

Equilibrium coefficients for the adsorption of colloidal stickies onto mineral suspension particulates to improve paper recycling

Christopher M. Gribble, G. Peter Matthews, Andrew Turner, Daniel Gantenbein, Joachim Schoelkopf and Patrick A. C. Gane

KEYWORDS: Adsorption, Bentonite, Equilibrium coefficients, Modified calcium carbonate, Paper recycling, Stickies, Talc.

SUMMARY : We present a study of the efficacy of four different minerals in adsorbing model ‘stickies’ – i.e. substances in recycled paper which derive from objects such as self-stick return envelopes, coating binders and waxes. Stickies cause numerous problems with paper quality and production. The minerals tested for their adsorption of seven model stickies, representing typical compounds encountered in a mill, were high and low surface area talc, modified calcium carbonate and bentonite. Equilibrium adsorption constants were calculated from measurements of dissolved organic carbon, and carbon measured by elemental analysis. Two different adsorption mechanisms, and a hybrid mechanism, were inferred from the results, and supported by electron microscopy. The formation of a layered ‘sandwich’ was most likely for the acrylic acid ester copolymer and styrene butadiene latex. An agglomeration mechanism was most probable for polyvinyl acetate and colophonium resin. The adsorption of fatty acid ester defoamer and mineral oil / silicone defoamer could be explained by a hybrid mechanism. Modified calcium carbonate was found to be the best adsorbent for acrylic acid ester copolymer, mineral oil / silicone defoamer, polyvinyl acetate and styrene-butadiene latex. The high surface area talc was the best adsorbent for alkyldiphenyloxide disulphonate, colophonium resin and fatty acid ester defoamer.

ADDRESSES OF THE AUTHORS:

Christopher M. Gribble¹ (christopher.gribble@plymouth.ac.uk)

G. Peter Matthews¹ (peter.matthews@plymouth.ac.uk)

Andrew Turner¹ (andrew.turner@plymouth.ac.uk)

Daniel Gantenbein^{1,2} (daniel.gantenbein@omya.com)

Joachim Schoelkopf² (joachim.schoelkopf@omya.com)

Patrick A.C. Gane^{2,3} (patrick.gane@omya.com)

¹School of Geography, Earth and Environmental sciences, University of Plymouth, Plymouth, PL4 8AA, U.K.

²Omya Development AG, Baslerstrasse 42, CH-4665, Oftringen, Switzerland

³Department of Forest Products Technology, Aalto University, Espoo, FI-00076 Aalto, Finland.

Corresponding Author: G.Peter Matthews

There continues to be considerable environmental pressure to increase the use of recycled paper, but its use is not without complications. Some of the most difficult problems result from the presence of adhesives, arising from hot melt glues, binders and other thermoplastic materials, for example from

book-backs and adhesive tape or from silicone based defoamers used in the paper making process. They tend to be pliable organic materials, such as styrene-butadiene and styrene acrylic latex binders, rubber, vinyl acrylates, polyisoprene, polybutadiene and hot melts (Doshi 1991; Douek et al. 1997; Doshi, Dyer 1998; Jones, Fitzhenry 2003). Under certain conditions, these compounds can become tacky and deposit as ‘stickies’ in the paper machine. Stickies have multiple deleterious effects on paper quality including sheet indentations, sheet structural defects, web breaks, and discolouration such as black spots (Olson, Letscher 1992; Hutten et al. 1997; Nguyen 1998). The correction of these faults increases production costs.

Once stickies are released by the pulping process, they can accumulate in the process water system of the recycled fibre section of a paper recycling mill. Similarly, fibre stock containing recycled fibre can suffer from a build-up of stickies on the paper making machine. As paper mills are continuing to reduce their fresh water usage to minimise costs, process water recycling is becoming more prevalent, increasing the concentration of stickies and thus making them even more problematic.

Studies of stickies that have been reported in the literature are mainly concerned with how the effects of these compounds may be reduced in paper mills (Nguyen 1998; Onusseit 2006), or the development of alternative paper additives that have less of a detrimental effect during paper recycling (Onusseit 2006; Delagoutte 2008). Some studies focus on the removal of stickies and pitch from the recycled fibre system by, for example, screening (Spiess, Renner 2004; Delagoutte 2005; Benecke et al. 2009), flotation (Kemper 1999; Heise et al. 2000; Delagoutte 2005) and adsorption (Douek, Allen 1991; Allen, Douek 1993; Rogan 1994), or from the process water in the paper mill (Holmbom, Sundberg 2003; Vähäsalo, Holmbom 2006). A study by Klunegnss et al. (2002) used precipitated calcium carbonate to study the pacification of micro and colloidal stickies in the process water. The report concluded that the efficacy of the precipitated calcium carbonate depended on the conditions of the system.

