

Aggregation and destabilisation of colloidal wood pitch by calcium ions in TMP suspensions

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SUMMARY: The colloidal stability of wood pitch against aggregation and destabilisation by CaCl_2 was assessed in suspensions of unbleached and peroxide-bleached thermomechanical pulp (TMP). The experiments were conducted at different pulp consistencies, at both pH 5 and pH 8, to determine pitch aggregation in acidic and neutral papermaking processes using TMP.

The colloidal pitch had low affinity to TMP fibres in the absence of CaCl_2 . At pH 8, a higher concentration of CaCl_2 was required to destabilise the colloidal pitch than at pH 5. Even low CaCl_2 -concentrations caused destabilisation of colloidal pitch in suspensions of TMP at pH 5.

More pitch was destabilised by CaCl_2 in suspensions of unbleached TMP than in suspensions of peroxide-bleached TMP. Resin acids were to a large extent found as stable calcium-soaps in the water phase at pH 8, even at high concentrations of CaCl_2 .

Water-soluble galactoglucomannans (GGM) stabilised pitch emulsions almost completely against calcium-induced aggregation both at pH 5 and 8. The colloidal stability of pitch in suspensions of TMP was not total, but was much higher when GGM was added, compared to when no GGM was added.

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A wide variety of wood components are released into the process waters during production of mechanical pulps, such as thermomechanical pulp (TMP) (Allen 1975; Örså et al. 1997). Among these are the lipophilic extractives, which consist of resin and fatty acids, sterols and their fatty acid esters and triglycerides (Ekman et al. 1990; Ekman, Holmbom 2000). A mixture of lipophilic extractives is commonly referred to as pitch. The pitch that enters the paper machine is located inside unbroken parenchyma cells, smeared onto fibre surfaces or dispersed in the process water as colloidal droplets (Allen 1975; 1980). The colloidal pitch has been deemed the most detrimental form of pitch for papermaking, and closure of the paper mill water system can cause further accumulation of colloidal pitch in the process waters. Uncontrolled aggregation of pitch may cause unwanted foaming, formation of deposits and runnability problems

(Hassler 1988; Ekman et al. 1990; Nylund et al. 1993; Örså, Holmbom 1994; Mosbye et al. 2008).

The pitch droplets have been shown to consist of two distinct parts; a core and a surface layer (Qin et al. 2003; Vercoe 2004). The core is composed of neutral substances, i.e. triglycerides and steryl esters, while the surface layer consists of amphiphilic resin and fatty acids (RFAs). The negative charge, from de-protonated RFAs in the surface layer, gives the colloidal pitch droplets electrostatic stabilisation towards aggregation. The electrostatic stability of a colloidal droplet is mainly dependent on the chemical composition of its surface layer, pH, temperature and electrolyte concentration (Back 1969; Scott 1996). The interaction between a colloidal pitch droplet and any other surface is determined by its surface layer (Back 2000; Qin et al. 2003; Vercoe 2004).

It has previously been shown that resin and fatty acids are attached to lipophilic colloidal droplets at pH 3 and below, while resin acids and short-chained unsaturated fatty acids dissolve into the water as sodium soaps at higher pH, in the absence of other multivalent metal ions (Sundberg, A., et al. 2009). Their distribution between lipophilic pitch droplets (l) and the water phase (w) has been described using pK_{lw} -values (Sundberg, A., et al. 2009; Strand et al. 2011). Phase distribution curves for individual resin and fatty acids, as a function of pH, electrolyte concentration and pitch composition have also been reported. From these results it was concluded that resin acids are dissolved into the water at a lower pH than fatty acids in general, probably due to the bulkiness of the resin acid structure.

Metal soaps, usually including Ca^{2+} , Mg^{2+} or Ba^{2+} , have previously been linked to formation of deposits in paper mills. The amount of formed soaps is a function of metal ion concentration as well as availability of soap anions, i.e. dependent on pH (Allen 1988). Phase distribution of RFAs as a function of pH has therefore been studied with added calcium, and the results showed that calcium soaps of fatty acids are less water-soluble than calcium soaps of resin acids (MacNeil et al. 2011). The destabilisation of colloidal pitch by electrolytes has previously been illustrated by additions of NaCl , CaCl_2 and LaCl_3 , followed by centrifugation and turbidity measurements at pH 5 and 8 (Sundberg, K., et al. 1994a; Sihvonen et al. 1998).

Deposition experiments of pitch with added calcium at varying pH have shown that the presence of fibres lowered the deposition of pitch onto steel plates (Hassler 1988). Deposition tests using pitch emulsions have shown that deposits were not formed on polypropylene surfaces at pH 5 or 8 without additions of calcium (Qin et al. 2004). The colloidal stability of pitch was also studied by NaCl additions to pitch emulsions in the presence of bleached kraft pulp at pH 5 (Sundberg, K., Holmbom 1997). It was concluded that pitch as such had little affinity to cellulosic fibres.

