Effect of increased levels of dissolved and colloidal substances from *Pinus radiata* on newsprint paper strength

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SUMMARY

The effect of increased levels of wood resins, salts and dissolved organics on newsprint tensile strength was evaluated. Significantly more *Pinus radiata* wood resins are adsorbed onto the fibre surface compared to reported results for Norwegian spruce. Differences in chemical composition may explain this. Tensile strength was found to decrease significantly and reach a limiting value as the level of wood resins in the handsheets increased to approximately 5 mg/g acetone extractives. High levels of calcium ions were found to cause precipitation of the wood resins onto the fibre surface and also reduced tensile strength. Increasing amounts of soluble polysaccharides, such as galactoglucomannans, were found to stabilize the wood resins in solution and reduce the amount adsorbed onto the fibre surface, resulting in increased tensile strength. The addition of polymeric fixatives was found to reduce the negative effect of the higher levels of extractives attached to the fibres.

KEYWORDS:
Wood resins, tensile strength, *Pinus radiata* extractives, recycling process water, dissolved organics, fixatives, calcium salts

INTRODUCTION

Water usage is an important issue facing many paper mills. In Australia, water shortages and restrictions are common and paper mills need to be concerned about eliminating unnecessary water wastage and finding ways to efficiently reuse water in order to reduce consumption. Because of its location on the Murray River, Norske Skog's Albury mill needs to explore options to minimise the amount of water it draws from the Murray River. The mill currently uses around 10 m^3/tonne of paper produced which is close to world's best practice for manufacture of mechanical paper grades. Water shortage issues within the Murray/Darling basin mean that further reductions may be needed. Norske Skog's Boyer mill uses 30-40 m^3/tonne, towards the top end of the typical water consumption of other modern newsprint manufacturers (20-40 m^3/tonne) and so needs to improve its water consumption to bring it closer to world best practice.

Increased process water recycling results in accumulation of substances that affect the wet end chemistry. These substances contribute to deposition problems as well as reduced paper machine efficiency and paper quality. The substances that accumulate in the process water include the wood resins and dissolved organic substances originating from the wood as well as dissolved salts and other dissolved process additives *(1)*. These dissolved and colloidal substances (DCS) are often referred to as 'detrimental substances' or 'anionic trash' because of the negative impact they have on paper machine operation and paper quality. The composition and concentration of these DCS varies depending on the mechanical pulping and bleaching processes *(1, 2)* as well as fibre source *(3)*.

The wood resins are a mixture of several different chemical classes. The main classes are the resin acids, fatty acids, triglycerides, sterols and the steryl esters. These are released into the process waters during pulping and, as the materials are lipophilic, form stable colloid suspensions in water in the form of a hydrophobic core of the triglycerides and steryl esters surrounded by an outer shell of fatty acids and resin acids *(4-6)*. It is well established that this colloidal material is responsible for deposition problems. One of the strategies employed by paper mills to reduce the level of the wood resins in the process water is to absorb the extractives onto the paper *(7-9)*.

Increased levels of inorganic metal ions such as sodium, calcium, magnesium and aluminium have been shown to cause aggregation of the wood resins and contribute to increased deposition problems *(10-12)*. Ca^{2+} and Al^{3+}, in particular, form insoluble precipitates with the fatty acids and resin acid components in the wood resins *(11, 13-16)* Strand *(15)* recently showed that the wood resin content in paper increased with the addition of calcium and magnesium metal ions. Calcium was found to retain more wood resins than magnesium. Lee *(17)* also found that greater deposition of wood resins onto model surfaces occurred with calcium ions compared to magnesium ions.

Dissolved organic material is also released into the process water consisting largely of the water soluble polysaccharides of hemicelluloses such as galactoglucomannans (GGM) and small amounts of lignin. This material has been found to sterically

stabilize the wood resins and prevent pitch deposition *(18-23)*.
The effect of DCS on paper properties has been investigated though differing effects have been observed depending on the pulp type and composition of the DCS. Wood resins have been found to decrease paper strength *(24-26)* while hemicelluloses have been found to improve it *(27-30)*.
This paper presents results of an investigation carried out to determine the effect on paper strength of increasing concentrations of DCS and adsorbed wood resins from *P. radiata* on TMP fibres. The key question being addressed is: what is the impact on paper strength of the strategies employed by the paper mill to increase water recycling and reduce wood resin concentration in the process water through fixation of the wood resins onto the paper?

