Comparison of Microstickies Measurement Methods Part II: Results and Discussion

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1. INTRODUCTION

In Part I of the article we discussed sample preparation procedure and described various methods used for the measurement of microstickies (1). Some of the important features of different methods are highlighted in Table 1. Temperatures used in the measurement methods vary from room temperature in some cases, 45 °C to 65 °C in other cases. Sample size ranges from as low as 0.25 g to as high as 50 g.

The working definition of microstickies, material passing through 150 µm or 100 µm slotted screen, is used in this study. Of the eight methods listed in Table 1, COD Method, PMV Microstickies Method and SCA Solvent Extraction Method employ slotted screen fractionation step. Two of the eight methods, namely Rotating-Wire-Mesh-Analyzer and Polyethylene Film Method, do not use fractionation step. UCM Deposition Test and Paprican's Thermogravimetric Test use 200-mesh screen (75 µm opening) for fractionation. IPST Method measures particles smaller than 25 µm and with molecular weight greater than 5,000 Dalton.

Measurement mechanisms used in various methods vary significantly. Three methods, UCM Deposition Test, Rotating-Wire-Mesh-Analyzer and Polyethylene Film Method take advantage ofthe deposition tendency of microstickies. IPST and COD methods relate miciostickies to TOC or COD respectively. Paprican's method is based on measuring the differences in the change in weight of the polymeric material on heating. PMV microstickies method is a modification of macrostickies method where stickies adsorb aluminum powder. In SCA method, stickies are dissolved in dichloromethane followed by FTIR analysis to identify and quantify dissolved material.

UCM Deposition Test was initially developed to study secondary stickies. However, it is also possible to use it to study microstickies smaller than 75 µm. Tests are conducted first without the addition of any chemicals to measure microstickies. Another filtrate sample is treated with a theoretical dosage of PEI (corresponding to isoelectric point) to measure secondary stickies.

Results from CTP solvent extraction method were submitted after the publication of Part I. The description of the method and data are presented in appendix.

In view of the differences in sample size, temperature and measurement mechanisms, it would be interesting to see how results from these methods correlate.

2. MICROSTICKIES DATA

In this section we will present the data obtained from each method followed by the comparison and discussion in the

Table 1. Features of microstickies measurement methods.

Method	Fractionation	Conditions	Sample Size	Mechanism
1 (a) UCM DepositionTest	-200mesh (75 µm)	Temp. 50°C, No chemical	~20 g	Collecton s.s. Plate; Int.:by collision; Ext: by transference
1 (b) UCM DepositionTest	-200mesh (75 µm)	Temp. 50°C, PEI(Theor.Dose)	~ 20 g	
2. Paprican's Thermogravimetric Method	- 200 mesh (75 µm), + 0.2 µm	NM	~ 0.25 g	Measure weight loss on heating
3.Rotating-Wire-Mesh-Analyzer	None	1%Consistency; Temp. 45 °C	8 g	Collecton polyesterwire
4. IPST Method	-25 µm, +5,000 Dalton	NM	Enough Pulp to generate 250 ml filtrate	Measure TOC (Total Organic Carbon)
5. Chemical OxygenDemand Method	-150 µm Centrifugeor -Whatman42	NM	5 g	MeasureCOD (Chemical Oxygen Demand)
6. PMV Micro-stickies Method	-100 µm slotted screen	NM	50 g	Usealuminum powder
7. SCA Solvent ExtractionMethod	-100 µm slotted screen	NM	5 g	Solventextraction
8.Polyethylene FilmMethod	None	500 ml at 1% Consistency Temp. 65 °C	4 beakers test. 5 g in each beaker for a total of 20 g.	Collect on LDPE film

Notes: (1) -200 mesh, -25 µm, etc. mean accepts or material that has passed through the corresponding screen or filter paper.
(2) NM: Not Material
(3) Details of CTP Solvent Extraction Method are given in Appendix 1.

next section. As mentioned in Part I, three pulps were sent to each of the participants:
Pulp A: Stickies-containing pulp
Pulp B: Stickics-free pulp
Pulp C: Deinked pulp.

Pulp samples were tested individually and blends of Pulp A and Pulp B in 25% increments were also tested.

2.1 UCM Deposition Test

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In this method, a pulp sample is fractionated using a DDJ fitted with 75 µm opening screen. The filtrate is then used in the UCM deposition tester. The stickies collected on the external and internal surfaces of the stainless steel coupons are measured by image analysis. The results of primary microstickies measurement are shown in Table 2. Secondary stickies (data shown in Table 3) are measured by adding the theoretical dosage of PEI to A fresh filtrate sample followed by the deposition test.

Results in Tables 2 and 3 indicate that the UCM deposition tester was able to collect sufficient amount of deposits on both external and internal surfaces ofthe coupon. However, the results do not follow the trend of increasing amount of stickies as one increases the proportion of stickies-containingpulp(PulpA)compared tothestickies-free pulp (Pulp B). Furthermore, the amount ofmicrostickies in the final deinked pulp (Pulp C) is about the same order ofmagnitude as that in other mixtures of Pulp A and B.