The colloidal pitch droplets can further be sterically stabilised against electrolyte-induced aggregation by addition of water-soluble polysaccharides released from wood, such as galactoglucomannans (GGM) (Welkener et al. 1993; Sundberg, K., et al. 1994b; 1996a; Hannuksela, Holmbom 2004). The steric stabilisation of pitch by GGM has previously been studied at slightly acidic pH, i.e. pH 5-6.5, in absence of fibres. The GGM in spruce is, however, to a large extent deacetylated during alkaline peroxide bleaching of mechanical pulps, rendering it insoluble in water, and thus unable to sterically stabilise the colloidal pitch (Sundberg, K., et al. 1996a; Thornton et al. 1994).

In this study, we have analysed the effect of calcium ions on the colloidal stability of wood pitch in TMP-suspensions, at both pH 5 and pH 8. The effect of pulp consistency on the destabilisation of wood pitch was also studied. The effect of water-soluble GGM on pitch stability was determined in TMP suspensions, at pH 5 and pH 8. Unbleached and peroxide-bleached TMP was used to further investigate if a difference in fibre charge played any role in the destabilisation of colloidal wood pitch.

Materials and Methods

Unbleached and peroxide-bleached TMP: Thermomechanical pulp (TMP) was obtained from a Finnish pulp mill using Norway spruce (*Picea abies*). The consistency was about 44% and the pulp was frozen until used. The TMP was freeze-dried and Soxhlet extracted for 12 h with hexane, and for an additional 12 h with a mixture of acetone: water: acetic acid (90:9:1) to remove as much lipophilic and saponified components as possible.

Some of the extracted TMP was peroxide-bleached according to a laboratory procedure with 0.2% DTPA, 0.05% MgSO₄, 3% H₂O₂ and about 3% NaOH, calculated on dry weight of TMP. The bleaching was performed at a pulp consistency of 10%, for 90 min at 60°C. No sodium silicate was added since metal ions were already removed from the TMP during extraction with acetone: water: acetic acid.

The extracted TMP, both peroxide-bleached and unbleached, was diluted to 3% with distilled water at 60°C and mixed for 1 h. The water was removed by filtering the pulp through a 200 mesh wire, and re-circulating the filtrate through the formed fibre cake to retain the fines in the pulp. This washing procedure was repeated 5 times for each pulp, until the TOC of the filtrate was below 40 mg/l. The fibre charge of the two pulps was determined by poly-electrolyte titration with 1,5-dimethyl-1,5-diazundecamethylene polymethobromide (polybrene, ~8×10³ Da, Sigma) and potassium polyvinyl sulphate (KPVS) through back-titration using a particle charge detector (Mütek PCD 03), also known as a streaming current detector (Holmbom et al. 2000). Suspensions of unbleached and peroxide-bleached TMP were prepared with de-ionized water, and different doses of polybrene were added to the suspensions during stirring. After 1 h the suspensions were filtered through glass fibre filters (VWR International, Glass microfiber, 691). The filtrates of the suspensions, as well as blank samples, were titrated with KPVS in the particle charge detector to determine the concentration of unadsorbed polybrene. The determined concentrations from the measurements were used to plot adsorption isotherms of polybrene, from which the charge of the TMP could be extrapolated. The determined charge of unbleached TMP was 84 µeq/g, and the charge of peroxide-bleached TMP was 199 µeq/g, which are in the same size range as previously published values of unbleached and peroxide-bleached spruce TMP (Fardim et al. 2002).

Pitch emulsion: Palmitic acid (16:0) and stearic acid (18:0) were extracted from a commercial soap (Raisapon 105, Ciba Specialty Chemicals). The soap was dissolved in a mixture of distilled water and acetone (6:1), which was then acidified with HCl and extracted with (tert-butyl)methylether (MTBE). Arachidic acid (20:0) was obtained from Fluka (Switzerland), and dissolved directly in acetone. Norway spruce TMP was Soxhlet extracted with hexane. The hexane was evaporated and the pitch components were re-dissolved in acetone. Pitch emulsions were prepared by injection of the acetone solution of pitch, with added saturated fatty acids, into distilled water during stirring. The acetone was removed from the emulsion by dialysis, according to a previously published procedure, resulting in a virtually acetone-free pitch emulsion (Sundberg, K., et al. 1996b; Sundberg, A. et al. 2009).

Galactoglucomannans (GGM) were isolated at a Finnish paper mill producing TMP from spruce by ultra filtration followed by spray-drying (Xu et al. 2007). The ratio of the sugar units Man:Glc:Gal was about 4:1:0.5, with an acetyl group on every

second mannose unit on average. The spray-dried GGM was dissolved in distilled water, and directly added to pitch emulsions for the experiments with added GGM.