EXPERIMENTAL

MATERIALS

Thermomechanical pulp (TMP) of *P. radiata* was obtained from the primary refiners of Norske Skog Boyer Paper Mill, Tasmania. The pulp was freeze-dried then soxhlet extracted with hexane for 8 hours. The wood resin extractives were recovered from the hexane by rotary evaporation. The concentrated wood resin extractives were stored at -24 ºC until required.
Dissolved organics (DOM) were obtained by aqueous extraction of the hexane extracted TMP pulp at 70 ºC using the method developed by Sundberg *(18)*. Five extractions were carried out using the filtrate collected from each extraction to dilute pulp to 2% consistency. The concentrated DOM was filtered through 0.45 µm filter paper and stored at 4 ºC.
Model compounds of abietic acid (Aldrich, technical grade 75% purity, impurities consist of other resin acids), oleic acid (Aldrich, technical grade, 90% purity, impurities consist of other fatty acids) and triolein (Aldrich, technical grade, 65% purity, impurities consist of other triglycerides) were also used to prepare model wood resin dispersions.
A commercial cationic fixative was obtained from Nalco. The fixative was a medium charge, medium molecular weight copolymer of polyacrylamide and poly(diallydimethylammonium chloride) (pDADMAC).
$CaCl_2$ and KNO_3 were purchased from BDH (99.8 purity %). All electrolytes used were dissolved in distilled water

METHODS

WOOD RESIN PREPARATION

Aqueous wood resin dispersions were prepared by the addition of dissolved extracted wood resin or a mixture of the model compounds (abietic acid, oleic acid and triolein) in acetone (99.5% purity, Sigma-Aldrich) to a 1 mM KNO_3 solution in distilled water with a pH of 5.5. Dialysis of the dispersion was performed using cellulose membrane tubing with a molecular mass cut off of 12,000 amu (Sigma-Aldrich D9402-100FT), to remove acetone. The wash water used was 1 mM KNO_3 pH adjusted to 5.5. This was changed every hour for the first 5 h and then at 24 h.

WOOD RESIN ADSORPTION STUDIES

Adsorption studies were carried out by adding the appropriate amounts of wood resin dispersion, DOM solution and a 5% pulp suspension of hexane extracted TMP pulp to a glass jar with distilled water containing 1 mM KNO_3 pH adjusted to 5.5. The final fibre consistency in the jar was 0.5%. The wood resin/DOM/fibre suspensions were stirred for 60 minutes using paddle stirrers (330 rpm) at 50 °C in a controlled temperature water bath.
The amount of wood resins bound onto the fibres was determined by centrifuging the sample to remove the fibres and then determining the amount of wood resin, that is the dissolved and colloidal fraction, left in the supernatant. The amount of wood resin bound onto the fibres was then determined by difference between the sample with no centrifugation (containing fibres) and the sample of centrifuged supernatant (not containing fibres).

WOOD RESIN ANALYSIS

The wood resins were extracted from the pulp samples using tertiary-butylmethylether (t-BME). They were then silylated and analysed by gas chromatography (GC) analysis as described previously (31).
Wood resins were extracted from handsheets by soxhlet extraction with acetone. They were then silylated and analysed in the same way as the wood resins from the pulp samples.

DOM ANALYSIS

The total soluble carbohydrate content was determined using the Oricinol method *(32,33)*.
The composition of the monosaccarides in the DOM was determined using acid methanolysis following the procedure of Sundberg *(34)*. Three mL of methanolysis reagent was added to 2.0 mL of freeze-dried DOM. The reaction was carried out using a Radley's reactor for 5 h at 70 °C. Samples were silylated and analysed using gas chromatography with sorbitol as the internal standard.

CATIONIC DEMAND

Wood polymer charge density was determined at a pH of 5.5 by titration of 10 mL of the sample with 0.001 N pDADMAC using a Mutek PCD-02 (Particle Charge Detector) to determine the charge neutralisation endpoint.