Table 2. **Microstickies in pulp filtrate** (no chemicals added).

	mm^2/g on the External film	mm^2/g on the Internal film	Total mm^2/g
100% A	237.6	20.7	258.3
75% A + 25% B	76.9	42.8	119.8
50% A + 50% B	85.8	43.1	128.9
25% A + 75% B	163.8	51.1	214.8
100% B	180.9	51.8	232.8
100% C	145.5	53.4	198.9

Table 3. **Secondary stickies in pulp filtrate** (with theoretical dosage of PEI added).

	mm^2/g on the External film	mm^2/g on the Internal film	Total mm^2/g
100% A	322.0	71.4	393.4
75% A + 25% B	202.0	53.8	255.8
50% A + 50% B	190.9	28.8	219.7
25% A + 75% B	421.4	68.1	489.6
100% B	309.3	43.2	352.5
100% C	161.6	46.0	207.6

2.2 Paprican's Thermogravimetric Method

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2.2.1 Microstickies content

Table 4 gives the microstickies content in Pulp A, determined in triplicate using thermogravimetry. Researchers at Paprican define microstickies as synthetic polymers with particle sizes ranging between 0.2 and 75 µm.

Table 4. **Microstickies content of stickies-containing pulp, Pulp A.**

Pulp Sample	Microstickies Content % (weight/weight)
Pulp A	0.02 0.04 0.05
Mean	0.04

These results show that the concentration of primary microstickies in Pulp A was about 0.02 % to 0.05 % or 200 ppm to 500 ppm. Because this microstickies content is close to the detection limit of our TG method, we did not find it useful to measure the microstickies content in samples of Pulp A diluted with increasing amounts of Pulp B.

2.2.2 Macrostickies

Because the microstickies content of Sample A was close to the detection limit, we carried out additional analysis to verify that the stickies added to the pulp were in the macrostickies class. Since the pulp was spiked with stickies only, to save time, we did not go through our usual procedure (TAPPI Test Method 277) but simply isolated the stickies with a Pulmac and scanned the black filter on which these macrostickies were collected. A view of the filter is shown on the left side of Figure 1 whereas the right image in Figure 1 presents a closer view of a typical particle.

Table 5 summarizes the observations on macrostickies. Though these measurements are not accurate, they strongly suggest that the stickies added to the pulp were probably not broken up enough in the repulping step to be brought in the size range of microstickies. Additionally, build up of stickies due to water loop closure in the mill is relatively difficult to simulate in a short pilot plant trial.

Table 5. **Macrostickies content in Pulp A.**

Measurement	Units	Macrostickies in Pulp A
Weight	(%)	0.26
Area	mm^2/kg	51600
Number	#/kg	31400
Mean area/sticky	mm^2	1.22
Mean Diameter	mm	1.25

2.2.3 Chloroform extract

Further confirmation that Pulp A was almost free of microstickies was sought by carrying out a series of chloroform extractions on Pulp A and Pulp B (i.e. as received). The extractions were then repeated on the passed 200-mesh fractions of the same two pulps. All extractions were done in duplicate. The results are summarized in Table 6. After addition of stickies to Pulp B to produce Pulp A, the extractive content rose from 0.35 % to 0.59 %. This increase of 0.24 % is close to the % weight of macrostickies in Sample A, determined from the rejects of the Pulmac (0.26 %) screening step. This suggests that these macrostickies

Table 6. **Chloroform extracts in Pulps A and B, before and after fractionation.**

Samples		$CHCl_3$ Extract % by weight
Pulp A (with stickies)	Whole pulp	0.59
	<200-mesh fraction	1.27
Pulp B (stickies-free)	Whole pulp	0.35
	<200-mesh fraction	1.22

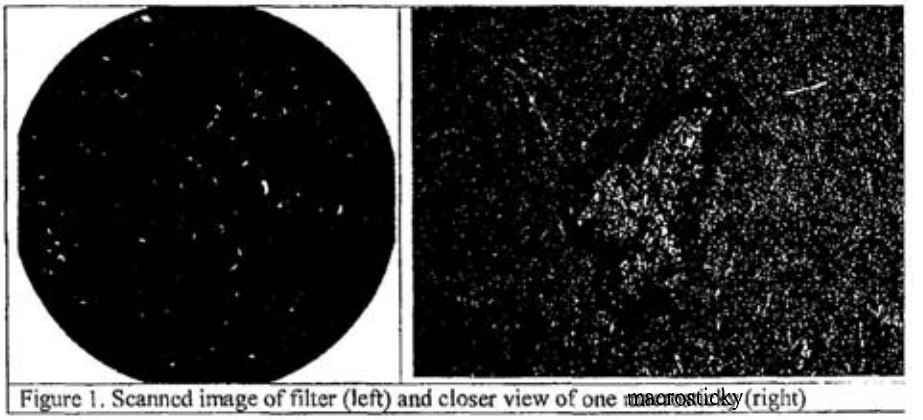

Figure 1. Scanned image of filter (left) and closer view of one macrosticky (right)

