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Evaluating the Effectiveness of Chemicals for Stickies Control

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Abstract

Mixing an aqueous suspension of stickies under turbulent conditions induces agglomeration, since the particles collide strongly enough to overcome their mutual repulsion. The turbidity of the water progressively decreases at a measurable rate, which increases with increasing turbulence and decreasing pH. Stickies-control additives can accelerate agglomeration, and the clarification rate can be used as a measure of the effectiveness of the additive. Talc and a chemical additive were examined. It was found that while talc did not alter the agglomeration rate it led to a detackified agglomerate. In contrast, the chemical additive greatly enhanced agglomeration, but did not reduce tack.

INTRODUCTION

Although additives for stickies control are widely used (1-3), an objective means of evaluating their performance is not available. One measure of a good additive is its ability to agglomerate and detackify stickies, which could then be caught in the web and purged from the system. Stickie particles are negatively charged. If two particles collide strongly enough to overcome their mutual repulsion, agglomeration will occur, the agglomerate will grow to the point where it destabilizes, and the turbidity of the water will decrease. Hence, a good additive will clarify water under turbulent conditions that promote interparticle collision, and the clarification kinetics could be used to evaluate the effectiveness of the additive. This study examines the agglomeration process in order to understand the function of different additives and develops a simple procedure for screening their effectiveness.

EXPERIMENTAL

Agglomeration studies were run in a 5L temperature-controlled glass mixing chamber (Bioflow 3000) obtained from New Brunswick Scientific. A stirrer with a radial flow impeller was controlled at between 50 and 1000 rpm. Four removable metal baffles reduced solid body rotation and minimized vortex formation. Agglomeration kinetics were measured under acidic conditions, since agglomeration either did not occur or occurred very slowly at pH>4. These conditions may be atypical, but since the additives are compared on a *relative* basis, the only assumption involved is that their *relative* behavior under acidic conditions will transfer to higher-pH environments.

Measurements were usually made at 50°C and at 1,000 rpm by periodically withdrawing samples and measuring their optical density at 650 nm, the wavelength typically used to measure turbidity. Zeta potential and particle size were measured with a Malvern Zetasizer 3000. Samples containing talc (whose particle size of >1.0 μ exceeded that of the acrylate stickies used) were allowed to settle for a day prior to the zeta measurement.

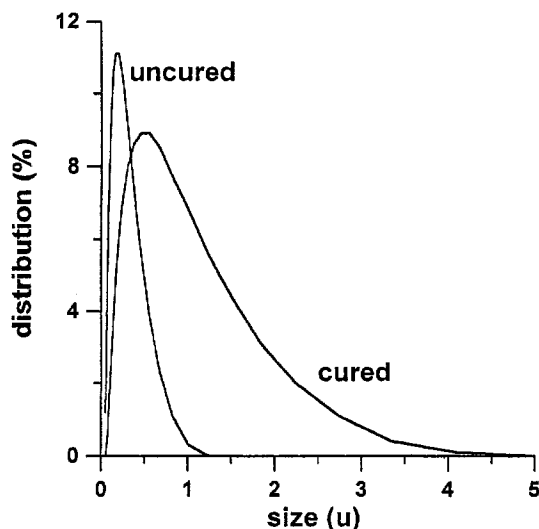


Figure 1: Comparison of particle size and dispersion for uncured and cured stickies.

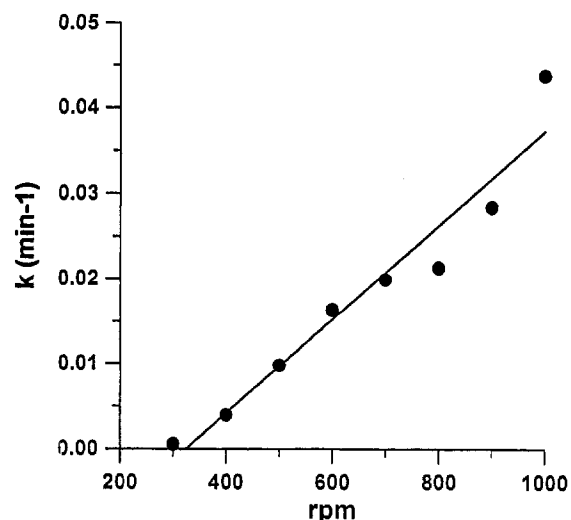


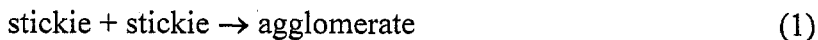
Figure 2: Effect of mixing rate on the rate of agglomeration.