Determination of pitch stability: Unbleached or peroxide-bleached TMP was weighed into a bottle, the dry weight depending on the targeted consistency. 53 g of pitch emulsion was mixed with the TMP. Different volumes of CaCl₂-solutions were added and the pH of the suspension was adjusted to 5 or 8 with NaOH at room temperature. The pulp suspensions were diluted, so that the final volume was 60 ml in all experiments. The total pitch concentration after dilution was about 200 mg/l, with 20–24 mg/l fatty acids, 48–57 mg/l resin acids, 30–34 mg/l steryl esters and 78–90 mg/l triglycerides. The suspensions were stirred at 200 rpm by a magnetic stirrer for 1 h. After 1 h, the pH of the suspensions was measured and the suspensions were then centrifuged at about 210 g for 15 min, to remove unstable aggregates of pitch, fines and fibres and the supernatant was collected. The pH of the suspensions at “pH 5” was between 5.0 and 5.2, and the pH at “pH 8” was between 7.8 and 8.0.

The selected Ca²⁺-concentrations were meant to reflect the conditions in three different papermaking processes. The concentrations were 0, 1, 3 and 10 mM, with the zero concentration acting as a reference. Ca²⁺-concentrations between 0–1 mM are typical when kaolin is used as filler, 1–3 mM when calcium carbonate is used, and about 10 mM when calcium sulphate is used.

Colloidal stability was in these experiments defined as the colloidal wood pitch that could withstand a centrifugation at 210 g for 15 min, and thus remained in the supernatant of the sample. The determined concentration of pitch in the supernatant was compared to the concentration in samples without added CaCl₂, which was subjected to the same procedure.

Analysis of pitch composition: Internal standard, containing heneicosanoic acid, betulinol, cholesteryl heptadecanoate, and 1,3-dipalmitoyl-2-oleyl glycerol in MTBE, was added to the samples (Örså, Holmbom 1994; Strand et al. 2011). The water samples were acidified with H₂SO₄ and the pitch components were extracted from the water samples with MTBE, dried under N₂ gas, and silylated with pyridine, N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA), and trimethylchlorosilane (TMCS) for 45 min at 70°C. The concentrations of pitch components in the samples were determined by gas chromatography (GC).

Analysis of different groups of pitch components was conducted on a short column GC (HP-1,

7 m x 0.53 mm) with on-column injection, equipped with a flame ionization detector (FID). Analysis of individual resin and fatty acids was conducted on a long column GC (HP-1, 25 m x 0.20 mm) with split injection, equipped with a FID detector.

Analysis of hemicelluloses: Water samples containing hemicelluloses were freeze dried (Sundberg, A. et al. 1996; Willför et al. 2009; Strand et al. 2011). Methanolysis reagent (water-free 2M HCl in MeOH) was added to the dry samples. The samples were placed in an oven at 100°C for 3 hours. Sorbitol in MeOH was added as internal standard. The samples were silylated using pyridine, hexamethyldisilazane (HMDS), and TMCS over night at room temperature. The analysis of sugar units was conducted with a long column GC (HP-1, 25 m x 0.20 mm) with split injection, equipped with a FID detector.

Results and discussion

Colloidal stability at pH 5

Previous work has shown that resin and fatty acids (RFAs) are found both in dissolved and colloidal form depending on pH, while the neutral substances are only found in colloidal form, because of their insolubility in water (Sundberg, A., et al. 2009; Strand et al. 2011). Information about colloidal stability of pitch can therefore be derived from the variations in concentration of neutral substances, i.e. steryl esters and triglycerides, in the supernatant of centrifuged samples. The experiments were conducted in the absence of water-soluble GGM.

The concentration of neutral substances in the supernatant decreased with increasing CaCl₂-concentration at pH 5 in absence of TMP. About 61% of the neutrals remained in the supernatant at 3 mM CaCl₂, and only 5% at 10 mM CaCl₂ (*Fig 1*). The mechanisms behind electrolyte-induced destabilisation of pitch have been described as compression of the electrical double layer, possibly combined with direct chemical reactions between soap anions and metal ions (Sundberg, K., et al. 1994a; Back 2000; Hannuksela, Holmbom 2004; Stack et al. 2011). The removal of the pitch was probably due to creaming, since no other available surfaces were present in the absence of TMP (Allen 1980).

The presence of unbleached TMP, at 0.25% or 1% consistency, did not result in a destabilisation of neutral components in the absence of CaCl₂; the concentration of neutrals was the same or higher when TMP was added (*Table 1*). It has previously also been shown that colloidal wood pitch has no affinity to bleached kraft pulp in the absence of NaCl, and that no deposition onto polypropylene surfaces in absence of electrolytes occurs

(Sundberg, K., Holmbom 1997; Qin et al. 2004). Addition of 1 mM CaCl₂ to the 0.25% suspension of unbleached TMP lowered the concentration of neutral substances in the supernatant to 19% (Fig 1). Only 6% of the neutral substances remained in the supernatant when the TMP consistency was 1%, at 1 mM CaCl₂. At pH 5, 1 mM of CaCl₂ was enough to cause extensive destabilisation of colloidal pitch in the presence of TMP.