are largely soluble in hot chloroform. The passed 200-fractions of Pulps A and B are both richer in extractives than the wholepulps due to some enrichment of lypophilic compounds in the fines. However, the difference of 0.05 % (1.27 vs. 1.22) between the fines in Samples B and A, indicates that the amount of microstickies in Sample A was relatively low. When the extractives contents in the two fine fractions are based on the weight of the whole pulps, the increase in extractives content due to microstickies upon addition of stickies to Pulp B is only 0.02 %, close to the estimate of 0.04 % made by the thermogravimetric method.

2.2.4 Summary and Comments

These results show that the microstickies content in Pulp A was about 200 ppm to 500 ppm as measured by thermogravimetric analysis while macrostickies content as determined by solvent extraction was about 2600 ppm. Since microstickies content of stickies-containing pulp, Pulp A, is close to the detection limit of TG method, we did not analyze microstickies content of stickics-free pulp, Pulp B, or various combinations of the two.

It appears that the mechanical action of the pilot plant pulper was not high enough to break up enough macrostickies to bring them in the size range of microstickies. This observation is in agreement with Paprican's experience on the formation of primary microstickies from the attrition of macrostickies in a laboratory repulper. Because these microstickies are abundant in mill recycled pulps, it is possible that the shearing forces in industrial repulpers are greater than in laboratory and pilot plant repulpers. Also, the extent of water loop closure in pilot plant is not the same as that in the mill system.

2.3 Rotating-Wire-Mesh-Analyzer

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The amount of microstickies deposited on polyester-wire varies from 9.3 mg/8g (1162.5 ppm) in stickies-containing pulp (Pulp A) to 1.2 mg/8g (150 ppm) in stickies-free pulp (Pulp B), as shown in Table 7. In this case whole pulp was used but only stickies smaller than 150 µm seem to deposit on the wire. Interestingly, results do show the expected trend that as more stickies-containing pulp is added to stickies-free pulp, Pulp B, greater amounts of stickies are deposited on the wire.

Table 7 **Microstickies collected on a rotating polyester wire.**

Samples	Adsorbed Mass, mg/8g			
	Rplct. 1	Rplct. 2	Rplct. 3	Average
100% A	9.4	9.1	9.5	9.3
75% A + 25% B	8.1	8.2	7.8	8.0
50% A + 50% B	5.0	4.9	4.7	4.9
25% A + 75% B	2.5	2.3	2.6	2.5
100% B	1.1	1.1	1.3	1.2
100% C	2.6	2.7	2.4	2.6

2.4 IPST Method

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The patented IPST method, described in Part I, measures total organic carbon (TOC) of filtrate from 25 µm Whatman filter and a 5,000 Dalton ultrafiltration membrane and reports the difference as related to the microstickies content of the sample. Pulp samples as received were filtered without dilution and various mixtures were prepared for microstickies measurement. Results shown in Table 8 indicate that the average values of microstickies content of stickies-containing pulp, Pulp A (1400 ppm), and stickies-free pulp, Pulp B (1348 ppm), are not significantly different. However, both pulps A and B have average stickies content much higher than that in the deinked pulp, Pulp C (224 ppm). Thus, it appears that microstickies content of the two pilot plant generated pulp samples are statistically similar. Similar conclusion is reached when pulp was diluted to 1 % consistency (as called for by the protocol) before making the measurements.

2.5 Chemical Oxygen Demand (COD) Method

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This method involves measuring COD of centrifuged and filtered samples and microstickies concentration is estimated by difference. Results presented in Table 9 indicate that samples containing 25% to 100% of stickies-contain-

Table 8. **Microstickies results by IPST method.**

Pulp Sample	TOC in Filtrate -25? m	TOC in Ultrafiltrate -5,000 Dalton	Microstickies, ppm (no pulp dilution)	Microstickies, ppm (pulp diluted to1 % consistency)
100% A	1512	113	1400 + 94	125 + 2.8
75% A + 25% B	1433	101	1332 + 99	123 + 0.8
50% A + 50% B	1396	119	1277 + 20	125 + 2.5
25% A + 75% B	1474	104	1370 + 52	126 + 2.0
100% B	1468	120	1348 + 50	127 + 3.5
100% C	285	60	224 + 12	7 + 1.0

Table 9 **Microstickies analysis by COD method.**

Pulp Sample	Centrifuged Sample COD, mg O_2/L (with 95% CI)	Filtered Sample COD, mg O_2/L (with 95% CI)	COD Difference mg O_2/L
100% A	6934 + 5404	6166 + 1225	769
75% A + 25% B	7276 + 10752	5762 + 2876	1514
50% A + 50% B	6672 + 3383	5814 + 1082	858
25% A + 75% B	6637 + 2804	5637 + 1772	1000
100% B	5794 + 279	5596 + 1310	198
100% C	2706 + 6408	3702 + 1738	-996

ing pulp, Pulp A, have COD difference values of 769 mg O_2/L to 1514 mg O_2/L while stickies-free pulp value is 198 mg O2/L. However, DIP COD difference value is negative.

