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Application of Cyclodextrins for Extractives Control—Non-Proprietary Version

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Interim Report, February 2010

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PRODUCT DESCRIPTION

PM35 is a typical Fourdrinier paper machine and produces a number of specialty paper grades, among them a wet-strength-containing grade that contains recycled fiber. During a PM35-run one-reel recycled fiber trial using cyclodextrins technology as a stickies detackifying aid, elevated scratch counts on the second coater halted the trial. Microstickies and tack tests were performed on process samples taken during the trial to determine the mechanisms responsible for the elevated scratch counts. Using these test results, a laboratory mixing analysis of recycled and virgin pulps was conducted in preparation for a future recycled fiber trial. Results of the laboratory mixing study are reported here.

Results & Findings

This report provides background on the PM35 cyclodextrins trial followed by an analysis of the results from the recycle mix study.

Challenges & Objective(s)

This study was conducted to check for interactions between different pulp types and to screen different treatment options with the goal of reducing scratch counts.

Applications, Values & Use

The procedure to quantify colloidal microstickies in recycled pulp offers a way to help paper machine operators recognize potential impacts or issues with a given recycled fiber shipment.

EPRI Perspective

This study originally began as an EPRI project in 2006 and focused on the use of cyclodextrins to control extractives. Over time, the project evolved into its current status aimed at using cyclodextrins to reduce the impact of stickies and microstickies in recycled fiber at paper mills. Stickies and microstickies are blamed for a number of downtime-related problems on paper machines, including deposition, quality upsets, and coater blade scratches.

Approach

The project team designed the study to

- determine the impact of pulp mixing, cyclodextrins (Eka TR 3911) treatment, and fixative treatment on recycled fiber;
- measure stability of incoming pulp samples;
- determine pulp interaction when using recycled fiber; and
- determine impact of Eka TR 3911 on stabilization.

The project team used Duluth high-quality recycled pulp for most of the work, except for recycled pulp (SFK Pulp) from an alternate supplier for a few experiments. Pulp samples were taken during the trial for evaluation using the microstickies measurement system for effective measurement of micro-organic accumulation (EMMA) and turbidity. Select samples also were tested at the Institute of Paper Science and Technology (IPST) for tackiness, a measurement of a material's stickiness.

Keywords
Cyclodextrins
Chemical process
Pulp and paper industry
Industrial productivity
Environmental control

EXECUTIVE SUMMARY

Summary

Paper Machine PM35 ran a one-reel recycled fiber trial using cyclodextrins technology as a stickies detackifying aid. The resulting elevated scratch counts on the second coater canceled the remainder of the trial. The process samples were taken during the trial to conduct microstickies and tack tests, suggesting that mixing of virgin and recycled pulps led to agglomeration of the stickies that promoted the elevated scratch counts. A laboratory pulp mixing analysis was held in December 2009 as a recommended as a path forward to prepare for a future recycled fiber trial.

Preliminary conclusions

Using recycled fiber resulted in an increase in scratch counts on the second coater. Application of cyclodextrins can reduce the tackiness of stickies in the recycled fiber, but the mixing of virgin kraft pulps with recycled fiber leads to elevated dissolved and colloidal organics in the system and the potential for process upsets.

Recommendations

The analysis of the process samples from the PM35 cyclodextrins trial has led to a proposal for the evaluation of mixing virgin and recycled pulps. A laboratory pulp mixing analysis was recommended as a path forward to prepare for a future recycled fiber trial.

Conclusions

1. The procedure to quantify colloidal micro-stickies in the recycled lap pulp offers a means to help paper machine operators know of potential impacts or issues with a given recycled fiber shipment.
2. Dilution and mixing of Duluth HQ recycled fiber with virgin kraft pulps dispersed fewer microstickies than with SFK recycled fiber.
3. When making an evaluation of colloidal organics, a key component of the evaluation is to look at changes and differences. The three biggest changes seen in this study were more associated with the stock and water from the papermaking process rather than with the recycled fiber.
    a. The coated broke saw a 19% drop in Effective Measurement of Micro-organic Accumulation (EMMA) potential, indicating agglomeration upon mixing.

b. The recycled pulp mixed with the dilution water had lower EMMA potentials than the dilution water. Normally an increase or additive effect of adding more colloidal organics is observed.

c. Treatment of the softwood virgin kraft fiber with cyclodextrins before blending with recycled fiber had the biggest impact, leaving a stable concentration of colloidal microstickies after the blending process.