We have measured the equilibrium constants for the adsorption of model stickies onto selected minerals – namely talc, modified calcium carbonate, and bentonite – in the special case where the adsorbent mineral is maintained in great excess in relation to the model sticky adsorbed on the surface and/or in a suspension. The determination of equilibria for the different mixtures of mineral and sticky provides information on whether the sticky remains in colloidal suspension or adsorbs onto the surface of the mineral, and is therefore a means of describing the efficacy of a chosen mineral for stickies control. The measurements of these equilibria are complicated by the fact that the species are colloidal both before, and possibly after, adsorption. Stickies are not easily defined, as they can have partially retained surfactant and charge stabilisation arising from their original product form, as delivered in water suspension. This current work is an extension of that reported by Benecke et al. (2009), who used turbidity, chemical oxygen demand and gravimetric techniques for the measurement of adsorption of stickies. The work was also continued in Gribble et al. (2010), where two additional analytical techniques, dissolved organic carbon and elemental analysis, were used to construct adsorption isotherms for two of the sticky systems reported by Benecke et al. (2009), adsorbing onto two talc and two modified calcium carbonate grades. In this work seven different sticky systems are investigated using dissolved organic carbon analysis and elemental analysis to measure the equilibrium coefficients of adsorption onto different minerals. The equilibrium results reported in this work are operationally defined for the conditions stated in the method, using a timescale representative of a paper mill.

The selected model compounds are often found in sticky deposits as stated in Benecke et al. (2009), although in real systems the stickies have undergone changes during paper production, use and recycling. Some of the tested compounds, such as defoamers, are process chemicals rather than stickies. In the paper mill stickies will be in competition with the process chemicals.

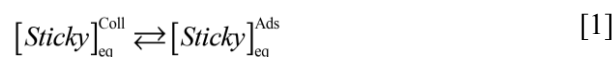
Our experimental approach is entirely different from those used in standard tests from TAPPI or INGEDE. In standard tests (Doshi et al. 2003), stickies are typically identified by filtering them onto filter paper, then dyeing the filter paper with black water-based ink, and then coating the paper with alumina. The quantity of sticky is then measured by image analysis of the white alumina. These methods measure total quantities of stickies in suspension, rather than the quantity of adsorbed sticky, so are not appropriate in the present work.

Background theory

The adsorption equilibrium is defined by the balance between concentrations of sticky in suspension and concentrations of sticky on the particle surface:

Sticky (colloidal suspension) \rightleftharpoons Sticky adsorbed on mineral (adsorbed)

The initial colloidal sticky concentration, $[Sticky]_0^{Coll}$ is determined by the amount of sticky added at the beginning of the experiment. The concentration of mineral added during the experiment is $[Mineral]^{Susp}$. The extent of movement toward equilibrium is initially zero, such that $[Sticky]_0^{Ads}$ is zero. On mixing the sticky and mineral suspension, an equilibrium is set up:



The equilibrium constant for the adsorption, is:

$$K_{eq} = \frac{[Sticky]_{eq}^{Ads}}{[Sticky]_{eq}^{Coll}} \quad [2]$$

This equilibrium constant does not involve $[Mineral]^{Susp}$, which was in great excess, *Fig 1a*. Such an equilibrium also applies to the situation shown in *Fig 1b*, where just enough mineral is present. The adsorption behaviour for *b* may not precisely equal that shown in *a*, because of adsorbate-adsorbate interactions, shown as \leftrightarrow in *Fig 1b*. *Fig 1c* illustrates alteration of the equilibrium by chemical or physical perturbation. *Fig 1d* shows the adsorption behaviour when the sticky is in excess, with adsorption entirely controlled by the mineral concentration.

The aqueous concentration can be determined by using a calibration series of sticky concentrations. When determining the aqueous concentration, we assume the mineral and sticky adsorbed onto mineral is completely removed by centrifugation, used to separate adsorbed material from non-adsorbed material. We also assume the mineral particle size does not affect the adsorption behaviour as the mineral is in excess.

The adsorbed concentration is determined by measuring the carbon content of the mineral before and after adsorption, having adopted a suitable separation technique for the mineral from the host suspension. The measurements assume uniform adsorption behaviour onto the mineral, i.e. *Fig 1a* rather than *Fig 1b*. The measurements are corrected for the initial carbon content of the mineral, so the additional carbon content is associated only with the sticky concentration on the surface.

The results presented in this work have industrial applications in optimising the control of stickies in a paper recycling mill. The adsorption mechanisms proposed for a controlled situation can be adapted for the multi-contaminant system in the paper recycling mill, so that the effect of stickies in the paper mill can be minimised.

Materials and methods

The artificial stickies used are commercially available analogues of typical products found to contribute to stickies found in a paper mill and are listed in *Table 1*. For those components obtained as a suspension, the solids contents have been measured experimentally, by evaporating the suspension at 130°C and measuring the weight change.

