Effects of metal ions and wood pitch on retention and physical properties of TMP

Lu, Xiaomin; Sundberg, Anna; Strand, Anders; Hubbe, Martin A.

Published in:
Nordic Pulp and Paper Research Journal

DOI:
10.1515/npprj-2020-0036

Published: 24/09/2020

Paper chemistry

Xiaomin Lu*, Anna Sundberg, Anders Strand and Martin A. Hubbe

Effects of metal ions and wood pitch on retention and physical properties of TMP

https://doi.org/10.1515/npprj-2020-0036
Received April 11, 2020; accepted August 25, 2020; previously published online September 24, 2020

Abstract: The influence of metal ions, Ca^{2+} and Mg^{2+}, on wood pitch retention at pH 8 was studied by investigating the pitch content of TMP-papers using both short- and long-column gas chromatography (GC). The effects of two different drying methods, air-drying and freeze-drying, on pitch retention were also compared in this work. The pitch emulsion was prepared with fatty acids, resin acids, and triglycerides at a certain ratio to simulate the pitch composition in closed water system in paper mill. At increasing pH, some of the resin and fatty acids will dissolve into the water phase as metal soaps. In this work, the retention of colloidal pitch in TMP-papers by metal ions at pH 8 was determined. The amount of 5 mM metal ions was found to retain more pitch. The tensile index decreased by the addition of metal ions, and the decrease became more pronounced as the increase of the metal ions concentration. Besides, the hydrophobicity of handsheets was found being changed only a little, which might because the morphology and pitch retained on the surface both affected the hydrophobicity.

Keywords: metal ions; papermaking; softwood; TMP; wood pitch.

Introduction

Wood extractives are located mainly in the resin canals and the parenchyma cells; a smaller amount of extractives are found in middle lamellae and cell walls of tracheids and libriform cells (Fengel and Wegener 1984). There are hydrophilic and lipophilic wood extractives. The composition of extractives varies from species to species, and the total amount of extractives in a given species depends on growth conditions and also on the geological site and the season (Sjöström 1993, Ekman and Holmbom 2000). Lipophilic extractives, or wood resins, consist of fatty acids, resin acids, sterols, steryl esters, and triglycerides. The composition changes during harvesting, transportation, and storage of wood (Ekman and Holmbom 2000). A mixture of lipophilic extractives can also be called pitch.

Many metal ions are present in pulping and papermaking. Examples of common metal ions are Na^{+}, Mg^{2+}, Ca^{2+}, and Al^{3+}. These metal ions originate from raw materials, additives, and impurities. In pulp suspensions, the fatty acids and resin acids are insoluble in water under acidic conditions. The wood pitch properties, *i. e.*, colloidal stability and deposition tendency, are dependent on the surface layer (Sundberg, A. et al. 1995, Sundberg, K. et al. 1995 Sundberg, K. et al. 1996, Qin et al. 2003, Qin et al. 2004, Tammelin et al. 2007). However, at pH above 6, the fatty acids and resin acids will gradually dissolve in water and react with available metal ions to form metal soaps (McLean et al. 2005). The formed soaps are either soluble or insoluble in water depending on the metal ion (Allen 1988, 2000). The presence of some dissolved softwood hemicellulose, *i. e.*, galactoglucomannans, has been shown to promote the stabilization of pitch (Welkener et al. 1993, Sundberg, K. et al. 1994a, Sundberg, K. et al. 1994b, Hannuksela and Holmbom 2004).

There are many reasons for pitch deposition, such as changes in pH and temperature, increased shear forces, and colloidal destabilisation of pitch (Allen 1975, 1980, Ekman et al. 1990). In the mechanical pulping process, the wood pitch exists in the form of colloidal droplets, with a diameter of 0.1 to 2 μm (Allen 1975, Sundberg, K. et al. 1994a, Sundberg, K. et al. 1994b, Hubbe et al. 2020). Deposits on paper machine equipment can affect the water removal on wires and cause problems on press and dryer rolls. Deposits can also result in spots and holes in the paper (Rying 1978, OLM 1984).

***Corresponding author: Xiaomin Lu,** Department of Forest Biomaterials, North Carolina State University, Raleigh, NC 27695, USA, e-mail: xlu13@ncsu.edu, ORCID: https://orcid.org/0000-0001-6717-525X
Anna Sundberg, Laboratory of Natural Materials Technology, Åbo Akademi University, Porthaninkatu 3, 20500 Turku, Finland, e-mail: anna.sundberg@abo.fi
Anders Strand, Mirka Ltd, Pensalavägen 210, 66850 Jeppo, Finland, e-mail: anders.strand@mirka.com
Martin A. Hubbe, Department of Forest Biomaterials, North Carolina State University, Raleigh, NC 27695, USA, e-mail: hubbe@ncsu.edu

In previous research, metal ions have been proved to affect the stability of wood pitch. The stability or deposition tendency of wood pitch was also discussed by other researchers. But the physical properties of paper sheets after adding metal ions has not been investigated. The aim of this work was to determine the effects of metal ions and wood pitch on retention and paper properties. Pitch emulsions, consisting of resin acids, fatty acids, and triglycerides, were added to suspensions of thermomechanical pulp (TMP). Different concentrations of Mg^{2+} and Ca^{2+} were also added. The content of pitch in papers, and the physical properties, including tensile index, air permeability and contact angle, were demonstrated in this paper.

Materials and methods

Materials

TMP of Norway spruce (*Picea abies*) was used in the experiments. TMP was obtained from a Finnish pulp mill. The pulp was stored in a freezer at −24 °C.

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 86 % distilled water and 14 % acetone. The mixture was acidified with concentrated HCl to pH 3 and extracted with methyl tert-butyl ether (MTBE). The MTBE was removed by evaporation and the fatty acids were re-dissolved in acetone. Pure linoleic acid (18:2) was obtained from Sigma and pure oleic acid (18:1) from Fluka. The pure fatty acids were directly dissolved in acetone.

A mixture of resin acids was obtained by extraction of solid oleoresin from Norway spruce (*Picea abies*) with hexane. The extract was filtrated through a filter paper (Blue Ribbon, Schleicher & Schuell), evaporated and re-dissolved in acetone.

The triglycerides used in this work were soybean oil (Oilio, Belgium). The triglycerides contained 14 % saturated fatty acids, 24 % monounsaturated fatty acids, and 62 % polyunsaturated fatty acids. The soy bean oil was directly dissolved in acetone.

Solutions of the metal ions Ca^{2+} and Mg^{2+} were used. These were prepared by dissolving $CaCl_2 \bullet 2H_2O$ (Assay: 99.0 %, J. T. Baker Company) to 1 M, $MgCl_2 \bullet 6H_2O$ (Assay: 100.7 %, PROLABO Company) to 1 M with distilled water.