HANDSHEET PREPARATION

The latency of the hexane extracted pulp was removed at 90 ºC in a British Standard Disintegrator and used for all handsheet preparation and some deposition experiments.
Handsheets were prepared according to Tappi Method T205 sp-95 using a Standard British sheet machine with water recirculation.

TENSILE STRENGTH TESTING

Handsheets were conditioned prior to strength testing in a humidity controlled room at 23 °C and 50% relative humidity according to Tappi Standard T402 om-93. A Lorentzen and Wettre Tensile Tester was used to test the tensile strength according to Tappi Standards method T 220 om-96.

RESULTS AND DISCUSSION

The composition of the aqueous wood resin dispersions prepared from the extracted wood resin and the model compounds is presented in Table 1. Dialysis of the dispersions resulted in significant loss of material due to deposition of the wood resins onto the dialysis tubing. The relative ratios of the components in the three dispersions were relatively similar.

	Fatty Acid [mg/L]	Resin Acid [mg/L]	Triolein [mg/L]	Total wood resin [mg/L]
Model wood resin undialysed	20.0 ± 2.5	56.0 ± 4.9	29.4 ± 1.3	105 ± 9
Extracted wood resin undialysed	14.2 ± 0.6	62.0 ± 2.7	31.4 ± 1.7	108 ± 5
Extracted wood resin dialysed	8.0 ± 0.1	41.3 ± 0.7	22.4 ± 0.1	72 ± 1

Table 1: Composition of model and extracted wood resin dispersions

EFFECT OF WOOD RESIN CONCENTRATION

The adsorption of the model and extracted wood resin onto TMP fibres was measured at increasing concentrations of resin added to an extractive free–fibre suspension. The results in Figure 1 show that all the dispersions behave the same at the same concentration over the range of 0 – 30 mg/g added wood resin. The amount of wood resin deposited onto the fibre surface increased as the wood resin concentration was increased up to 30 – 40 mg/g fibre. A maximum of 14 – 18 mg wood resin /g fibre was found to adsorb onto the fibre surface. The results indicate that the wood resins have a strong affinity with the TMP fibres with 30 – 50% being absorbed onto the hexane extracted fibres. This result is higher than the 10-25% Picea abies extractives retained in Kraft and Kraft/TMP handsheets reported by Sundberg *(24)*. The difference in behaviour between the *P.abies* and *P.radatia* is likely due to the differences in composition of the extractives from the two species *(3)*.

Figure 2 shows a comparison of deposition behaviour of undialysed wood resin onto extractive free TMP fibres at pH 5.5 and 7.0. The results indicate that there is a dramatic decrease in the amount of wood resin deposited onto the fibre surface as the pH increases. At pH 5.5 components were mostly in their undissociated form with low solubility. It is well known that pH will affect both the chemical nature of the carboxylic acid groups of the resin acid and fatty acid, and their physical properties, through affecting the solubility of the components. As the pH is raised to 7.0, the solubility of the resin acid increased. Abietic and oleic acid have a 'colloidal' pKa of 6.4 and 9.85, respectively *(35)*.

Figure 3 shows the effect of the amount of wood resin (acetone extracted) present in the handsheet on the tensile index of the handsheets. Tensile strength significantly decreased with increasing levels of wood resin in the handsheets. A minimum in strength was reached at approximately 5 mg wood resin/g fibre. The results follow similar trends in the decrease in tensile strength reported in the literature, although the minimum in strength found in Figure 3 occurred at slightly higher levels of wood resins in the handsheets than the 2 mg/g reported by Sundberg *(24)*. The difference in the wood resin level at which the tensile strength minimum occurs may be due to differences in the composition of the wood resins extractives of *P.radiata* and *P.abies*. The higher resin acid content of *P.radiata* has been shown to absorb more strongly onto fibres than fatty acids and triglycerides that are at significantly higher levels in *P.abies (3)*. The constant value in tensile strength after the minimum was reached can be attributed to the wood resin no longer being retained on the fibre surface but rather between fibres in the fibre-fibre network at higher wood resin additions *(24)*.