When the concentrations of neutral substances in the supernatants were compared, it was seen that a higher pulp consistency caused more destabilisation of colloidal pitch. A higher pulp consistency resulted in more colloid-fibre interactions which lead to a higher degree of destabilisation (Hassler 1988; Back 2000).

About 30% of the neutral substances remained in the supernatant at 1 mM CaCl₂ in a 1% suspension of peroxide-bleached TMP at pH 5 (Fig 2). This means that there was a higher concentration of stable pitch in suspensions of 1% peroxide-bleached TMP than in suspensions of 1% unbleached TMP at 1 mM of CaCl₂. The higher pitch stability against CaCl₂ in suspensions of peroxide-bleached TMP compared to unbleached TMP was probably due to the difference in fibre-charge. The fibre-charge of peroxide-bleached TMP was 199 µeq/g, while the charge of unbleached TMP was 84 µeq/g. Charged groups are formed during peroxide bleaching due to demethylation of methyl-esterified galacturonic acid groups (Holmbom et al. 2000). The added calcium ions probably adsorbed primarily to the fibres, since the pK_a-values of the charged groups on fibres are lower than the pK_a of RFAs, 3.5-4.0 and 5.5-6.4 respectively (Holmbom et al. 2000). The peroxide-bleached TMP could therefore retain more calcium ions, meaning that less free calcium was available for destabilisation of colloidal pitch in the presence of peroxide-bleached TMP. Another explanation could be that more calcium ions were needed to neutralise the peroxide-bleached TMP, and colloid-fibre repulsion was therefore stronger at 1 mM of CaCl₂ in suspensions of peroxide-bleached TMP compared to with unbleached TMP. Free calcium ions, as well colloid-fibre repulsion, were therefore likely to be the decisive factors behind the destabilisation of pitch in these experiments. The concentration of hemicelluloses released from 1% unbleached TMP was about 2.7 mg/l, while 3.3 mg/l was released from peroxide-bleached TMP. These concentrations were too low to significantly affect the colloidal stability of pitch (Fig 2). At 3 mM of CaCl₂ the neutral substances were completely destabilised in the presence of 1% peroxide-bleached TMP or 1% unbleached TMP (Fig 2).

The concentration of RFAs in the supernatant at

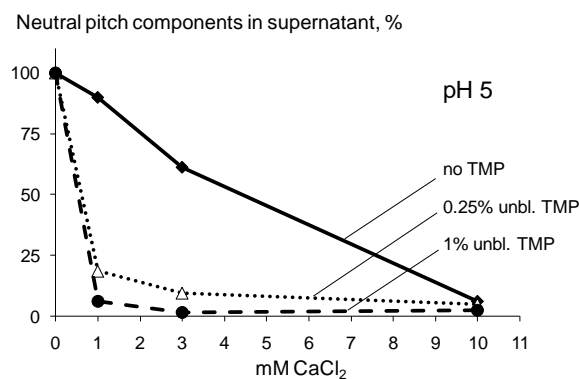


Fig 1. Relative amount of neutral substances remaining in the supernatant after CaCl₂-additions to suspensions of 0, 0.25 and 1% unbleached (unbl.) TMP at pH 5.

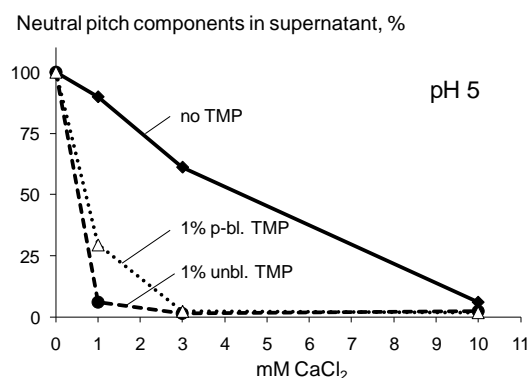


Fig 2. Relative amounts of neutral substances in the supernatant after CaCl₂-additions to suspensions of no TMP, 1% peroxide-bleached (p-bl.) TMP and 1% unbleached (unbl.) TMP at pH 5.

pH 5 decreased with increasing CaCl₂-addition in the absence of TMP (Fig 3), like in the case of the neutral substances (Fig 2). This indicated that colloidal destabilisation occurred while the amphiphilic RFAs were attached to the colloidal pitch at pH 5. Studies on the phase distribution of resin and fatty acids between colloidal pitch droplets and the water phase, as a function of pH, have shown that most of the RFAs are attached to the colloidal pitch at pH 5 (Sundberg, A., et al. 2009; MacNeil et al. 2011; Strand et al. 2011). The results are also in agreement with previously determined colloidal pK_a-values for RFAs, and the fact that protonated acids tend to be attached to available surfaces (Kanicky et al. 2000; McLean et al. 2005a).

