

Pitch detackification with natural and modified talcs

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ABSTRACT: Pitch deposition in pulp or in different parts of the manufacturing system can lead to a decrease in the quality of the final paper produced and to manufacturing efficiency problems. One of the methods to control pitch deposition is the use of talc. Talc acts primarily as a detackifier and must be part of the deposit to control further deposition. The effectiveness of talc as a control agent depends on its structural and surface characteristics (e.g., specific surface, surface energy, surface charge, and ratio of lyophobic to hydrophilic surface), which are related to its mineral composition and the thermal and surface treatments it has undergone. For this study, we tested five commercial talcs, corresponding to two groups of different mineralogical compositions, to determine their detackification capacity using a deposition tester developed by the Complutense University of Madrid, Spain. In this method, the quantification of the deposits is carried out by an image analysis of stainless steel collectors on which the deposit has formed. After image analysis, a qualitative analysis to determine the deposit organic fraction is carried out by gas chromatography after deposit extraction. The detackification capacity is expressed as the reduction of the deposits formed on the collectors when the different talcs at several concentrations are added to the pulp suspensions. The results show that pitch detackiness by talc addition is related to talc concentration and mineral surface properties, as for example, chlorite proportion, surface area, and surface treatment, and to the adsorption capacity of pitch on talcs. In general, the talc having the highest quantity of mineral talc presents the best detackification capability, and the detackification of all talcs studied was appreciably reduced at low proportion of addition.

Application: This study highlights the high pitch detackification capacity of five talcs with different mineralogical compositions and surface characteristics used at various concentrations.

Wood pitch is released from fibers into process water during the production of thermomechanical pulp (TMP). The dispersion of pitch takes the form of colloidal droplets with a hydrophobic core, composed mainly of steryl esters and triglycerides, and a thin surface layer of sterols, fatty acids, and resins acids [1-3]. The changes in pH and salt concentration (ionic force) produced during bleaching, the oxidant treatment stages, and the extraction stages destabilize the dissolved and colloidal matter from the pulp extractive, forming sticky deposits called “pitch” [4]. The characteristics of the wood pitch, including hydrophobicity, deformability, tackiness, and low surface energy, can cause deposition problems, decreasing the final product quality and papermaking efficiency [5]. The tendency of organic material to form deposits is related to its nature, and therefore to its tackiness. Tack is defined as the stickiness of a particle, qualitatively determined by touch. More specifically, tack is the energy required to separate two particles not permanently bound together. One of the technologies commonly used to control pitch deposition today is detackification. Detackification technology involves eliminating the tackiness associated with the pitch, but also can involve stabilizing pitch particles to prevent their agglomeration [6,7].

Talc is one of the additives used traditionally for pitch control [7]. Guará [8] proposed that, in the mechanism of detackification, talc becomes incorporated in pitch deposits, which causes a decrease in tackiness and inhibits further de-

position. Guará theorized the existence of a second step after the adsorption of pitch onto talc [8]. This second step occurs when talc particles with adsorbed resins form “sandwich structures” with very thin intercalates constituting a sort of nano-composite material. The detackification occurs firstly through immobilization of the sticky materials [9].

“Talc” describes a mineral in a generic way; in the market it is possible to find talc products with different mineralogical compositions and surface properties. Talc is a mineral composed of hydrated magnesium silicate with the chemical formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. The main or basal surfaces of this elementary sheet do not contain hydroxyl groups or active ions, which explains talc’s hydrophobicity and inertness. Highly lamellar talcs have large, individual platelets, whereas platelets are much smaller in a compact (microcrystalline) talc. The elementary sheets are stacked on top of one another, like flaky pastry, and because the binding forces (van der Waals forces) linking one elementary sheet to its neighbors are very weak, the platelets slide apart at the slightest touch, giving talc its characteristic softness [10-12]. Various studies have reported the water contact angle to be 66° – 90° [7].

For this paper, we studied the capacity of different talcs, modified or not, for use as pitch detackification agents by measuring the deposition tendency of water-containing extractives. For this, calcium chloride was added to approach to the actual destabilization conditions that occur as a consequence of the presence of Ca^{2+} in process waters in pa-

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permaking. The deposits were measured with a deposition tester developed by the Complutense University of Madrid (UCM) research group in Spain. The efficiency of the talcs on extractives reduction was measured by gas chromatography (GC) analysis.

