

Changes in extractives and wetting properties of TMP paper during ageing

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SUMMARY: TMP-based newsprint paper was submitted to accelerated ageing at 60°C for up to 7 days, natural ageing at room temperature for a year, and storage in a freezer for two years. Already after 2 days of accelerated ageing, only 20% of the original lipophilic extractives could be extracted with acetone and analysed by gas chromatography. The contact angle with water increased remarkably during accelerated ageing, already within 2 h, indicating a rapid migration of lipophilic extractives to the surface of the fibres. After this, the contact angle continued to rise slightly, and the contact angle remained high even after extraction of the paper with acetone. During this later phase the extractives are oxidised and further also polymerised, thus preventing their extraction. Similar changes were observed also in paper stored at room temperature (natural ageing), and even in paper stored in a freezer. For pre-extracted paper, the contact angle decreased, verifying that the extractives play the key role in the so-called self-sizing of paper during storage. To manage and control the surface and printing properties of paper, appropriate attention should be paid to the amount and composition of extractives and to the storage conditions, especially for paper made from mechanical pulps.

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Paper produced from mechanical pulp, so-called wood-containing paper, contains almost all of the original wood components. Lipophilic extractives, also called wood resin or wood pitch, are causing many problems in papermaking. The lipophilic extractives are hydrophobic substances that can be extracted from wood or paper with various organic solvents such as hexane or acetone. Spruce wood, which is primarily used in mechanical pulping, contains about 1% of lipophilic extractives that are mainly composed of free fatty acids, resin acids, sterols, steryl esters and triglycerides (Ekman, Holmbom 2000). Most of the fatty acids are

unsaturated, containing 1-3 double bonds. The steryl esters and triglycerides are esters of sterols or glycerol with fatty acids.

During production of mechanical pulp, the extractives are to a large extent dispersed in the water phase as colloidal droplets, with a size of about 0.1-2 µm (Sundberg et al. 1994). Part of the extractives, however, remains attached to the fibres and fines and are retained in the paper. Aggregated pitch droplets are also retained. Aggregation depends on the process conditions and the added chemicals such as polymers or electrolytes. The most severe problems caused by extractives in papermaking originate from uncontrolled aggregation and formation of sticky deposits leading to web breaks and spots in the paper.

The lipophilic extractives can influence the sorption of water and other solvents and consequently, affect the printability of the paper. Unsaturated extractives can be oxidized during wood storage and further during pulping, bleaching and papermaking, and in particular during storage of the paper. The oxidized products are generally more hydrophilic, but degradation products can cause odour and taste problems (Holmback et al. 2007). It is also known that extractives in pulp and paper can migrate and accumulate on fibre surfaces during storage, in this way increasing the hydrophobic character of the paper surface (Swanson, Cordingly 1959; Hubbe 2006). This phenomenon is called self-sizing. The occurrence, mechanism and extent of self-sizing is influenced by many parameters in paper production, such as pH, bleaching agents used or presence of metals (e.g. aluminium) (Zhuang et al. 1997; Ness, Hodgson 1999; Hodgson, Ness 2002). In wood-containing paper, resin and fatty acids have been stated to be responsible for the self-sizing phenomenon due to their ability to bond with fibres through ester bonds (Hodgson, Ness 2002). Self-sizing can also occur in bleached chemical pulps. Here it is attributed to non-saponifiable extractives that can be removed by acetone, indicating no covalent bonding; hence the mechanism is different than for extractive-rich papers. The second mechanism might, however, also happen in wood-containing paper.

Recycled paper is a raw material of increasing importance. Recycled paper, however, also contains adhesives, coating binders, ink residues and chemicals added during deinking, beside the fibres

and the extractives especially from paper grades containing mechanical pulp (Blanco et al. 2002). It is believed that the main reason for poor deinking of uncoated paper is ageing of the ink (Haynes 2000), but the ageing of extractives can also play an important role. Less attention has been given to the base paper itself; however, old newsprint paper shows the highest fibre loss during flotation deinking (Deng 2000).

