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STICKIE INTERACTIONS IN FIBER-WATER SYSTEMS

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ABSTRACT

A Britt jar approach was used to study the distribution of a model stickie material in a fiber-water system when the water was separated from the fiber through a 200 mesh screen. The model stickie chosen was a polyvinyl acetate (PVAc) homopolymer in methanol solution. A gravimetric technique determined how much of the stickie went with the water and how much stayed with the fiber. A mass ratio factor, M_r, was used to ratio the amount of stickie that stayed with the fiber over the amount that went with the water; the higher the M_r, the more the amount of stickie staying with the fiber. Factors evaluated included Kappa number, surfactant level, pH, and refining. Refining, low pH, and high Kappa number all tended to increase M_r. A retention system also worked very well in retaining the model stickie in the fiber structure. It was demonstrated that the stickie will agglomerate and/or coalesce in pure or dilute water systems; however, this tendency to agglomerate and/or coalesce is inhibited by the presence of a fibrous network. This study demonstrated that the procedure may be an effective tool for studying stickie interactions in fiber-water systems.

INTRODUCTION

Stickies are one form of contaminant in recycle paper streams that causes processing problems in recycle plants and paper machines. If they stay with the fiber in the finished paper product, they can stick to downstream paper processing equipment such as forming fabrics, wet pressing felts and rolls, dryer cans, calender rolls, and other paper machine processing equipment. In addition, stickies may have a negative effect on critical paper properties such as strength, aesthetic appearance, friction, printability, et al. In the recycle plant, several types of separation operations are utilized to remove stickie materials from the fiber stream. These include screening, flotation, and various forms of centrifugal cleaning. There are also points in the recycle process where water is separated from the fiber stream. Such separation occurs in thickeners, washers, and in the paper forming process itself. Drum savealls and disc filters used for paper machine fiber recovery are also examples of a fiber-water separation.

The recycle plant is designed to separate stickies from the fiber and cause them to go with the white water (or gray water), either for disposal or for recycle. Nevertheless, a small percentage of stickies make it through the recycle plant to the paper machine. At this point, it is generally preferred that stickies go with the fiber and not with the white water; otherwise build-up and agglomeration may occur in the white water recycle process. Retention systems are often employed to help stickies stay with the fiber on the paper machine.

One reason that stickies are not completely separated in the recycle plant is because they are often very fine in particle size, less than five micrometers. Recycle fiber process steps, such as dispersion, kneading, and refining, further attempt to reduce stickies to smaller and smaller particles. It can be argued that the fine particularization of stickies minimizes their impact on paper properties; however, it also increases their tendency to go with the white water of the paper machine process. Fine particles also contribute to drainage difficulties on the paper machine.

The continuing persistence of stickie problems in recycle mills and paper mills indicates that the interactions of stickies with fiber in water systems are still not well understood. A fundamental study to develop better knowledge of these interactions is necessary.

DESCRIPTIVE INFORMATION

This study is the first part of a program to identify the interactions of stickies in water-fiber systems. The basic purpose is to identify the factors that cause stickies to go with the fiber or with the water in a separation process. In this presentation, a procedure for studying these interactions is described. Some of the early experimental results will be presented.

METHODS AND MATERIALS

The procedure is based on the Britt jar apparatus, depicted in Figure 1. A measured amount of a model stickie material is added, slowly from a syringe, to a fiber slurry in the Britt jar that already contains predetermined amounts of fiber and water. The slurry, with stickie, is agitated for 15 minutes at 300 RPM, then the water is drained and separated through a 200 mesh screen. The fiber collected on the screen is dried and weighed. The solids content of the drained water is measured to determine the amount of solids that passed through the screen. A blank experiment, without the stickie, is conducted in an identical manner. By weight difference, the amount of stickie in the fiber and the amount in the water is determined.

The model stickie chosen for these experiments is a 3% solution of Polyvinyl Acetate (PVAc) homopolymer in methanol. The homopolymer has a glass transition

temperature (T_G) of 29°C. When the solution is added slowly to an agitated fiber slurry, PVAc instantly precipitates into a white amorphous gel that has stickie-like properties and is very small in particle size.