Whitewater was obtained from the East Millinocket, ME, mill, owned at the time by Bowater. The various additives used were supplied by the mill. Polyvinyl acetate (PVAc) of molecular weight 12,800 was obtained from the Aldrich Chemical Co. Acrylates were obtained from B.F. Goodrich (Carbotac latex). Acrylates and PVAc are commonly found in the mill (4, 5). EXPN-3405 and ACCURAC-181 (manufactured by Nalco) and (Mistron-400 from Luzenac) were provided by the mill.

A stable suspension of cured acrylate was prepared as follows. The latex (10 mL) was spread evenly on a glass plate, dried with a stream of hot air, and cured overnight. The film was then scraped off and added to 600 mL of hot deionized water with 1 mL 1.0N KOH and 50 μ L BRD surfactant, a blend of fatty acids and a nonionic surfactant obtained from Buckman Laboratories (6). The suspension was then chopped into smaller particles with a high-speed homogenizer. Most of the particles were quite large and settled to the bottom of the beaker, and the yield of dispersed fine material was quite small. After being cooled to room temperature, the solids were further homogenized to produce a milky suspension, from which some further settling occurred. The decanted liquid was then used for the kinetic work. A comparison of the particle size distribution of cured and uncured material is provided in Figure 1. The reaction chamber was charged with either deionized water or whitewater, and the resuspended cured latex was added. The pH was then stabilized to a target value with 1N HCl or KOH, and the kinetic run begun. Runs were generally continued to about 1-3 half-lives.

DISCUSSION

Clarification kinetics were usually of the first-order ($r^2 > 0.99$). The uncertainty in rate constants was about 20% for the uncured stickies but was much higher (at about 100%) for the cured material, probably because of its wider size distribution. If the kinetics followed the scheme



where the agglomerate was removed from the process, then the agglomeration should be of the second-order (7). On the other hand, if the properties of the agglomerate were similar to that of the initial stickie, i.e., the process



had the same rate constant as process (1), then the reaction would be first-order. Since the stickie will grow and fall out of suspension at some point, mixed-order kinetics are anticipated, with the process being initially first-order and then becoming more complex.

In order to determine the effect of mixing intensity on the agglomeration rate, PVAc was added as a 9.9% solution in methanol to water at pH 2.6. In order to eliminate batch-to-batch inconsistencies, agglomeration rates at different mixing intensities were measured with a single batch of a stickie suspension. The kinetics were measured at a given mixing rate, the rpm of the impeller was then progressively increased, and the rate was measured at each step. The results, illustrated in Figure 2, show that agglomeration increases linearly with mixing intensity. Reproducible rates could not be measured below 300 rpm because the agglomeration was too slow. The Figure 2 relationship is linear only because the data were acquired over a single run. Rates measured across different runs were highly variable, probably because the size distribution of PVAc particles in suspension varied across each batch.

Agglomeration rates of uncured acrylate in distilled water and whitewater are compared in Table 1. While the whitewater rates are slightly faster than those in distilled water, the differences are within a factor of two. Hence, the conclusions reached for distilled water should also apply to whitewater. The agglomeration rates of cured and resuspended acrylates are listed in Table 2 and display a much higher variability than those in Table 1 for the uncured material. However, the median rate of 0.15 min^{-1} is roughly comparable to the rates in Table 1 for uncured acrylate, confirming that there are no order-of-magnitude differences in behavior. The high variability of the rates in Table 2 appears to be principally associated with differences in particle size. The changes in particle size that accompany the decrease in turbidity are illustrated in Figure 3. As expected, the large particles agglomerate rapidly. Hence, the wider distribution in particle size present in a suspension of cured stickies leads to scatter in the agglomeration rate. The remainder of the study was conducted with uncured stickies with the expectation that the conclusions will also apply to cured resuspended material.

The dependence of the rate of agglomeration of acrylates on pH is illustrated in Figure 4. The break at $\text{pH} \approx 4$ indicates that stickies will resist agglomeration at higher pH, most likely because the zeta potential becomes less negative under acidic conditions. The rate is quite sensitive to pH in the pH range of 4-5. Mills that deliver acid shocks to remove stickies should, therefore, target a pH of slightly less than 4 to ensure that they operate in the plateau region of the curve where the agglomeration rate is maximal.