Methods

Preparation of pitch emulsion

Acetone solutions of fatty acids, resin acids and triglycerides were mixed in the ratio of 15:32:53. The acetone was evaporated under nitrogen gas, and the residue was re-dissolved in acetone to a concentration of 30 g/L. The acetone solution was stored in the cold room at 4 °C. 13.3 mL acetone solution was injected in 2000 mL distilled water under agitation (Sundberg, K. et al. 1996). This emulsion was dialyzed eight times against distilled water using a dialysis membrane (Medicell International Ltd., cut off 12000 to 14000 Dalton). Before being added to the TMP suspension, the pitch emulsion after dialysis was heated to 60 °C, and the pH was adjusted to 8 with H_2SO_4 or NaOH solution.

Preparation of TMP suspension

An amount of 16 g dry-weight TMP was used for each of the test series. The TMP was diluted to a consistency of 2.2 % with 60 °C distilled water and defibrated for two minutes using a handmixer. The TMP was alkali-treated at pH 11 for one hour at 60 °C, which should be enough to deacetylate all galactoglucomannans in the TMP, rendering them insoluble in water (Hannuksela et al. 2002). The pH of the suspension was then adjusted to 8 with 0.5 M H_2SO_4. The TMP suspension was diluted to a consistency of 0.5 % with the pitch emulsion and distilled water, and was agitated at 60 °C and pH 8 for half an hour. A certain amount of metal ions was added to the suspension. The TMP-suspension was further diluted to a consistency of 0.1 % with distilled water, making the total weight of the suspension 16 kg. The pH was once again measured and readjusted to 8 if needed.

Papermaking

Handsheets were prepared with a laboratory sheet former using 800 mL of the TMP suspension for each paper sheet. Each of the wet paper sheets was placed in between two blotters, and the sandwiched “blotter-papers sheet-blotter” was subjected to a heavy cylinder to remove the extra water. Finally, three paper sheets were then freeze-dried and the rest were air-dried at room temperature in a paper testing room. The additives in each of the test series are shown in Table 1.

Table 1: Additives in each Test Series.

	Test series
1	TMP
2	TMP + Pitch
3	TMP + Pitch + 1 mM Ca^{2+}
4	TMP + Pitch + 5 mM Ca^{2+}
5	TMP + Pitch + 10 mM Ca^{2+}
6	TMP + Pitch + 1 mM Mg^{2+}
7	TMP + Pitch + 5 mM Mg^{2+}
8	TMP + Pitch + 10 mM Mg^{2+}

Calendering

The wire side of the air-dried papers was calendered twice using a laboratory calender at 60 °C (outer temperature) with a steel nip pressure of 30 bars prior to the contact angle measurement and the determination of tensile index. Three of sheets were stored in freezer prior to contact angle measurements, and the rest of the sheets were stored in a paper testing room at 23 and 50 % relative humidity prior to determination of tensile index and air permeability.

Contact angle measurements

The hydrophobicity of the papers was tested with a Contact Angle and Surface Tension Meter with 3 µL de-ionised water in air. The contact angle was captured after 1 second after touching the surface of handsheet. The device was equipped with long camera lens. CAM 200 included a FireWire video camera, an adjustable sample stage and a LED light source.

Physical properties

The sheets were weighed using a laboratory scale with an accuracy of 0.0001 g. Thickness of the sheets was determined by measuring the thickness of 5 papers together with an L&W Micrometer SE 250. The air permeability of the sheets was measured using an L&W Air Permeance SE 166. Tensile index of the sheets was determined using an L&W Tensile Strength Tester SE 060. The physical properties were carried out after at least 48 hours preconditioning at 23 and 50 % relative humidity.

Determinations and analysis

A scheme of the pretreatments of the papers, and the determinations and analysis is shown in Figure 1.

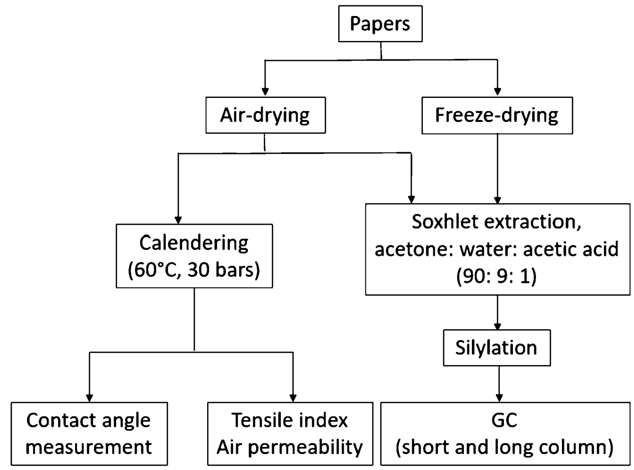

Figure 1: Analytical procedure of papers.

Determination of TMP dryness

About one gram of TMP was put in an aluminium pan (Φ = 100 mm, h = 7 mm), and the dryness was determined gravimetrically with a Sartorius MA 30 Moisture Analyzer at 105 °C. The moisture analyzer was equipped with two infrared dark radiators which provide heat for the determination of moisture. The chamber was fully heated to reach the set temperature at the beginning and the heat stopped automatically when the weight of the sample reached a constant value (Electronic Moisture Analyzer Installation and Operating Instructions, Sartorius, 1990). The dry content in the TMP was 44 %.

Pitch analysis

The papers were extracted with a mixture of acetone, distilled water, and acetic acid in the ratio of 90:9:1. This mixture was used to ensure extraction of resin acids and fatty acids that were present in soap form. For each parallel sample, three freeze-dried papers and three air-dried papers were extracted in 100 mL soxhlet apparatuses with 50 mL acetone-mixture solution. The volume of the extracts was adjusted to 50 mL at room temperature after the extractions. The extracts were stored in a cold room until further used.

A certain volume of the extract (Table 2) was transferred to a test tube, and 2 mL standard solution, containing 0.02 mg/mL heneicosanoic acid (C21), betulinol, cholesteryl heptadecanoate (CH17), and 1,3-dipalmitoyl-2-oleyl glucerol (TG-std), was added. The extract was then evaporated under nitrogen gas at 40 °C. The extract was further dried in a vacuum desiccator at 40 °C for 15 min. The samples were silylated for 45 min at 70 °C with 20 µL pyridine, 80 µL bis-(trimethylsilyl)-trifluoro acetamide (BSTFA) and 20 µL trimethyl chlorosilane (TMCS) (Örså and Holmbom 1994).

Table 2: The Volume of Extract Used in Analysis of Pitch.