Table 1 is the experimental model. The distribution of stickie is determined from the differences in solids between the experiment with stickie and the blank without stickie. The amount of stickie, in gm, remaining in the filtered fiber mat is $m_{mat}-m'_{mat}$. The amount of stickie in the effluent water is $m_{water}-m'_{water}$. If the experiment is to be successful, the following material balances have to be satisfied:

(1) $m_{fiber} + m_{stickie} = m_{mat} + m_{water}$
for the experiment with stickie.

(2) $m_{fiber} = m'_{mat} + m'_{water}$
for the control without stickie.

(3) $m_{stickie} = (m_{mat}-m'_{mat}) + (m_{water}-m'_{water})$
for the stickie balance.

The data results from a typical experiment are tabulated in Table 2. The material balances as expressed by Equations (1) and (2) generally check to within +/- 2%. The $(m_{mat}-m'_{mat})$ and $(m_{water}-m'_{water})$ quantities in Equation(3) are determined as small differences between relatively large numbers and therefore have a much larger variation, approximately =/- 20%.

A mass ratio factor (M_r) is defined as the concentration of stickie in the fiber mat to that in water, i.e.,

(4) $M_r = ((m_{mat}-m'_{mat})/m'_{mat})/((m_{water}-m'_{water})/V)$

where V is the volume of water used in the experiment. Table 2 shows how M_r is calculated from the numerical data in accordance with Equation (4). M_r is a small number if most of the stickie goes with the water. It becomes a very large number if most of the stickie stays with the fiber. If the stickie is equally distributed between fiber and water, then M_r = 1. If all of the stickie stays with the fiber, then $m_{water}-m'_{water}$, the denominator in Equation (4), goes to zero and M_r goes to infinity. In certain situations, M_r will be a negative number. An example would be an experiment where there is a strong retention system and the presence of the stickie enhances retention. In a parallel study, Diaz(1) demonstrated such an effect when using SBR latex as a model stickie and alum as the retention aid. The retention of fines and stickies with the fiber was such that there was less solids in the water from the experiment than in the blank. The term, $m_{water}-m'_{water}$, became a negative number and, accordingly, so did M_r.

RESULTS

Kappa Number and Surfactant Concentration

Mass ratio factors (M_r) were measured for a variety of softwood Kraft pulps, both with and without the presence of a surfactant. The surfactant was a nonionic commonly used as a collector in deinking processes. The results are illustrated in Figure 2. It appears that M_r increases linearly with Kappa number suggesting that the model stickie (PVAc) will associate more strongly with brown pulp than with the zero Kappa bleached pulp. Surfactant level generally tends to increase the tendency of the stickie to go with the water (i.e., lower M_r); however, the effect is inconsistent. M_r for Kappa 81 pulp drops steeply at the highest surfactant concentration. This result does not appear to be an artifact since it occurred reproducibly. It may be an associative thickener effect and/or an effect of critical micelle concentration.

Microscopic examination of the water effluents from both the high Kappa (Kappa = 81) unbleached pulp and the zero Kappa bleached pulp revealed that many of the stickie particles were in the range of one to five micrometers in diameter. The examination also revealed a tendency of these particles to cluster with themselves and also with fiber fines in the effluent.

Refining

In principal, the stickie can be associated with domains of higher specific surface, or be freely suspended in water. Domains of higher specific surface include fiber fines and the frayed fibrils that stick out from pulp fibers as a result of the refining process. In order to distinguish between the two possible associations, the effect of fiber surface area on M_r was studied. Bleached pulp was beaten to different Candian Standard Freeness levels and measurements made at each level. The results illustrated in Figure 3 demonstrate that M_r is inversely proportional to freeness.

The root cause of this dependence can be appreciated from the data presented in Table 3. The "fines in water" column measures the fines in the water effluent without stickie (m'_{mat} in Table 1 and Equation (3)). "Stickie in Water" represents the mass of stickie in the water effluent, i.e., ($m_{water}-m'_{water}$) from Table 1 and Equation (3). The final column is the mass ratio of stickie in the water effluent to that of fines in effluent. Both masses, m'_{mat} and ($m_{water}-m'_{water}$), decrease with increased refining. This reflects on the improved filtration efficiency of the mat as its surface area is increased due to refining. However, the relative constancy of the mass ratio suggests an association of stickies with the fines.