Addition of 1 mM CaCl₂, in combination with 1% unbleached or peroxide-bleached TMP, was enough to remove most of the RFAs from the supernatant at pH 5 (Fig 3). The concentration of RFAs in the supernatant, at 1 mM CaCl₂, was only 9% in suspensions of 1% unbleached TMP, while it was 28-32% in suspensions of 1% peroxide-bleached TMP. A concentration of 3 mM CaCl₂ was enough to destabilise almost all of the RFAs, as with the neutral substances, in 1% TMP-suspensions of unbleached and peroxide-bleached TMP.

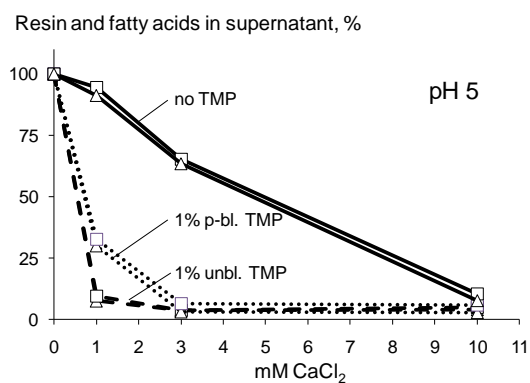


Fig 3. Relative amounts of resin and fatty acids in the supernatant after CaCl_2 -additions to suspensions of no TMP, 1% peroxide-bleached (p-bl.) TMP and 1% unbleached (unbl.) TMP at pH 5. Δ = resin acids, \square = fatty acids.

Colloidal stability at pH 8

CaCl_2 -concentrations of 1 and 3 mM did not cause much destabilisation of colloidal pitch at pH 8 in the absence of TMP; the concentration of neutral substances in the supernatant remained at 97% even though the concentration of CaCl_2 was 3 mM (Fig 4). The corresponding value at pH 5 was 67% with 3 mM CaCl_2 (Fig 2). This shows that the colloidal pitch was more stable towards electrolyte-induced aggregation at pH 8 than at pH 5 in the absence of TMP. This was probably caused by the pitch having a higher surface charge at pH 8, and perhaps also by a higher concentration of dissolved RFAs in the water phase at pH 8 compared to at pH 5 (Sundberg, K., et al. 1996b; Sundberg, A., et al. 2009). A CaCl_2 -concentration of 10 mM resulted in almost complete destabilisation of the colloidal pitch.

It has previously been reported that deposits of pitch will be formed at alkaline conditions if sufficient Ca^{2+} is present (Hassler 1988). It has also been shown that pitch with a high degree of free acids is more stable against CaCl_2 additions at pH 8 than at pH 5 by deposition tests onto polypropylene surfaces (Qin et al. 2004). Others have, however, reported that colloidal pitch is less stable against CaCl_2 -additions at pH 8 than at pH 5, by the use of turbidity-measurements of pitch emulsions after centrifugation, which would imply that turbidity measurements are not always reliable (Sihvonen et al. 1998).

The concentration of neutral substances was not changed significantly when 1% unbleached or peroxide-bleached TMP was added to pitch emulsions at pH 8, as was also the case at pH 5 (Table 1). More neutral substances were destabilised at 1 mM CaCl_2 in the presence of 1% unbleached TMP than with 1% peroxide-bleached TMP (Fig 4).

Further increasing the CaCl_2 -concentration to 3 and 10 mM resulted in similar destabilisation of

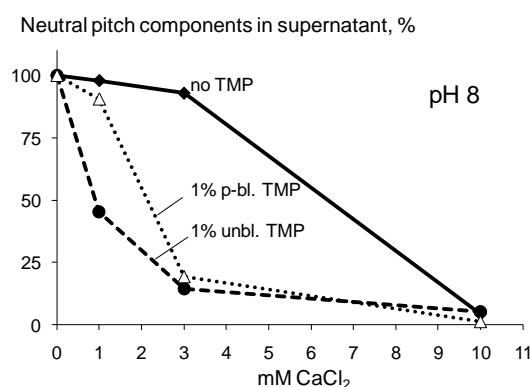


Fig 4. Relative amounts of neutral substances in the supernatant after CaCl_2 -additions to suspensions of no TMP, 1% peroxide-bleached (p-bl.) TMP and 1% unbleached (unbl.) TMP at pH 8.

pitch with both unbleached and peroxide-bleached TMP. The hemicelluloses released from 1% peroxide-bleached and 1% unbleached TMP during the experiments was 3.9 mg/l and 5.0 mg/l, respectively, which should not be enough to cause the difference seen in colloidal stability.

The difference in pitch stability was most likely, as in the experiments at pH 5, caused by the difference in the fibre charge of peroxide-bleached TMP compared to unbleached TMP. More Ca^{2+} was bound to the peroxide-bleached TMP with higher charge, resulting in less free calcium ions to cause destabilisation of colloidal pitch at 1 mM CaCl_2 .

The colloidal stability of pitch towards electrolyte-induced aggregation in suspensions of unbleached and peroxide-bleached TMP was higher at pH 8 (Fig 4) than at pH 5 (Fig 2) with 1 mM CaCl_2 . At 10 mM CaCl_2 , the colloidal pitch was more or less completely destabilised at both pH 8 and 5. The affinity of colloidal pitch to talc has also been shown to decrease with increasing pH (Gantenbein et al. 2010).