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CYCLODEXTRINS INDUSTRIAL TRIAL ON PM35

Background

This project originally began as an EPRI project in 2006 focused toward the use of cyclodextrins to control extractives. Over time, the project evolved into its current status aimed at using cyclodextrins to reduce the impact of stickies in recycled fiber used at a paper mill.

Stickies are blamed for a host of downtime-related problems on the paper machine including deposition, quality upsets, and coater blade scratches. Yan et al. estimated in 2003 that the annual cost of stickies to the U.S. paper industry totaled over $500 million,[1] due mainly to production losses from extra washing and cleaning. Microstickies are estimated to cost the industry $500,000 per mill annually.[2]

Cyclodextrins were discovered by the Institute of Paper Science and Technology (IPST) as a potential product for the detackification of stickies. Cyclodextrins are made up of 6-8 glucose units in a cyclical arrangement surrounding a hydrophobic core, as shown in Figure 1-1. Cyclodextrins are theorized to deactivate the stickies by capping the highly hydrophobic sites on the molecule, which changes the wettability of the stickies by making them more hydrophilic and reducing their ability to agglomerate.[3] However, this pulp was not traced to its end user to learn if the cyclodextrins prevented stickies problems on the paper machine.

PM35 is a typical Fourdrinier paper machine through the press section and main drying section with on-machine coaters. One of the quality parameters monitored on this machine is scratch counts. Typical scratch levels for the grades using recycled fiber manufactured on PM35 are three to five scratches in a ten-minute counting period.

[1] Yan, D. and Deng. Y. "Water-soluble/dispersible cationic pressure-sensitive adhesives. I. Adhesives from solution polymerization." *Journal of Applied Polymer Science*, Wiley Periodicals, Vol. 90, 6:1624-1630 (2003).

[2] Banerjee, S., IPST at Georgia Institute of Technology, private communication, 2003.

[3] Haynes, R.D. "Using Cyclodextrin to Stabilize and Control Colloidal Micro-stickies to Improve Paper Machine Runnability", *Proceedings of the TAPPI Engineering, Pulping, and Environmental Conference*, Memphis, TN, 2009.

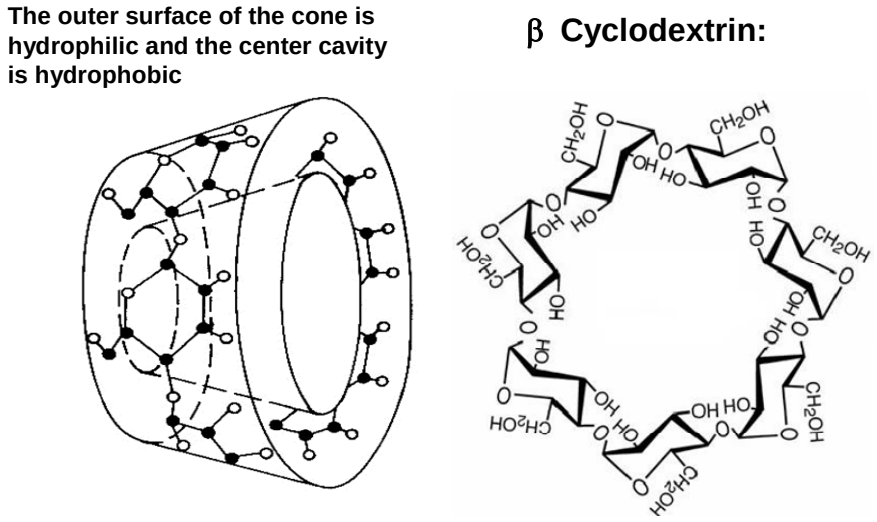

Figure 1-1
Structure for a β-cyclodextrin Molecule

PM35 manufactures a number of specialty grades, among them a wet-strength containing grade that contains recycled fiber. During previous trials with recycled fiber, scratch counts at the coater were elevated into the 40-50 scratches per 10-minute counting period. The scratches are attributed to stickies that are pulled out of the sheet by the coater blade and leave scratches or streaks in the machine direction. The use of cyclodextrins was offered as a potential means to reduce the level of scratches when using recycled fiber for the manufacture of the wet-strength containing grade.