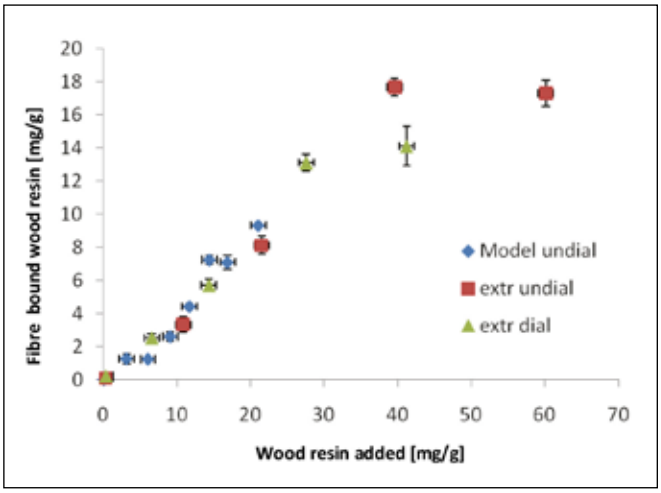

Fig. 1: Deposition behaviour of undialysed model and extracted wood resin, and dialysed extracted wood resin at pH 5.5. (Error bars in this and subsequent figures indicate ± one standard deviation from the mean).

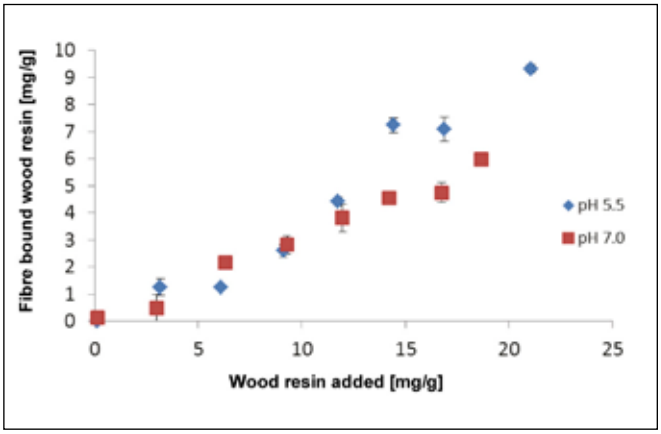

Fig. 2: Adsorption of undialysed model wood resin onto extractive-free TMP fibres at pH 5.5 and pH 7.0.

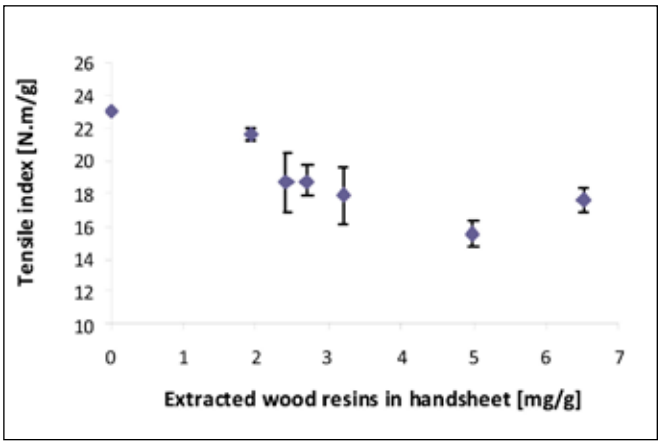

Fig. 3: Effect of wood resin (acetone extracted) content on tensile strength of TMP handsheets

EFFECT OF DISSOLVED ORGANIC MATERIAL

Dissolved organic material (DOM) was obtained from TMP pulp by five repeated extractions using the filtrate from previous extractions in order to concentrate the dissolved organic material released from the fibres. Table 2 summarises the chemical properties of the DOM.

Average wood polymer concentration	2324 mg/L
Carbohydrate (orcinol method)	95.3 ± 2 %
Lignin (UV adsorption method)	7.6 ± 0.2 %
Total sugars (acid methanolysis method)	72 ± 10 %
Cationic Demand [mmol/g equiv charge]	0.42
Galactose : glucose : mannose ratio	0.4: 1: 2.4

Table 2. Characterisation of dissolved organic material obtained from *P.radiata* TMP pulp by hot aqueous extraction.