In the absence of TMP, about 96% of the fatty acids were found in the supernatant at 3 mM of CaCl_2 at pH 8 (Fig 5), much like the neutral substances (Fig 4). The concentration of fatty acids in the supernatant decreased from 96% to only 11% when the CaCl_2 -concentration was increased from 3 to 10 mM (Fig 5). The decrease in fatty acid concentration was very similar to the decrease in the concentration of neutral substances in the supernatant (Fig 4). Addition of CaCl_2 lowered the solubility of fatty acids in water. Previously published results have showed that the $\text{pK}_{\text{a}}^{\text{w}}$ -values of most RFAs are strongly shifted towards higher pH in the presence of CaCl_2 , and the solubility in water of RFAs in the presence of calcium is decreased (Qin et al. 2004; MacNeil et al. 2011). It has also been shown that the formation of calcium

soaps is dependent on the concentration of calcium ions as well as the availability of soap anions, which is highly pH-dependent (Allen 1988). The threshold pH for metal soap depositions was shown to be about pH 6.

In suspensions of unbleached or peroxide-bleached TMP, the concentration of fatty acids in the supernatant decreased when CaCl₂ was added, and only 6-11% remained in the supernatant at 10 mM CaCl₂ (Fig 5). This also implies that the fatty acids were mainly attached to pitch droplets at pH 8.

About 95% of the resin acids were found in the supernatant at pH 8 with 3 mM CaCl₂ in the absence of TMP (Fig 5). The concentration of resin acids in the supernatant at 10 mM CaCl₂ was 44% of the initial concentration. Hence, the resin acids were not removed to the same extent as fatty acids and neutral substances at high CaCl₂-concentration. The excess of calcium ions at 10 mM of CaCl₂ and the abundance of available soap anions leads to formation of calcium soaps of resin acids (Allen 1988). The solubility of calcium soaps of resin acids in water is much higher than the solubility of calcium soaps of fatty acids (MacNeil et al. 2011). The formation of calcium soaps of resin acids at pH 8 may also have stabilised the neutral substances (Fig 4) at 1-3 mM CaCl₂ by decreasing the concentration of free calcium ions.

A CaCl₂-concentration of 1 mM in a suspension of 1% unbleached TMP lowered the concentration of resin acids in the supernatant to 72%; while the corresponding value in suspensions of 1% peroxide-bleached TMP was 90% (Fig 5). The amount of resin acids remaining in the supernatant at 10 mM CaCl₂ was about 40% regardless if TMP was present or not. These resin acids were either dissolved or present as stable calcium-soap aggregates, since the neutral substances were almost completely removed at these conditions (Fig 5). It has been reported that deposits contain less resin acids at pH 8 than at pH 5 in the presence of calcium, by deposition tests onto steel foils (Saarimaa et al. 2006), which is probably due to the solubility of resin acids in water at high pH and CaCl₂-concentrations. Adding resin acid to the pulp washing stage has been shown to increase removal of neutral substances, indicating that the resin acids have emulsifying properties (Palonen et al. 1982).

The composition of resin acids in the supernatant was different at 0 mM and 10 mM CaCl₂, in a suspension of 1% of peroxide-bleached TMP (Fig 6). The total concentration of resin acids in the supernatant was 48.5 mg/l at 0 mM CaCl₂, and 18.3 mg/l at 10 mM CaCl₂. The dominating dehydroabietic acid had a concentration of 12.7 mg/l at 0 mM CaCl₂, and a concentration of 8.2 mg/l at

10 mM CaCl₂, i.e. only a decrease of 35%. The decrease of e.g. isopimaric acid in the supernatant was about 79%. This indicates that the calcium soap of dehydroabietic acid is more water-soluble than other calcium soaps. The same was seen from RFA phase distribution experiments, with added CaCl₂, and was described as an effect of the hydrophilic aromatic ring in the structure of dehydroabietic acid (MacNeil et al. 2011). The deposition behaviour of colloidal pitch has been linked to the solubility of the different groups of pitch components at varying pH; especially the solubility of resin acids in papermaking processes using *Pinus radiata* (McLean et al. 2005b).

TMP-suspensions with water-soluble GGM

Addition of 90 mg/l of water-soluble galactoglucomannans (GGM) to colloidal pitch emulsions completely stabilised the pitch toward electrolyte-induced aggregation both at pH 5 and 8, even at 10 mM of CaCl₂ (Fig 7). It has previously been shown that 100 mg/l of native O-acetyl-GGM can completely stabilise a colloidal pitch emulsion against even 30 mM of CaCl₂ at low pH (Hannuksela, Holmbom 2004). The stabilising mechanism was described as steric stabilisation (Welkener et al. 1993; Sundberg, K., et al. 1994a; 1996a; Puro et al. 2011).