Many studies on paper permanence have been done by accelerated ageing at elevated temperatures (Wilson et al. 1955; Browning, Wink 1968; Luner 1969). A wide range of paper properties have been measured, such as folding, tearing, tensile strength, pH, colour, cellulose types (alpha, beta, gamma) or water-soluble acidity. Accelerated ageing tests were criticized in the past for poor prediction of physical properties (Bansa, Hofer 1989; Shahani 1995). This criticism should probably be carried over to chemical properties as well. However, accelerated ageing is still a relevant technique to assess the behaviour of such complex materials as paper. Standard procedures for accelerated ageing are using temperatures of 80 to 150°C at different relative humidity levels (e.g. ISO 5630-1, 5630-3, SCAN-CM 32:78). The higher the temperature the greater is the risk of alteration/degradation of sensitive components, especially the extractives.

In this study, we applied an old standard method for accelerated ageing (DIN 54606-1, -2) with a temperature of 60°C. The aim of the study was to analyse the changes occurring in extractives in TMP paper during ageing at different temperatures and times, and to monitor how ageing alters the surface properties of the paper by measuring the contact angle with water.

Materials and Methods

TMP-based newsprint paper with a grammage of 45 g/m² was obtained from a Swedish paper mill. It was produced from 100% spruce (*Picea abies*) thermomechanical pulp. During the course of the study, the TMP paper was stored in black sealed polyethylene bags in a freezer at -18°C ± 3°C. The dry mass content was determined with an electronic moisture analyser (Sartorius MA 30) at 105°C. For the determination, one paper sheet was used parallel to papers submitted to ageing or extraction.

For accelerated ageing, small sheets of the TMP paper were placed in an oven with circulating air at 60°C ± 3°C according to DIN 54606-1 and -2 for 0 (reference sample), 15, 60, 120 (2 h), 240 (4 h), 1020 (17 h), 2880 (2 days) and 10800 min (7 days). The relative humidity varied between 23 and 30%. Care was taken to avoid contamination of the paper surface.

Natural ageing was performed by keeping TMP papers hanging in closed cardboard boxes in darkness, to prevent light-induced oxidation, for up to 332 days, at ambient temperature and relative humidity. TMP paper was also stored in a freezer at -18°C ± 3°C for about two years.

The treatments and determinations done on the TMP paper are outlined in Fig 1.

Analysis of extractives

Small sheets, weighing between 0.4 and 1.6 g, were extracted in Soxhlet extractors with acetone:water (9:1 by vol.) for at least 20 cycles. The extract was filtered on a glass fibre filter and diluted. Internal standards were added as an MTBE solution (0.02 mg/mL). Three parallel samples for each point were analyzed. Standard deviation was between 4 and 10 %. The contents of free fatty acids (FA), resin acids (RA), sterols (S), lignans, steryl esters