EXPERIMENTAL

Characterization of talcs

Five commercial talcs were used for this study. The talcs correspond to two groups of different mineralogical compositions: A, with high concentrations of talc and some dolomite; and B, with medium concentrations of talc and chlorite. The A group is formed by a natural talc (A) and superficially modified anionic (AT) and cationic (AK) talcs. The B group is formed by a natural anionic talc (B) and modified cationic talc (BK). These talcs were characterized by X-ray diffraction, scanning electron microscopy, and analysis by dispersive energies, zeta potential, and surface area measurements. The analyses showed that the type of chlorite present in talc B was clinocllore. The zeta potential was determined with a particle charge detector (at pH 7) and particle size distribution was determined with a particle size analyzer [13]. **Table I** shows the mineralogical composition measured by X-ray diffraction of both talc groups. **Table II** summarizes the physical properties. Mineralogically, the main component in all of them is talc, although the group B talcs include a high proportion of chlorite.

Preparation of the extractive dispersions

The colloidal dispersions of extractives were obtained by extraction of *Eucalyptus globulus* wood sawdust in pilot plant scale with acetone (30 L), evaporation of the solvent, and re-extraction with hexane to increase the selectivity of lypophilic compound extraction, according to SCAN-CN 50:93 [14]. Subsequently, the solvent was evaporated in a rotary evaporator. Colloidal dispersions were obtained after alkaline hydrolysis with potassium hydroxide solution and a new extraction of lipophilic compounds with hexane. A concentrated solution of pitch in acetone was obtained by evaporation to a 3000 mg/L concentration. Pitch dispersions were obtained by dilution of this concentrated solution with distilled water.

Preparation of the talc suspensions

Talc suspensions were prepared at 5 wt% in ultrapure (Milli-Q) water and stirred overnight at the natural pH to be used as slurry.

Deposition experiments

The depositions experiments were carried out with the deposition tester developed by the UCM Research Group and previously described in more detail [15-18]. The tester consists of an axial flow propeller, a rotor assembly with open ends, and a cylinder support with removable steel foils as collector surfaces. The propeller creates a flow parallel to the outer steel foil. The flow mechanism transfers the sticky material to the

	Group A		Group B		
	A	AT	AK	B	BK
Talc (1), Mg ₃ Si ₄ O ₁₀ (OH) ₂	85.4	82.4	94.3	61.7	55.7
Talc (2), Mg ₃ Si ₄ O ₁₁ nH ₂ O	13.2	16.0	-	-	-
Dolomite, CaMg(CO ₃) ₂	1.3	1.5	4.2	-	-
Calcite, CaCO ₃	-	-	0.3	-	-
Quarz, SiO ₂	0.1	1.5	0.3	0.5	0.4
Clinocllore, Mg ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈	-	-	-	37.0	42.1
Ferrous and calcium oxide, Ca ₂ Fe ₇ O ₁₁	-	-	-	0.9	1.8

I. Mineralogical composition of talcs (%).

	Group A		Group B		
	A	AT	AK	B	BK
Talc					
Specific area BET (m²/g)	12	14	12	8.5	8.5
Density (g/cm³)	2.80	2.78	2.80	2.78	2.78
Hardness (Mohs)	1	1	1	1-2	1-2
Zeta potential (mV)	-69	-69	+45	-55	+30
H ₂ O adsorbed (%)	15 at 120°C	<1	1 at 120°C	>0.5	>0.5
pH (dispersion 10%)	9	8.5	9	9.5	9.5
d ₅₀ (µm)	4.2	4.5	4.2	3.5	3.5

II. Physical properties of talcs.

outer cylinder surface. On the inner cylinder surface, depositions occur via an impact mechanism.