The recycled fiber and cyclodextrins trial ran on PM35 on October 1st, 2009, using two pounds per ton of cyclodextrins product (TR-3911) added to the recycle pulper. The trial was halted due to high scratch counts after one reel was manufactured. The scratch counts were greater than 80 scratches per 10-minute period (as stated previously, three to five scratches per 10-minute period is normal).

Pulp samples were taken during the trial for evaluation by using the microstickies measurement system for EMMA (Effective Measurement of Micro-organic Accumulation) and turbidity. Select samples were also tested at IPST for tackiness, a measurement of the stickiness of a material.

2
UNDERSTANDING THE MIXING OF RECYCLED AND VIRGIN PULPS

Background

This project originally began as an EPRI project in 2006 focused toward the use of cyclodextrins to control extractives. Cyclodextrins are torus shaped, cyclic oligomeric sugar-based molecules that resemble a short ice cream cone and consist of a 6 (α), 7 (β), or 8 (γ) glucose unit. They are non-toxic, have a low cationic demand charge, and contain a hydrophobic cavity and a hydrophilic exterior. Their ability to form complexes with a variety of organic compounds makes these molecules valuable in medical and industrial applications.

Over time, the project evolved into its current status aimed at using cyclodextrins to reduce the impact of stickies in recycled fiber used at a paper mill. The results indicated that the elevated scratches that occurred may have been caused by microstickies agglomeration that was initiated by mixing of virgin kraft and recycled fiber. The results of laboratory mixing study was are reported here.

Basically, the EMMA potential measures the level of microstickies in solution and can be used to determine the capacity a paper machine system has to carry the load of colloidal material without said material depositing or agglomerating. Figure 2-1 illustrates the relationship of EMMA potential to the stability of the wet end of the paper machine. An arbitrary value of 500 ppm EMMA is selected as the average EMMA potential, with one standard deviation to either side of the average representing a stable zone in which to operate. Greater or lower than one standard deviation from the average EMMA potential represents unstable zones. In the low EMMA potential zone, the colloidal microstickies have already fallen out of solution by agglomerating to macrostickies or depositing onto surfaces. In the high EMMA potential zone, there is more colloidal material in solution that could lead to a high concentration of colloidal organics on the surface of the sheet, which could transfer to the paper machine rolls, dryer cans, calender stacks and coater blades. Treatment of the colloidal microstickies in these examples could result in either an increase or decrease in the EMMA potential in order to get into the stable zone.

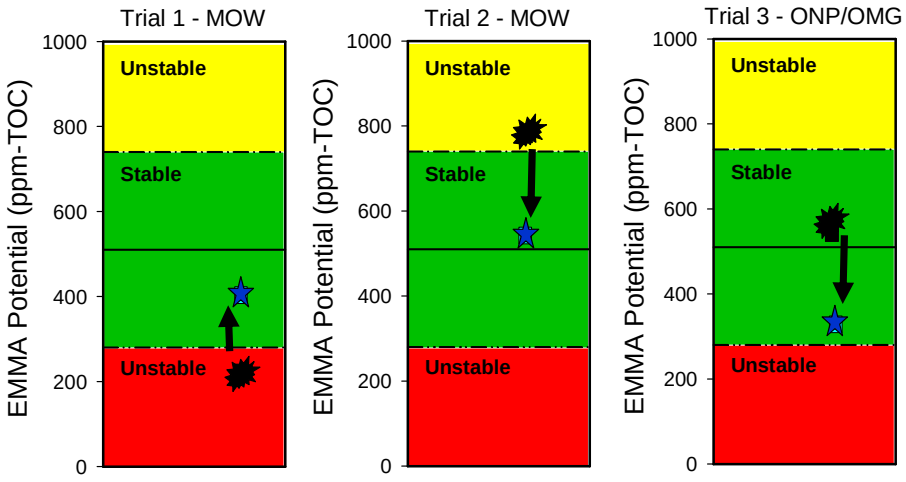

Figure 2-1
Colloidal Organic Response toward Stability with Treatment at Dump Chest

Mix Study

While trying to produce a certain wet strength grade, the Mill is experiencing problems with deposits that appear to be related to recycled fiber. This study was initiated to check for interactions between the different pulp types and to screen different treatment options. Duluth high quality (HQ) recycled pulp was used for most of the work except for a few experiments with a recycled pulp from an alternate supplier, SFK Pulp.