Test series	Volume of extracts, mL (air-dried papers)	Volume of extracts, mL (freeze-dried papers)
TMP	20	20
TMP + Pitch	20	20
TMP + Pitch + 1 mM Ca^{2+}	20	12
TMP + Pitch + 5 mM Ca^{2+}	20	12
TMP + Pitch + 10 mM Ca^{2+}	12	6
TMP + Pitch + 1 mM Mg^{2+}	20	20
TMP + Pitch + 5 mM Mg^{2+}	20	20
TMP + Pitch + 10 mM Mg^{2+}	12	6

The silylated extracts were transferred to auto sampler vials using clean Pasteur pipettes. The pitch was analyzed as groups by short column GC (Perkinelmer Clarus 500) and individual resin and fatty acid were analysed by long column GC (Perkinelmer Clarus 500).

The short column was a HP-1, 7 m (L) × 0.53 mm (ID) and the film thickness was 0.15 µm. Hydrogen was used as carrier gas, with a flow of 7.0 mL/min. The temperature programmes for the heated zones were: oven: 100 °C, 0.5 min, 12 °C/min, 340 °C, 5 min, injector: 80 °C, 0.1 min, 50 °C/min, 110 °C, 15 °C/min, 330 °C, 7 min, detector: 340 °C. The injection volume was 0.5 µL, on-column, and the detector used was a flame ionization detector (FID).

The long column of channel A was a HP-1, 25 m (L) × 0.199 mm (ID) and the film thickness was 0.11 µm. The column of channel B was a HP-1, 25 m (L) × 0.204 mm (ID) and the film thickness was 0.11 µm. Hydrogen was used as carrier gas, with the pressure of 14 psi. The temperature programmes for the heated zones were: oven: 120 °C, 1 min, 6 °C/min, 320 °C, 15 min, injector: 160 °C, 0 min, 8 °C/min, 260 °C, 15 min, detector: 320 °C. The injection volume was 1 µL, split 25:1, and the detector was a FID.

Results and discussions

Paper sheets were prepared from TMP, with addition of pitch emulsion and different amounts of metal ions. The pitch content in the papers and some physical properties were determined. The pitch content in the papers is a measure of the interactions between colloidal pitch and metal ions, *i. e.* aggregation, leading to retention in the papers. Tensile index, contact angle and air permeability were measured to assess the effect of the retained pitch-metal ion aggregates in handsheets.

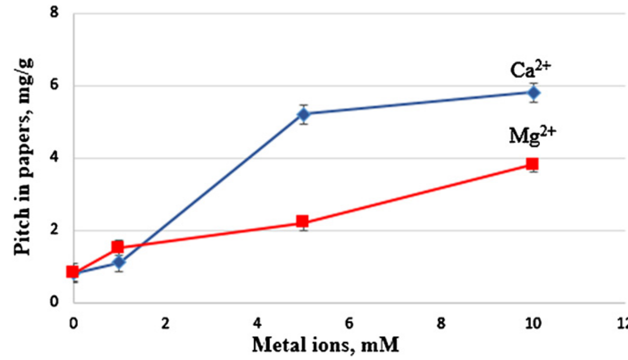

Figure 2: The total amounts of pitch in air-dried papers, after adding pitch emulsion and 1, 5 or 10 mM Ca^{2+} or Mg^{2+} to TMP suspensions.

The pitch content in papers

Papers air-dried at room temperature

The total amount of pitch in the papers increased with increasing concentration of Ca^{2+} (Figure 2). In the absence of electrolyte, the aggregation and deposition of pitch was low, since the pitch dispersion was well stabilized electrostatically at pH 8 (Sundberg, K. et al. 1994a, Sundberg, K. et al. 1994b). Qin et al. discovered the same results in 2004. At pH 8, the colloidal droplets of pitch are negatively charged due to the presence of the carboxylic groups in fatty acids and resin acids (Allen 2000). The repulsive force between the droplets prevented the droplets from aggregating. Besides, the fatty acids acted as emulsifiers at higher pH, preventing the pitch deposition (Hassler 1988, Sihvonen et al. 1998). Increasing the Ca^{2+} concentration from 0 mM to 1 mM resulted in only a slight increase of pitch in the papers, while increasing the Ca^{2+} concentration from 1 mM to 5 mM resulted in a large increase of pitch in the papers, from 1.1 mg/g to 5.2 mg/g. This indicates that 5 mM Ca^{2+} caused aggregation of colloidal pitch at pH 8, while 1 mM Ca^{2+} was not enough to cause significant aggregation. Increasing the Ca^{2+} concentration from 5 mM to 10 mM, increased the amount of pitch in the papers from 5.2 to 5.8 mg/g, *i. e.* an increase of only 0.6 mg/g (Appendix Table A1). This shows that the aggregation of colloidal pitch against the Ca^{2+} does not have a linear regression. The results are consistent with what MacNeil found. They claimed the addition of Ca^{2+} could decrease solubility of fatty and resin acids (MacNeil et al. 2011).

The addition of Mg^{2+} to the furnish also caused retention probably due to the aggregation of colloidal pitch, and retention of pitch in the papers (Figure 3). However, the retention of pitch by Mg^{2+} was not as high as in the case of Ca^{2+} at the same concentration of metal ions. A Mg^{2+} concentration of 1 mM resulted in similar amount of re-

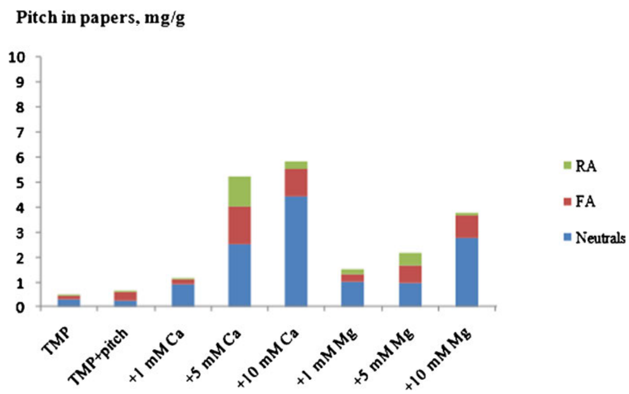

Figure 3: The amounts of resin acids (RA), fatty acids (FA) and neutrals in air-dried papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions.

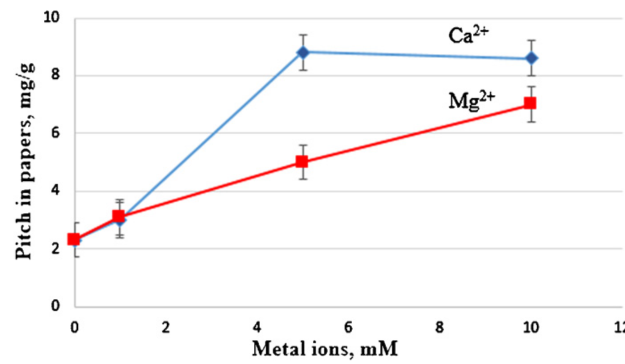

Figure 4: The total amounts of pitch in freeze-dried papers, after adding pitch emulsion and 1, 5 or 10 mM Ca^{2+} or Mg^{2+} to TMP suspensions.

tained pitch as 1 mM Ca^{2+}, but the pitch content with 5 mM Mg^{2+} was much lower than with 5 mM Ca^{2+}. About 3.8 mg/g pitch was retained in the papers by 10 mM Mg^{2+}, while the corresponding value with 10 mM of Ca^{2+} was 5.8 mg/g. The aggregates formed between Ca^{2+} and pitch might be larger and tackier, and were therefore more easily retained in papers than the aggregates formed between pitch and Mg^{2+}. The tacky properties of pitch can change greatly, depending on whether it has become air-oxidized, polymerized, when the temperature changes, or when it is mixed with other materials (Dreisbach and Michalopoulos 1989).