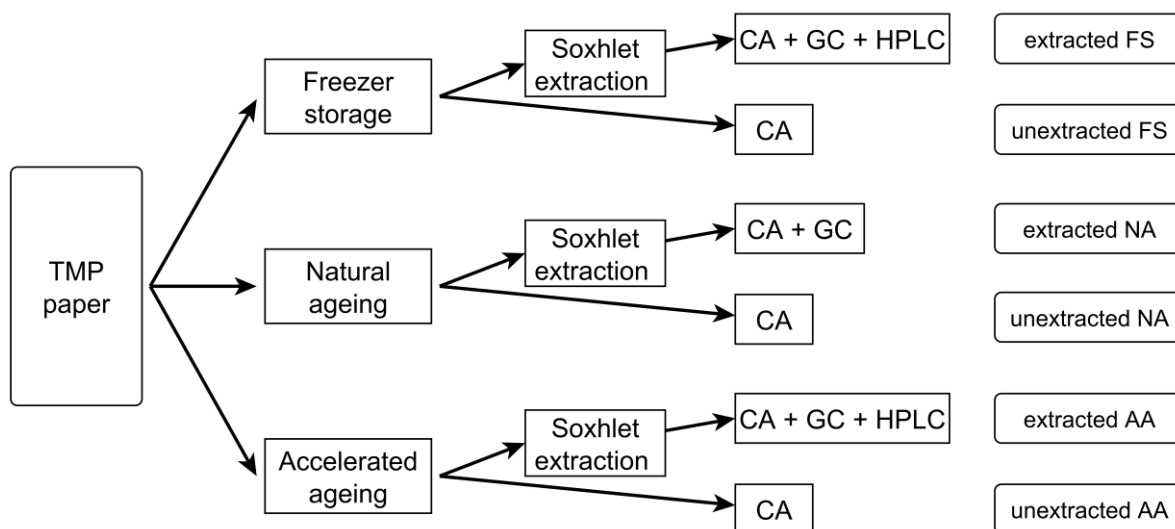


Fig 1. Scheme of treatments and determinations of TMP papers. CA: contact angle, GC: gas chromatography, HPLC: liquid chromatography, FS: freezer storage, NA: natural ageing, AA: accelerated ageing.

(StE) and triglycerides (TriG) were determined after silylation by gas chromatography (GC) using both a short and a long column. The internal standards used are heneicosanoic acid (S1), betulinol (S2), cholesteryl heptadecanoate (S3) and 1,3-dipalmitoyl-2-oleyl-glycerol (S4) (Örså, Holmbom 1994).

The extractives were analysed also by high-pressure liquid chromatography with a size exclusion column (HPLC-SEC). The acetone extracts were dried in a stream of nitrogen at 40°C, dissolved in THF, and filtered through a syringe filter before injection in a HPLC-SEC instrument (Shimadzu), using THF as eluent, a Sedere LT-ELSD detector and 2 x Jordi Gel DVB 500A (300 mm x 7.8 mm) column. Two different length guard columns have been used (7.5 x 4.6 mm in first analysis and 50 x 7.8 mm in later ones).

Contact angle determination

The wetting properties of paper were assessed by contact angle (CA) measurements. CA was determined with distilled water using a CAM 200 Optical Contact Angle Meter (KSV Instruments, Finland). The volume of the water droplet was 3.5 µl. The contact angle was determined at least at five different positions on the paper, always in the same machine direction of the paper. From the contact angle kinetic curves, contact angle values at 0.6 s were chosen. At this point of time the water droplet had reached a quasi-equilibrium and the process of accelerated absorption had not yet started.

Results and discussion

Changes in extractives during ageing

Accelerated ageing

Ageing of paper depends on the surrounding conditions, mainly temperature and humidity (Luner 1969). In this work, heat treatment of papers was used to accelerate ageing. The DIN standard suggests that heat treatment at 60°C for 7 days corresponds to ageing in room temperature for 3–12 months.

The total amount of extractives, that could be extracted from the paper sheets with acetone:water (9:1) and analysed by GC, increased slightly during the first 60 min of accelerated ageing (Fig 2). This might be due to migration of extractives, facilitating the extraction. However, the amount of extractible extractives in paper decreased significantly after 2–4 h, and after 17 h only about 20% of the extrac-

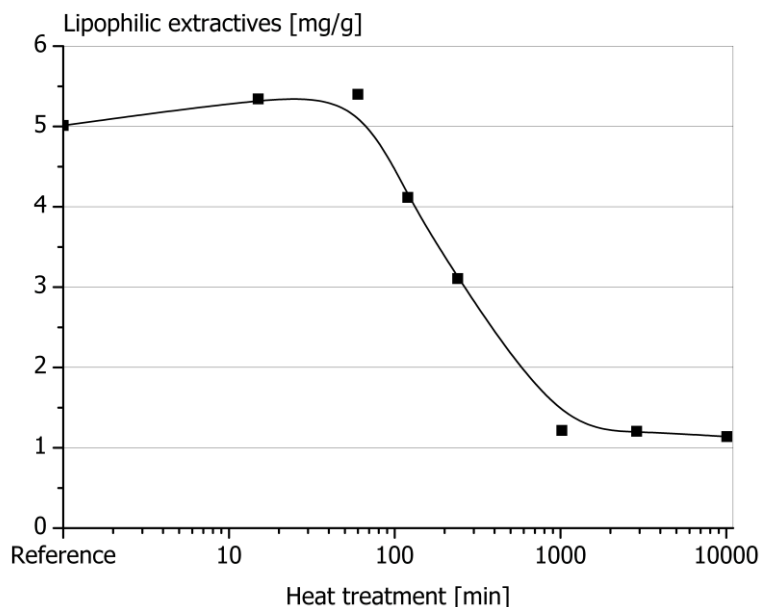


Fig 2. Amounts of lipophilic extractives in TMP paper after accelerated ageing, determined by extraction with acetone:water (9:1) and GC analysis.

tives could be removed and detected by GC analysis.

