Prediction of breaks caused by lipophilic extractives using on-line turbidity measurement

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SUMMARY: Thermomechanical pulp (TMP) was sampled from paper mill using a mixture of deinked pulp and TMP to produce newsprint. After validation of a correlation between extractives level and associated centrifuged turbidities of TMP, the latter parameter was compared to the paper machine runnability according to stickies related break risk. The development and the implementation of an automated turbidity sensor in the paper mill permitted regular measurement of the turbidity parameter, thus allowing prediction of periods during which stickies break are more important. As expected, the results indicate that a high level of TMP turbidity and consequently a high amount of extractives involves a higher stickies break risk.

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Worldwide, the contribution of recovered paper to paper manufacturing has been steeply increasing during the last years. Environmental and social concerns have necessitated the use of recovered paper in larger volumes for paper production. One of the challenging issues when utilising the recovered paper is the amount of adhering contaminants associated with the incoming furnishes. In addition, for several years, there is substantial progress in closing water circuits to minimise freshwater consumption and reduce discharges to the environment. As a results, the concentration of dissolved colloidal substances increases (Allen 1975; Benecke et al. 2009; Miranda et al. 2009; Liang et al. 2011) in the papermaking process waters, which is critical for paper machine runnability and paper quality. Moreover, paper mills using mixtures of thermomechanical pulp (TMP) and deinked pulp (DIP) are often confronted to important problems of stickies breaks which give rise to important economic losses (Garver et al. 1997; Lenes et al. 2001; Allen 2002; Castro, Dorris 2004; Haynes 2008; Monte et al. 2010). Indeed, mills using such mixtures face increased deposition phenomena, which are believed to result from interactions occurring between some of the TMP and DIP components. This phenomenon is however not very well understood and seems to originate from precipitation of colloidal substances promoted by the physico-chemical changes induced by the pulp mixing.

Both DIP and TMP contain colloidal substances dispersed in the water phase. However, the nature and quantity of these materials is different in the two pulps. In TMP, they are mainly composed of resinous materials originating from the wood, including a mixture of different substances such as fatty acids or fatty acids esters, resin acids, sterols and steryl esters (Allen 1975; Thornton 1993). These substances are dispersed in water during the wood defibration step and form microscopic, hydrophobic droplets having diameters in the range 0.1 to 2 μm (Holmbom, Sundberg 2002). These colloidal resin particles present a negatively charged surface, which enables to maintain them in a dispersed state. In addition, colloidal resin droplets are reported to adsorb hemicelluloses dissolved in the water phase resulting in a steric stabilisation of the dispersion (Sundberg et al. 1996; Mosbye et al. 2003a; Delagoutte et al. 2007; Otero et al. 2000). In DIP, both compounds, similar to those found in mechanical pulps, and synthetic compounds such as polyvinyl acetate, polyacrylate originating from coatings or adhesives materials are found. Nevertheless, the colloidal content of DIP is generally much lower than that of TMP (Castro, Dorris 2004). This is mainly due to the presence of two loops deinking systems including two thickening steps responsible for a significant washing effect.

These colloidal materials, as such, are not so problematic during papermaking, particularly with regard to deposits formation, provided they remain stable, that is to say, finely dispersed in the water phase (Carre et al. 1995; Ekman et al. 1990). However, particular conditions can induce the destabilisation of the dispersion and lead to the agglomeration of the particles resulting in the generation of more or less tacky precipitates. This phenomenon is the cause of the formation of pitch deposits (Laudbach, Greer 1991) or secondary stickies (Carre et al. 1995) in various locations in the paper machine (formation wires, presses, drying section) and is responsible for breaks of the paper sheet during production (Guo, Douek 1996; Qin et al. 2004). There are several possible origins of colloidal materials destabilisation: changes of pH or conductivity, temperature shocks, neutralisation of the anionic charge

carried by the particles due to the addition of cationic polymer in the wet end (Carre et al. 1995). Stability of these colloidal materials is therefore a key factor which seems to be negatively affected during DIP and TMP mixing, resulting in the stickies troubles observed in paper-machines (Willför et al. 2000; Allen 2002).

The work reported here focuses on stickies problems encountered by the Norske Skog paper mill located in Golbey in the east of France using a mixture of DIP/TMP (70/30, w/w) to produce newsprint. The mill faced numerous crises of breaks attributed to the generation of stickies deposits during the papermaking operation. The amounts of macro-stickies (residual adhesives particles) in the DIP were found to be relatively low suggesting problems arising from secondary stickies formation, probably related to the destabilisation of colloidal substances contained in both TMP and DIP. Thus, the aim of this work was devoted to the identification of a process indicator able to predict the risk of breaks related to stickies. For this purpose, dissolved and colloidal materials were characterised both in nature and quantity in DIP (results not shown) and TMP during periods of good and poor runnability of the paper machine. Turbidity of TMP was investigated as a potential parameter to quantify lipophilic extractives content and consequently predict risk of breaks. Finally, an automated measurement was developed and tested regarding its ability to estimate the risk of occurrence of stickies related breaks.

