively in paper recycling, and their performance is frequently less than optimal, suggesting that other factors might come into play. A wide variety of contaminants ranging from heavy particles such as ink and clay to lighter materials such as organic adhesives are encountered. Typically, the heavy contaminants are removed more successfully than are the adhesives. In a survey of stickies from various process streams at two newsprint mills we found that clay was frequently associated with stickies even after passage through both forward and reverse cleaners (23). This was curious since clay has a specific gravity of 1.8 g/cm^3, and should have been easily removed. In this paper we demonstrate that clay can associate with polyvinyl acetate (PVAc) to form neutral-buoyancy aggregates that would be transparent to centri-cleaners.

Polyvinyl acetate (MW 500,000) was obtained from Polysciences Inc. Kaolin clay (DB KOTE 2 Spray Dried) was acquired from Dry Branch Kaolin Company. A relationship (equation 1) between total suspended solids (TSS) and turbidity was established by preparing several suspensions of clay in water and measuring both TSS and turbidity.

Table 55 Effect of sparking on clay-stickie agglomerates[1].		
	before	**after 50 sparks**
size (nm)	269 (2)	272 (1)
zeta potential (mv)	39 (2)	39 (1)
[1]the numbers in brackets are average deviations from 3 determinations		

No measurable turbidity was recorded from suspensions of only PVAc in water. A series of experiments was run where mixtures of clay (0.1-0.4%) and PVAc (0.2%) were added to water at various temperatures with stirring. TSS measurements (expressed as a percentage of solids in water) were made in triplicate. An aliquot was centrifuged in an insulated vessel (to maintain temperature) at 400 g for 15 minutes, and the turbidity measured and converted to TSS through equation (1). The uncertainty in TSS was about 7%. The stirring period did not affect the results, indicating that steady-state conditions are reached rapidly. No change in TSS was observed when a 0.4% clay and 0.2% PVAc mixture in water was stirred at 60^{o}C for 0.5 to 4 hours. Hence, a stirring period of 30 minutes was used throughout. All measurements were made in triplicate.

$$\textbf{TSS (g/L) = 0.0002 turbidity (NTU) –0.0015 } (r^2 = 0.92, n=4) \qquad (1)$$

For the electron microscopy work, a 0.4% clay suspension in water was centrifuged as above and PVAc (0.2%) added to the centrifugate at 70^{o}C with stirring. The suspension was then filtered through an YM1 membrane (Millipore Corp., Bedford, MA), and images were taken of the residue with an JSM-6400 instrument. For the particle size measurements, suspensions of clay in water (0.1-0.4%) were centrifuged. PVAc (0.2%) was added, the suspension heated to 70^{o}C with strong stirring. Particle size measured with a Malvern Zetasizer.

For the sparking experiments, a 1-liter sample of 1% clay + 1% PVAc was prepared at 70^{0}C. The sample was then centrifuged for 15 minutes to isolate the clay-stickie aggregates, and the supernatant diluted to 8 L. The diluted sample was subjected to 50 sparks, and the average particle size and zeta potential obtained. The results, listed in Table 55, show that sparking does not induce a significant change.

The specific gravity of PVAc in water is temperature-dependent (24); the polymer used in this study floats at temperatures above 50^{o}C and sinks at cooler temperatures. We reasoned that if PVAc and clay (which is heavier than water) were added to water, then at high temperatures we would have one floating and one sinking component, whereas at temperatures below 50^{o}C, both components would sink. Hence, there is a potential for neutral-buoyancy clay/PVAc agglomerates to develop in the former situation, but not in the latter.

Figure 28 compares the TSS of clay alone to that of mixtures of clay and PVAc at 60^{o}C. The TSS of the mixture is substantially higher than those of the individual components. Similar results were obtained at 70 and 80^{o}C. Contrasting results were obtained at 45^{o}C and are included in Figure 28. Here, the presence of PVAc makes no significant difference to the TSS. Interpretation of these results is straightforward. At the higher temperature, the light PVAc partially