There was a difference in the behaviour of unsaturated and saturated fatty acids during ageing. After 4 h of accelerated ageing, the content of unsaturated fatty acids (18:3, 18:2 and 18:1) that could be analysed was 78% of the original value, while 84% saturated fatty acids could be analysed (Table 1). After 7 days, only 23% of the unsaturated fatty acids could be analysed while 38% of the saturated fatty acids could be extracted and identified. The decrease in unsaturated fatty acids is most likely due to their oxidation and further polymerisation. The saturated fatty acids were more stable against oxidation, since they do not contain any double bonds. Nevertheless, the amount of saturated fatty acids also decreased significantly during accelerated ageing. A possible explanation to this disappearance of saturated fatty acids is that the acids are somehow bound to the paper, eventually through ester bonds with hydroxyl groups in the paper (Swanson 1978; Hodgson, Ness 2002).

About 70% of the initial amount of resin acids could be analysed after 4 h of accelerated ageing but only 38% after 17 h (Table 1). The amount of individual resin acids varied a lot in the paper. After 7 days, 28% of isopimaric acid (IP), 31% of sandaracopimaric acid (Sa), 27% of pimaric acid (P) could be analysed compared to 47% of dehydroabietic acid (DeAb). The structure of dehydroabietic acid includes an aromatic ring, which makes this acid more hydrophilic and also more stable against oxidation or polymerization than other resin acids.

Table 1. Extractives in TMP paper after accelerated ageing, extracted with acetone:water (9:1) and analysed by short and long column GC. sFA: saturated fatty acids (16:0, 17:0, 18:0, 20:0, 22:0, 23:0), uFA: unsaturated fatty acids (18:1, 18:2, 18:3), RA: resin acids, St.: sterols, TriG: triglycerides, StE: steryl esters, Lig.: lignans, Sa: sandaracopimaric acid, P: pimaric acid, IP: isopimaric acid, DeAb: dehydroabietic acid, Ab: abietic acid.

Time	Extractives [mg/g]						
	sFA	uFA	RA	St	TriG	StE	Lig
0 min	0.26	0.31	0.93	0.13	2.10	1.01	0.21
15 min	0.26	0.34	1.00	0.14	2.25	1.06	0.26
60 min	0.26	0.35	1.01	0.14	2.21	1.12	0.29
4 h	0.22	0.24	0.74	0.11	0.91	0.63	0.20
17 h	0.15	0.13	0.36	0.05	< 0.01	< 0.01	0.19
2 days	0.12	0.09	0.35	0.04	< 0.01	< 0.01	0.23
7 days	0.10	0.07	0.31	0.04	< 0.01	< 0.01	0.24

Time	Resin acids [mg/g]						
	Total	Sa	P	IP	DeAb	Ab	
0 min	0.94	0.07	0.03	0.20	0.34	0.15	
15 min	1.00	0.08	0.03	0.21	0.36	0.16	
60 min	1.01	0.08	0.03	0.22	0.40	0.14	
4 h	0.74	0.06	0.02	0.15	0.33	0.09	
17 h	0.36	0.03	0.01	0.06	0.20	0.05	
2 days	0.35	0.02	0.01	0.06	0.19	0.03	
7 days	0.31	0.02	0.01	0.06	0.16	0.04	

Abietic acid was especially sensitive to oxidation, only 18% could be analysed after 7 days. Abietic acid and other related abietic-type acids can also be converted to dehydroabietic acid during oxidative conditions.

About two thirds of the extractives in the fresh TMP paper were steryl esters and triglycerides (Table 1). After 4 h of heat treatment, 62% of the steryl esters, but only 43% of the triglycerides could be analysed. After 17 h, and longer, only very small peaks could be seen in the chromatogram where triglycerides and steryl esters typically occur (Fig 3). Only about 3% of the original steryl esters and triglycerides values could be detected after accelerated ageing. The decrease in extractives can be due to oxidation and polymerization (cross-linking) of the components. The extractives may also be attached to the paper through radical formation, thus preventing their extraction. A further possibility is that the components

are oxidized and degraded and can therefore not be detected by GC analysis.