2.6 PMV Microstickies Method

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In this method image analysis is used to evaluate microstickies area of 100 µm slotted plate screen accepts dewatered on a filter paper. The method is similar to that used for macrostickies measurment. The image analysis method detects stickies with equivalent circle diameter greater than 100 µm. The method seems to give reproducible and meaningful results even though only a portion of the microstickies population is considered in the measurement. Interestingly, results, shown in Table 10, indicate that stickies in the size range of 100 µm to 2000 µm are measured in the accepts of the laboratory 100 µm slotted screen. This could at least in part be due to the use of high temperature and pressure during the drying step of the method.

Table 10 **Microstickies image analysis results by PMV method.**

Pulp Sample	Cumulative Sticky Area, mm2/kg				
	100-200	100-400	100-600	100-1000	100-2000
100% A	3,541	4,855	5,545	5,846	10,304
75% A + 25% B	3,837	5,233	5,429	5,954	5,954
50% A + 50% B	3,054	4,352	4,558	4,829	4,829
25% A + 75% B	2,814	3,901	4,267	4,634	4,634
100% B	321	438	438	438	438
100% C	847	1,242	1,242	1,412	1,412

2.7 SCA Solvent Extraciton Methos

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The amount of material soluble in dichloromethane is determined in the whole pulp and in the pulp retained on 0.10 mm slotted Pulmac screen. Microstickies concentration is then calculated by the difference, as shown in Table 11. Microstickies content in stickies-containing pulp, Pulp A, is only 0.4 % (400 ppm) while that in the stickies-free pulp, Pulp B, is 0.12 % (1200 ppm).

Table 11. **Solvent extraction results.**

Pulp Sample	% Total Stickies + Std. Dev.	% Macrostickies + Std. Dev.	% Microstickies
100% A	0.38 + 0.042	0.34 + 0.101	0.04
75% A + 25% B	0.38 + 0.093	0.17 + 0.026	0.21
50% A + 50% B	0.28 + 0.027	0.09 + 0.050	0.19
25% A + 75% B	0.21 + 0.035	0.12 + 0.069	0.09
100% B	0.13 + 0.006	0.01 + 0.004	0.12
100% C	0.07 + 0.006	0.01 + 0.000	0.06

Microstickies content in deinked pulp, Pulp C, is estimated to be about 0.06 % (600 ppm).

FTIR analysis of all the extracts was carried out to identify percent of wood extractives, synthetic polymers and other unidentified material. Results are shown in Table 12. Interestingly, wood extractives and unexplained material constitutes a significant portion of the extracts.

2.8 Polyethylene Film Method

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The amount of material collected on polyethylene film immersed in the whole pulp is expressed as mg/kg in Table 13. The results show a systematic decrease in the material collected on the film as the stickies-containing pulp, Pulp A, is diluted with stickies-free pulp, Pulp B. The amount of material collected on the film is 8 mg/kg in the case of stickies-free pulp compared to the amount collected in the case of deinked pulp, Pulp C, 385 mg/kg.

An example micrograph of adsorbed material, shown in Figure 2, reveals a majority of particles with a size around 20 µm that were the most prevalent adsorbed material throughout all of the samples studied. Under high magnification (50X) it was observed that these particles had rounded edges, indicative of a soft, deformable amorphous material. Also apparent in Figure 2 is a fiber, about 100 µm long. It is possible that the fiber itself is tacky or that it has adhered to the film via the other depositable material. The error involved in these fibers being attached is worthy of discussion.

The measurements made of deposited material ranged from about 0-150 mg of material. From microscopic observations over many areas of the film we estimated that about 10 such fibers were present on each piece of the film with the 25 % stickies-containing pulp sample. For each experiment there

Table 12 **FTIR analysis of extracts of total stickies and macrostickies shown in Table 10.**

Pulp Sample	Total Stickies Composition			Macrostickies Composition		
	% Wood Extractives	% Synthetic Polymers	% Unexplained	% Wood Extractives	% Synthetic Polymers	% Unexplained
100% A	55	17	28	28	30	41
75% A + 25% B	43	23	35	33	25	43
50% A + 50% B	55	12	34	35	18	47
25% A + 75% B	61	10	29	30	23	47
100% B	82	8	10	53	13	35
100% C	60	10	30	60	13	28