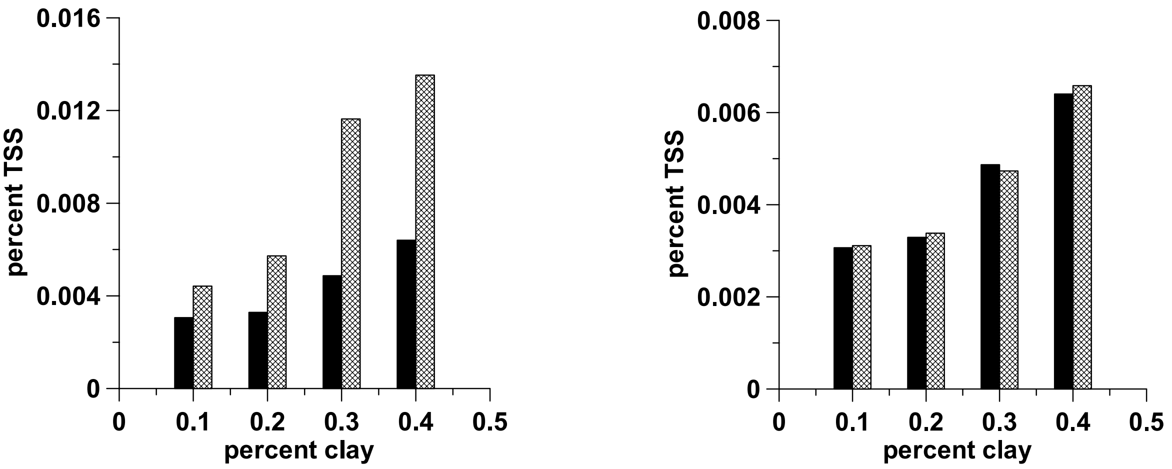

Figure 28: Effect of 0.2% PVAc on the TSS of clay in water at 60^{o}C (left) and 45^{o}C (right). The bold and hatched bars represents clay and the clay/PVAc mixture, respectively.

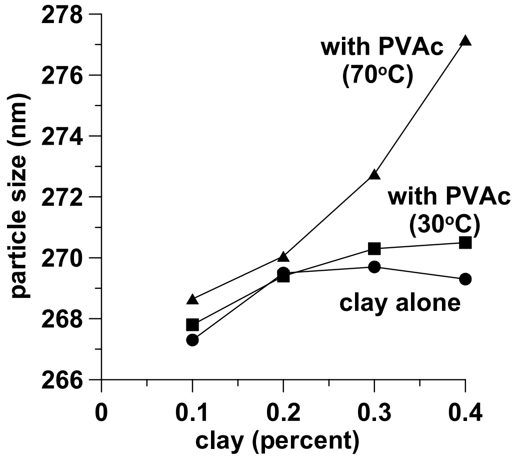

Figure 29: Particle size of solids in clay-PVAc centrifugate. The clay values reflect the quantities initially added.

agglomerates with the heavy clay to form a neutral-buoyancy mixture. Both components are heavy at the lower temperature, and agglomeration does not bring the clay into suspension.

Clay is much heavier than water, and the TSS of the suspension derived from clay alone must be due to particles that are too small to be centrifuged down (25). It is likely that the adhesive coats the clay particles and reduces their specific gravity at the higher temperature. This brings a subset of the population into the neutral-buoyancy region. Increasing the quantity of clay relative to that of PVAc increases the subset affected. The difference in TSS in Figure 28 increases almost linearly with clay content, which suggests at least a quasi-equilibrium situation. A value of 0.0016 g^{-1}L was calculated for the ratio [TSS]/[clay][PVAc]. We believe that this value is a measure of the sub-population that is brought to neutral buoyancy.

Aggregate formation should increase particle size, and measurements were first made on the centrifugate from suspensions of 0.1-0.4% clay in water. The results, presented in Figure 29 demonstrate that the particle size stabilizes at 269-270 nm. The particles grow in the presence of PVAc at 70^{o}C in keeping with the formation of aggregates. In contrast, the 30^{o}C profile is similar to that of clay alone. The differences in particle size are barely outside experimental uncertainty, but they are consistent with the TSS results in Figure 28. The particle size increases by a maximum of only 3% in Figure 29, and the aggregate is still much heavier than water. We believe that a clay particle of a size range just large enough to be centrifuged down in the absence of PVAc is brought into suspension through agglomeration with the polymer. Sparking did not alter the particle size or the zeta potential, possibly because of the orientation of the stickie on the particle as will be discussed later.

Finally, SEM images provide direct evidence for the association of PVAc and clay. Images of aggregates are compared to those of clay alone in Figure 30, and a relatively uniform coating of polymer on clay is visible. Considered together, our results demonstrate that clay associates with PVAc (and probably other stickies) and that a fraction of the aggregate is of neutral buoyancy and is transparent to centrifugal cleaners. This explains why clay and stickies can be found together downstream of the cleaners. Since the stickie coats the clay particles, the clay increases the effective concentration of the stickie, and mills that process high-ash furnish may find stickies control to be especially challenging.