Effect of pH

Low pH (less than 5.0) increases the tendency of the stickie to stay with the fiber. The effect as demonstrated in Table 4 is more pronounced with

unbleached, high Kappa, kraft pulp (Kappa = 81) than with bleached kraft (Kappa = 0). A possible reason for this is that acid may be increasing lignin hydrophobicity by protonating carboxylic acid groups.

Retention Systems

A study was made to compare how well the model stickie worked in retention systems as compared to more traditional latex polymer emulsions. Two PVAc latex systems were chosen. One was a flexible crosslinking PVAc latex generally used as a pressure sensitive adhesive (T_g, = -36°c). The other was a more rigid PVAc latex generally used for paper coatings (T_g = 29°C). The retention system chosen was based on anionic colloidal silica, cationic starch, and alum. The quantities were .06 g of silica, .06 g of cationic starch and .03 g of alum added to 3 g of bleached kraft. The PVAc resin added was .2 g, bone-dry basis. The slurry was mixed in 600 ml of water. A controlled experiment was run by eliminating the cationic starch from the above formulation. In both cases, experiment and control, the distribution of chemicals in the fiber and in the water effluent was determined by subtracting a blank without chemicals, in accordance with the format of Table 1. Since starch is in the experiment and not in the control, comparison by M_r is biased. Therefore, the retention efficiency, R_e, of the system was based on the reduction of solids in the water effluent.

(5) $R_e = ((m_{water}-m'_{water})_{exp}/(m_{water}-m'_{water})_{cont})*100$

where $(m_{water}-m'_{water})_{exp}$ is the solids or chemical content of the water effluent from the experiment with starch, and $(m_{water}-m'_{water})_{cont}$ is the solids or chemical content of the water effluent from the control experiment without starch. Both $(m_{water}-m'_{water})_{exp}$ and $(m_{water}-m'_{water})_{cont}$ are determined in accordance with the format of Table 1.

The results are presented in Table 5. It shows that R_e of the model stickie is comparable to the latex materials. It appears that the model stickie follows the behavior of real life stickies and polymeric materials in the retention systems of recycle mills. It also appears that the procedure as described here is a viable tool for measuring the effectiveness of such systems in retaining sticky materials.

Agglomeration

Figure 4 presents one of the important results that has emerged from this study. It shows that the model sticky will agglomerate into larger particles when dispersed in water, but not when dispersed in a fiber network. In this set of experiments, the model stickie was added to the water prior to adding the fiber and the effect was compared to adding the stickie to the slurry after the fiber. There were three agitation time levels; 25 minutes, one hour, and 24 hours. The stickie was added to the water and in successive experiments agitated at 300 rpm for 25 minutes before the fiber was added, one hour before the fiber was added, and 24 hours before

the fiber was added, respectively. After the fiber was added, the agitation was continued for an additional 15 minutes before draining the water. In the comparison experiments, the fiber was added to the water, agitated for 15 minutes and then the sticky added. In successive experiments, the slurry was agitated for 25 minutes, one hour, and 24 hours, respectively, before draining the water.

It happened that $(m_{water}-m'_{water})$ was near zero in the experiments where the sticky was added before the fiber. Since this term is in the denominator of Equation (4), it makes M_r an awkward comparator therefore, the experiments were compared by the concentration of stickie in the water, $(m_{water}-m'_{water})/V$.

Figure 4 shows that the concentration of the sticky is zero or near zero, across the board, when the stickie is added to the water first. The concentration is higher and ranges from 100-150 mg/l, for the experiments where the fiber is added first. The explanation is that when the stickie is added slowly to the water from a syringe and while the water is being agitated, small particles are formed, that quickly coalesce into larger particles. This is very observable. By the end of 24 hours, all the stickies have coalesced into one large aggregate. The large stickie particles are too large to pass through the 200 mesh screen of the Britt jar and that is why zero stickies are observed in the water effluent.

On the other hand, if the stickie is added after the fibers, the fibrous network inhibits the stickie particles from coalescing with each other. The particles remain small, small enough that many of them are able to pass through the 200 mesh screen and show up in the water effluent. The relative size of fibers (20-40 μm) compared to the much smaller observed stickie diameters (less than 5 μm) suggests that it has to be the fines that are networking around the stickie particles and protecting them from coalescing with other stickie particles.