The minerals used in this investigation are talc, modified calcium carbonate (MCC) and bentonite. All are used in paper manufacture either as a paper coating pigment or filler. However, the minerals already in the recycled paper are usually dispersed, and may be covered with latex if the paper source is coated broke. Therefore the existing mineral surfaces tend to be inactive. In this work, we are studying the effect of adding additional mineral with fully active surfaces.

The low surface area (LSA) talc (Finntalc PO5) was obtained in undispersed form from Mondo Minerals, Finland¹. It was further processed by delaminating and grinding to give an additional surface area and particle size grade referred to as high surface area (HSA) talc (Gantenbein et al. 2009). The LSA talc has less exposed facial surface, and, thus, relatively more edges which are dominated by hydrophilic interactions (Gribble et al. 2010). By contrast the HSA talc is dominated by the hydrophobic interaction on the relatively greater area of exposed talc faces. The talc used in this investigation is undispersed. However commercial talc often contains dispersants and hence has surface properties that differ from the LSA and HSA talc used.

The MCC was obtained from Omya Development AG² and the sodium bentonite was sourced from Morocco³. The modified calcium carbonate is a speciality mineral produced from ground calcium carbonate by Omya Development AG (Ridgway et al. 2004).

¹ Mondo Minerals B.V. Kasarmikatu 22, Helsinki, Finland

² Omya Development AG, Baslerstrasse 42, CH-4665, Oftringen, Switzerland

³ S&B Industrial. Minerals. Morocco S.A.R.L

Table 1. Stickies used in investigation

Illustrative Sticky	Product name	Supplier	Solids Content / (%)
Acrylic acid ester copolymer	Acronal V 212	BASF	68.29
Alkyldiphenyloxide disulphonate	Dowfax 2A1	DOW Corning	45.00
Colophonium resin	Colophonium	Resina AG	Not applicable
Fatty acid ester defoamer	Afranil RS	BASF	30.31
Mineral oil / silicone defoamer	Agitan 700	Münzing Chemie	83.61
Polyvinyl acetate	Vinnapas B 17	Wacker	Not applicable
Styrene-butadiene latex	Styronal D 809	BASF	53.21

Table 2. Summary of mineral properties.

Mineral Name	Specific Surface Area / m ² g ⁻¹	Particle Size-Weight Distribution* / μm			Particle Size-Number distribution / μm
		d ₁₀	d ₅₀	d ₉₀	d _{mode}
LSA talc	7.13	2.24	4.50	10.1	0.557
HSA talc	45.30	1.56	5.02	21.0	0.521
MCC	36.13	2.55	5.49	9.85	0.537
Sodium bentonite	100.13	0.11	1.84	19.72	0.064

* d_N represents the particle diameter for which N % of the sample mass has particles finer than diameter (d).

The surface areas were measured and calculated using the BET approximation (Brunauer et al. 1938), *Table 2*, on a Micromeritics Gemini 2360 surface area analyser⁴. The particle size distributions of the minerals were obtained using time averaged light scattering measured by a Malvern Mastersizer 2000⁵. The light scattering results were processed applying Mie theory (Mie 1908) to obtain the particle size distribution, based on the assumption that the particles are spherical. The weight median particle diameters, d₅₀, are reported in *Table 2*. The surface area of the sodium bentonite measured by gas adsorption is not representative since the mineral swells in water as a function of salt concentration, degree of activation etc.

Table 2 also shows the mode of the particle size distribution by number of particles, which allows comparison with the diameter of the stickies. The particle size number distribution calculated using Mie theory is shown in *Fig 2*.

⁴ Micromeritics U.K. Ltd, 178-182 High Street North, Dunstable, Bedfordshire, U.K.

⁵ Malvern Instruments Ltd, Enigma Business Park, Grovewood Rd, Malvern, U.K.

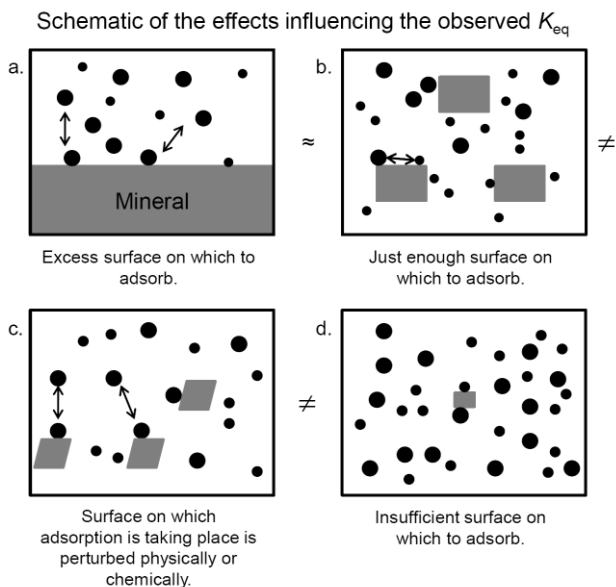


Fig 1. Schematic highlighting how the equilibrium adsorption behaviour is modified by mineral concentration. Fig 1a the mineral concentration is in great excess, Fig 1b the mineral concentration is just in excess, Fig 1c the mineral concentration is just in excess but the surface of mineral has been perturbed chemically or physically, influencing the adsorption. Fig 1d the sticky is in great excess. In this publication, the results and conclusions refer to the system where the mineral is in excess, i.e. Fig 1a, or just sufficient, Fig 1b.