Objectives of Mix Study

The objectives of the study were to

- Determine the impact of pulp mixing, cyclodextrins (Eka TR 3911) treatment, and fixative treatment on recycled fiber used at the Mill;
- Measure stability of the incoming pulp samples;
- Determine pulp interaction when using recycled fiber; and
- Determine impact of Eka TR 3911 on stabilization.

SWD/HWD/Recycle Mix Study with Chemical Control

Five pulp stocks were collected while mill was on a wet strength grade:

1. Softwood (SWD) kraft – used at 41%;
2. Hardwood (HWD) kraft – used at 34%;
3. Coated broke;

4. Recycled wet lap pulp from Duluth (Duluth HQ); and
5. Recycled pulp dry lap from SFK (SFK).

Recycled fiber and coated paper was made down to 5% stock using paper machine whitewater or dilution water commonly used.

Samples were collected while the mill was producing a wet strength grade. (This is the grade that will have recycle added in normal production. Note: SWD kraft was made down with fresh water during this grade run; it is normally made down with white water.)

Results – Quantify Colloidal Micro-stickies of Recycle Lap Pulp

For this study it is unknown if the recycle lap pulps were produced under stable conditions. Test results show that the Duluth HQ sample has a low concentration of colloidal microstickies and that SFK is at the industry average of colloidal microstickies. Mixing of tap water with the recycled pulps saw a doubling of EMMA potential for both pulps with Duluth HQ at about 1/3rd the value of the SFK pulp sample (see Figure 2-2 and Figure 2-3). Mixing took the SFK sample to about the industry high and, typically, it is desired to have a pulp within the 25 to 75% quartile with no agglomeration when mixed. (Neither pulp saw a drop in EMMA with mixing). These results indicate that there were microstickies adsorbed onto the fiber surfaces that dispersed into solution once the pulps were slushed with tap water. If it is desirable to reduce the amount of colloidal microstickies that get into the paper machine system, these results indicate that the Duluth HQ pulp appears to have fewer microstickies.

The recycled lap pulp was mixed with the pulper dilution water (Figure 2-4) used while the paper machine was on a grade using wet strength (similar to when the machine produces the grade requiring recycled fiber). The Duluth HQ sample saw a slight increase in EMMA potential, which was within 10% of no mixing. SFK saw a drop in EMMA potential of 13%. Typically, a change within 10% of no mixing is considered a stable process.[4]

[4] Haynes, R.D., Eka Chemicals, private communication, 2009.

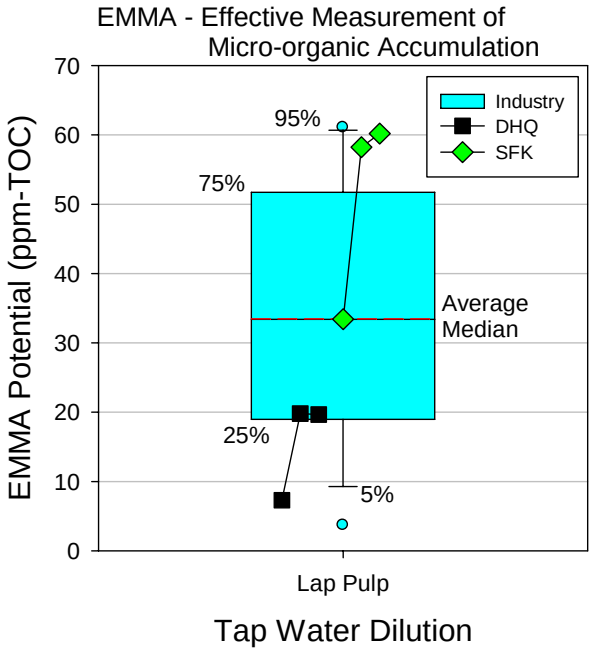

Figure 2-2
EMMA Comparison of Duluth HQ and SFK Recycled Pulps Before (Lower Point) and After Tap Water Dilution (Upper Points)

