Process factors affecting colloid stability and deposit formation in manufacture of newsprint from TMP and recycled fibre

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SUMMARY

Formation of pitch and sticky deposits through the destabilisation of colloidal material present in paper manufacture continues to be a challenge in improving machine efficiency in newsprint manufacture from a furnish comprising thermo-mechanical pulp (TMP) and recycled fibre (RCF), and in an environment where water usage efficiency is at best practice. Findings from laboratory studies that have investigated colloid structure, impact of multiple and multi-valent cations, pH, temperature, shear and dissolved organic matter on Pinus radiata extractive colloid stability have been used, along with observations of process conditions in Norske Skog’s Albury mill to determine which properties are most important in maintaining colloid stability.

Developments in our understanding of wood extractive colloid structure have led to an explanation as to why pitch deposition is more likely during summer months. A parameter called the “ester to acid ratio” has been shown to exhibit both short and long-term trends when applied to process stream extractive levels. This greater propensity for deposition during summer months is exacerbated by elevated soluble calcium levels during summer time. Dissolved organic wood polymers also affect colloid stability and their behaviour is further modified by the presence of soluble calcium. More stable colloids are obtained under conditions of neutral pH, avoidance of downward temperature shocks and avoidance of shear forces.

KEYWORDS:
Pitch deposits, colloid stability, wood extractives, resin acids, fatty acids, glycerides, TMP, recycled fibre, newsprint manufacture.

INTRODUCTION

The manufacture of newsprint using a mixture of mechanical pulp and recycled pulp has consistently proved a challenge with respect to formation of troublesome deposits. Deposit formation has continued to occur at an unacceptable level as water reduction initiatives have been progressively implemented in recent years. Experience at Norske Skog’s Albury mill has been that these deposits have been dominated by hydrophobic extractives derived from P. radiata (1).

The focus of our research has been to understand the factors that influence extractive colloid stability, in particular those factors that may be different for pine compared to the more extensively studied spruce.

DEPOSIT COMPOSITION

Deposits can take a variety of forms and can occur in a range of locations from the stock approach circuit, through the forming and press sections to the calender stack. Deposit analysis entails microscopic examination, analysis of the sample using Fourier Transform Infra Red (FTIR) spectroscopy, extraction with acetone, determination of wood extractives using Gas Chromatography (GC) and determination of filler content. Two types of solvent extraction are used, the first with just acetone to extract neutral extractives and free organic acids and the second, acidic acetone extraction, to enable determination of the salt forms of organic acids such as resin and fatty acids. FTIR analysis determines the broad classes of compounds present, and in particular is the main tool for determining if stickies from recycled fibre are present. Typical analysis determines for each deposit type the percentages of extractives, free resin acids, resin acids in salt form, fatty acids, glycerides, calcium carbonate, and other fillers as well as the presence/absence of stickies. Table 1 indicates typical compositions for samples of deposits taken from paper machine uhle boxes. Figure 1 give an indication of the variability in the presence of stickies over a range of uhle box locations over a range of days.

Table 1. Typical average composition of deposits taken from paper machine uhle boxes.

<table>
<thead>
<tr>
<th>% Acet. Extr.</th>
<th>% Free Resin Acids</th>
<th>% Resin Acid Salts</th>
<th>% Fatty Acids</th>
<th>% Glyc.</th>
<th>% CaCO₃</th>
<th>% Other Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>3.4</td>
<td>3.9</td>
<td>1.1</td>
<td>5.2</td>
<td>32</td>
<td>9</td>
</tr>
</tbody>
</table>

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moving average.

Appita should provide clues as to how to control and reduce deposit understand how they interact in the papermaking environment play a significant role in the formation of deposits, so steps to component in comparison, and there is no evidence of their absorbance signals in the FTIR spectra relative to that of the not measured quantitatively, the magnitude of the stickies' around 40% of samples. Although their mass percentage was (32% calcium carbonate, 9% “other” fillers) whilst the balance, recycled fibre. polymerised extractives, as well as, sometimes, stickies from (32% calcium carbonate, 9% “other” fillers) whilst the balance, recycled fibre. Deposits consist of approximately 36% extractive material, of which almost 40% is resin acids (in roughly equal proportions of free and calcium salt forms), glycerides and fatty acids. It is assumed that the remaining 60% of the acetone extract contains neutral components (sterols and steryl esters), oxidised and polymerised extractives, as well as, sometimes, stickies from recycled fibre.