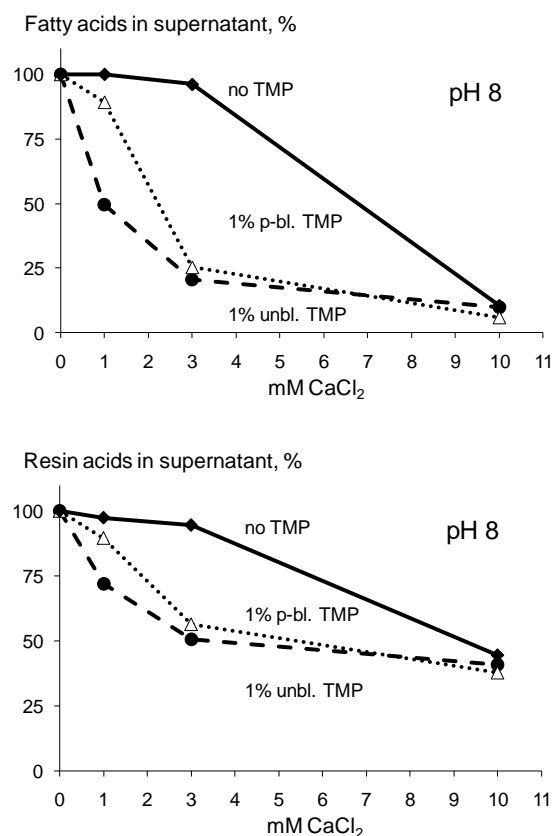


Fig 5. Relative amounts of resin and fatty acids in the supernatant after CaCl₂-additions to suspensions of no TMP, 1% peroxide-bleached (p-bl.) TMP and 1% unbleached (unbl.) TMP at pH 8.

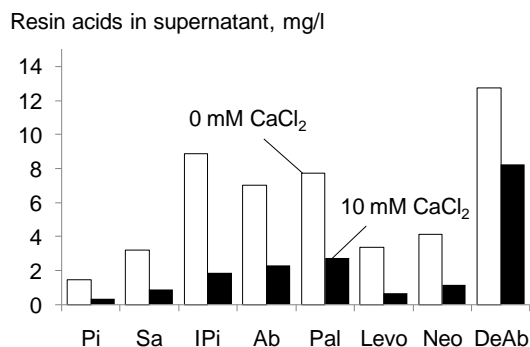


Fig 6. Composition of resin acids in the supernatant with 1% peroxide-bleached TMP and CaCl₂ concentrations of 0 mM and 10 mM. The total concentration of resin acids was 48.5 mg/l at 0 mM and 18.3 mg/l at 10 mM CaCl₂ at pH 8. Pi = pimaric acid, Sa = sandaracopimaric acid, IPi = isopimaric acid, Ab = abietic acid, Pal = palustric acid, Levo = levopimaric acid, Neo = neoabietic acid, DeAb = dehydroabietic acid.

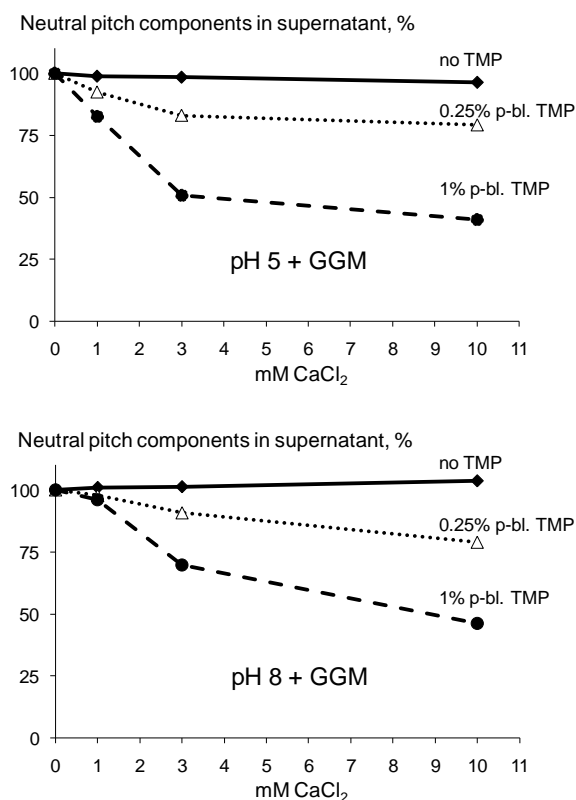


Fig 7. Relative amounts of neutral substances in the supernatant after CaCl₂-additions to suspensions of no TMP, 0.25% and 1% peroxide-bleached (p-bl.) TMP with added GGM, at pH 5 and pH 8.

At pH 5, in suspensions of 0.25% peroxide-bleached TMP about 83% of the neutral substances remained stable with 3 mM CaCl₂, and 51% in suspensions of 1% peroxide-bleached TMP (Fig 7). The destabilisation of colloidal pitch was dependent on the concentration of CaCl₂, as well as the pulp consistency even though the pitch particles were sterically stabilised by the addition of GGM.