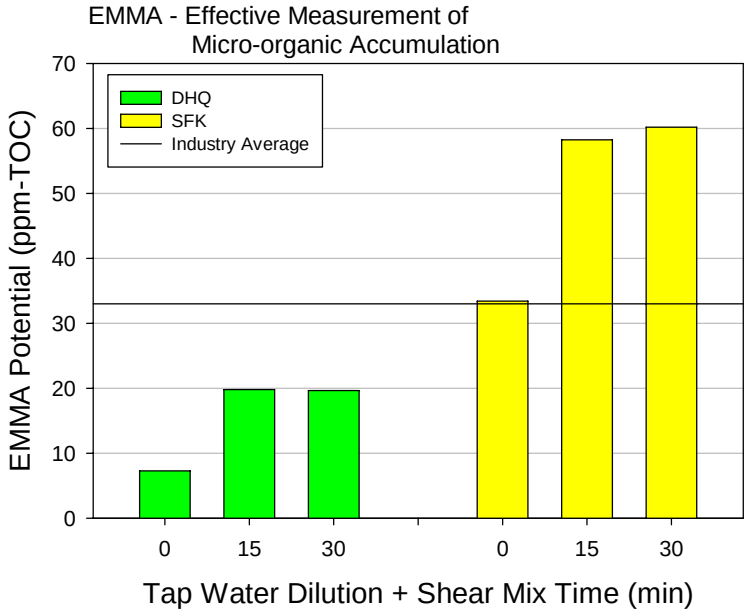

Figure 2-3
Results of EMMA Potential Following Dilution with Tap Water for Industry Benchmarking and 15 and 30 Minute Shear Stress Tests

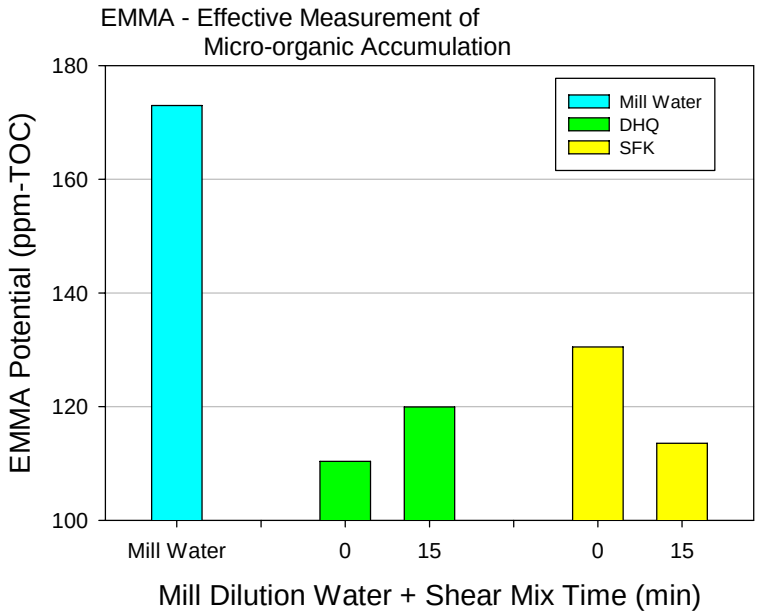

Figure 2-4
EMMA Potential Following Dilution with Pulper Dilution Water for 15 and 30 Minute Shear Stress Tests

Results – Measure Stability of the Incoming Pulp Samples

Based on these results, the Duluth HQ recycled pulp should cause the least issues. A significant concern is that the made down pulps had a lower EMMA potential than the dilution water; this could indicate agglomeration of colloidal organics in the water onto the fiber, which could cause deposit issues.

The next step was to look at the individual pulps and to determine the response to the shear stress of mixing and how treatment of the individual pulps with cyclodextrins (1 lb/ton was the dosage) responded (see Figure 2-5). For the individual pulps, the HWD and the Duluth HQ pulps saw the smallest change. The coated broke sample saw a significant drop of 19% in EMMA and indicates agglomeration of colloidal organics out of the filtrate. The SFK pulp samples saw a 13% drop in EMMA with treatment of the cyclodextrins returning the pulp to pre-mix levels. Treatment of coated broke and Duluth HQ did not return them to pre-mix levels of EMMA potential.