Filler material makes up approximately 41% of the deposits (32% calcium carbonate, 9% “other” fillers) whilst the balance, 23%, is believed to be fibre and fines. Stickies are present in around 40% of samples. Although their mass percentage was not measured quantitatively, the magnitude of the stickies’ absorbance signals in the FTIR spectra relative to that of the wood extractives, indicates that they may only be a minor component in comparison, and there is no evidence of their presence in GC analysis of the acetone extracts. Deposit analysis therefore suggests that tacky wood extractives play a significant role in the formation of deposits, so steps to understand how they interact in the papermaking environment should provide clues as to how to control and reduce deposit formation.

COLLOID STRUCTURE

Resin acids, fatty acids and glycerides are hydrophobic compounds that organise themselves into colloids in aqueous environments. Several studies have investigated the structure of these colloids and the work of multiple research groups (2-4) indicate that the structure is likely to be as proposed in Figure 2. The most recent work from our group (4) proposes that the colloid is characterised by a surface layer of resin acids but may also contain fatty acids. The extent to which the fatty acids share the surface with the resin acids is dependent on the proportion of glycerides present in the colloid. Lower proportions of glycerides result in withdrawal of the fatty acids from the surface and their retreat to the core. This transition of fatty acids from outer surface to inner core in turn affects the stability of the colloid. A more unstable colloid results from the depletion of fatty acids in the surface layer when glyceride levels decrease.

Fig. 1. Presence/absence of stickies in deposits.

Fig. 2. Proposed colloid structure for wood extractives derived from softwoods.

Fig. 3. Ratio of glycerides (fatty acid esters) to free resin and fatty acids in thermomechanical pulp at the Albury mill. The solid line is a 7 point moving average.
Knowing this fundamental relationship between glyceride levels and colloid stability led us to a closer analysis of extractive levels over time in process streams at the Albury mill. The concentration of glycerides, resin acids and fatty acids has been measured in process stream at Norske Skog’s Albury mill for over 14 years thus enabling construction of a long term trend of the ratio of the glycerides (also known as fatty acid esters) to the free resin and fatty acids. We propose that this “Ester to Acid Ratio”, (EAR) is in effect a colloid stability indicator. Figure 3 summarises over 14 years of this data for extractives in TMP taken at the proportioners, just prior to mixing with recycled fibre stock. It shows both long and short term trends. In the late 1990’s the EAR varied between a winter minimum of around 0.4 to a summer maximum of around 0.8 to 0.9. However from around 2002 onwards the cycles changed to lower maxima and lower minima, to the extent that the 2011 maximum is below the 1990’s minima. Therefore, combining our knowledge of the colloid structure (and its tendency to unstable behaviour at low EAR) with process stream data leads to the suggestion that colloids in the process streams should be less stable now than they were 10-14 years ago. A similar pattern of variation over time in the EAR indicator was found for headbox stock.

Analysis of the EAR parameter in pitch deposits taken from the paper machine over a three year period (Fig. 4) showed two data populations, one with EAR values between 0.2 and 0.9, and another (the red bars) with values less than 0.1. This latter population was also generally characterised by a higher proportion of resin acid salts, most likely of calcium. In these instances at least, it could be inferred that calcium was a direct participant in the formation of the deposit, presumably via reaction between soluble calcium and soluble resin acids.

**IMPACT OF DISSOLVED INORGANIC AND ORGANIC SPECIES ON COLLOID STABILITY**

According to the DLVO colloid chemistry theory, the presence of cations such as sodium (Na⁺), calcium (Ca²⁺) and potentially aluminium (Al³⁺) or iron (Fe³⁺) in process whitewater would be expected to affect colloid stability. We have recently conducted studies to explore the impact of inorganic species on the deposition behaviour of wood extractive colloids (5-8). A Photometric Dispersion Analyser (PDA) was used (5) to determine the Critical Coagulation Concentration (CCC) of several inorganic cations. (The CCC is that concentration of a particular species that induces destabilisation and coagulation of colloids.) The CCC’s for a number of cations in colloidal wood extractive suspensions are listed in Table 2.