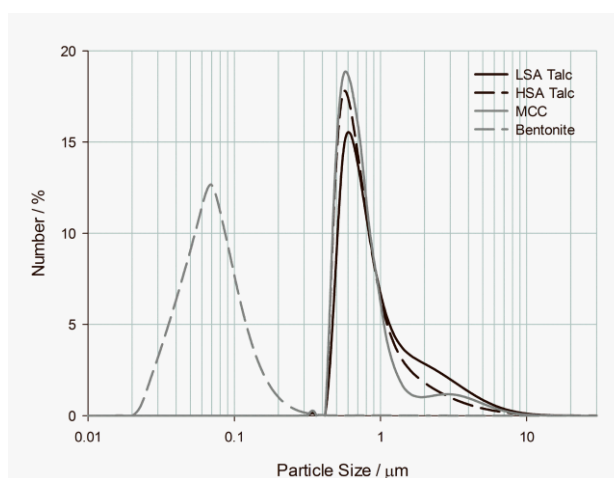


Fig 2. Particle size number distribution for the minerals used to study the adsorption of stickies. The number distribution shows the significant difference in size between the bentonite and the three other minerals used in the investigation.

Artificial sticky preparation

All the stickies were prepared to form colloidal stable suspensions with an initial concentration of 0.5 g dm^{-3} with pH between 7 and 7.5 and conductivity in the range of 1000 to $1500 \text{ } \mu\text{S cm}^{-1}$, mixing with mechanical stirrers at a minimum of 500 revolutions per minute. They were adjusted to these ranges where necessary using dilute analytical grade hydrochloric acid, analytical grade sodium hydroxide and laboratory grade sodium chloride.

Most of the artificial stickies were available as colloidal suspensions. However, for the colophonium resin and polyvinyl acetate, which were not in suspension, the following procedures were followed, and the samples then adjusted to the correct pH and conductivity range.

Colophonium: 5 g of colophonium was saponified in 10000 g deionised water by the addition of 5 g sodium hydroxide. The pH was afterwards adjusted back to 7.5 by the addition of hydrochloric acid with a resulting turbidity of 130 nephelometric turbidity units and a chemical oxygen demand of $813 \text{ mg O}_2 \text{ per dm}^3$.

Polyvinyl acetate: 5 g polyvinyl acetate was dissolved in 100 cm^3 acetone (propanone). The solution was added under vigorous stirring to a solution of 5 g polyvinyl alcohol and 10 litres of deionised water. The acetone was evaporated at 60°C overnight to give a colloidal stable suspension with a turbidity of 64 nephelometric turbidity units and a chemical oxygen demand of $1280 \text{ mg O}_2 \text{ dm}^{-3}$.

All sticky suspensions were then diluted to 0.1, 0.05, 0.01 and 0.005 g dm^{-3} , and reference samples of each concentration were taken to construct a calibration series. The sticky suspensions then had mineral suspension added to give a mineral concentration of 2 g dm^{-3} .

Equilibration

The mineral and sticky suspensions were mixed for 30 minutes at 150 revolutions per minute on an orbital shaker. The minerals with adsorbed sticky were removed by centrifuging at 2000 g for 15 minutes for talc and MCC, whereas the bentonite samples were centrifuged for 20 minutes. The supernatant was stored in clean glass bottles. The mineral precipitates with adsorbed stickies were kept in the centrifuge tubes for freeze drying for a period of 48 hours before elemental analysis.

Analysis

The experiments were replicated three times with the aqueous and adsorbed concentration determined a minimum of three times for each experiment. The average data was then used for all subsequent calculations.

The aqueous sticky concentration was determined using dissolved organic carbon analysis, and the adsorbed sticky concentration was determined using elemental analysis. The dissolved organic carbon data was converted from $\mu\text{mol dm}^{-3}$ to mg dm^{-3} of dissolved organic carbon. The elemental analysis results were converted from % of adsorbed carbon to mg g^{-1} of adsorbed carbon. The two results were then combined to give the equilibrium constants with the units of $\text{dm}^3 \text{ g}^{-1}$.