The lignans in the sheets were not affected at all by the heat treatment (Table 1). The lignans are antioxidants and are therefore more stable. They may even inhibit the oxidation of the lipophilic extractives (Holmback et al. 2007).

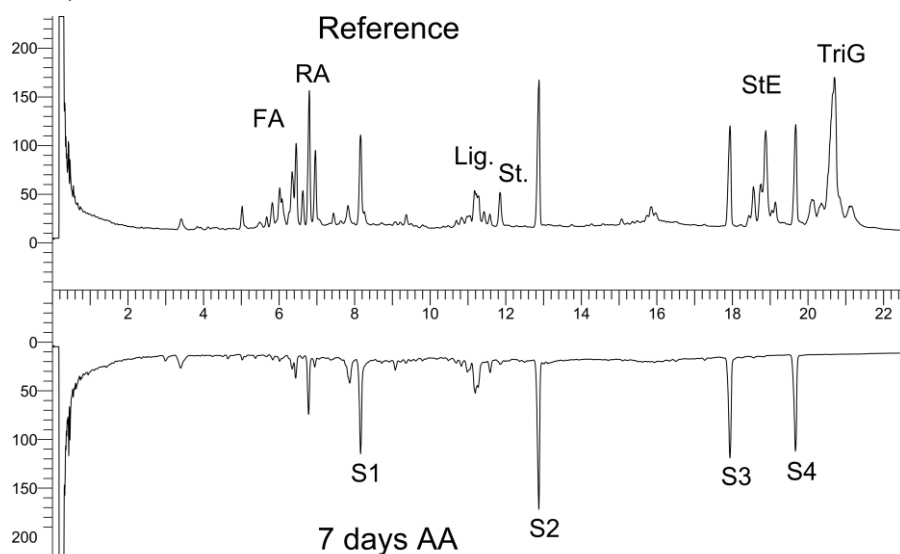


Fig 3. GC of acetone extracts of TMP paper on a short column of original paper (reference) and paper after 7 days of accelerated ageing (AA). S1 – S4: internal standards. FA: fatty acids, RA: resin acids, Lig.: lignans, St.: sterols, StE: steryl esters, TriG: triglycerides.

Natural ageing and freezer storage

Ageing of the paper sheets at room temperature (natural ageing) or storing paper in a freezer also caused changes in the extractives (Table 2). Already after 25 days, the extractives had decreased. The amount of saturated fatty acids decreased only slightly, even up to 332 days of natural ageing. The amount of unsaturated fatty acids and sterols, however, decreased significantly already during 25 days at room temperature. The steryl esters and triglycerides had disappeared almost completely already after 25 days and even after storing in a freezer for 2 years. The steryl esters and triglycerides seem to be particularly sensitive to oxidation and other reactions during storage.

The amount of resin acids decreased during the first 25 days, but did not change much after that. Oxidised products of resin acids, i.e. a complex

mixture of oxo- and hydroxy-derivatives, gradually appeared during natural ageing and were observed also after freezer storage.

Analysis of extractives by HPLC-SEC

The extract of fresh TMP paper analysed by HPLC-SEC shows four distinct peaks, mainly consisting of triglycerides, steryl esters, fatty acids, and resin acids (Reference in Fig 4A). After accelerated ageing for 7 days, the extract exhibited a very different profile (Fig 4B). The triglycerides and steryl esters had disappeared, probably due to oxidation and further degradation, and polymerization (cross-linking) so they no longer could be extracted. The SEC profile of the extract of paper stored for 2 years in the freezer was similar to the accelerated aged paper, verifying that extensive changes in extractives can take place also at very low temperatures (Fig 4C).

Table 2. Extractives in TMP paper after natural ageing and storage in a freezer, extracted with acetone:water (9:1) and analysed by long (and short) column GC. Other RA: oxo- and hydroxy-resin acids. For abbreviations see Table 1 and Fig 1.