<table>
<thead>
<tr>
<th>Salt</th>
<th>CCC [mM]</th>
</tr>
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<tbody>
<tr>
<td>NaCl</td>
<td>720±36</td>
</tr>
<tr>
<td>KCl</td>
<td>670±33</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>7.8±0.3</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>6.5±0.4</td>
</tr>
<tr>
<td>Al₂(SO₄)₃</td>
<td>0.065±0.003</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>0.075±0.005</td>
</tr>
</tbody>
</table>

A very clear relationship between valency and the CCC is indicated by this data, with each unit increase in valency leading to a reduction of the CCC by around two orders of magnitude. The use of sodium based chemicals for deinking of recycled fibre and brightening of TMP fibre and the presence of calcium carbonate filler in recycled paper leads to the presence of both sodium and calcium cations in process waters. Sodium levels in paper machine whitewater averaged around 14 mM when the mill was operating on a caustic/silicate/soap/ hydrogen peroxide deinking recipe, but with a change to neutral deinking in 2007, sodium levels have decreased. They are well below the levels (Table 2) where sodium by itself would induce colloid destabilisation. Calcium on the other hand requires closer scrutiny. Data showing the concentration of soluble calcium in the recycled pulp stream (Fig. 5) indicates that the introduction of neutral deinking in 2007 resulted in an abrupt and significant increase in soluble calcium present in the system, and that its variability also increased significantly, taking it on occasions closer to the CCC for calcium. An additional feature of the data in Figure...
IMPACT OF pH, TEMPERATURE AND SHEAR ON COLLOID STABILITY

pH has a significant influence on wood extractive behaviour within the operating pH band for paper-making, particularly where the process contains extractives from high organic acid extractive woods such as P. radiata. Resin acids have a colloidal pK\textsubscript{a} of around 6-7 (10), which means that above pH=6 they become available for reaction with other soluble multi-valent species such as calcium and aluminium, to form a metal-resinate salt. Low pH environments result in a low CCC for calcium (Table 3), but it increases as pH increases. This has several implications for paper-making. Firstly, deposition of pitch colloids is more likely in the acidic environment associated with thermo mechanical pulp manufacture (neglecting other factors such as steric stabilisation of colloids). This can have an important consequence where process whitewater from a higher pH environment (eg the paper machine in neutral paper-making) returns to the lower pH environment in the pulp mill. The decrease in pH will generate destabilising conditions that could result in deposition of pitch colloids onto fibre surfaces, which when carried forward to the paper mill, are more prone to forming sticky deposits on critical surfaces such as press fabrics and uhle box surfaces. A process solution to this situation is to introduce a dissolved air flotation stage whereby whitewater

### Table 3. Influence of pH on the CCC for calcium interacting with wood extractive colloids at 25 °C.

<table>
<thead>
<tr>
<th>pH</th>
<th>CCC-calcium [mM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>1.6 ±0.2</td>
</tr>
<tr>
<td>4.0</td>
<td>1.7 ±0.4</td>
</tr>
<tr>
<td>5.5</td>
<td>7.8 ±0.3</td>
</tr>
<tr>
<td>7.0</td>
<td>8.8 ±0.4</td>
</tr>
<tr>
<td>8.0</td>
<td>12 ±0.6</td>
</tr>
</tbody>
</table>

5 is that for the post-neutral deinking data, the maxima tend to be during the warmer months (November to March), whilst the minima tend to be during the cooler winter months (May to August). The coincidence of elevated levels of destabilising soluble calcium with less stable wood extractives during these warmer months thus makes the process more vulnerable to pitch deposition during the summer, and this is borne out by analysis of production breaks.

The presence of multiple salts and their impact on wood extractive colloid stability was investigated by determining the CCC for calcium and aluminium in the presence of variable amounts of sodium (9). The resultant non-linear relationship for the sodium/calcium combination (Fig. 6) indicated that, whilst there is a significant reduction in the CCC for calcium, the sodium levels needed to induce it are well above the likely practical concentration for sodium in process water circuits. Thus it was concluded that varying levels of sodium alone would not significantly increase pitch deposition risk.
returned to the pulp mill from the paper mill has any extractives taken out. Secondly, it reinforces the importance of keeping the paper making process at a neutral pH in order that a more stable colloidal environment is maintained. Neutral pH also ensures that dissolution of the destabilising calcium is minimised. Typical process pH values for the TMP, recycled fibre and headbox streams are shown in Figure 7 for Albury mill process streams. The pH of headbox stock is strongly buffered at around pH 6.7 – 7.0. The recycled fibre pH has generally varied between 6.0 and 6.5 since neutral deinking was introduced in 2007, whilst TMP varies between 4.5 and 6.0. The largest pH differential exists between TMP stock and headbox stock.