The chemical composition of the retained pitch in air-dried papers is shown in Figure 4. The pitch content in papers with TMP and pitch emulsion but without added metal ions were quite similar to the papers of only TMP. This indicates that the pitch was colloidally stable and only small amounts were retained in the papers at pH 8. Pitch has been shown to have low affinity to TMP in the absence of metal ions (Strand et al. 2011). Some resin acids and fatty acids are further soluble in water at pH 8 as sodium soaps (Sundberg, A. et al. 2009). It has also been shown that the calcium soaps of resin acids can be soluble in water at pH 8, while almost no fatty acids are dissolved at pH 8 and 10 mM Ca^{2+} (MacNeil et al. 2011).

Significantly more resin acids but also fatty acids were retained in the papers at 5 mM Ca^{2+} than at 10 mM (Figure 4). Less resin acids were retained at 10 mM Ca^{2+}, possibly due to the formation of water-soluble resin acid soaps, or colloidally stable aggregates of resin acids at high concentration of Ca^{2+}. Calcium soaps of resin acids have been shown to have a higher solubility in water than calcium soaps of fatty acids (MacNeil et al. 2011), which could explain why the amount of resin acids in the papers decreased more than the amount of fatty acids at high Ca^{2+} concentration. The amount of neutrals in the papers increased with increasing concentration of Ca^{2+} (Figure 4). It has been shown that the major part of colloidal pitch was destabilized in unbleached TMP at pH 8 and at 10 mM Ca^{2+} (Strand et al. 2011).

More resin acids were also retained at 5 mM Mg^{2+} than 10 mM Mg^{2+} (Figure 4). It is possible that the resin acid-Mg^{2+}-soap aggregates were colloidally stable, or more resin acid-Mg^{2+}-soaps were dissolved in water at high concentration of Mg^{2+} at pH 8. The fatty acids retained in papers increased with the increase of Mg^{2+} concentration from 1 to 5 mM, while the amount of fatty acids retained in the papers were quite similar with 5 or 10 mM Mg^{2+} were quite similar. The reason might be that the fatty acid-Mg^{2+}-soaps were colloidally unstable when the Mg^{2+}-concentration was 5 mM. The amount of neutrals in the papers was approximately the same with 1 and 5 mM Mg^{2+}, while the amount of neutrals in the papers with 10 mM Mg^{2+} was as three times larger than with 5 mM Mg^{2+}.

Freeze-dried papers

The total amount of pitch in freeze-dried papers increased with increasing concentration of Ca^{2+} or Mg^{2+} (Figure 4). The addition of Calcium ions has been found to induce the precipitation of colloids, which can further coagulate (Stack et al. 2014). Compared to air-dried papers, more pitch was retained in the freeze-dried paper.

The chemical composition of the retained pitch in freeze-dried papers is shown in Figure 5. The pitch content in the papers increased significantly after the addition of pitch emulsion. Especially more neutrals were found in freeze-dried papers after addition of pitch emulsion. This was not seen with air-dried papers. The reason might be that neutrals could not be removed to the same extent from

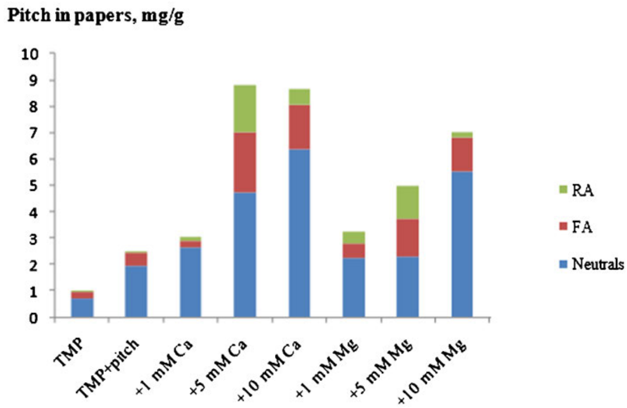

Figure 5: The amounts of resin acids (RA), fatty acids (FA) and neutrals in freeze-dried papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions.

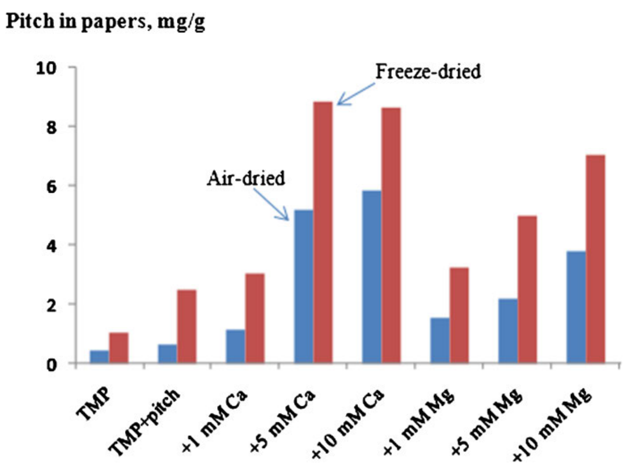

Figure 6: Total pitch in air-dried and freeze-dried papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions.

air-dried papers or that neutrals were attached to the blotting papers during air-drying.

Comparison of drying methods

More pitch could be extracted from freeze-dried papers than from air-dried papers (Figure 6). It is possible that bonds in pitch or between pitch and fibres were formed during the air-drying, which decreased the extractability of the pitch. In previous research, it has been found that air-drying resulted in a more compact morphological structure and increased density of foam-formed paper samples (Korehei et al. 2016). Another possibility is that the pitch in air-dried paper is covered by a layer of substances during drying, which may decrease the extractability. Some of the pitch in the air-dried papers might also be removed by the blotting papers during the drying process. Freeze-drying could furthermore preserve the porous structure of the papers, leaving the pitch more accessible to extraction with solvents.

The amounts of resin and fatty acids found in freeze-dried papers of TMP, or TMP and pitch emulsion were similar as in air-dried papers, while the amount of neutrals was significantly higher in freeze-dried papers than in air-dried TMP papers (Figure 3 and 5).