Materials and Methods

Raw materials

Dithionite-bleached TMP was supplied by the Norske Skog paper mill (Golbey, France) using mainly Norway Spruce (Picea Abies) and Silver Fir (Abies Alba). The dry content was about 10% w/w and pulp was stored in a freezer until needed.

Sample preparation – lipophilic extraction

TMP samples were thawed in a 50°C bath for 2 hours. Then, pulp was manually pressed on a 150 µm sieve. The filtrate was centrifuged for 10 min at 3000 g to keep only the dissolved and colloidal fraction of samples. Supernatant obtained is lyophilised. Freeze-dried samples were then extracted with 99% GC grade methyl tert-butyl ether, MTBE (Sigma-Aldrich), using an accelerated solvent extractor Dionex ASE-200.

GC-MS analysis

Samples were analysed as trimethylsilyl derivatives using the following procedure. In a screw-capped vial, a sample of approximately 1 mg of dry extract was dissolved in 200 µl of N,O-bis-(trimethylsilyl) trifluoroacetamide containing 1% trimethylchlorosilane (Acros Organics). The solution was sonicated for about 1 min and heated at 60°C for 20 min. After evaporation of the solvent in a stream of dry nitrogen, the residue was diluted in 1 ml of anhydrous ethyl acetate. GC-MS analysis was performed on a Clarus® 500 GC gas chromatograph (Perkin Elmer Inc., USA) coupled to a Clarus® 500 MS quadrupole mass spectrometer (Perkin Elmer Inc., USA). Gas chromatography was carried out on a 5% diphenyl / 95% dimethyl polysiloxane fused-silica capillary column (DB-5ms, 30 m x 0.25 mm, 0.25 mm film thickness, J&W Scientific, USA). The gas chromatograph was equipped with an electronically controlled split / splitless injection port. The injection (1 µl) was performed at 250°C in the split mode (split flow of 40 ml/min). Helium was used as carrier gas, with a constant flow of 1 ml/min. The oven temperature program was as follows: 80°C constant for 2 min, 80°C to 190°C at a rate of 10°C/min, 190°C to 280°C at a rate of 15°C/min, 280°C to 300°C at a rate of 5°C/min and then constant for 17 min. Ionisation was achieved under the electron impact mode (ionisation energy of 70 eV). The source and transfer line temperatures were 250°C and 330°C, respectively. Detection was carried out in scan mode: m/z 35 to m/z 700. The detector was switched off in the initial 2 min (solvent delay). Compounds were identified by comparison with spectra from the NIST (US National Institute of Standards and Technology, Gaithersburg, MD, USA) mass spectral library.

Enrichment of colloidal substances in TMP process water

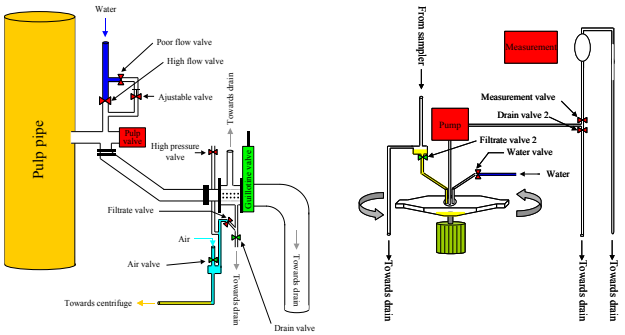
TMP at 10%w/w consistency was pressed on a 150 µm sieve to generate a filtrate. During this filtration stage, poor retention of the colloid in the fibrous web is achieved and most of them are recovered in the filtrate. A part of this filtrate was kept separate while the remaining was used to dilute fresh TMP from 10% down to 3% consistency. This diluted pulp was then filtered on a Buchner filter to form a fibre pad allowing the retention of most of the colloidal materials. The produced pad, enriched in colloids, was then diluted with the separate TMP filtrate allowing the dispersion of colloids previously recovered. The pulp was again pressed on a 150 µm sieve (filtration with low retention). The generated filtrate was then centrifuged 10 min at 3000G before determination of turbidity. This operation could be carried out several times to obtain filtrates of different turbidity.