Time	Extractives [mg/g]						
	sFA	uFA	RA	Other RA	St	TriG	StE
Reference	0.26	0.31	0.94	< 0.01	0.13	2.10	1.01
2 years FS	0.25	0.18	1.06	0.19	0.11	< 0.01	< 0.01
25 days NA	0.23	0.10	0.58	0.25	0.05	< 0.01	< 0.01
197 days NA	0.21	0.07	0.56	0.27	0.05	< 0.01	< 0.01
332 days NA	0.22	0.06	0.61	0.32	0.03	< 0.01	< 0.01

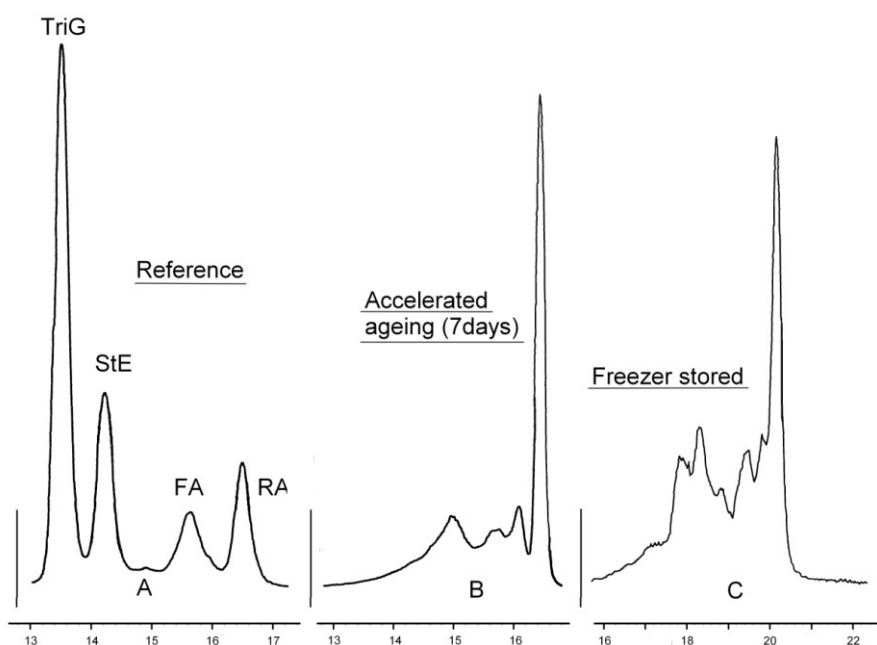


Fig 4. HPLC-SEC chromatograms of extract from fresh TMP paper (A), paper submitted to accelerated ageing at 60°C for 7 days (B) and paper stored in the freezer at -18°C for 2 years (C). TriG: triglycerides, StE: steryl esters, FA: fatty acids, RA: resin acids. C was done with a longer guard column, hence the difference in the time scales.

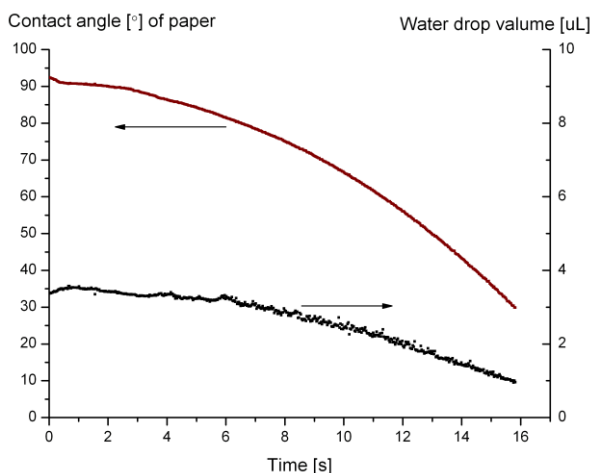


Fig 5. An example of a kinetic curve of wetting on unextracted TMP paper, aged for 7 days by accelerated ageing.

Contact angle

The wetting properties of paper were assessed by dynamic contact angle measurements with distilled water. An example of a kinetic curve can be seen in Fig 5. To compare all samples, values of the dynamic contact angle at 0.6 s were chosen.