The effect of DOM on adsorption of wood resin (dialysed extracted wood resin) onto the fibre surface was investigated at pH 5.5. The pulp used in this set of experiments was prepared for handsheet preparation and it was found that that in the process of removing latency, further DOM was generated so the background DOM level increased to 70 mg/L carbohydrate. Figure 4 indicates that there is a significant decrease in the amount of wood resin adsorbed onto the fibre surface when DOM is added to the fibre/wood resin suspension. The results suggest that the DOM is stabilizing the wood resins in solution and so less is adsorbed onto the fibre surface.

The corresponding effect on the handsheet tensile strength of the varying DOM to wood resin ratio added is presented in Figure 5. A significant increase in the handsheet tensile strength was observed as the DOM to wood resin ratio added to the handsheets increased. The increase that occurred is largely a result of the corresponding decrease in the actual amount of wood resin adsorbed onto the handsheet as shown in Figure 6.

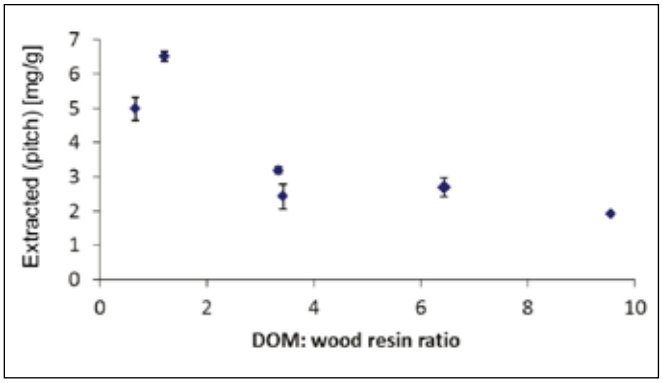

Fig. 6: Influence of dissolved organic materials on amount of dialysed extracted wood resin in latency free TMP handsheets pulp at pH 5.5.

EFFECT OF CALCIUM IONS

The effect of calcium ions on the adsorption of wood resin and the corresponding effect on paper strength were also investigated. The amount of wood resin adsorbing onto the fibre surface, from a pulp suspension to which 28 mg/g dialysed

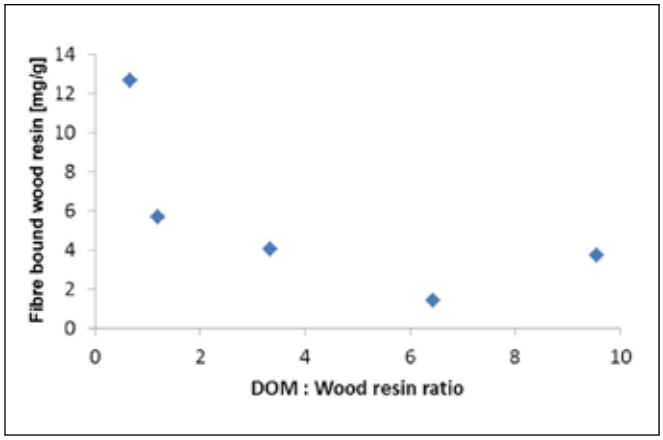

Fig. 4: Effect of dissolved organic materials on dialysed wood resin adsorbed onto latency and extractive free TMP pulp at pH 5.5.

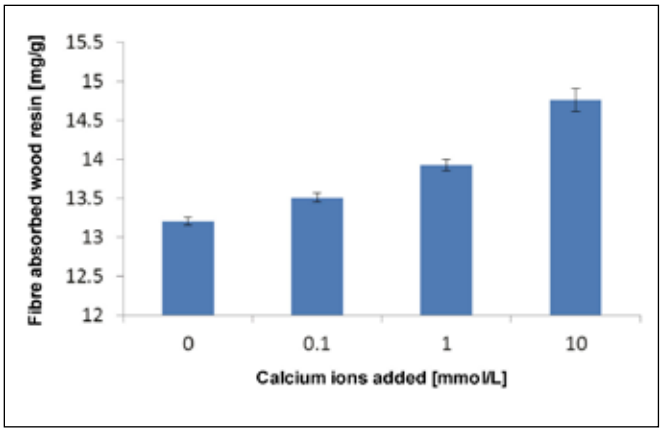

Fig. 7: Effect of calcium ions on the amount of dialysed extracted wood resin adsorbed onto extractive free TMP pulp at pH 5.5