The experiments were carried out at 50°C for 2 h at a rotor rotation speed of 250 rpm. The beaker was filled with 1.8 L of pitch dispersion and contained about 50 mg/L of extractives. The experiments were carried out at pH 8, at talc concentrations of 50, 100, and 200 mg/L. We conducted a trial without talc addition as a control against which to determine the performance of the different talcs. Calcium chloride was added 1 min after the talc addition to obtain the maximum amount of pitch aggregates to study in the deposition. Pitch droplets are susceptible to an electrolyte-induced aggregation with Ca^{2+} that led to the formation of deposits. The concentration of Ca^{2+} added was 10 mmol/L of Ca^{2+} [19, 20].

When the deposition experiment was finished, the stainless steel foils with the deposits were withdrawn from the cylinder support and dried at room temperature before scanning with a commercial computer flatbed scanner at 600 dpi. The resulting scanned images were analyzed using the image analysis system "Stickies Measurement System," developed by the British Research Centre, PIRA International, and the UCM. The results are expressed as follows: covered area of deposits expressed as square micrometers (mm^2), mm^2 of deposits per square meter (m^2) of surface (ppm), and percentage of covered area of deposits (%). In this paper, the sum of the internal and external deposits, expressed in mm^2 , (total deposits) are shown, representing the deposition on the entire collector. Therefore, the reduction of the depositability by image analysis is obtained by Eq. (1):

$$\text{Reduction (\%)} = \frac{\text{Total deposits without talc (mm}^2\text{)} - \text{Total deposits with talc (mm}^2\text{)}}{\text{Total deposits without talc (mm}^2\text{)}} \times 100 \quad (1)$$

GC analysis

The analysis of extractives was carried out using a GC with a flame ionization detector, coupled with an autosampler, and with a capillary injector for liquids. The capillary column was 15 m long and 0.53 mm in diameter; film thickness was 0.15 μm . The chromatograph was programmed from 100°C (0.5 min) to 340°C at a rate of 12°C/min. The injector was programmed from 100°C (0.5 min) to 340°C at 200°C/min. After the experiments, the steel foils were removed and extracted with a solution of methyl tertiary-butyl ether (MTBE) (40 mL) and acetic acid (1 mL) in an ultrasonic bath. Lypophilic extractives were silylated and determined by GC [21]. Lypophilic extractives in water were determined by extraction with MBTE and analysis by GC.

To correlate the deposits obtained by the deposition rotor with their composition, the results of the analyses by GC were referred to the deposits obtained in the foils, from the corresponding blank values, and according to the following equation:

$$\text{SCG (mm}^2\text{)} = \frac{\text{BSI (mm}^2\text{)}}{\text{BSG (mg)}} \times \text{SMG (mg)} \quad (2)$$

where

SCG = total deposits measured by GC in mm^2

BSI = total deposits without talc measured by image analysis

BSG = total deposits without talc measured by GC

SMG = total deposits with talc measured by GC

The blank surface measured by image analysis (BSI) corresponds to the measures of the foils surface covered with pitch, in the absence of talc. These values are the most reliable because of their reproducibility, two tests per talc series, and the lack of interference by talc deposition. The blank mass measured by GC (BSG) was obtained from the analysis of the blank by GC. The sample mass by GC (SMG) was obtained by means of the GC analysis of each of the samples studied.

From Eq. (2), we assumed that the pitch deposits measured by image analysis are proportional to the mass of pitch measured by GC. This hypothesis is exact when the average thickness of the layer deposited is constant in all the foils analyzed. Therefore, if the surface covered by pitch is proportional to the mass, the relation between blank covered surface and pitch mass of the blank can be expressed by the following proportionality constant:

$$K = \frac{\text{BSI (mm}^2\text{)}}{\text{BSG (mg)}} \quad (3)$$

According to this hypothesis, Eq. (2) can be reformulated as:

$$\text{SCG} = K \times \text{SMG} \quad (4)$$

With this mathematical treatment, the total deposits measured by GC are expressed as square millimetres (mm^2). On the other hand, the reduction of the depositability measured by GC is obtained from Eq. (5):

$$\text{Reduction (\%)} = \frac{\text{Deposited pitch without talc (mg m}^{-2}\text{)} - \text{Deposited pitch with talc (mg m}^{-2}\text{)}}{\text{Deposited pitch without talc (mg m}^{-2}\text{)}} \times 100 \quad (5)$$

As a summary, **Fig. 1** shows the schematic representation of the experiments.