8. Conclusions

Firing a high-intensity spark underwater leads to a shock wave that then propagates as a sound wave. The sound wave breaks down water into hydroxyl radicals that are strong oxidants. Stickies and pitch are commonly-found contaminants in recycle mills and they cost the industry several hundred million dollars. The radicals generated by the sparker are able to oxidize these contaminants, which reduces their tack and makes them more benign. They also promote agglomeration of these contaminants, which makes them more screenable.

Mechanistically, the effects caused by the sparker are no different than those caused by ultrasound, but the sparker offers two distinct advantages. It does not heat up the water and it can treat a large volume of water. These attributes make it economical for mill applications. Several mill trials were run. One mill purchased the unit after finding that stickie deposits on the dryer felts were reduced. The sparker induced agglomeration of a mixture of pitch, fines and clay deposits at one newsprint mill. This can be detrimental if the deposits are unexpected. Laboratory work shows that these deposits are mainly the result of a high alum concentration. Sparking reduced hole counts and increased yield at another newsprint mill, but this could not be confirmed elsewhere. However, sparking reduced hydrosulfite bleach use by about 1 lb/ton in both mills, by inhibiting ink reagglomeration to fiber. The reduced bleach use and the decreease in tack of stickie deposits are presently the most useful features of the device. The payback for either application is attractive.

Sparking also degases water and is able to oxidize odor-causing sulfur compounds. It can be used to manage particulates, although this application is complex and depends on the chemicals present in the stream. It can decolorize pulp mill filtrates. It does not refine fiber or clean wires and felts as was initially hypothesized. Finally, a short study was conducted to determine

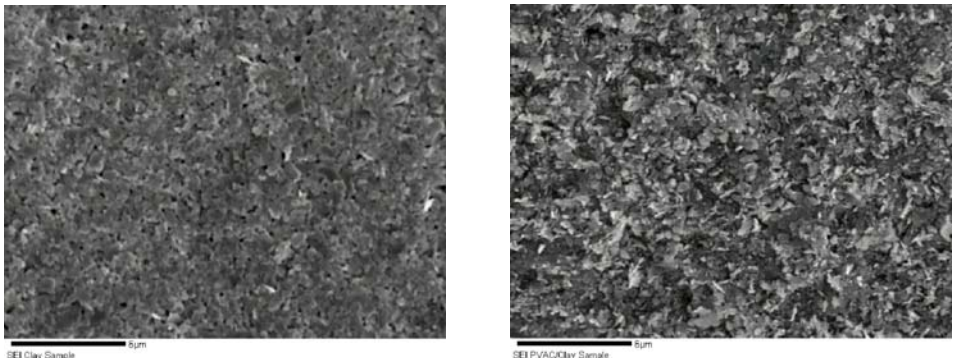

Figure 30: SEM images of clay (left) and clay-PVAc aggregates (right).

whether sparking would inactivate stickie-clay aggregates. It did not, but in the course of the study it was noted that these aggregates can be of neutral buoyancy, which explains why they are able to pass through cleaners and contribute to product defects.

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10. Publications and technology transfer

Patents

Two US patent applications:

- H.Corcoran, S.Banerjee, System and method for altering the tack of materials using an electrohydraulic discharge, US patent allowed.
- S.Banerjee, System and method for altering characteristics of materials using an electrohydraulic discharge, US patent pending.

have been filed. The technology has been licensed to Sparktec Inc.

Publications

- H. Corcoran, D-J. Sung, S. Banerjee, Electrohydraulic discharge detackifies polymer surfaces in water, *Industrial & Engineering Chemistry Research*, 40, 152 (2001).
- J.Yang, S.Banerjee, Effect of clay-stickie interaction on centrifugal cleaner efficiency, *Tappi J.*, in press.
- H. Corcoran, Ph.D. thesis, IPST, Atlanta, GA, 2001.

Presentations

H.Corcoran, D-J.Sung, and S.Banerjee, Control of Stickies through Electrotechnology, 1st CTP-PTS Packaging, Paper and Board Symposium, Grenoble, France, 1999.

H.Corcoran, D-J.Sung, and S.Banerjee, Detackification of stickies using plasma-spark technology, TAPPI Papermaker's Conference, Vancouver, 2000.