Manual measurements of turbidity on centrifuged filtrate

Pulp was pressed on a 150 µm sieve to extract a filtrate (filtration without retention) which was then centrifuged with Sigma 3-16 centrifuge. The measures of turbidity of generated supernatant were made with a turbidimeter HACH Model 2100 P ISO.

Development of the automated turbidity measurement on centrifuged filtrate

To allow a regular follow-up of turbidity on TMP (centrifuged supernatant) of the paper mill, an automated sensor was developed. It consists in two modules: a pulp sampler and an analysis unit. The sampler, *Fig 1a*, is connected to a TMP pulp pipe. The sampler allows the generation of a filtrate from a 10% pulp consistency. A small quantity of the pulp is taken and forced, by pressure, through a tube whose wall is pierced with small



a) b)

Fig 1. a) schematic blueprint of the sampler
b) schematic blueprint of the analysis cell

holes allowing separation of fibres and filtrate. The produced filtrate is temporarily stored before being sent towards the analysis unit with airflow. Between two samplings, the system is totally cleaned with fresh water.

Then, the filtrate is centrifuged (1500 g for 8 min) and transferred by a pump into the turbidity measurement cell, *Fig 1b*. Turbidity measurement is done using a light beam obtained from a diode at 870 nm wavelength. Transmitted and 90° scattered light intensities are measured by two photodetectors. The turbidity is then given by the *Eq 1*:

$$T_c = \frac{I_{Diff}}{I_{Trans}} \qquad [1]$$

With T_c = turbidity after centrifugation, I_{Diff} = scattered intensity and I_{Trans} = transmitted intensity.

The data generated by the sensor are recorded in the mill database system.

Definition of machine runnability

The partner mill possesses a database, which records all stickies related breaks. According to the daily frequency of stickies breaks, the paper machine runnability is classified as follow:

- Good runnability = 0 to 2 stickies breaks per day
- Poor runnability = 3 or 4 stickies breaks per day
- Bad runnability = 5 and more stickies breaks per day

Results and discussion

Effect of chemical composition of lipophilic extractives on paper machine runnability

TMP lipohilic extractives were obtained from freeze dried DCS by extraction with MTBE. GC-MS analysis of extractives corresponding to periods of good runnability with less than two stickies related breaks per day, indicated the presence of numerous compounds similar to those already described in the literature (Nugent et al. 1977; Ekman et al. 1990; Mosbye et al. 2003b; Willför et al. 2000). To evaluate the effect of extractives chemical composition on the paper machine runnability, MTBE extracts of TMP collected during periods of good and bad runnability were subjected to GC-MS analysis. A comparison of chromatograms of lipophilic extractives obtained during periods of good runnability (A) or bad runnability (B) is reported in *Fig 2*. In both cases, more than 50% of compounds were identified in the mixture. These extractives are in majority fatty acids and alcohols, resin acids, terpenes, sterols and phenolic compounds. Chromatograms present very similar profiles with very few variations, which tends to indicate that TMP lipophilic compounds are very similar independently of the paper machine runnability. Thus, the chemical composition of extractives seems to have very low impact on the phenomenon of stickies breaks.

Effect of lipophilic extractives quantity on paper machine runnability

According to the results described previously, paper machine runnability did not depend on the composition of the lipophilic extractives. Other parameters should be therefore envisaged to explain the higher formation of secondary stickies or pitch at the occurrence of paper sheet breaks during periods of bad runnability. *Fig 3* describes the variation of the extractives level according to the paper machine runnability.

Several samplings of TMP pulp were made with different operating states (good, poor and bad