The dissolved organic carbon analysis was measured using a Shimadzu⁶ TOC-5000A total organic carbon analyser coupled to a Shimadzu ASI-5000A auto sampler using standard operating procedures for the analysis of dissolved organic carbon (Pan et al. 2005).

Analytical quality assurance

Accuracy was checked against two certified reference materials which reflected this instrument's normal use for marine applications - namely deep sea water from the Sargasso, collected at 2600 m, from Hansell Laboratory, University of Miami with a certified dissolved organic carbon content of 44 – 45 $\mu\text{M C}$ within a 95% confidence limit. Our results agreed with these reference values: our DOC value was $44.3 \pm 3.8 \mu\text{M C}$ within the 95% confidence limit from 34 analyses.

Elemental analysis was performed on a Carlo Erba⁷ EA-1110 CHNS elemental analyser, following standard operating procedures. The results were cross checked against a reference marine sediment, PACS-1 (NRC, Canada) with a certified carbon concentration of $3.69 \pm 0.11\%$ with a 95% confidence limit, which compares well with $3.58 \pm 0.15\%$ with a 95% confidence limit for our measurements.

Results and discussion

To confirm the excess concentration and to justify the exclusion of $[\text{Mineral}]^{\text{Susp}}$ from the equilibrium calculation, an experiment using modified calcium carbonate and alkyldiphenyloxide disulphonate was carried out in which the mineral concentration was changed from $0.25 - 20 \text{ g dm}^{-3}$, using 12 different mineral concentrations and constant sticky concentration. The equilibrium constant with mineral concentration in the calculation, stayed in the range $0.001360 \pm 0.000041 \text{ dm}^3 \text{ g}^{-1}$.

The concentration of adsorbed carbon was measured by elemental analysis. However, because of the likely presence of unknown carbon-containing surfactants it was not possible to calculate the precise sticky concentration on a molar basis.

Equilibrium constants

The equilibrium constants for all the sticky and mineral systems were calculated using the dissolved organic carbon data and elemental analysis carbon data, Eq 2. The results are shown in Fig 3. The error bars in Fig 3 represent two standard deviations for

each of the equilibrium constants as used by Gribble et al. (2010), i.e. 95% of the assumed statistical distribution of the calculated equilibrium constants at each different concentration are within the error bars. We are assuming linearity across the experimental range and this is discussed later.

The applicability of Eq 2 depends on various factors, including the particle size of both the mineral and sticky, and the location of adsorption sites on the surface. For example, with talc the diameter of the hydrophobic surface is much greater than the hydrophilic edge diameter. With modified calcium carbonate the active adsorption site is within a porous particle. Therefore, the adsorption site may not be on the surface but could be located within the mineral particle. The results do not distinguish the exact method of sticky removal, but provide information about the efficiency of sticky removal when the mineral is in great excess relative to the sticky concentration. The exact adsorption location for each sticky would need further investigation, using different techniques, although inferences can be made about the adsorption sites, and also the structure of the resulting agglomerates as discussed overleaf.

Fig 3 shows that the equilibrium constants are higher for HSA talc than LSA talc by a ratio of between 1.10 and 3.88. This ratio provides clues about the adsorption mechanism, specifically whether the sticky preferentially adsorbs on hydrophobic or hydrophilic species. The ratio for the acrylic acid ester copolymer is 1.10, which implies hydrophilic adsorption, since the increased hydrophobic surface relative to hydrophilic surface makes little difference. The ratio for alkyldiphenyloxide disulphonate is 3.88, which implies that adsorption onto hydrophobic surfaces is preferred relative to hydrophilic surfaces. For the fatty acid ester defoamer and colophonium, the ratios of 2.18 and 2.61 respectively suggest HSA talc is better at adsorbing stickies from colloidal suspension, implying the adsorption is dominated by hydrophobic forces. However, it must be borne in mind that the adsorption may also be assisted by unknown surfactants present in the commercial suspension.

The MCC used in this investigation had the highest equilibrium constants for the adsorption of acrylic acid ester copolymer, mineral oil/silicone defoamer, polyvinyl acetate and styrene-butadiene latex. MCC is a charged species, so the dominant adsorption mechanism is likely to be charge related (Ridgway et al. 2004). Adsorption onto bentonite is also charge related (Asselman, Garnier 2000).