Temperature has a moderating effect on the CCC for sodium and calcium, and to a lesser extent for aluminium (Table 4). Increasing the temperature results in an environment in which the colloids will be more stable. Decreasing temperature by contrast has the opposite effect. This characteristic of colloid stability therefore means that downward temperature shocks associated with introduction of cold freshwater at times such as start-up make the process more prone to pitch deposit formation. The Albury mill has certainly encountered this and has made changes to water management practices as a result. Substitution of cold mill filtered water by warm clear filtrate obtained by sending machine chest stock to the saveall and returning the resulting clear filtrate to the super clear filtrate tank, from which shower water is obtained, has led to less temperature shock at start-up and less propensity for deposits to form on the press section clothing.

Temperature [°C] Na⁺[mM] Ca²⁺[mM] Al³⁺[mM]
--- | --- | --- | ---
25 | 720 | 7.8 | 0.065
50 | 1600 | 24 | 0.09

Table 4. Effect of temperature on CCC for sodium, calcium and aluminium.

Application of high shear forces has been shown to reduce the CCC for calcium quite significantly (Fig. 8). Therefore high shear environments such as uhle box lips and press nip points are more prone to deposition.

![Fig. 8. Impact of shear force on CCC for calcium interacting with wood extractive colloids at 25 °C.](image)

**IMPACT OF DISSOLVED ORGANIC MATTER ON COLLOID STABILITY**

Thermo mechanical pulping at temperatures in excess of 100 °C results in some dissolution of hemicellulose material to generate dissolved organic material, otherwise known as wood polymers. These wood polymers have been shown to interact with wood extractive colloids by various processes, one of which is known as steric stabilisation (11-15).
We recently reported the impact of dissolved wood polymers on the stability ratio of wood extractives (where the colloidal stability ratio, W, is defined as the ratio of collisions between particles to the number of collisions that result in coagulation) and found a complex pattern of behaviour (6). The data reproduced in Figure 9 was obtained by measuring the stability ratio, using a PDA, of wood extractive colloids that had been prepared by dialysis and recombined with varying quantities of wood polymers that had been extracted from TMP using hot water. A complex pattern of increasing and decreasing colloid stability was observed. The successive increase, decrease, increase, followed by another decrease and increase in the stability ratio was explained in terms of successive destabilising and stabilising processes: bridging flocculation; steric stabilisation, depletion flocculation and depletion stabilisation (Fig. 9) (16).

In a more complex set of experiments a similar combination of wood extractive colloids and soluble wood polymers were combined in the presence of 10 mM CaCl2. This was done to more closely imitate the presence of inorganic cations known to be present in the Albury mill process water circuit. A significantly different pattern of behaviour was observed (Fig. 10). Destabilisation of the colloids occurred at quite low wood polymer concentration (<50 mg/L), after which increasing wood polymer concentration caused the colloids to become more stable. Clearly, the introduction of an inorganic cation has significantly altered the behaviour of the wood extractive colloid. Measurement of the soluble wood polymer concentration in Albury mill process water has shown that a concentration of around 100 mg/L is present. For the case where no calcium was present (Fig. 9) this corresponds to a region where the wood extractive colloids are the most stable. By contrast, when 10 mM Ca2+ was present (Fig. 10), this corresponded to the least stable behaviour of the colloid. It is therefore clear that variation in either wood polymer or Ca2+ concentration will significantly affect wood extractive colloid stability.