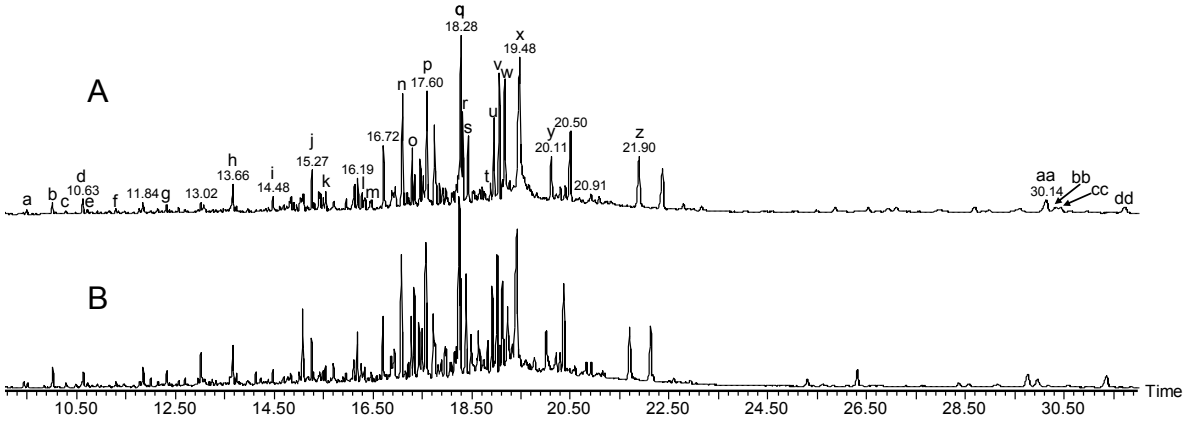


Fig 2. a. terpin ; b. nonanoic acid, TMS; c. benzaldehyde, 4-[(tri-methylsilyl)oxy]-; d. vanillin; e. myrtenoic acid, TMS; f. capric acid, TMS; g. vanillin, TMS; h. lauric acid, TMS; i. eugenol; j. 3-vanilpropanol, bis(trimethylsilyl)-; k. myristic acid, TMS; l. n-Pentadecanoic acid, TMS; m. hexadecanol, TMS ether; n. palmitic acid, TMS; o. epimanool; p. margaric acid, TMS; q.r. oleic acid, TMS; s. stearic acid; t. nonadecanoic acid, TMS; u. pimaric acid, TMS; v. sandacaropimaric acid, TMS; w. isopimaric acid, TMS; x. dehydroabietic acid, TMS; y. nonadecanol; z. 1-Eicosanol; aa. β-sitosterol; bb. stigmastanol; cc. β-sitosterol, TMS ether; dd. stigmasta-3,5-dien-7-one.

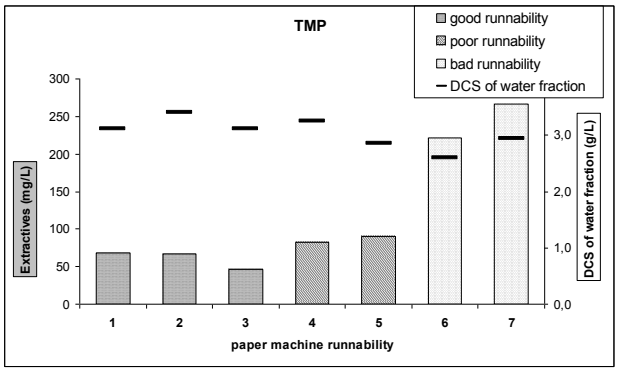


Fig 3. Extractives level according to paper machine runnability.

runnabilities) and their DCS contents determined. The measurements of dry extracts (*Fig 3* right scale) show that the quantities of DCS (≈ 3g/l) were very similar in all situations. On the other hand, the amounts of MTBE extractives (*Fig 3* left scale) in the dry extracts were very different. Particularly, there was a noticeable difference between periods of good or poor runnabilities (samples 1-5) and bad runnabilities (samples 6 and 7). The extractives contents of these last samples were very high compared to previous ones. These measurements indicate that the lipophilic extractives content of TMP pulp is a key factor influencing the phenomenon of stickies break. However, other parameters like interactions between DIP and TMP may be involved to explain the differences observed during periods of bad or poor runnability. According to these results, the development of an appropriate method to quantify lipophilic extractives during paper making process appears as a valuable tool to predict paper machine runnability.

Identification of an automatable parameter

Due to the difficulty to follow extractives level in mill, the utilisation of a simpler parameter, easy to automate online, was imperative. According to literature (Mosbye et al. 2003b; Sarja et al. 2003), the measurement of centrifuged turbidity gives a good estimation of the extractives level. Our work was primarily aimed to confirm the correlation between the centrifuged supernatant turbidity of a given sample and its extractives amount. Thus, TMP filtrates of different extractives contents were prepared and associated centrifuged supernatant turbidities were determinate. *Fig 4* shows the correlations between extractives content and the centrifuged supernatant turbidity. Results show a good correlation, indicating that centrifuged supernatant turbidity measurement could to be a reliable parameter to predict lipophilic extractives content and consequently predict the risks of stickies break. Furthermore, this measurement is also technically easier to implement on-line.