Table 13. **The amount of material collected on polyethylene film, mg/kg**

Pulp Sample	Round 1	Round 2	Round 3	Average	Std. Dev	95% CI	%COV
100% A	8270	7525	7255	7683	526	1308	7.0
75% A + 25% B	4070	4465	4720	4418	328	815	7.0
50% A + 50% B	3280	3725	3394.5	3467	231	575	7.0
25% A + 75% B	1100	1290	1240	1210	98	245	8.0
100% B	10	5	10	8	3	7	3.5
100% C	325	380	450	385	63	156	1.6

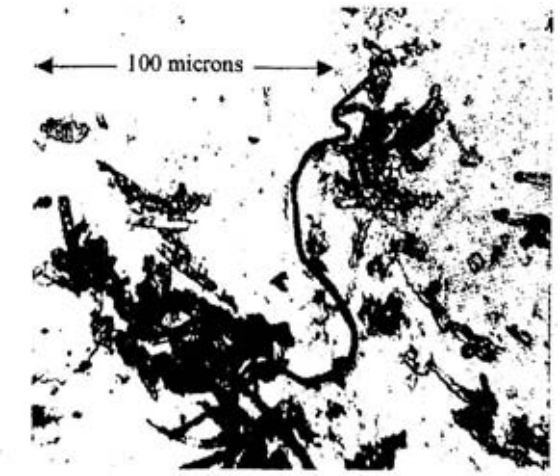

Figure 2. **Low density polyethylene film after deposition with 25 % stickies-containing pulp and 75 % stickies-free pulp as viewed using a light microscope. The darker material is the adsorbed material. A fiber is apparent. There is both globular and fibrous material on the film.**

were 5 pieces of film in each of the 4 beakers so a total of 200 fibers were estimated in this case. It is estimated that the individual fiber weighed approximately 0.5 micrograms (as estimated from a fiber model utilizing the cell wall density as 1.55 g/cm^3, and a fiber length and diameter of 0.17 and .045 mm, respectively) so that the percentage weight of the fibers to the total adsorbed material is only about 0.07%, which is negligible compared to the coefficient of variation in Table 13.

3. DISCUSSION

We prepared two pulps - one stickies-containing pulp (Pulp A) and the other stickies-free pulp (Pulp B), by running deinking pilot plant at the Forest Products Laboratory. We also included final deinked pulp (Pulp C). All participants agreed to measure the amount of microstickies in the three pulps. They also were requested to dilute Pulp A by adding Pulp B in 25 % increment. Our purpose was to observe the trend of decreasing amount of measured microstickies as we dilute stickies-containing pulp with stickies-free pulp,

First we offer general comments and observations followed by discussion on stickies classification to help us interpret all of the data from different measurement methods.

One factor that is important in the microstickies measurement is the sample size. If microstickies concentration is say 100 mg/kg, 1 g pulp sample will have 0.1 mg microstickies. Thus, a method has to be quite precise and sensitive to be able to detect small amount of microstickies. We note from Table 1 that PMV Microstickies Method utilizes 50 g sample while all other methods use anywhere from 20 g to 0.25 g. Sampling error can amplify small measurement errors. The error can be further amplified if the method calls for subtracting two small numbers. All methods that utilize relatively small sample size and/or require subtraction of two small measurements are inherently at disadvantage compared to the other methods.

Solvent extraction results are reported by Dorris and Castro (Table 6), Johansson (Table 11) and by Delagoutte and Brun (Appendix). Unfortunately, there is no universal

solvent that dissolves stickies and nothing but stickies. As a result, a solvent will dissolve some stickies but not all. Some of the highly cross-linked adhesives will be difficult to dissolve in solvents such as dichloromethane and chloroform. On the other hand, these solvents will dissolve a portion of wood material and other components of the pulp as shown by Johansson (Table 12).

Dorris and Castro (Table 6) use chloroform while Johansson (Table 11) and Delagoutte and Brun (Appendix) use dichloromethane as the solvent. Their results for the three pulps vary considerably as shown in Table 14. We also calculated solvent extractible synthetic polymer (SCA/S.P.) portion. It is clear from the results of Table 14 that solvent extraction data do not correlate.

Table 14. **Solvent extraction data.**

Method	Solvent Extractibles, ppm		
	Pulp A	Pulp B	Pulp C
TG	200 to 500	**	**
SCA	400	1200	600
SCA/S.P.*	negative	91	57
CTP	20	710	**

* Synthetic polymer portion of the extractibles
** Not measured

All methods except two present data as weight fraction in percent or ppm. Two methods report stickies area, mm^2/g or mm^2/kg. Our overall objective, as mentioned earlier, was to see which methods exhibit the trend of decreasing stickies as stickies-containing pulp (Pulp A) is diluted in 25 % increment with stickies-free pulp (Pulp B). Three methods were successful in exhibiting the trend:

- Rotating-Wire-Mesh-Analyzer (Section 2.3)
- PMV Microstickies Method (Section 2.6)
- Polyethylene Film Method (Section 2.8)

Two methods show essentially no change:

- UCM Method (Section 2.1)
- IPST Method (Section 2.4)

The following two methods exhibited sinusoidal behavior, i.e., stickies content of mixture is greater than either of the two individual pulps:

- SCA Solvent Extraction Method (Section 2.7)
- COD Method (Section 2.5)

Measurements were not carried out by TG Method (Section 2.2) due to the detection limit while CTP Solvent Extraction Method (Appendix) exhibited reverse trend, i.e., microstickies content increasing with the dilution of stickies-containing Pulp A with stickies-free Pulp B.