More pitch could be extracted from freeze-dried papers than from air-dried papers also after addition of Ca^{2+} or Mg^{2+}. Especially more neutral substances could be found in freeze-dried papers. Freeze-drying was a more gentle method, which left the pitch components more unchanged and accessible for extraction also in the presence of metal ions (Korehei et al. 2016).

Paper properties

Tensile index

Papers made of TMP without pitch emulsion had the highest tensile index of all papers tested, about 30 kNm/kg (Figure 7). This paper also contained the lowest amount of pitch (Appendix Table A3), about 0.43 mg/g in air-dried paper (Appendix Table A1).

When pitch emulsion was added to the TMP suspension, the tensile index decreased from 30 to 27 kNm/kg (Figure 7; Appendix Table A3), even if the pitch content increased only slightly, from 0.43 mg/g to 0.62 mg/g (Appendix Table A1). When 1 or 5 mM Ca^{2+} was added together with the pitch emulsion, the tensile index decreased further to 26 and 22 kNm/kg, respectively. There was no further decrease in tensile index in the papers when the Ca^{2+}

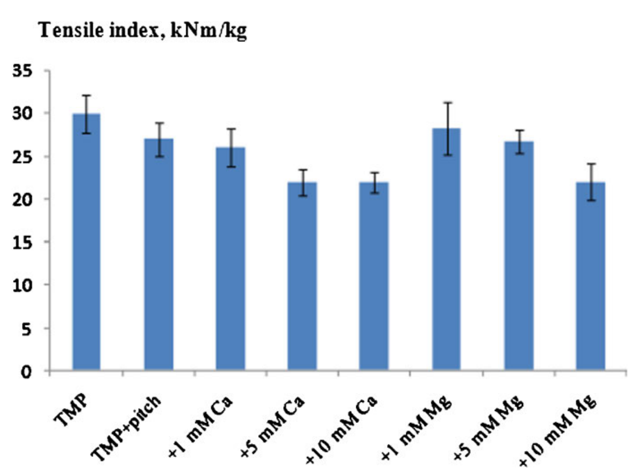

Figure 7: The tensile index of air-dried and calendered papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions.

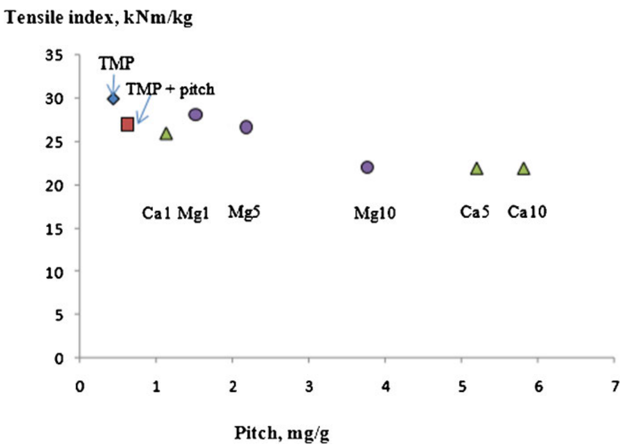

Figure 8: The tensile index as a function of pitch content of air-dried and calendered papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions. ◆: TMP, ■: TMP + pitch, △: +$CaCl_2$, ●: +$MgCl_2$.

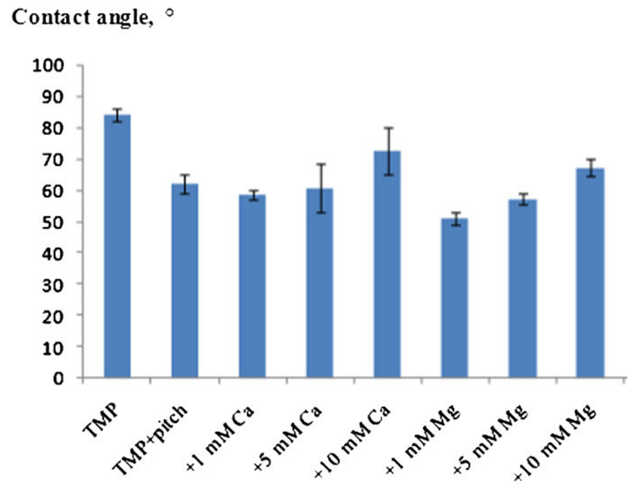

Figure 9: The contact angle after 0.2 s of air-dried papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions.

concentration was 10 mM. 0–2 mg/g pitch has been shown to decrease the tensile index of paper, and no further decrease was seen when the pitch content was 2–10 mg/g. Similar phenomena were observed by the other research groups (Zhang et al. 1999, Sundberg, A. et al. 2000).

When 1 and 5 mM Mg^{2+} was added to the furnish, the tensile index was similar or even higher than for papers of only TMP and pitch emulsion (Figure 7). The tensile index decreased when 10 mM Mg^{2+} was added.

The tensile index versus pitch content of the papers can be seen in Figure 8. No significant decrease in tensile index was seen upon addition of 1 mM Ca^{2+}, 1 or 5 mM Mg^{2+} to suspensions of TMP and pitch emulsion, even if the pitch content increased from 0.6 mg/g (TMP and pitch) to 2.2 mg/g (5 mM Mg^{2+}). It has previously been shown that the tensile index decreases when the pitch content increases from 0 to 2 mg/g in papers made of chemical pulp and thermal mechanical pulp (Sundberg, A. et al. 2000). Ca^{2+} or organic polymers were then used to aggregate the pitch and increase the retention, but the papers were not calendered. The calendering might press the fibres together and thereby diminish the effect of the pitch, or the pitch aggregates of Mg^{2+} might be retained differently than aggregates of Ca^{2+} and pitch.

The tensile index decreased when 10 mM Mg^{2+}, or 5 or 10 mM Ca^{2+} was added to the furnish together with the pitch emulsion (Figure 8). The pitch content was then 3.8–5.8 mg/g. A pitch content of about 4 mg/g might be high enough weaken the fiber-fiber bonds in the handsheets even if the handsheets were calendered. This claim is consistent with previous work done by Rundlöf and his colleagues that pitch decreased the strength of handsheets (Rundlöf et al. 2000) In addition to what Rundlöf's group, Sundberg A. also discovered the weakening function of pitch on paper strength (Sundberg, A. et al. 2000).

Contact angle

The contact angle of water droplets after 0.2 s of contact time was determined on air-dried and calendered papers. The contact angle of the TMP papers was the highest, 83° (Figure 9). When pitch emulsion was added to the furnish prior to papermaking, the contact angle decreased to 63°, indicating the papers become less hydrophobic by the added pitch emulsion at pH 8. This is opposite to what could be expected. The contact angle might be interfered by the soluble metal soap which was found to affect the surface tension of water droplets (Strand et al. 2011, Strand 2013). It appears that the added pitch emulsion and the dissolved resin and fatty acids at pH 8 can act as a detergent, removing hydrophobic substances from the surface.