The dynamic contact angle of the TMP papers increased significantly during the first 2 h of accelerated ageing (*AA unextracted*) (Fig 6). After that, up to 7 days, there was only a small additional increase in the contact angle. This implies that some of the extractives were relocated fast in the paper sheets, after only 2 h at 60°C, making the paper surface clearly less hydrophilic, i.e. undergoing self-sizing (Swanson, Cordingly 1959).

The contact angle was measured also on the aged papers after extraction with acetone-water (*AA extracted*). The contact angle of extracted fresh paper was lower than that of unextracted paper, 46° and 56°, respectively, as was expected (Reference in Fig 6). After 60 min of ageing, the contact angle of extracted papers started to increase strongly, and was close to the value of unextracted papers after 7 days. This implies that the lipophilic extractives are altered and become non-extractable, probably explained by oxidation of unsaturated extractives followed by polymerisation (cross-linking). Unsaturated fatty acids are known to polymerise through oxidation forming non-soluble polymer films (Formo et al. 1979). To assess the overall role of the extractives, contact angle was also measured on papers which had been extracted before ageing. The contact angle of papers without extractives did not increase during ageing, but, on the contrary, gradually decreased slightly during ageing. This is most likely due to oxidation of carbohydrates or lignin on the paper surface, thus increasing the hydrophilic character of the paper.

For papers submitted to natural ageing at room temperature the contact angle was about 90° already after a month and reached a level of about 100° after 2.5 months. It is evident that self-sizing occurs by storing of paper even at room temperature. This should be taken into consideration in connection to paper testing, especially when testing surface properties.

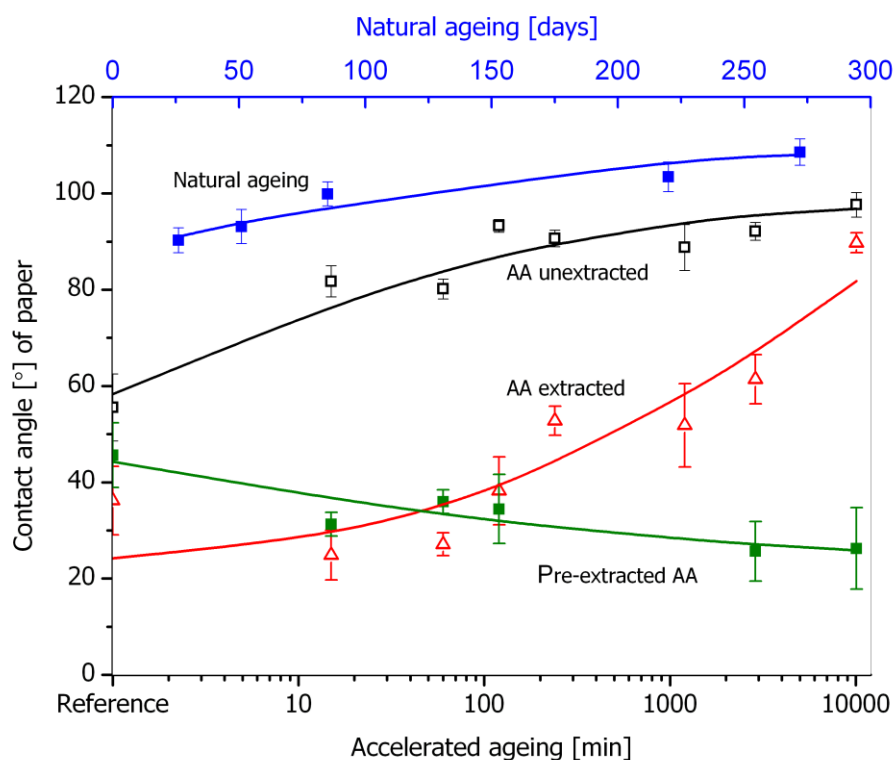


Fig 6. Dynamic contact angle values determined with distilled water. The contact angle values were read 0.6 seconds after having introduced the droplet onto the sample surface. AA: accelerated ageing.