⁶ Shimadzu Corp, Japan

⁷ Thermo Fisher Scientific, USA

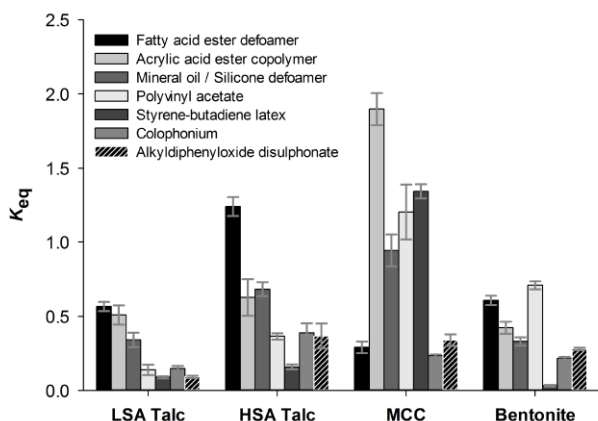


Fig 3. Average equilibrium constants for all experimental systems investigated, calculated from the dissolved organic carbon and elemental analysis carbon data. The error bars represent double the standard deviation determined from a minimum of three replicates of elemental analysis and dissolved organic carbon analysis over the linear range.

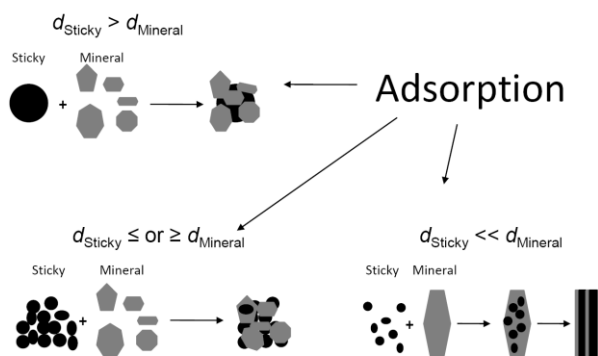


Fig 4. Schematic representation of how adsorption can vary dependent on the diameter of the mineral particle or sticky species. The concentration of mineral is always in excess, Fig 1a.

However, the particle size of the bentonite is smaller than the MCC in this investigation. The results imply that for the alkyldiphenyloxide disulphonate system one should preferably use HSA talc, MCC or bentonite to remove the sticky, and that the sticky is able to be removed using either hydrophobic or charge interaction sites for adsorption. These are not the only possible removal mechanisms that could occur during the experiment. One other mechanism is that the calcium soap could precipitate for alkyldiphenyloxide disulphonate.

Limitations on adsorption and the assumption of linearity (K_{eq})

Three different mechanisms for possible adsorption of stickies are shown schematically in Fig 4. The particle size of the mineral and the arrangement of adsorption sites affect the arrangement of sticky and mineral. When the mineral is much larger than the sticky, a sandwich of sticky particles can be formed between mineral particles, bottom right of Fig 4. The sandwich adsorption mechanism is most likely

for the acrylic acid ester copolymer and styrene butadiene latex because of their smaller median particle diameter of 0.77 and 0.19 μm (Benecke et al. 2009).

The mechanism represented in the top left schematic occurs when the sticky molecule is larger than the diameter of the mineral particle. The agglomeration mechanism is most probable for polyvinyl acetate and colophonium resin as the median particle diameters are 125.5 and 128.7 μm , respectively (Benecke et al. 2009) in relation to mineral modal particle sizes ranging from 0.064 to 0.557 μm . This mechanism requires more mineral particles adsorbed onto the surface before the sticky is detackified.

The schematic in the bottom left of Fig 4 represents a hybrid adsorption mechanism between that of the sandwich system and the agglomeration system, described above, and is likely to occur when the diameter of the sticky particle is of a similar size to the mineral particle. The hybrid mechanism is likely to occur with the fatty acid ester defoamer and mineral oil / silicone defoamer as the median particle diameters are 3.9 and 3.1 μm , respectively (Benecke et al. 2009).

The particle size is different for each sticky and each sticky will have a preferred adsorption site on the adsorbent. The adsorbent may not be completely covered at all available active adsorption sites for all the stickies. Sometimes the adsorption sites will be located close together on the adsorbent. Neighbouring adsorbate particles will compete with each other spatially, and this will affect the adsorption equilibrium constant. Therefore, at higher concentrations of stickies as the sticky concentration approaches the mineral concentration, as in Fig 1b, the equilibrium constant may deviate from being linear.

An electron micrograph of a hybrid structure is shown on Fig 5, for the case of fatty acid ester defoamer with LSA talc. Only the mineral can be seen, because of the much lower density to electrons of the sticky relative to the mineral. An example of the sandwich structure, shown in the bottom right of Fig 4, is shown for the case of styrene-butadiene with sodium bentonite in Fig. 6.

The equilibrium constant was calculated for every concentration and mineral to determine the linear range which applies to the sticky adsorbing onto the mineral. The linear range calculated for the equilibrium constants is shown in Table 3. The equilibrium constants were tested using the Q test for outliers, (Miller, Miller 2005) and all instances when the linear range is 0.1 – 0.005 instead of 0.5 – 0.005 g dm^{-3} could be rejected with 95% confidence.