A Ca^{2+} concentration of 1 mM in the furnish resulted in a slight decrease in contact angle of the papers, from 63° to 59° (Figure 9). The pitch content increased slightly in the papers as a result of 1 mM Ca^{2+}, only 0.5 mg/g (Appendix Table A1), which would explain why there was no significant change in contact angle. The contact angle on papers with 5 mM Ca^{2+} was almost the same as when 1 mM Ca^{2+} was added. The pitch content was, however, about five times higher in papers with 5 mM Ca^{2+} compared to papers with 1 mM Ca^{2+} (Appendix Table A1). This implied that the contact angle of the calendered papers did not directly correlate with the pitch content in these papers. The pitch content in the papers increased from 5.2 mg/g to 5.8 mg/g when the Ca^{2+} concentration in the furnish was increased

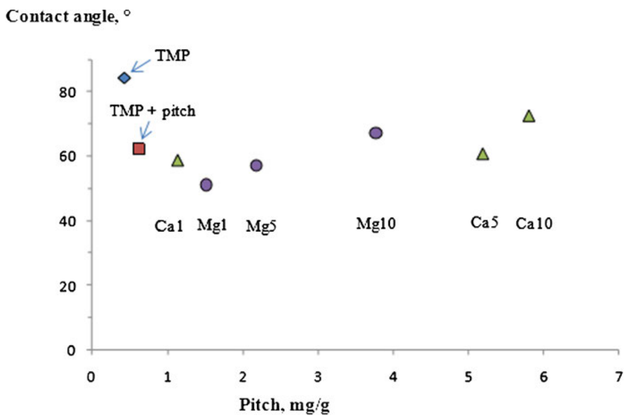

Figure 10: The contact angle after 0.2 s as a function of pitch content of air-dried and calendered papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions. ◆: TMP, ■: TMP + pitch, ▲: $+CaCl_2$, ●: $+MgCl_2$.

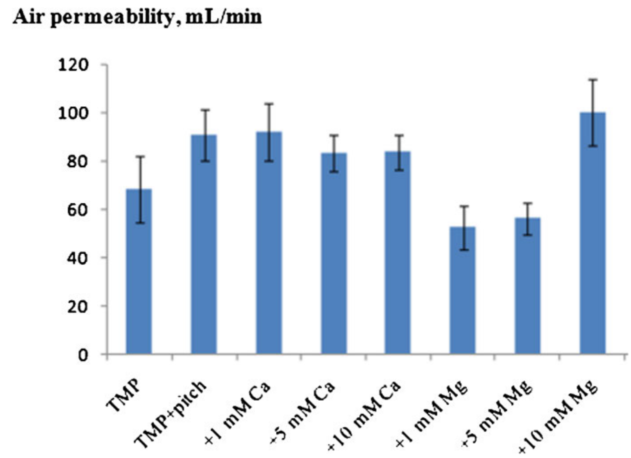

Figure 11: The air permeability of air-dried papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions.

from 5 mM to 10 mM (Appendix Table A1). There was a significant increase in contact angle when 10 mM Ca^{2+} was added to the furnish (Figure 9).

The contact angle of the papers after addition of Mg^{2+} increased with the increase of Mg^{2+} concentration (Figure 9). The contact angle of the papers was only 55° when 1 mM Mg^{2+} was added to the furnish. The contact angle with 1 mM Mg^{2+} was lower than the contact angle with 1 mM Ca^{2+}, even though the pitch content in these papers were on the same level, 1.5 mg/g compared to 1.0 mg/g. This indicated that the type of metal ions present in the furnish was important regarding the contact angle of the papers.

In Figure 10, the contact angle versus pitch content can be seen. There was no clear relationship between pitch content and contact angle, which indicates the pitch content is not the only factor influencing the hydrophobicity of the papers, and there are also other factors, e. g. as the type of metal ion and the morphology of the paper surface. Swanson and Cordingley (1956) suggested that the relatively brittle nature of fatty acid soap films stabilized by the presence of divalent ions can favor crumpling of the material.

Air permeability

After addition of pitch emulsion to the furnish, the air permeability increased from 69 mL/min to 90 mL/min (Figure 11). This indicates that the retained pitch made the paper structure less dense. The pitch was most likely embedded in the fibre matrix, and probably resulted in a more porous structure, which was more permeable to air.

Increasing Ca^{2+} concentration to 1 or 5 mM caused a decrease in air permeability of papers (Figure 11). However, no further decrease was seen when the Ca^{2+} concentration was increased from 5 mM to 10 mM; the air permeability of papers with Ca^{2+} leveled off at 84 mL/min. The air permeability of papers increased, however, with increased Mg^{2+} concentrations. When the concentration of Mg^{2+} was 1 or 5 mM, the air permeability of papers was lower than the papers of TMP and pitch emulsion. The papers with 10 mM Mg^{2+} had higher air permeability than the papers of TMP and pitch emulsion. This indicates that the effect of different metal ions on air permeability of papers varies considerably and that some other property is more important.

Figure 12 shows the air permeability as a function of pitch content of the air-dried papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions. No clear relationship between air permeability of papers and pitch content was found. This indicates that the pitch content is not a unique factor influencing air permeability in air-dried papers.

The air permeability versus paper density is shown in Figure 13. The air permeability of papers decreased with the increase of paper density. Density is therefore a much more important property for air permeability than pitch content.

Conclusions

The pitch content in TMP papers increased with increasing concentration of metal ions. More pitch was retained by addition of Ca^{2+} than Mg^{2+} when the same concentration was compared. Larger amounts of resin acids were found

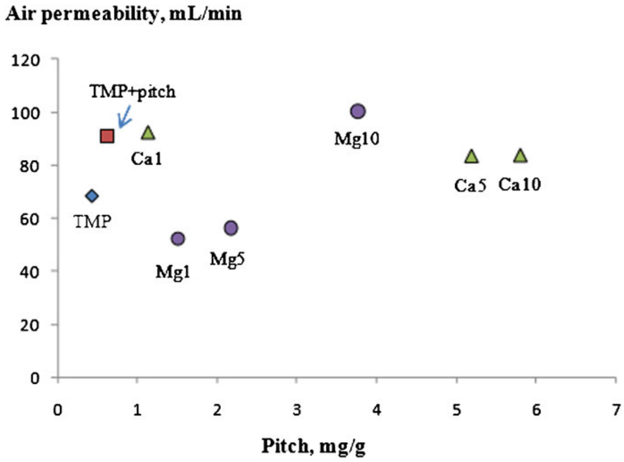

Figure 12: The air permeability as a function of pitch content of air-dried and calendered papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions. ◆: TMP, ■: TMP + pitch, ▲: $+CaCl_2$, ●: $+MgCl_2$.