Table 1: Comparison of agglomeration of acrylate ¹ in distilled water and whitewater				
pH	type of water	$k \times 10^3 \text{ (min}^{-1}\text{)}$	r^2	absolute difference (%)
4.89	whitewater	6.3	0.95	15
4.80	distilled	5.5	0.95	
3.05	whitewater	200	0.995	
3.01	whitewater	370	0.99	100
3.04	distilled	140	0.9997	
2.51	whitewater	190	0.97	36
2.47	distilled	130	0.999	
2.45	distilled	150	0.990	
¹ 0.5-5 mL of a 50% acrylate suspension (0.33 μ) added to 2 L of water at 1,000 rpm;				

Table 2: Agglomeration of cured/resuspended acrylate ¹		
pH	$k \times 10^3 \text{ (min}^{-1}\text{)}$	r^2
4.1-4.5	150	0.99
3.5-3.7	150	0.997
2.7-3.0	190	0.9992
2.5	63	0.999
2.5	33	0.986
¹ in water except for the first entry which refers to whitewater		

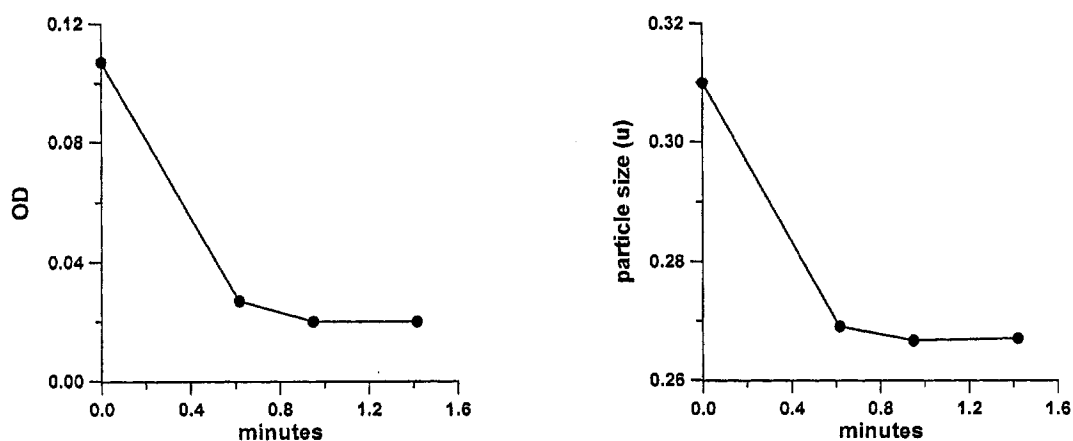


Figure 3: Optical density and particle size changes during cured PSA agglomeration in water at pH 3.3.

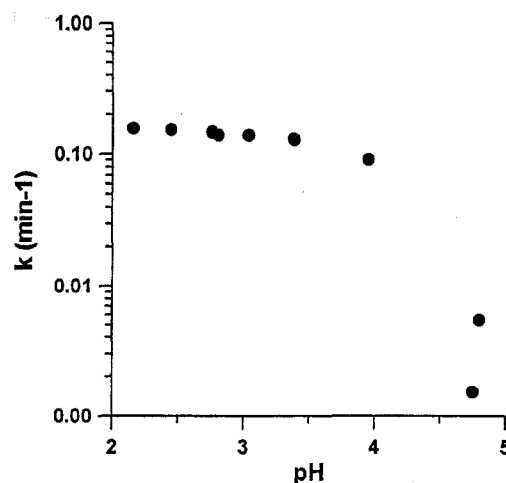


Figure 4: Dependence of acrylate agglomeration on pH.