RESULTS AND DISCUSSION

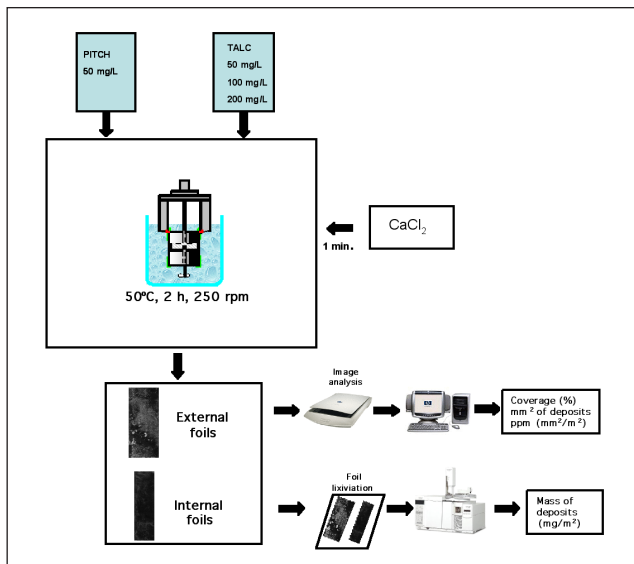
Table III shows the results of the extractive characterization and the composition of the lypophilic fraction determined by GC. The extractive content of the Eucalyptus globulus wood used in these experiments was very low compared with other species. This justifies the need to use a pilot plant extractor.

The composition of the lypophilic fraction was 33% of ste-

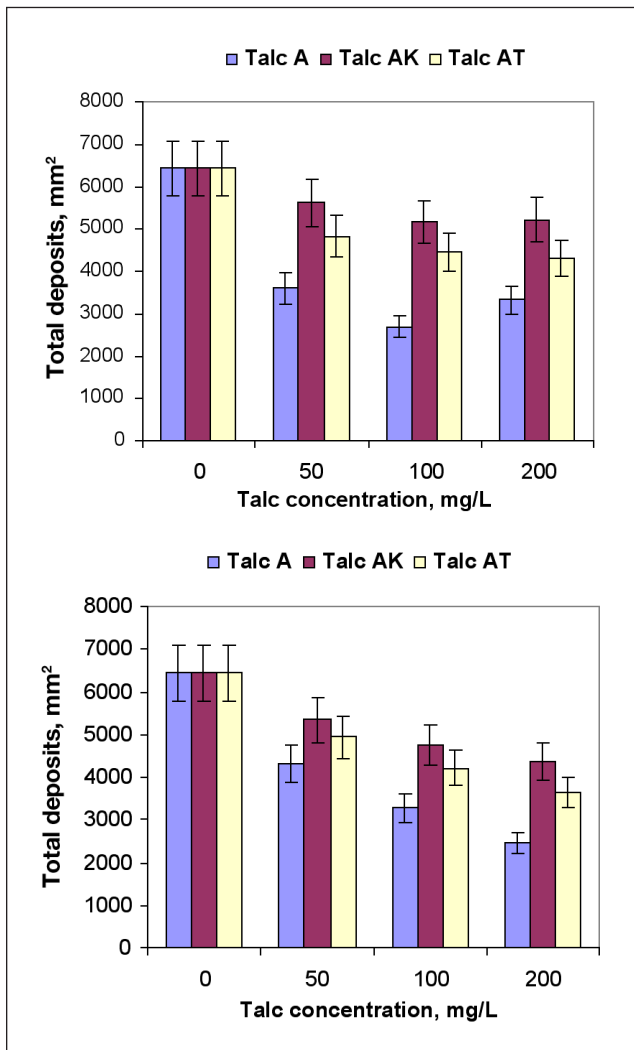
Total Extractives (%)	Total Lypophilic Fraction (%)	Lypophilic Fraction on Total Extractives (%)
0.75±0.5	0.10	13.50