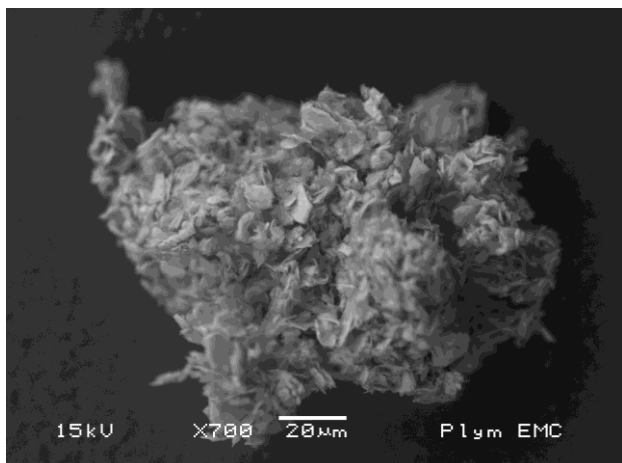


Fig 5. Scanning electron micrograph image of fatty acid ester defoamer with LSA talc.

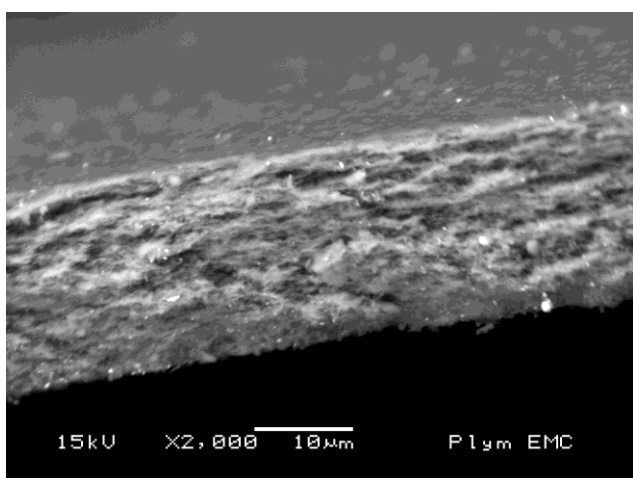


Fig 6. Scanning electron micrograph image of styrene-butadiene latex with sodium bentonite.

Acknowledgements

The authors wish to acknowledge Omya Development AG Switzerland, and the HEIF 3 program UK for funding the project. Omya Development AG is thanked for supporting cooperation between the University of Plymouth and its industrial Mineral and Surface Chemistry Research and Development.

Literature

Allen, L. H. and Douek, M. (1993): Effectiveness of Talc for Pitch Control in Kraft Pulp Manufacture, *J. Pulp Pap. Sci.*, 19 (3), J131.

Asselman, T. and Garnier, G. (2000): Adsorption of model wood polymers and colloids on bentonites, *Colloids Surf. A.*, 168 (2), 175.

Benecke, F., Gantenbein, D., Schoelkopf, J., Gane, P. A. C. and Gliese, T. (2009): Organic contaminants in recycled paper: a model study of the adsorbent properties of talc for idealised component suspensions, *Nord. Pulp Pap. Res. J.*, 24 (2), 219.

Table 3. Maximum of linear range (g dm^{-3}) applicable for adsorption of stickies onto different minerals. The minimum value of the linear range is 0.005 g dm^{-3} .

Sticky	LSA Talc	HSA Talc	MCC	Bentonite
Fatty acid ester defoamer	0.1	0.1	0.5	0.5
Acrylic acid ester copolymer	0.1	0.1	0.1	0.5
Mineral oil / silicone defoamer	0.5	0.1	0.1	0.5
Polyvinyl acetate	0.5	0.1	0.1	0.5
Styrene butadiene latex	0.1	0.1	0.1	0.5
Colophonium resin	0.5	0.5	0.5	0.5
Alkyldiphenyloxide disulphonate	0.5	0.5	0.5	0.1

Conclusions

We have derived equilibrium constants that provide fundamental information about the interaction of these model stickies with different minerals. *Fig 3* compared seven different stickies adsorbing onto four different minerals. The comparison of equilibrium constants with differing mineral properties helps identify conditions that could be used to remove a particular species of sticky in a paper mill. The results do not take account of adsorption kinetics; certain minerals may adsorb the stickies more quickly than others. Furthermore, the results are only for adsorption phenomena onto the mineral surface; in a paper mill with fluctuating sticky concentrations, the stickies could also desorb from the surface of the mineral.

Brunauer, S., Emmett, P. H. and Teller, E. (1938): Adsorption of Gases in Multimolecular Layers, *J. Am. Chem. Soc.*, 60 (2), 309.

Delagoutte, T. (2005): Management and control of stickies, *Prog. Pap. Recycl.*, 15 (1), 31.

Delagoutte, T. (2008): Stickies tackiness reduction with silanes, *Prog. Pap. Recycl.*, 17 (3), 9.