It may be that this is a case of kinetic-thermodynamic control. It is hypothesized that the association of stickies with fines competes with their ability to coalesce with other stickies. The association with fines is the much faster reaction; however, it is an intermediate state that is reversible. On the other hand, the coalescence of stickies is a slower, but irreversible, reaction. If the stickie in fiber slurry were allowed to agitate long enough, eventually the small stickie particles would find each other and coalesce into larger particles.

For the short-term effect, this study shows that the model stickie agglomerates in dilute water systems, but not in water-fiber slurries. If this effect can be related to real life stickies in a recycle mill, it helps explain why stickies remain small in fiber slurries and than build up into large aggregates in the white water systems of recycle mills and paper machines.

CONCLUSIONS

This study has demonstrated that the Britt jar approach may be a viable tool for studying stickie-fiber-water interactions. The model stickie as chosen for these experiments still has to be verified as having properties similar to real-life stickies in recycle mills. The procedure allows for other types of stickie materials, such as hot melts, waxes, and pressure-sensitive adhesives to be studied. Based on the authors' experience, it does appear that the behavior of the model stickie in fiber-water systems is consistent to what has been observed in recycle mills. Some of the behavioral aspects that have been observed here are as follows:

1. Higher Kappa number increases a pulp's ability to retain stickies in its fiber structure.

2. Refining increases the association of stickies with fines and thereby increases the retentivity of stickies into the fiber structure.

3. Low pH (that is less than pH = 5) increases the retentivity of stickies into the fiber structure, possibly by generating hydrophobic domains on the fiber surface.

4. The model stickie of this study appears to respond to retention systems in a manner similar to other polymers. The Britt Jar technique described here provides a way for studying and optimizing stickie retention systems.

5. The model stickie of this study will agglomerate and/or coalesce in pure or dilute water systems; however, its ability to coalesce and/or agglomerate is inhibited by the presence of a fibrous network. The competing tendency of the stickie to either associate with fines or to coalesce may be governed by kinetic-thermodynamic control.

FUTURE

It was mentioned above that this report is the first part of a continuing study to better understand stickie interactions in fiber-water systems. Other variables to be investigated will include temperature and consistency. Other types of suspected stickie materials will be studied. Possibilities include latex materials, hot melts, wax, and pressure-sensitive adhesives. A plan is being formulated to verify some of the results by actual trials in pilot facilities.

REFERENCES

(1) Diaz, R. "Measurement of Interactions Between Fibers and Styrene Butadiene Rubber Based Pressure Sensitive Adhesives (PSA), - A Final Report of Independent Research" Institute of Paper Science and Technology, Atlanta, Georgia, May 19, 1995

TABLE I - MODEL FOR STICKIE, FIBER, WATER INTERACTION EXPERIMENT

	Solids In		Solids Out	
	Fiber	Stickie	Fiber	Water
Experiment with Stickie	m_{fiber}	$m_{stickie}$	m_{mat}	m_{water}
Blank without Stickie	m_{fiber}	0	m'_{mat}	m'_{water}
Stickie Balance	0	$m_{stickie}$	$m_{mat}-m'_{mat}$	$m_{water}-m'_{water}$

TABLE II - TYPICAL DATA FOR STICKIE, FIBER, WATER INTERACTION EXPERIMENT
Water Volume = 300 ml

	Solids In (g)			Solids Out (g)		
	Fiber	Stickie	Total In	Fiber	Water	Total Out
Experiment with Stickie	1.5308	0.1000	1.6308	1.5077	0.1141	1.6218
Blank without Stickie	1.5308	0	1.5308	1.4973	0.0206	1.5179
Stickie Balance	0	0.1000	0.1000	0.0104	0.0935	0.1039

$M_r = (0.0104/1.4973)/0.0935/300) = 22.29$

TABLE III - EFFECT OF pH ON M_R

pH	M_r (Kappa = 0)	M_r (Kappa = 81)
4.0	156	410
4.5	-	122
5.0	-	78
5.5	-	39
7.0	131	96
9.0	113	149

TABLE IV - EFFECT OF REFINING ON PVAC/FIBER DISTRIBUTION IN WATER

Freeness, ml	Fiber in water, g	PVAc in water, g	PVAc/fiber
641	.0854	.2093	2.45
575	.0408	.1447	3.59
441	.0285	.1489	5.22
335	.0264	.0901	3.45
200	.0202	.0612	3.03