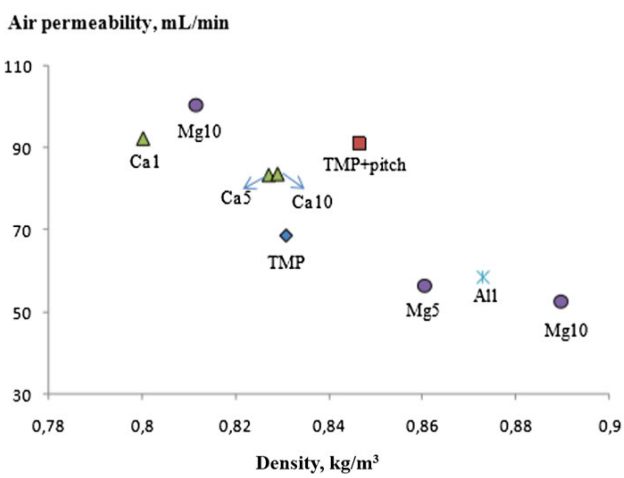

Figure 13: The air permeability as a function of density of air-dried and calendered papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions. ◆: TMP, ■: TMP + pitch, ▲: $+CaCl_2$, ●: $+MgCl_2$.

in paper made with 5 mM Ca^{2+} or Mg^{2+} than at 10 mM. Colloidally stable aggregates of resin acid and metal ions were formed at 10 mM, which were not retained in the papers.

The extractable amount of pitch in freeze-dried papers was significantly higher than in air-dried papers. Freeze-drying probably preserved the porous structure of the paper, which enhanced the accessibility of pitch extraction. Another possibility was that the pitch in air-dried papers was removed by the blotting papers, or that the pitch was covered with a layer of substances during drying, which decreased the extractability.

The tensile index of handsheets were changed since the pitch could alter or weaken the fiber-fiber interaction. The tensile index of air-dried and calendered papers was not significantly affected after addition of 1 mM metal ions or 5 mM of Mg^{2+}. The tensile index decreased slightly when 10 mM Mg^{2+}, or 5 or 10 mM Ca^{2+} were added. The contact angle of the TMP-papers was not much affected by the pitch content. The effect of pitch might get offset by the change of surface morphology.

The air permeability did not correlate with pitch content or the type of metal ions, but was dependent on the density of the papers

Funding: Authors state no funding involved.

Conflict of interest: The authors declare no conflicts of interest.

Appendix

Table A1: Pitch content in air-dried papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions.

Air-dried	Unit	TMP	TMP+pitch	$+Ca^{2+}$ 1 mM	$+Ca^{2+}$ 5 mM	$+Ca^{2+}$ 10 mM
Fatty acids	mg/g	0.15	0.34	0.18	1.49	1.07
Resin acids	mg/g	0.01	0.02	0.05	1.19	0.31
Neutrals	mg/g	0.28	0.27	0.90	2.51	4.44
Total pitch	mg/g	0.43	0.62	1.13	5.20	5.81

Air-dried	Unit	$+Mg^{2+}$ 1 mM	$+Mg^{2+}$ 5 mM	$+Mg^{2+}$ 10 mM	$+Al^{3+}$ 1 mM
Fatty acids	mg/g	0.30	0.71	0.88	0.61
Resin acids	mg/g	0.23	0.54	0.13	0.17
Neutrals	mg/g	0.98	0.94	2.76	1.08
Total pitch	mg/g	1.51	2.18	3.77	1.86

Table A2: Pitch content in freeze-dried papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions.

Freeze-dried	Unit	TMP	TMP+pitch	$+Ca^{2+}$ 1 mM	$+Ca^{2+}$ 5 mM	$+Ca^{2+}$ 10 mM
Fatty acids	mg/g	0.28	0.50	0.27	2.32	1.65
Resin add	mg/g	0.06	0.07	0.13	1.78	0.59
Neutrals	mg/g	0.67	1.94	2.62	4.70	6.38
Total pitch	mg/g	1.02	2.51	3.02	8.81	8.63

Freeze-dried	Unit	$+Mg^{2+}$ 1 mM	$+Mg^{2+}$ 5 mM	$+Mg^{2+}$ 10 mM	$+Al^{3+}$ 1 mM
Fatty acids	mg/g	0.56	1.46	1.30	0.97
Resin add	mg/g	0.46	1.22	0.19	0.30
Neutrals	mg/g	2.22	2.29	5.54	3.78
Total pitch	mg/g	3.25	4.97	7.02	5.06

Table A3: Total pitch content of air-dried papers of TMP, TMP and pitch emulsion, and TMP, pitch emulsion and metal ions, contact angle, tensile index, air permeability, thickness, weight.

	Total pitch mg/g	Contact angle °	Tensile index kNm/kg	Air permeability mL/min	Thickness µm	Weight g
TMP	0.43	84.3	30.0	68.6	88.8	0.74
TMP+pitch	0.62	62.2	27.0	90.9	90.3	0.76
+1 mM Ca^{2+}	1.13	58.7	26.0	92.2	92.6	0.74
+5 mM Ca^{2+}	5.20	60.7	22.0	83.5	93.9	0.78
+10 mM Ca^{2+}	5.81	72.5	21.9	83.7	93.1	0.77
+1 mM Mg^{2+}	1.51	51.1	28.2	52.5	85.7	0.76
+5 mM Mg^{2+}	2.18	57.2	26.7	56.4	87.0	0.75
+10 mM Mg^{2+}	3.77	67.3	22.0	100.4	92.6	0.75
+1 mM Al^{3+}	1.86	73.9	27.6	58.5	88.8	0.78