**PRACTICAL IMPLEMENTATIONS**

Many factors affect wood extractive colloid stability in the case where softwood TMP made from _P. radiata_ mixes with recycled fibre to form the furnish for newsprint. Ca2+ ions, derived from calcium carbonate coming into the process via recycled paper, significantly affect the behaviour of wood extractive colloids. Investigations at the molecular level have also reinforced that both long and short term changes in wood extractives composition also affect colloid stability. The combination of these two primary factors with other secondary factors such as pH, temperature, shear and dissolved wood polymers mean that deposit control, in an environment where as little water as possible is being used, is a complex process. Nevertheless the following principles are important for control of pitch deposition:

1. **Remove extractive material as early as possible in the process.** Elevated levels of wood extractive colloids increase the risk of deposit formation. Extractives removal via processes such as chip pre-treatment (17), flocculation and dissolved air flotation of pressate water (18, 19) should therefore be high on the priority list of strategies to minimise deposit formation. The use of dissolved air flotation (DAF) to treat filtrate from a TMP screw press has been used at Albury mill for several years. However, this strategy is not as effective as chip pre-treatment because wood extractive colloids prefer to associate with the fibre phase rather than the liquid phase. They therefore follow the fibre, which means that removal of extractives inevitably results in fibre loss as well. Fibre loss may be minimised by installation of a screen on a filtrate stream ahead of the DAF stage, and careful choice of screen mesh size is needed to optimise fibre recovery whilst maximising extractives removal.

2. **Minimise the level of soluble calcium in process water.** The presence of soluble calcium destabilises wood extractive colloids both directly and by reducing the positive effects of dissolved wood polymers. Decreasing pH results in higher levels of soluble calcium so pH needs to be carefully managed. The factors that lead to decreases in pH can also be quite subtle. For example, development of anaerobic conditions in pulp storage chests will generate organic acids that lower the pH. The use of brightening agents such as sodium hydrosulphite will provide a source of sulphur oxide anions that are an oxygen source for anaerobic bacteria, thus encouraging anaerobic bacteria development and pH depression. Therefore another important control strategy in
minimising soluble calcium levels is to minimise the amount of sulphur bearing brightening agents. It is also important to keep pulp storage chests well mixed and at as low a level consistent with production and process stability requirements. Return of process water containing soluble calcium back to the pulp mill will have a greater tendency to destabilise colloids in the pulp mill, so process water management strategies must take this into consideration. It is intended that the current Albury mill practice of using dissolved air flotation to remove extractives from paper machine press filtrate together with TMP press filtrate will cease, with the paper machine stream being sent to the recycled fibre dissolved air flotation device instead. This will prevent soluble calcium being returned to the pulp mill.

3. Manipulate dissolved polymer concentration. Recent studies reported by Strand et al. show that addition of galactoglucomannans to TMP suspensions significantly improved colloid stability, even when calcium ions were present (20). Guar gum is chemically quite similar to galactoglucomannans (21), so its addition to headbox stock is also an option for improving the stability of wood colloids in manufacture of newsprint from TMP and recycled fibre.

4. Manage pH carefully. Operation at a higher pH leads to more stable wood extractive colloids and lower levels of soluble calcium, although this creates a dilemma for maintaining product brightness for mechanical paper grades where alkaline darkening is a known phenomenon of lignin-rich TMP.

5. Avoid downward temperature shocks. Pitch deposition can be particularly troublesome during start-ups after a maintenance shut on the paper machine, and a significant contributor is the use of cold fresh water make-up. These studies highlight the importance of avoiding downward temperature shocks caused by introducing cold water.

CONCLUSIONS

The conceptual model of a wood extractive colloid has been further developed to show that the extent to which fatty acids share the surface with resin acids is dependent on the proportion of glycerides in the colloid. This in turn affects colloid stability, with a lower proportion of glycerides leading to a less stable colloid. This feature may be captured by defining a parameter called the Ester to Acid Ratio (EAR), with less stable colloids being characterised by a low EAR. Tracking of the EAR in process streams over a 14 year period has shown that it undergoes an annual cycle with lower stability in the summer. There has also been a long term decline in the EAR, suggesting that the process is now more susceptible to other factors affecting colloid stability, particularly in summer.

These other factors include the concentration of soluble inorganic and organic species. The coincidence of elevated levels of soluble calcium with low colloid stability during the warmer months makes the process more susceptible to pitch deposition during the summer. Dissolved wood polymers (e.g. galactoglucomannans) also affect colloid stability, although the extent to which they do this is affected by the presence of soluble calcium.

Temperature and pH both have a significant effect on colloid stability. Colloids are more stable in the presence of inorganic ions such as calcium at neutral pH than at low pH. Decreases in temperature lead to destabilisation of colloids and deposition. Increased shear forces also lead to greater tendency for colloids to aggregate and deposit.

REFERENCES


(13) Sirvonen, A-L., Sundberg, K., Sundberg, A. and Holmbom, B.


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