In an attempt to make sense out of these data we propose the classification of microstickies in the next section. We then identify size range covered by various methods and explain differences in observed trends.

3.1 Stickies Classification

Approximate classification of stickies based on size is shown schematically in Figure 3. We should acknowledge that in reality, demarcation lines between different size classes is quite fuzzy and not as sharp as we display at the bottom of Figure 3. We have shown approximate size range for each category for illustration and discussion purposes.

Most of the macrostickies are removed by screens, cleaners, flotation cells and washers. Stickies smaller than macrostickies, those that pass through the laboratory 100 µm slotted screen, are termed microstickies. Microstickies may muse problems by depositing on paper machine clothing and dryer cylinders or may affect paper or board quality. These stickies can be classified further as suspended stickies, dispersed stickies. colloidal stickies and dissolved stickies (see Figure 3). Various methods used for measuring microstickies are also identified in Figure 3 together with approximate size range of stickies measured.

We note from Figure 3 that most of the methods that primarily measure dispersed, colloidal and dissolved stickies exclude long fibers as well as macrostickies from the sample. On the other hand, those methods that primarily measure microstickies in the suspended solids size range include long fibers of the sample.

In addition to macrostickies and microstickies, we need to be concerned about secondary stickies that precipitate out of the pulp slurry due to change in pH, temperature or chemical environment. UCM Deposition Test results of secondary stickies are reported in Table 3.

Macrostickies and microstickies primarily originate from adhesives such as SBR, EVA, and polyacrylates. On the other hand, dispersed, colloidal and dissolved stickies arise from adhesives as well as starches, wood pitch, and PVAc. Stickies-containing pulp, Pulp A, and stickies-free pulp, Pulp B, probably contain similar amounts of dispersed, colloidal and dissolved stickies. However, macrostickies and suspended stickies are abundant in Pulp A but not in Pulp B. As a result, methods that measure primarily suspended stickies or depositable stickies (Rotating-Wire-Mesh-Analyzer, PMV Microstickies Method and Polyethylene Film Method) were able to distinguish between stickies content of the two pulps while the other methods that included dispersed, colloidal and/or dissolved stickies were not able to observe much difference between the stickies content of the two pulps.

3.2 Microstickies Test Methods

Three methods that primarily measure suspended stickies are listed in Table 15. Results from these methods were fitted to linear regression. Percent standard error and r^2 values are reported in Table 15. All three methods include