III. Composition of Eucalyptus globulus extractives.

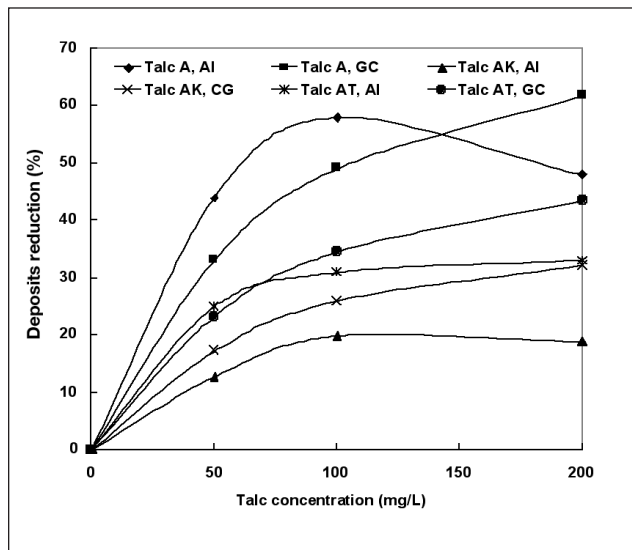
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1. Experimental protocol.



2. Total deposits obtained with the addition of group A talcs by image analysis and gas chromatography (GC).



3. Deposition reduction versus talc concentration by image analysis and by GC for group A talcs.

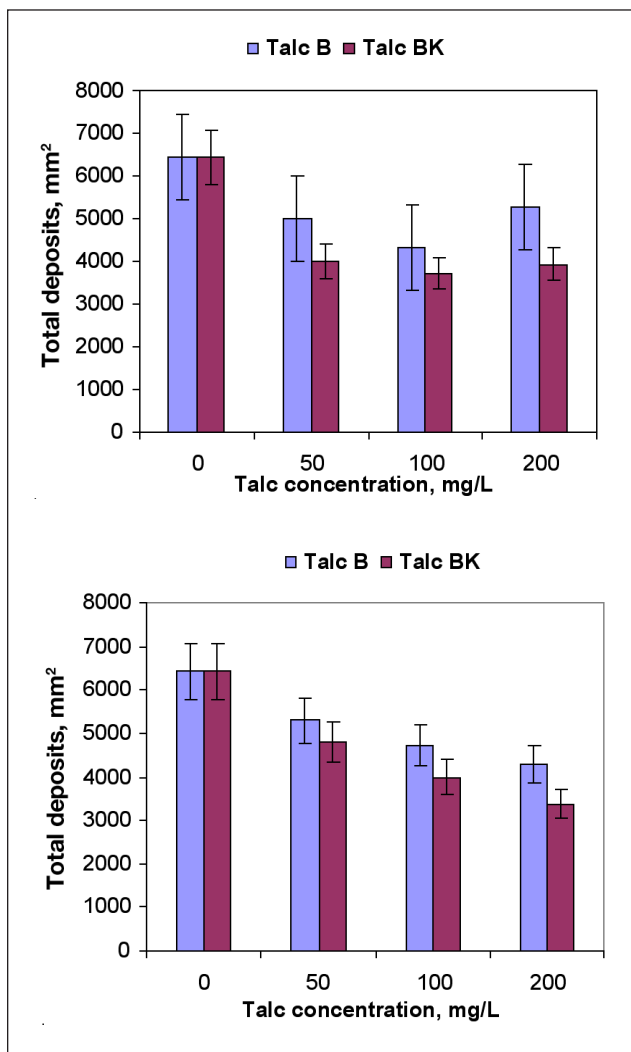
rol esters, 8% of triglycerides, 17% of fatty acids, and 42% of sterols [13]. **Figure 2** shows the total deposit obtained with the addition of different talc concentrations of the A group, by image analysis and by GC, respectively. In all cases, the amount of deposits decreases with respect to the blanks when talc was added.

The results obtained with the two deposits determination techniques used in the study showed slightly different trends. The deposits obtained by the deposition rotor and analyzed by image analysis show a slightly higher degree of deposition than those obtained by GC analysis. The results measured by GC show a regular decrease of the deposits with the addition of talcs. Both image analysis and GC analysis show that the lowest amount of deposits was achieved with talc A. The best performance obtained with this talc was at 100 mg/L, according to the measurements performed with image analysis, and 200 mg/L when measured by GC. **Figure 3** shows the difference between the reduction results obtained by image analysis and by GC for talc A. The ordinate axis represents the decrease of the property considered as a reduction percentage of the formed deposits or as a percentage of pitch retained by adsorption on talc.