TABLE V - BRITT JAR RETENTION OF PVAc POLYMER USING THE COLLOIDAL SILICA, CATIONIC STARCH, ALUM RETENTION SYSTEM

Polymer	Retention % (R_e)
PVAc Homopolymer in MeOH sol'n, $T_g = 29°C$	67.2
PVAc Latex Emulsion, $T_g = 29°C$	72.5
PVAc Latex Emulsion, $T_g = -36°C$	75.2

Speed Controlled
Stirrer 300 RPM

Britt Jar Assembly

200 Mesh Screen

Filtrate
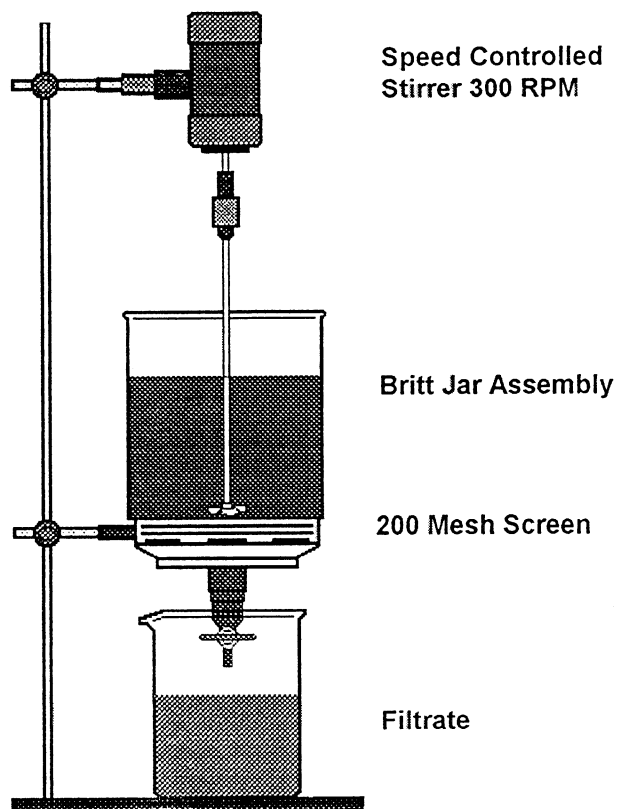
Figure 1 - Britt Jar Apparatus
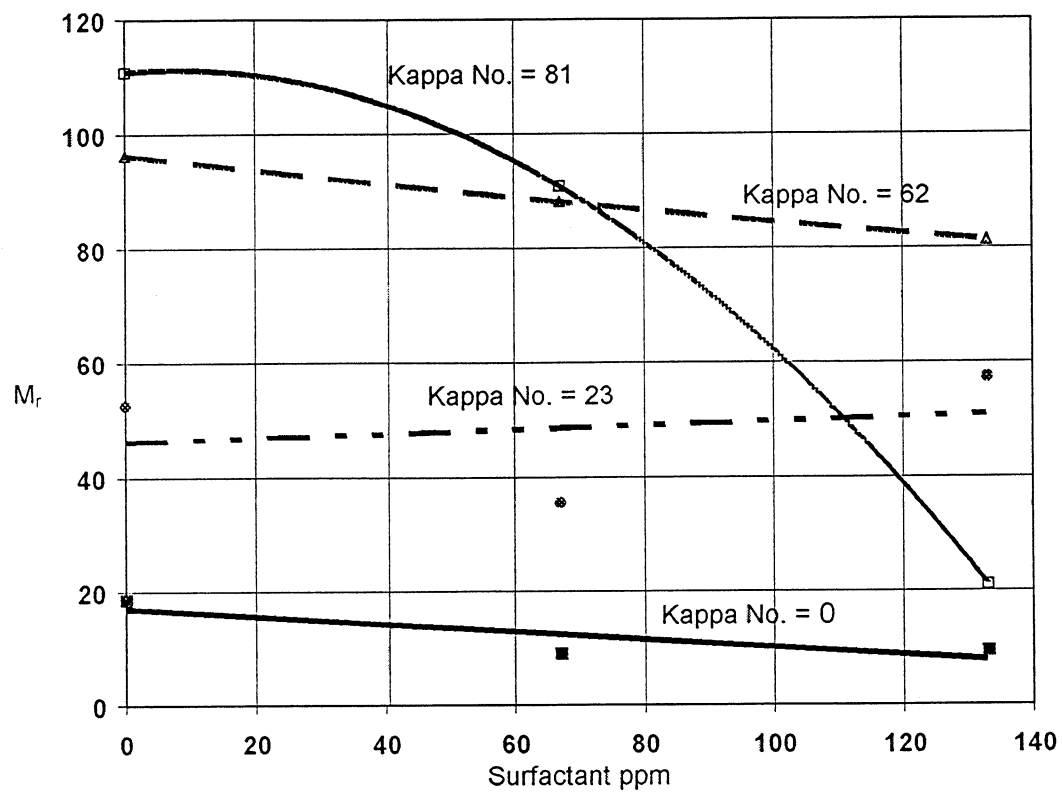
Figure 2 - Stickies Distribution Based on Surfactant Level and Kappa Number
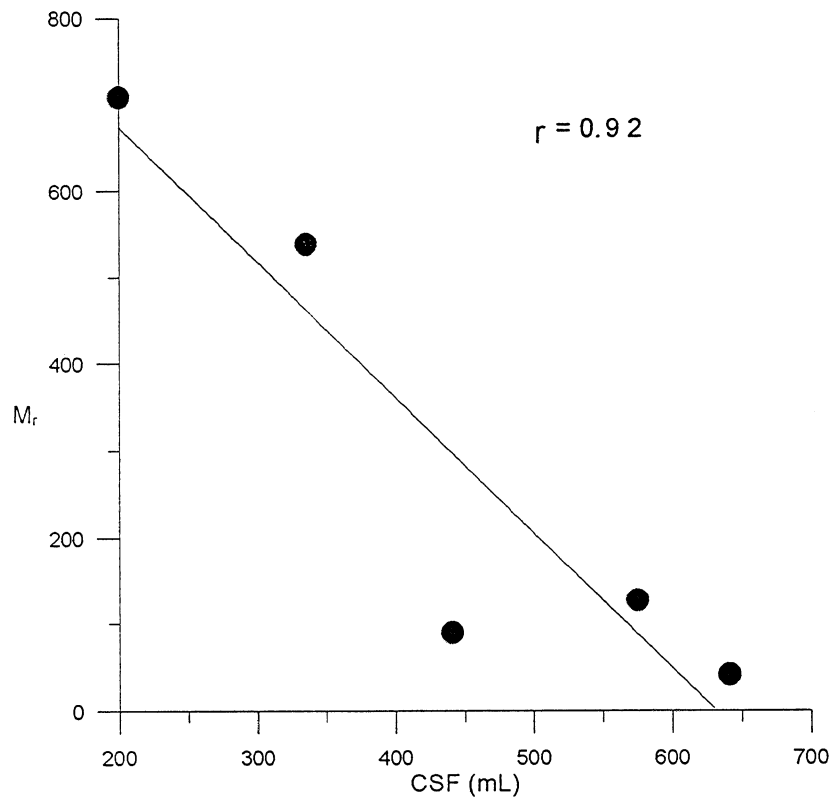
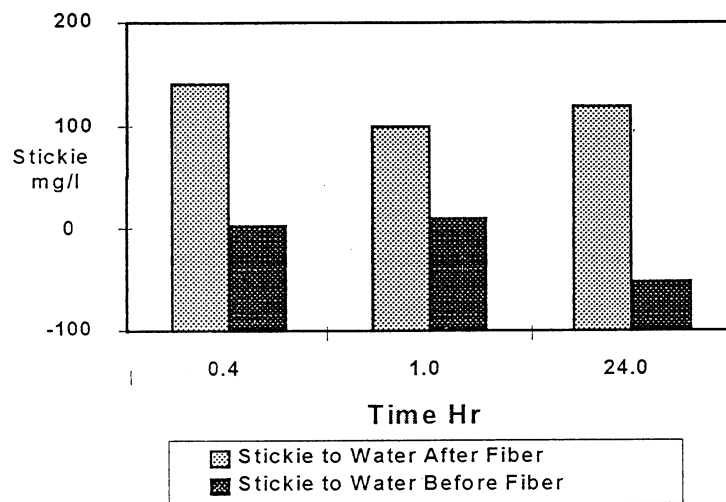Figure 3 - Effect of Refining on M_r - M_r vs. Canadian Standard Freeness

Figure 4 - Stickie in the Water Layer