Conclusions

The amount and composition of extractives, and the wetting properties, changed dramatically during storage/ageing of TMP-paper. Already after 2 h ageing at 60°C the contact angle is increased remarkably, probably due to migration of lipophilic extractives to the surface of paper. The amount of extractives decreases strongly after 2 days of ageing. At the same time the contact angle increases further, i.e. the paper surface becomes less wettable. This implies that the relocated extractives at the surface of paper are polymerised, after oxidation, and can no longer be removed by extraction. Polymers could not be observed in the acetone extracts by HPLC-SEC analysis, probably because they are insoluble in acetone. However, such cross-linked polymeric structures are probably formed. Similar effects on the extractives and the surface properties were also seen for paper sheets stored at room temperature and even for papers stored in a freezer at -18°C.

The migration of extractives, leading to so-called self-sizing, happens quite fast even at low temperatures. This should be taken into account in particular when studying surface properties of papers, especially for wood-containing papers containing substantial amounts of extractives.

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Literature

Bansa, H. and Hofer, H.H. (1989): Artificial aging as a predictor of paper's future useful life, *Abbey Newsletter Monograph Supplement 1*.

Blanco, A., Negro, C., Monte, M.C., Fuente, H. and Tijero, J. (2002): Overview of two major deposit problems in recycling: slime and stickies. Part II: Stickies problems in recycling, *Prog. Pap. Recycl.* 11(2), 26-37.

Browning, B.L. and Wink, W.A. (1968): Studies on the permanence and durability of paper, *Tappi* 51(4), 156-163.

Deng, Y. (2000): Effect of fiber surface chemistry on the fiber loss in flotation deinking, *Tappi J.* 83(6), 61.

Ekman, R. and Holmbom, B. (2000): The chemistry of wood resin. In Back, E.L. and Allen, L.H: *Pitch Control, Wood Resin and Deresination*, Atlanta: Tappi Press, 2000, pp. 37-76.

Formo, M.W., Jungermann, E., Norris, F.A., Sonntag, N.O.V., and Ed. Swern, D. (1979): *Bailey's Industrial oil and fat products*, 4th ed. Vol. 1, Wiley, New York, pp.796-805.

Haynes, R.D. (2000): The impact of the summer effect on ink detachment and removal, *Tappi J.* 83(3), 56-65.

Hodgson, K.T. and Ness, J.M. (2002): Self-sizing mechanism of thermomechanical pulps used in newsprint production, 56th Appita Annual Conference, 18-20 March 2002, Rotorua, New Zealand, Appita Inc. 419-427.

Holmback, J., Pranovich, A., Auer, M. and Holmbom, B. (2007): Influence of knotwood extracts on formation of hexanal in paper, The 14th International Symposium for Wood, Fiber, and Pulping Chemistry. Durban, South Africa, 25-28 June 2007, Tappsa, 4.

Hubbe, M. (2006): Paper's resistance to wetting – a review of internal sizing chemicals and their effects, *Bioresources* 2, 106-145.

Luner, P. (1969): Paper Permanence, *Tappi* 52(5), 796-805.

Ness, J. and Hodgson, K.T. (1999): The effects of peroxide bleaching on thermo-mechanical pulp self-sizing, *Nord. Pulp Paper Res. J.* 14(2), 111-115.

Örså, F. and Holmbom, B. (1994): A convenient method for the determination of wood extractives in papermaking process waters and effluents, *J. Pulp Pap. Sci.* 20, 361-366.

Shahani, C.J. (1995): Accelerated aging of paper: can it really foretell the permanence of paper, Report, Preservation Research and Testing Office, Washington, D.C, USA.

Sundberg, K., Thornton, J., Ekman, R. and Holmbom, B. (1994): Interactions between simple electrolytes and dissolved and colloidal substances in mechanical pulp, *Nord. Pulp Paper Res. J.* 9(2), 125-128.

Swanson, J.W. and Cordingly, S. (1959): Surface chemical studies on pitch. II The mechanism of the loss of absorbency and development of self-sizing in papers made from wood pulps, *Tappi* 42(10), 812-819.

Swanson, R.E. (1978): Mechanism of cellulose sizing produced by vapor phase adsorption, *Tappi* 61(7), 77-80.

Wilson, W.K., Harvey, J.L., Mandel, J. and Worksman, T. (1955): Accelerated aging of record papers compared with normal aging, *Tappi* 38(9), 543-548.

Zhuang, J., Chen, M. and Biermann, C.J. (1997): Rosin soap sizing without mordants by immersion in size solution, *Tappi J.* 80(1), 271-276

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