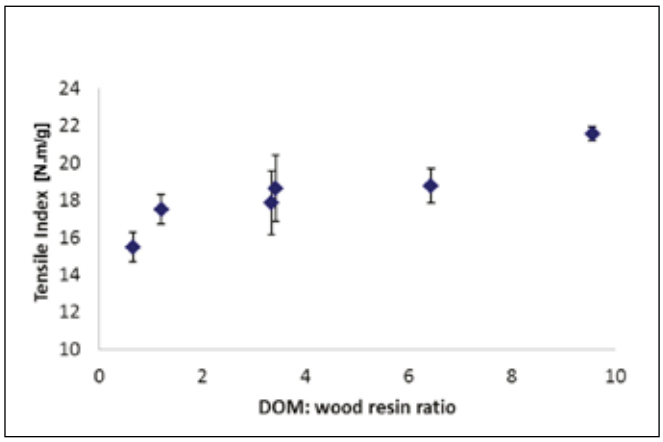

Fig. 5: Influence of dissolved organic materials on tensile strength of latency and extractive free TMP pulp at pH 5.5.

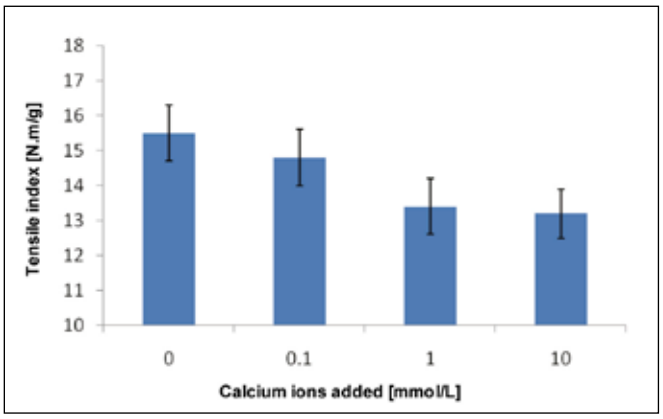

Fig. 8: Effect of addition of calcium ions on the tensile strength of latency and extractive free TMP at pH 5.5 containing dialysed extracted wood resins.

extracted wood resin was added, was found to increase as the concentration of calcium ions increased from 0 to 10 mM as shown in Figure 7. Strand *(36)* reported similar behaviour.
The addition of calcium was found to reduce the tensile strength of handsheets as shown in Figure 8. The observed decrease in strength can be attributed to the increased level of wood resins adsorbed onto the fibre surface.

EFFECT OF FIXATIVE

The effect, on the amount of wood resin adsorbed, of the addition of commercial polymeric fixative was carried out by adding 2 kg/t (mg/g) fixative to the TMP pulp containing 28 mg/g dialysed extracted wood resin and varying concentrations of DOM. Cationic polymers are used in the papermaking process to control pitch deposition by adsorbing the pitch onto the fibre surface. As shown in Figure 9, the fixative enabled greater amounts of wood resin to be adsorbed onto the fibres even in the presence of DOM though the amount adsorbed did decrease as the level of DOM in the suspension increased.
The tensile index of handsheets containing varying amounts of

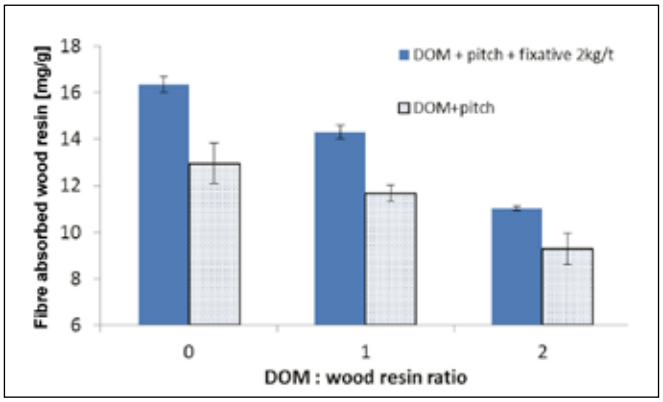

Fig. 9: Effect of addition of fixative and DOM on the adsorption of dialysed extracted wood resin onto extractive free TMP pulp at pH 5.5