For the Duluth HQ recycle lap, neither the addition of a stabilizer like Eka TR 3911 (cyclodextrin) or fixatives such as Eka TR 3642 (a polyamine) or Eka TR 3682 (a polydadmac) significantly changed the amount of stable colloidal organics. Adding more cyclodextrin tended to lower the number (see Figure 2-6). The SFK recycled pulp sample did benefit from the addition of 1 lb/ton of cyclodextrin, but had a significant amount of agglomeration at a dosage of 2 lb/ton.

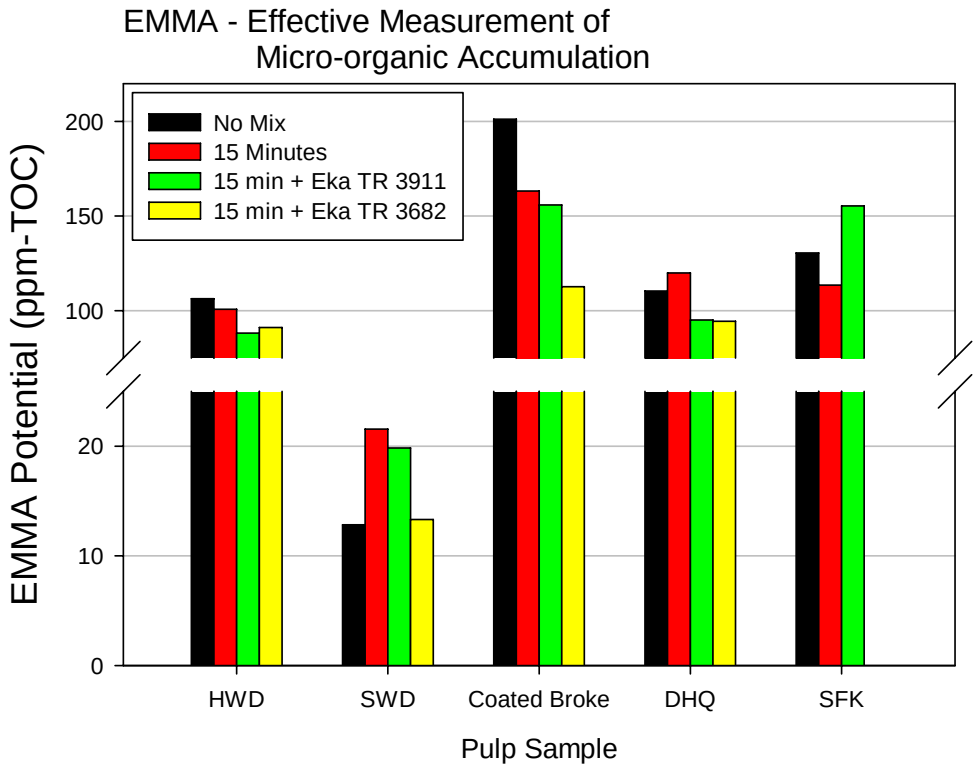

Figure 2-5
Stability of Pulp Samples Following Mixing with Pulper Dilution Water With and Without Additives