A CaCl₂-concentration of 3 mM in suspensions of 1% peroxide-bleached TMP with added GGM

resulted in 51% of the neutral substances remaining in the supernatant (Fig 7), while only 2% remained in the supernatant when no GGM was added at pH 5 (Fig 2).

At pH 8, the concentration of neutral substances remained at 70% in the supernatant with 3 mM CaCl₂, and at 46% with 10 mM CaCl₂, in suspensions of 1% peroxide-bleached TMP (Fig 7). The corresponding value was only 19% when no GGM was added with 3 mM of CaCl₂ (Fig 4). It is evident that the steric stabilisation of colloidal pitch by GGM in TMP-suspensions is also effective at pH 8.

The stabilisation of colloidal pitch by GGM was as effective at pH 5 and 8 against 10 mM of CaCl₂ (Fig 7). The concentration of neutral substances in the supernatant was slightly higher at 1 and 3 mM CaCl₂ at pH 8, than at pH 5, in suspensions of 1% peroxide-bleached TMP. The pitch was somewhat more stable at pH 8 than at pH 5, because of additional sorption of free calcium ions to the pulp, a higher surface charge of the colloids, and removal of free calcium ions due to the formation of calcium soaps of resin acids.

The concentration of GGM in the supernatant was not significantly affected by the changes in pitch composition throughout the experiments, neither at pH 5 nor at pH 8. This implies that the water-soluble GGM had no mentionable tendency to be attached to TMP or colloid surfaces, which is agreement with previous studies (Hannuksela et al. 2003, Qin et al. 2004).

Table 1. Concentrations of pitch components in the supernatant of TMP-suspensions, without addition of CaCl₂.

	Neutral substances mg/l	Fatty acids mg/l	Resin acids mg/l
pH 5			
No TMP	121	24	58
0.25% unbl. TMP	120	23	54
1% unbl. TMP	127	23	49
No TMP	121	20	48
1% p-bl. TMP	125	20	46
pH 8			
No TMP	129	23	57
1% unbl. TMP	132	23	55
No TMP	114	21	49
1% p-bl. TMP	115	22	49
With GGM			
pH 5			
No TMP	124	24	49
1% p-bl. TMP	129	25	47
pH 8			
No TMP	119	22	48
1% p-bl. TMP	125	23	48

Conclusions

At pH 8, a higher concentration of CaCl₂ was required to aggregate and destabilise the colloidal pitch than at pH 5, in absence of water-soluble hemicelluloses. Even low CaCl₂-concentrations destabilised the colloidal pitch almost completely in TMP suspensions at pH 5, implying that the colloids were more susceptible to destabilisation when the resin and fatty acids were associated with the pitch droplets. A higher TMP consistency resulted in less stable pitch if CaCl₂ was added. The mechanisms behind pitch destabilisation were most likely aggregation by calcium ions, followed by retention of the aggregates by fibres and fines.

The colloidal pitch was not destabilised by addition of unbleached or peroxide-bleached TMP to pitch emulsions at pH 5 and 8 in the absence of CaCl₂, which indicated that colloidal wood pitch has low affinity to TMP fibres on its own. At low CaCl₂-concentrations, more pitch was destabilised by addition of unbleached TMP than with peroxide-bleached TMP. The high negative charge of peroxide-bleached TMP probably adsorbed more calcium ions, leaving less free calcium available to destabilise the colloidal pitch. TMP fibres can therefore act as adsorbing surfaces and prevent uncontrolled aggregation of pitch in the presence of CaCl₂.

At pH 8, some of the resin acids remained in the supernatant of TMP suspensions even at high concentration of CaCl₂. The resin acids most likely remained in the supernatant in the form of dissolved calcium soaps or stable calcium-soap aggregates. The formed calcium soaps of resin acids at higher pH can cause pitch problems, and can be difficult to control since these soaps are quite stable and do not have affinity to either pitch particles or TMP.

Water-soluble galactoglucomannans (GGM) stabilised the pitch droplets sterically against aggregation by CaCl₂ in the absence of TMP, at both pH 5 and pH 8. Addition of peroxide-bleached TMP diminished the steric stabilisation of colloidal pitch in the presence of CaCl₂. The GGM-addition stabilised the colloidal pitch to the same extent at pH 8 and pH 5 in TMP suspensions. This indicated that the surface composition of the pitch droplets is not a decisive factor behind the mechanisms of steric stabilisation.

This study has shown that the colloidal pitch system is essentially different at pH 5 and pH 8, especially because of the resin acid distribution between the colloids and water. The colloidal systems in paper machines running at acidic or neutral conditions may also in this sense be completely different, even though the same raw

material is used. It was also shown that wood pitch can be sterically stabilised, to some extent, by GGM even in suspensions of peroxide-bleached TMP at both pH 5 and pH 8. These results support the conclusion that a high concentration of dissolved GGM is essential for the colloidal stability of pitch, and consequently for avoiding pitch deposits at acidic and neutral conditions.

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