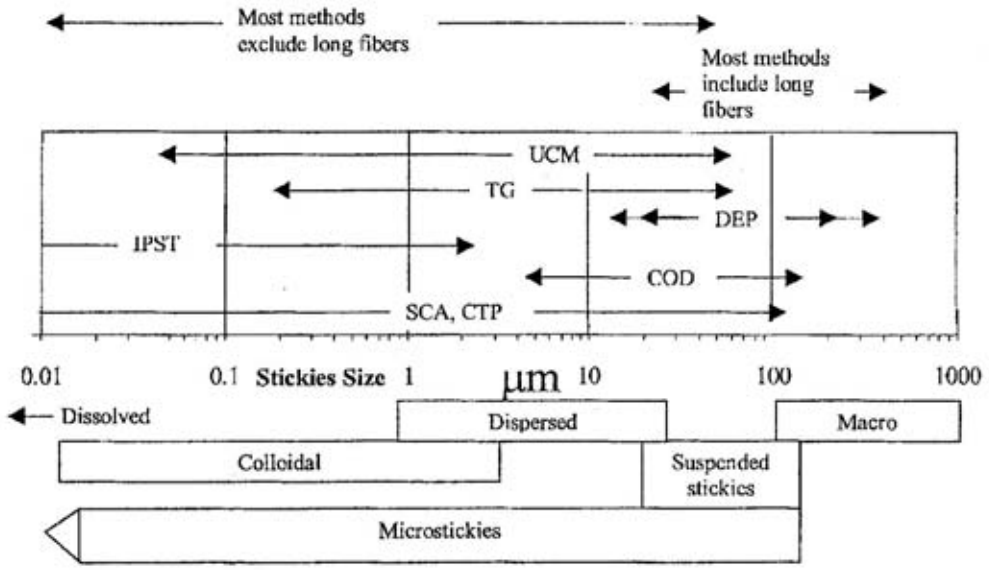

Figure 3. **Stickies - classification and measurement based approximately on size.**
Classification: Macrostickies: > 100 µm, stickies in rejects from 100 µm slotted screen.
Microstickies: < 100 µm, stickies in accepts from 100 µm slotted screen
Suspended stickies: 20 µm to 100 µm, in sample obtained as accepts from 100 µm slotted screen.
Dispersed stickies: 1 µm to 25 µm **Colloidal stickies: 5 µm to 0.01 µm**
Dissolved stickies: < 0.01 µm
Measurement methods: DEP: Microstickies deposition test includes Rotating-Wire-Mesh-Analyzer, PMV Microstickies Method and Polyethylene Film Method
UCM: UCM Deposition Test **TG Paprican's Thermogravimetric Method**
IPST IPST Method **COD: Chemical Oxygen Demand Method**
SCA, CTP: SCA and CTP Solvent Extraction Method
Note: Most of the methods that primarily measure dispersed, colloidal and/or dissolved stickies exclude long fibers while methods that primarily measure microstickies include long fibers as indicated at the top.

long fibers in their measurement. Results from these three methods are plotted in Figure 4. Correlation coefficient values among these methods vary froin 0.90 to 0.96.

While Rotating-Wire-Mesh-Analyzer and Polyethylene Film Method do not fractionate, PMV Microstickies Method uses slotted screen to remove macrostickies. It is not clear what are the size ranges of stickies that will and will not deposit on the wire or the film. Also, one would like to know what is the lower limit beyond which the stickies are too small to deposit. It would be enlightening to repeat the deposition test with and without slotted screen fractionation to evaluate the impact of macrostickies on the final results. In any event, in view of an excellent correlation of these two deposition tests with PMV Microstickies Method (that removes macrostickies before measuring microstickies), we feel that these three methods appear to be promising for measuring the concentration of suspended stickies.

Table 15. **correlation among three microstickies measurement methods.**

Microstickies Methods (Suspended solids)	Correlation Coefficient			% Error, (Linear Regression, r^2)
	Rotating Wire	PMV Method	PE Film	
Rotating Wire	1.0	0.895	0.963	5 (0.99)
PMV Method	0.895	1.0	0.949	10 (0.94)
PE Film	0.963	0.949	1.0	6 (0.98)

4. CONCLUSIONS AND COMMENTS

PMV Microstickies Method is the only one of all the methods examined here that fractionates to remove macrostickies and exhibits the desired trend for the sus-

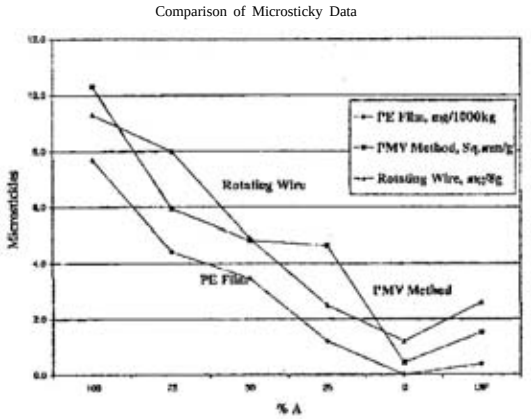

Figure 4. **Comparison of microstickies data from the three methods: Rotating-Wire-Mesh-Analyzer, PMV Microstickies Method, and Polyethylene Film Method. Note that a multiplying factor is used to fit all data in single figure with reasonable clarity.**

pended solids portion of microstickies. All other methods either failed to exhibit the trend or did not remove macrostickies. Results from Relating-Wire-Mesh-Analyzer and Polyethylene Film Method do exhibit the desired trend and do correlate well with the PMV Method. We therefore consider these two methods to be promising pending further development to evaluate the size ranges of stickies collected on the wire or the film.

Those methods that failed to exhibit the trend excluded suspended stickies in their measurement. It is quite possible that samples of Pulp A and Pulp B contain similar amounts of dispersed, colloidal and dissolved stickies. This may explain why some of the methods did not detect the expected trend.

Stickies measurement methods discussed here consider different regimes of stickies distribution as shown in Figure 3. Stickies smaller than macrostickies, those that pass through 100 µm slotted screen, are termed microstickies. Microstickies are further classified as suspended, dispersed, colloidal and dissolved stickies. Suspended stickies may lead to deposition on paper machine clothings; dispersed, colloidal and dissolved stickies may precipitate out on the dryer cylinders; while colloidal and soluble material could potentially form secondary stickies. Thus, depending on paper mill situation and associated problems with stickies, one may need to measure one or more of the stickies smaller than macrostickies. In many practical situations, it is quite likely that there is a good correlation among the concentration values of various classes of stickies so that any one of the methods considered here may be applicable. More research is needed to confirm this hypothesis.

Our ultimate goal is to improve paper mill efficiency by reducing stickies related downtime or product downgrade. Certainly, extensive research in the development of a method for measuring the concentration of stickies smaller than macrostickies will lead to further progress in paper recycling.