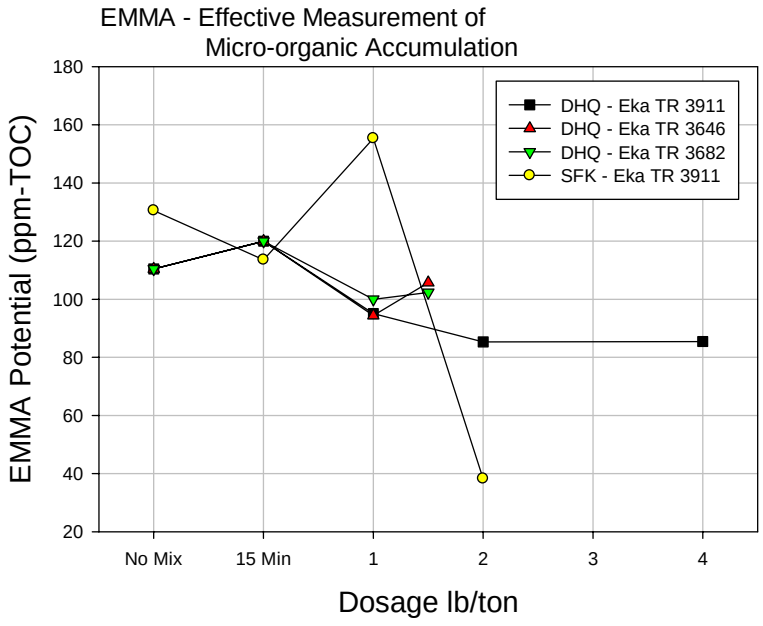

Figure 2-6
Response of Recycled Pulps to Cyclodextrins (Eka TR 3911) and Fixative (Eka TR 3646, TR3682) Addition

Results – Determine Pulp Interaction when Using Recycled Fiber

In general, the actual mix results show a decrease in EMMA potential with blending of the recycled fiber with the virgin kraft pulps. This would suggest an unstable mix with a potential for agglomeration and/or deposition (see Figure 2-7). The actual mixture appears to show little difference between 10% recycled fiber in the mixture and 25% recycled fiber. Duluth HQ recycled fiber would seem to be favored over SFK, as the EMMA potential does not decrease as much when mixing recycled fiber with the virgin kraft pulps.

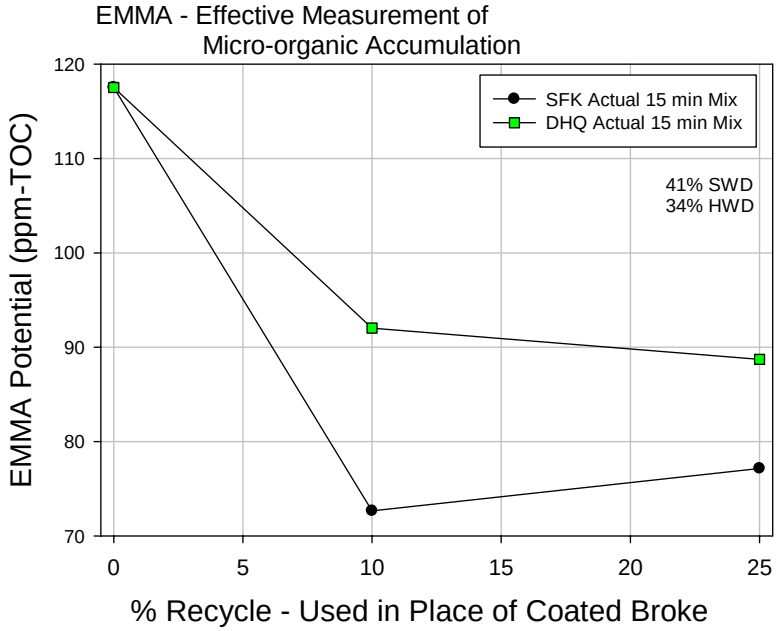

Figure 2-7
Impact on EMMA Potential of Partial Replacement of Coated Broke with Recycled Fiber. Replacement with SFK Appears to be Less Stable than with Duluth HQ, i.e., Lower EMMA Potential Suggesting Dispersion of Microstickies that could Lead to Agglomeration and/or Deposition of Microstickies

Results – Evaluation of Treatment Options

Figure 2-8 shows the impact of treating different components in the stock mixture with increasing dosages of cyclodextrins (Eka TR 3911). There is little benefit from increasing the dosage of cyclodextrins to recycled fiber; the same response was obtained at 1 lb/ton as at 4 lb/ton. Increasing the dosage for coated broke increased the stability, but it was more efficient to treat recycled fiber. Treating both coated broke and recycled fiber did not help more than just treating recycled fiber. The surprise in the results came from treating the SWD kraft virgin fiber; based on these results the best place to treat is the SWD kraft. These results could point to the drop in EMMA potential when recycled fiber was added to the dilution water – treating a larger portion of the stock helped stabilize the blending. We recommend additional testing to confirm this result.