Table 3: Effect of talc on acrylate agglomeration			
pH	talc (%) ¹	k x 10 ³ (min ⁻¹)	r ²
<i>1,000 rpm</i>			
3.01	0	370	0.987
2.97	0.03	210	0.987
	0.12		
3.09	0.24	440	0.985
<i>750 rpm</i>			
3.08	0	67	0.99
2.98	0.03	66	0.996
3.08	0.12	71	0.993
3.09	0.24	63	0.94
¹ of the talc concentrate (0.9 lb/gallon); the mill dosage is 0.4%			

Effect of additives on acrylate agglomeration

Talc is commonly used to deactivate stickies (8, 9), and its mode of action was probed by adding it to whitewater and measuring the rate of stickie agglomeration. Whitewater (2.5 L) was spiked with 0.6 mL of a 50% suspension of acrylate, and data were taken at various impeller speeds. Only the 750 and 1,000 rpm conditions led to first-order kinetics; agglomeration was too slow at lower rates. The kinetic data summarized in Table 3 show that the rates are not significantly increased by the presence of talc. Although some of the values in Table 3 are flagged as zero-talc, the whitewater contained some residual talc. Importantly, in the absence of talc, the agglomerate was compact and tacky and attached to the sides of the chamber. In its presence, the agglomerated stickie was feathery, and floated on the surface, and the walls of the chamber

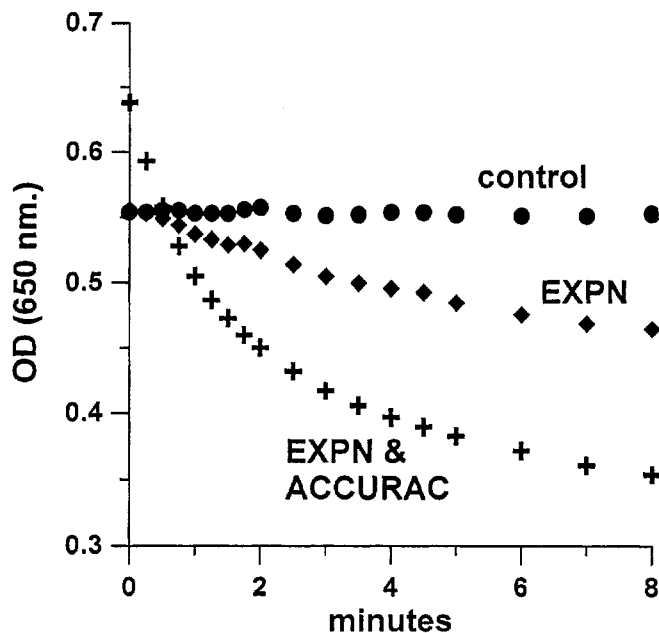


Figure 5: Agglomeration rates in the presence of EXPN and ACCURAC.

were relatively clean. Hence, tack should be useful in keeping stickies from depositing on machine surfaces. The degree of detackification was qualitatively the same at all the concentrations listed in Table 3. The level of stickies used in these experiments far exceeds levels likely to be encountered in the mill, and there should be a sufficient reserve of talc even under reduced dosage to handle stickie surges. Hence, the dose used by the mill may be unnecessarily high. Our results suggest that while talc is ineffective for agglomerating stickies to one another, it is a powerful detackifier.

The Millinocket mill used a combination of EXPN-3405 and ACCURAC-181. EXPN-3405, a mixture of polyethyleneimine and a mixed polyamide polyamine polymer, was applied at 3 lb/ton. ACCURAC is cationic polyacrylamide and is applied at 2.5 lb/ton. The effect of the combination of agglomeration is compared to corresponding data for EXPN alone and to a control in Figure 5. The rate enhancement is sizeable. As before, the stickie alone did not agglomerate, whereas the combination rapidly removed the stickie from suspension. Only minor differences in particle size were observed among the three sets. In contrast to the action of talc, the agglomerate remained quite tacky and adhered strongly to the sides of the vessel from which they had to be scraped off.

The two examples illustrated above show different extremes. Talc does not enhance agglomeration (at least by our measure) but is unique in its ability to detackify acrylates. EXPN/ACCURAC greatly enhances agglomeration but does not appear to reduce the tack significantly. The agglomeration is useful, since microstickies can be converted to macrostickies and then be potentially removed through flotation (10) in the clarifier or screening. Numerous other chemicals were evaluated, many of which affected neither the agglomeration rate nor the tack. While we recognize that our test may not capture all the attributes of a stickies-control ad-

ditive, it does provide an objective measure of the efficiency of an additive and an understanding of its mechanism of action. Two facilities (including the Millinocket mill) have successfully used the technique for selecting their stickies-control chemicals and optimizing the dosage, with considerable cost savings.

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