Doshi, M. R. (1991): Properties and Control of Stickies, *Prog. Pap. Recycl.*, 1, 54.

Doshi, M. R. and Dyer, J. M. (1998): Management and Control of Stickies, *Paper Recycling Chal.* 3, 195.

Doshi, M. R., Moore, W. J., Venditti, R. A., Copeland, K., Chang, H. M., Putz, H. J., Delagoutte, T., Houtman, C., Tan, F., Davie, L., Sauve, G., Dahl, T. and Robinson, D. (2003): Comparison of Macrostickies Measurement Methods, *Prog. Pap. Recycl.*, 12 (3), 34.

Douek, M. and Allen, L. H. (1991): Some Aspects of Pitch Control with Talc in Unbleached Kraft Pulps, *J. Pulp Pap. Sci.*, 17 (5), J171.

- Douek, M., Guo, X. Y. and Ing, J.** (1997): An overview of the chemical nature of deposits stickies in mills using recycled fibre, Recycling Symposium, 313.
- Gantenbein, D., Schoelkopf, J., Hunziker, P., Matthews, G. P. and Gane, P. A. C.** (2009): Efficiency of colloidal pitch adsorption onto phyllosilicates: Comparing talc, chlorite and pyrophyllite, Nord. Pulp Pap. Res. J., 24 (4), 448.
- Gribble, C. M., Matthews, G. P., Gantenbein, D., Turner, A., Schoelkopf, J. and Gane, P. A. C.** (2010): Adsorption of surfactant-rich stickies onto mineral surfaces, J. Colloid Interf. Sci., 352 (2), 483.
- Heise, O. U., Kemper, M., Wiese, H. and Krauthauf, E. A.** (2000): Removal of residual stickies at Haindl Paper using new flotation technology, Tappi J., 83 (3), 73.
- Holmbom, B. and Sundberg, A.** (2003): Dissolved and colloidal substances accumulating in papermaking process waters, Wochenbl. Papierfabr., 131 (21), 1305.
- Hutten, I. M., Diaz, R., Roberts, M. K., Jeffrey, C. and Banerjee, S.** (1997): Fiber to water distribution of stickies, Tappi J., 80 (4), 193.
- Jones, D. R. and Fitzhenry, J. W.** (2003): Esterase-type Enzymes Offer Recycled Mills An Alternative Approach to Stickies Control, Pulp Paper, 77 (2), 28.
- Kemper, M.** (1999): State-of-the-art and new technologies in flotation deinking, Int. J. Miner. Process., 56 (1-4), 317.
- Klungness, J. H., Gleisner, R. L. and Sykes, M. S.** (2002): Micro and colloidal stickie pacification with precipitated calcium carbonate, Conference 7th Recycling Technology, Crowne Plaza Hotel, Brussels, Belgium.
- Mie, G.** (1908): Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen, Ann. Phys-Leipzig, 330 (3), 377.
- Miller, J. N. and Miller, J. C.** (2005): Statistics and chemometrics for analytical chemistry, Pearson Prentice Hall, Harlow, England ; New York.
- Nguyen, D. T.** (1998): Prevention of pitch and stickies deposition on paper-forming wires via adsorption of a cationic polymer associated with anionic species, Tappi J., 81 (6), 143.
- Olson, C. R. and Letscher, M. K.** (1992): Increasing the Use of Secondary Fiber - An Overview of Deinking Chemistry and Stickies Control, Appita J., 45 (2), 125.
- Onusseit, H.** (2006): The influences of adhesives on recycling, Resour. Conserv. Recy., 46 (2), 168.
- Pan, X., Sanders, R., Tappin, A. D., Worsfold, P. J. and Achterberg, E. P.** (2005): Simultaneous Determination of Dissolved Organic Carbon and Total Dissolved Nitrogen on a Coupled High-Temperature Combustion Total Organic Carbon-Nitrogen Chemiluminescence Detection (HTC TOC-NCD) System, J. Autom. Method. Manag., 2005 (4), 240.
- Ridgway, C. J., Gane, P. A. C. and Schoelkopf, J.** (2004): Modified calcium carbonate coatings with rapid absorption and extensive liquid uptake capacity, Colloids Surf. A., 236 (1-3), 91.
- Rogan, K. R.** (1994): Adsorption of oleic acid and triolein onto various minerals and surface treated minerals, Colloid Polym. Sci., 272 (1), 82.
- Spiess, W. and Renner, K.** (2004): Improving the efficiency of recovered paper screening or: How to effectively control stickies, Wochenbl. Papierfabr., 132 (17), 1002.
- Vähäsalo, L. J. and Holmbom, B. R.** (2006): White pitch deposition and styrene-butadiene-rubber binder content in paper mill process waters, Appita J., 59 (4), 280.

**Manuscript received April 12, 2011
Accepted June 14, 2011**