Implementation and validation of the automated turbidity measurement

According to these results, it seems relevant to envisage the use of an on-line device to measure turbidity. Such measurements can give useful information to predict and avoid stickies breaks. In order to validate that the amount of extractives contained in TMP pulp can be a predictive

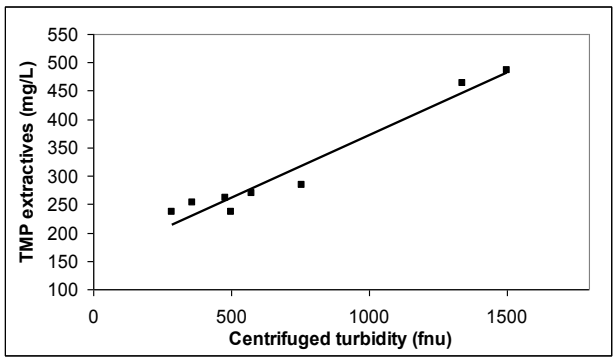


Fig. 4. Extractives level according to centrifuged turbidity of TMP samples

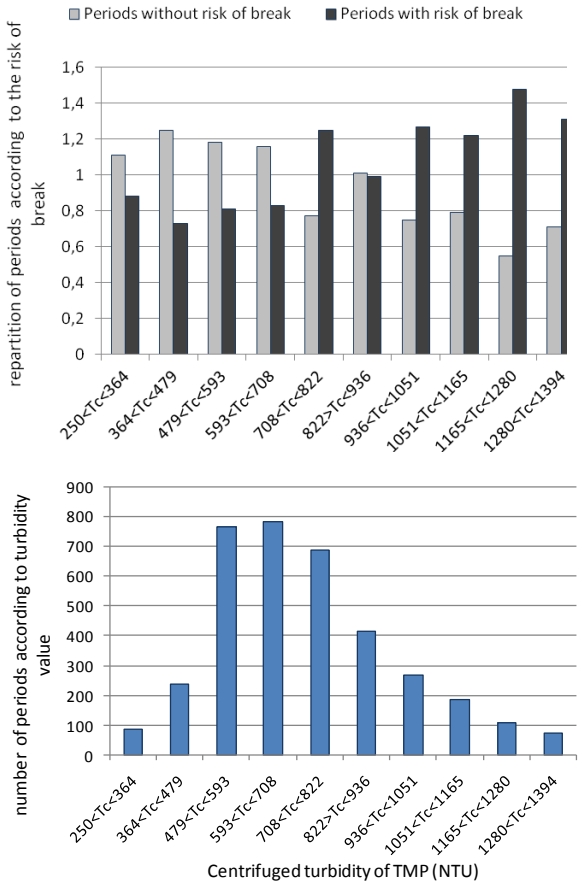


Fig 5. Correlation between turbidity level of TMP pulp and paper web break.

parameter of stickies break phenomenon, the data acquired by the turbidity sensor were analyzed and correlated to the mill paper web break. Data were analysed using a non statistical approach with the Br@incube software (ip leanware SARL). Results of this analysis are given in *Fig 5*.

This figure shows values of turbidity (bottom histogram) in relation to the risks of stickies break (top grey histograms). To achieve analysis, the stickies breaks were expressed in "risk of break" in a range of time. The average of breaks was calculated over a period of 6 hours instead of considering the breaks themselves. The stickies break risk was divided into 2 populations: one corresponding to periods without break (left grey histogram) and the other corresponding to periods with stickies breaks (right dark grey histogram). The results

indicate an increasing trend of risk of break with high turbidity level, while the periods with low risks of stickies breaks were dominant for the smaller values of turbidity. This confirms the impact of the high turbidity levels of the TMP pulp and consequently the effect of high amounts of extractives on the number of stickies breaks. However, more investigations are needed to explain the mechanism of destabilization of colloidal substances at the origin of stickies formation, which may be influenced by other parameters than the sole quantity of extractives.

Conclusion

This study highlights that extractives contained in spruce TMP pulp were quite similar to those described in the literature. More than extractives chemical composition, the extractives content of TMP pulp appeared to be a key factor resulting in stickies breaks phenomenon occurring in a newsprint machine using a mixture of DIP and TMP. Bad runnability of the paper machine seems associated to higher lipophilic extractives contents, while good runnability is associated to lower lipophilic extractives content. Due to the difficulty to follow on-line extractives content, an automated sensor was developed to allow a regular measurement of TMP pulp turbidity in mill and consequently the extractives content which is directly correlated with turbidity. The results indicated that high turbidity levels are favourable to stickies breaks risks, while low levels of turbidity resulted in lower risks of stickies breaks. Even if turbidity seems to be an important parameter responsible for stickies formation, other parameters should be involved to explain the destabilization mechanisms of colloidal substances. Indeed, high levels of turbidity do not always result in periods with stickies breaks, while low levels of turbidity lead generally to lower risks of stickies formations. The online follow-up of turbidity level could be however a valuable parameter to monitor and reduce the problems caused by stickies formations.

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