dialysed extracted wood resins at a constant addition of 2 kg/t fixative was found to be slightly higher than handsheets with just wood resin (Fig. 10). As the level of wood resins increased, the tensile index decreased. The tensile strengths of handsheets prepared with 28 mg wood resin/g fibre containing 2 kg/t fixative were found to be slightly higher than the handsheets containing either calcium, DOM or wood resins alone as shown in Figure 11. The results in both Figures 10 and 11 suggest that fixative may have a beneficial effect on handsheet strength and is able to improve fibre bonding as well as adsorb wood resins. The improvement in fibre bonding may be a result of the fixative increasing the retention of anionic polysaccharides from the DOM. These results are important in demonstrating the benefit of using cationic fixatives as a pitch control strategy, because they can remove troublesome pitch colloids from the process water (by adhering them to fibres) with less impact on paper strength. A limit to the amount of wood resin adsorption onto the surface before tensile strength is detrimentally affected was found to exist even with the addition of cationic fixative.

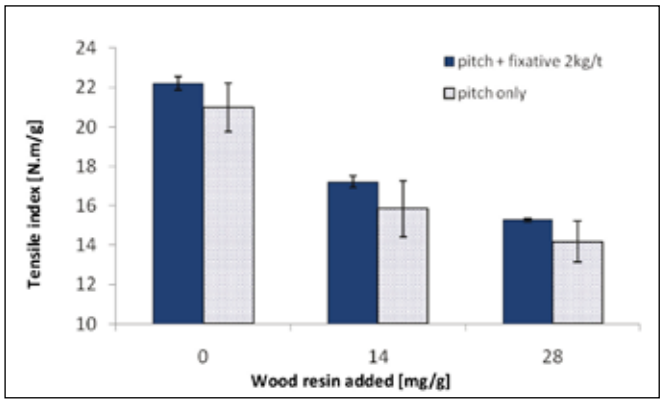

Fig. 10: Effect of addition of dialysed extracted wood resin in the presence of 2 kg/t fixative on tensile index of latency and extractive free TMP at pH 5.5.

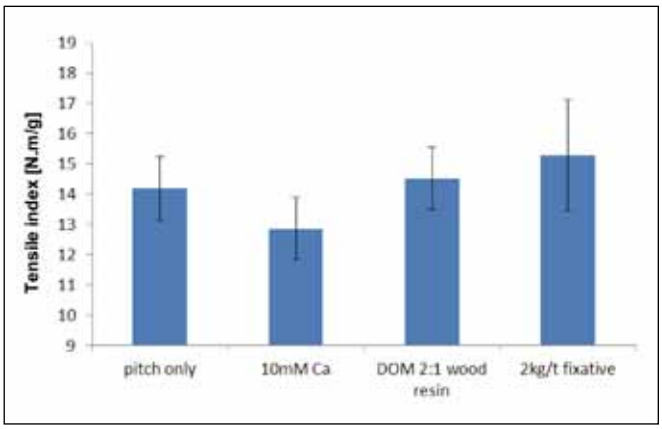

Fig. 11: Effect of various additives on the tensile index of latency and extractive free TMP pulp at pH 5.5 with 28 mg/g dialysed extracted wood resin added.

CONCLUSIONS

Wood resins from *P. radiata* have a detrimental effect on the tensile strength of TMP pulp. The tensile strength appears to reach a minimum at approximately 5 mg/g acetone extractives in the handsheet. High levels of calcium increases precipitation of the wood resins on the fibre surface and causes further reduction in tensile strength. The presence of DOM reduces the adsorption of wood resins onto the fibre surface and stabilises the wood resins in solution. This reduced level of extractives in the handsheets results in higher tensile strength.
The addition of fixative to handsheets (to attach more wood resins onto the fibre surface in order to reduce the concentration in solution) reduces the negative effect of the higher levels of extractives attached to the fibres. There appears to be a limit to the amount of wood resins that can be adsorbed onto the fibre surface, even with the beneficial effects of DOM and fixatives, before paper strength is adversely affected.

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