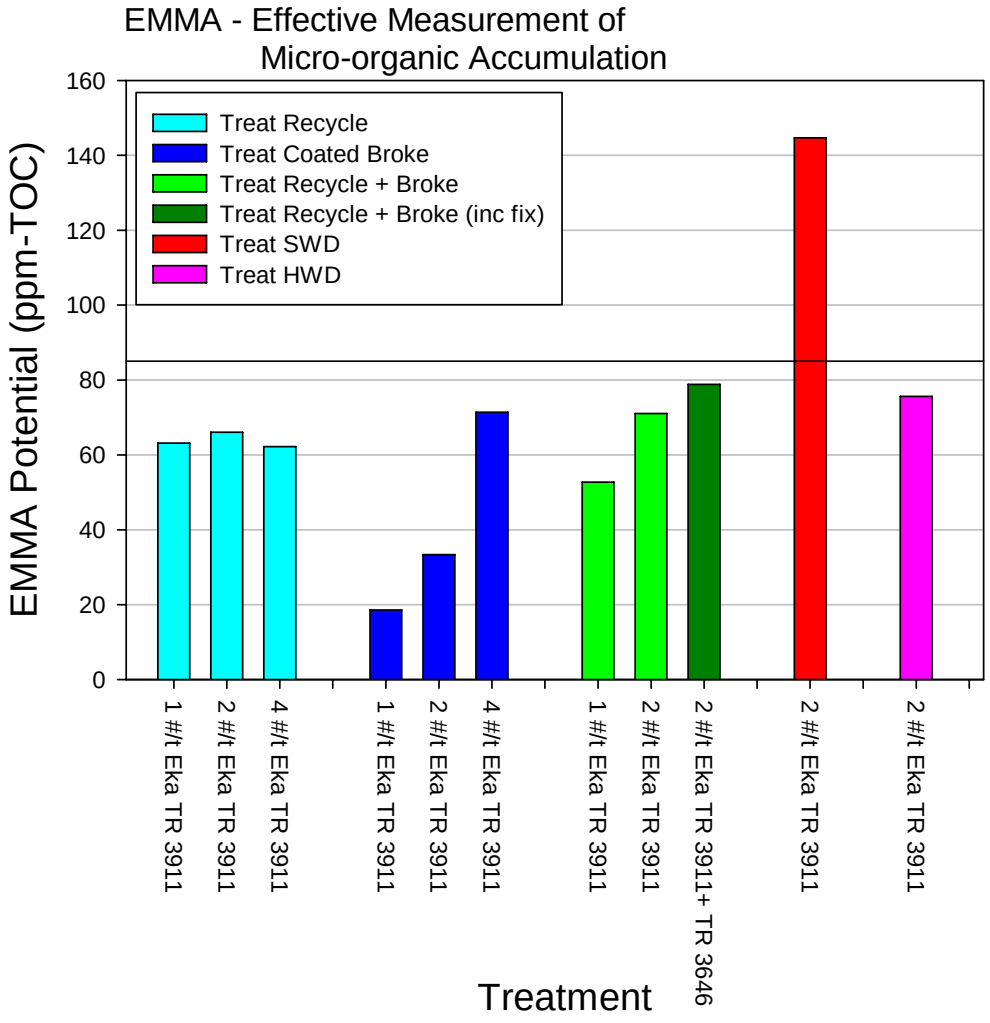

Figure 2-8
Treating Softwood Kraft has the Greatest Impact on EMMA Potential of Treating Individual Stock Components with Increasing Dosages of Cyclodextrins

Conclusions

1. The procedure to quantify colloidal micro-stickies in the recycled lap pulp offers a means to help paper machine operations know of potential impacts or issues with a given recycled fiber shipment.
2. Dilution and mixing of Duluth HQ recycled fiber with the virgin kraft pulps dispersed fewer microstickies than with SFK recycled fiber.
3. When making an evaluation of colloidal organics, a key component of the evaluation is to look at changes and differences. The three biggest changes seen in this study were more associated with the stock and water from the papermaking process than with the recycled fiber.
4. The coated broke saw a 19% drop in EMMA potential, indicating agglomeration upon mixing.

5. The recycled pulp mixed with the dilution water had lower EMMA potentials than the dilution water. Normally an increase or additive effect of adding more colloidal organics is observed.
6. Treatment of the SWD virgin kraft fiber with cyclodextrins before blending with recycled fiber had the biggest impact, leaving a stable concentration of colloidal microstickies after the blending process.

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