5. LITERATURE CITED

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6. ABREVIATIONS

COD: Chemical Oxygen Demand
DDJ: Dynamic Drainage Jar
IPST: Institute of Paper Science and Technology
PEI: Polyethylene-imine
PMV: Papierfabrikation und Mechanische Verfahrenstechnik (Paper Technology and Mechanical Process Engineering)
SCA: Svenska Cellulosa Aktiebolaget
UCM: Complutense University, Madrid

APPENDIX 1
CTP Method for Microstickies Measurement

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CTP methodology is based on the characterization of the different stickies species in a recycled pulp: macro-, micro-, and colloidal stickies.
Three different pulp Fractions making up the entire pulp are considered:

A. The fibrous fraction: Suspended solids retained on a 100 µm wire after intense washing (= hypewashing) with tap water. This fraction contains only the macrostickies.

B. The fine elements fraction: The fraction of suspended solids which is washed away during the hyperwashing step. In the fine element fraction, only microstickies are contained.

C. The dissolved and colloidal fraction: The fraction contained in the supernatant obtained after the centrifugation (3000 g - 15 min) of the water which accompanies the pulp sample. This fraction is only composed of dissolved and colloidal stickies.

Dichloromethane extractable materials contained in three pulp fractions are assessed:

1. Entire pulp: This extract represents the total stickies content (macro, micro and colloidal stickies) of the pulp fraction (extraction result ER 1). The sample to extract is prepared by evaporating an entire pulp sample in an aluminum cup; this sample is then extracted.
2. Hyperwashed pulp: This extract represents only the macrostickies content of the pulp (extraction result ER 2).
3. Dry residue: Comes from the supernatant of the water, that accompanies the pulp: This extract represents the dissolved and colloidal stickies (extraction result ER 3).

Dichloromethane extractions were performed in Soxhlet apparatus for 6 hours on these three different fractions of the pulp. After evaporation of the solvent, the residue is dried and weighed. The result is first expressed in g extract per g of dried material extracted. Then it is possible to express this result in g extractable materials per 100 g of entire pulp, and calculate the contribution of the three fractions.

• The fibrous fraction contribution (almost macrostickies) is represented by ER2
• The tine elements fraction contribution (microstickies) is calculated as: ER1 - (ER2 + ER3)
• The soluble and colloidal fraction contribution is represented by ER3.

Application example : pilot plant pulp mixture

This method was performed to characterize the microstickies content of 3 pulp samples: Pulp A (with stickies), pulp B (stickies-free) and pulp C (a deinked pulp). Mixtures of Pulp A and Pulp B were also analyzed and the results are reported in table A-1.

These measurements show that the microstickies content of these pulps samples vary from almost 0 to 0.1 g/100g (or from 0 ppm to 1020 ppm). The extracted amounts after hypewashing are very close to the values obtained with the whole pulps. There is a small difference certainly due to the removal of solvent extractable soluble materials during hyperwashing. This is observed in the sticky-free pulp, meaning that these compounds don't come from the adhesives introduced in the trials. Moreover, this is confirmed by the reject rate of a Somerville screening test (measuring the macrostickies content) performed on the stickies-containing pulp: around 0.5% of macrostickies were recovered which corresponds roughly to the amount of adhesive materials introduced in the pulp.

Table A-1. **Solvent extraction results of testing pulps mixtures.**

Stickies content represented by DCM extract expressed in g per 100g of pulp			
	Macro-stickies (ER2)	**Colloidal and micro-stickies	Total Stickies (ER1)
100% Pulp A	0.418	0.002	0.42
75% Pulp A + 25% pulp B	0.373	0.000	0.37
50% Pulp A + 50% pulp B	0.277	0.063	0.34
25% Pulp A + 75% Pulp B	0.149	0.071	0.22
100% Pulp B	0.068	0.102	0.17
100% Pulp C			0.15
** Colloidal and microstickies are calculated together, in this case ER3 was not performed			

Application example : industrial DIP pulp

An example or measurements performed at CTP on an industrial pulp is reported hereafter.
When this procedure was applied to stickies-containing pulp, Pulp A, the amount of microstickies was found to be too small or close to zero. When DIP, Pulp C, was analyzed we found that virtually all of the stickies are macrostickies. Therefore, to illustrate the method, we used industrial DIP. Results are shown in Table A-2.

The results show that :
• The stickies content of this pulp is low. It corresponds to
• final pulp (end of DIP process)
• The microstickies represents the major stickies source which is usually the case according to our experience. ■

Table A-2. **Solvent extraction results of testing industrial DIP.**

	Stickies content: g DCM extract for 100g of whole pulp			
	Colloidal stickies	Macrostickies	Microstickies	Total
Deinked pulp sample, Replicate 1	0.006	0.13	0.30	0.43
Deinked pulp sample, Replicate 2	0.002	0.10	0.28	0.38

Note: Pulp used in this illustration is different from Pulps A, B and C.