References

Allen, L.H. (1975) Pitch in wood pulps. Pulp Pap. Can. 765:T139–T146.
Allen, L.H. (1980) Mechanisms and control of pitch deposition in newsprint mills. Tappi J. 63(2):81–87.
Allen, L.H. (1988) The importance of pH in controlling metal-soap deposition. Tappi J. 71(1):61–64.
Allen, L.H. (2000) Pitch control in paper mill. In: Pitch Control, Wood Resin and Deresination. Eds. Back, E.L., Allen, L.H. TAPPI Press, Atlanta, GA. pp. 307328.
Dreisbach, D.D., Michalopoulos, D.L. (1989) Understanding the behavior of pitch in pulp and paper mills. Tappi J. 72(6):129–134.
Ekman, R., Eckerman, C., Holmbom, B. (1990) Studies on the behavior of extractives in mechanical pulp suspensions. Nord. Pulp Pap. Res. J. 5(2):96–103. 10.3183/npprj-1990-05-02-p096-103.
Ekman, R., Holmbom, B. (2000) The chemistry of wood resin. In: Pitch Control, Wood Resin and Deresination. Eds. Back, E.L., Allen, L.H. TAPPI Press, Atlanta, GA. pp. 37–76.
Fengel, D., Wegener, G. (1984) Structure and ultrastructure. In: Wood: Chemistry, Ultrastructure, Reactions. W. de Gruyter, Berlin, New York. pp. 6–25.
Hannuksela, T., Holmbom, B. (2004) Stabilization of wood-resin emulsions by dissolved galactoglucomannans and galactomannans. J. Pulp Pap. Sci. 30(6):159–164.
Hannuksela, T., Tenkanen, M., Holmbom, B. (2002) Sorption of dissolved galactoglucomannans and Galactomannans to Bleached Kraft Pulp. Cellulose 9(3):251–261. 10.1023/A:102117842.
Hassler, T. (1988) Pitch deposition in papermaking and function of pitch-control agents. Tappi J. 71(6):195–201.
Hubbe, M.A., McLean, D.S., Stack, K.R., Lu, X., Strand, A., Sundberg, A. (2020) Self-assembly of alkyl chains of fatty acids in papermaking systems: a review of related pitch issues, hydrophobic sizing, and pH effects. BioResources 15(2):4591–4635.
Korehei, R., Jahangiri, P., Nikbakht, A., Martinez, M., Olson, J. (2016) Effects of drying strategies and microfibrillatedc fiber content on the properties of foam-formed paper. J. Wood Chem. Technol. 36(4):235–249. 10.1080/02773813.2015.1116012.
MacNeil, D., Sundberg, A., Vähäsalo, L., Holmbom, B. (2011) Effect of calcium on the phase distribution of resin and fatty acids in pitch emulsions. J. Dispers. Sci. Technol. 32(2):269–276. 10.1080/01932691003659270.
McLean, D.S., Stack, K.R., Richardson, D.E. (2005) The effect of wood extractives composition, pH and temperature on pitch deposition. Appita J. 58(1):52–55.
OLM, L. (1984) Pitch problems and their control in kraft mills using hardwoods from temperate and tropical zones. Appita J. 37(6):479–483.
Qin, M., Hannuksela, T., Holmbom, B. (2003) Physical-chemical characterisation of TMP resin and related model mixtures. Colloids Surf. A 221(1–3):243–254. 10.1016/S0927-7757(03)00146-8.
Qin, M., Hannuksela, T., Holmbom, B. (2004) Deposition tendency of TMP resin and related model mixtures. J. Pulp Pap. Sci. 30(10):279–283.
Rundlöf, M., Sjölund, A.K., Ström, H., Åsell, I. (2000) The Effects of Dissolved and Colloidal Substances Released from TMP on the Properties of TMP fines. Nord. Pulp Pap. Res. J. 15(4):256–265.
Rying, S. (1978) Groundwood mills use specialty chemicals to solve pitch problems. Pulp Pap. 52(3):177–179.
Sihvonen, A.-L., et al. (1998) Stability and deposition tendency of colloidal wood resin. Nord. Pulp Pap. Res. J. 13(1):64–67. 10.3183/npprj-1998-13-01-p064-067.
Sjöström, E. Wood chemistry – fundamentals and applications. 2nd edition. Academic Press, San Diego, USA, 1993. pp. 21–108.
Stack, K., Lee, R., Richardson, D., Lewis, T., Garnier, G. (2014) Complex formation and stability of colloidal wood resin pitch suspensions with hemicellulose polymers. Colloids Surf. A 441:101–108. 10.1016/j.colsurfa.2013.08.057.
Strand, A. The pH-Dependent Phase Distribution of Wood Pitch Components in Papermaking Processes. PhD Dissertation, Laboratory of Wood and Paper Chemistry, Dept. of Chem. Eng., Åbo Akademi University, 2013.
Strand, A., Sundberg, A., Vähäsalo, L., Holmbom, B. (2011) Influence of pitch composition and wood substances on the phase distribution of resin and fatty acids at different pH levels. J. Dispers. Sci. Technol. 32(5):702–709. 10.1080/01932691.2010.480853.
Sundberg, A., Ekman, R., Holmbom, B., Sundberg, K., Thornton, J. (1995) Interactions between dissolved and colloidal

substances and a cationic fixing agent in mechanical pulp suspensions. Nord. Pulp Pap. Res. J. 8(1):226–231. 10.3183/NPPRJ-1993-08-01-p226-231.
Sundberg, A., Holmbom, B., Willför, S., Pranovich, A. (2000) Weakening of paper strength by wood resin. Nord. Pulp Pap. Res. J. 15(1):46–53. 10.3183/npprj-2000-15-01-p046-053.
Sundberg, A., Strand, A., Vähäsalo, L., Holmbom, B. (2009) Phase distribution of resin and fatty acids in colloidal wood pitch emulsions at different pH-levels. J. Dispers. Sci. Technol. 30(6):912–919. 10.1080/01932690802646249.
Sundberg, K., Thornton, J., Ekman, R., Holmbom, B. (1994a) Interactions between simple electrolytes and dissolved and colloidal substances in mechanical pulp. Nord. Pulp Pap. Res. J. 9(2):125–128.
Sundberg, K., Thornton, J., Petterson, B., Holmbom, B. (1994b) Calcium-induced aggregation of dissolved and colloidal substances in mechanicalpulp suspensions. J. Pulp Pap. Sci. 20(11):J317–J322.
Sundberg, K., Ekman, R., Holmbom, B. (1995) Dissolved air flotation with calcium and polygalacturonic acids. Nord. Pulp Pap. Res. J. 10(3):201–203.
Sundberg, K., Petterson, C., Eckerman, C., Holmhom, B. (1996) Preparation and properties of a model dispersion of colloidal wood resin from Norway spruce. J. Pulp Pap. Sci. 20(7):J248–J252.
Swanson, J.W., Cordingley, R.H. (1956) Surface chemical studies on pitch. I. A new approach to the pitch problem in papermaking. Tappi J. 39(10):684–690.
Örså, F., Holmbom, B. (1994) A convenient method for the determination of wood extractives in papermaking process waters and effluents. J. Pulp Pap. Sci. 20(12):J361–J365.
Tammelin, T., Österberg, M., Johnsen, I.A. (2007) Adsorption of colloidal extractives and dissolved hemicelluloses on thermomechanical pulp fiber components studied by QCM-D. Nord. Pulp Pap. Res. J. 22(1):93–101. 10.3183/npprj-2007-22-01-p093-101.
Welkener, U., Hassler, T., McDermott, M. (1993) The effect of furnish components on depositability of ptch and stickies. Nord. Pulp Pap. Res. J. 8(1):223–225.
Zhang, X., Beatson, R.P., Cai, Y.J., Saddler, J.N. (1999) Accumulation of specific dissolved and colloidal substances during white water recycling affects paper properties. J. Pulp Pap. Sci. 25(6):206–210.