The talc A deposits reductions measured by image analysis present a maximum of 57% at 100 mg/L of talc concentration and decrease at 200 mg/L. A similar tendency was shown in all talcs when depositability reduction was determined with image analysis, except with talc AT, which showed a slight increase in the reduction of deposit at 200 mg/L.

These results indicate that the initial hypothesis that the mass of extractives are proportional to the covered surface is only an approximation; the main deviation from this hypothesis could be the result of talc deposition.

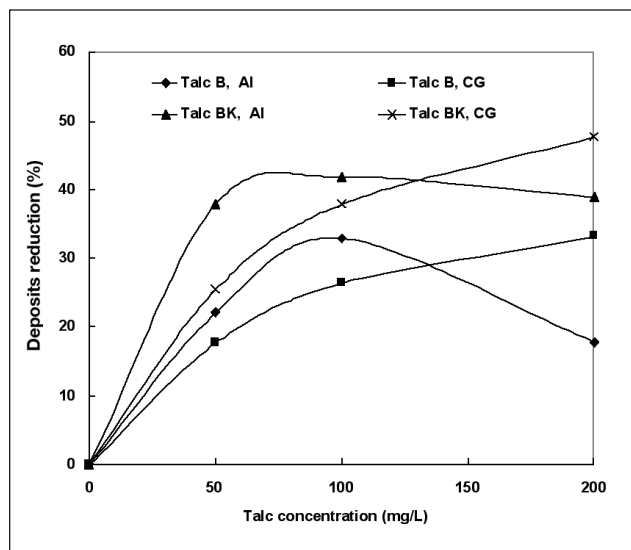
The highest detackification capacity was shown by talc A, high talc mineral grade, with a deposits reduction effective-



4. Total deposits obtained with the addition of group B talcs by image analysis (left) and GC (right).

ness obtained by GC of 62%. This reduction of deposits, with initial pitch concentration of 50 mg/L and talc addition of 200 mg/L, is significant because it reduces the accumulative effect of pitch in the recirculation water.

Talc AK (high mineral grade cationized talc) presents a similar mineralogic composition to A talc, although it differs in its surface properties. The superficial nature of this cationic talc is the result of a treatment by adsorption with a cationic polyelectrolyte, such as poly-diallyl-di methyl ammonium chloride (polydadmac). The reduction of deposits reached using talc AK was only 32% by GC. The lower detackification capacity of cationized talc AK could be explained by assuming that the presence of cationic charges does not increase the affinity of talc to lipophilic compounds. The presence of cationic groups, such as quaternary ammonium salts of polydadmac, would form a layer of water molecules attached to the polyelectrolyte through the negative polar charges that it partially occupies along with the adsorbed molecules of polyelectrolyte.



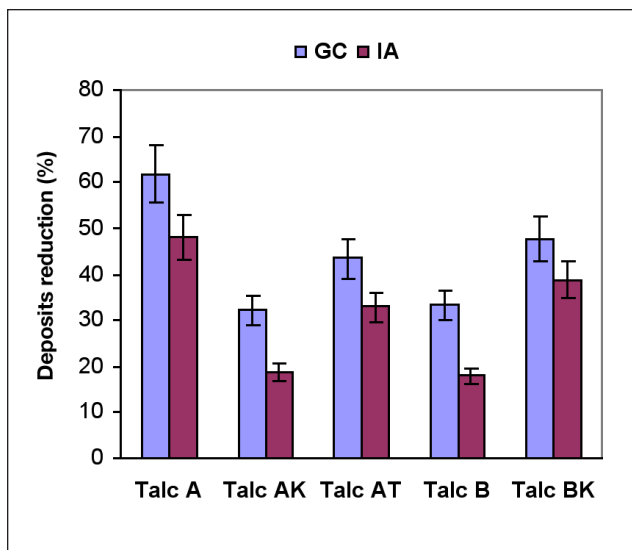
5. Deposition reduction versus talc concentration by image analysis and by GC for group B talcs.

The superficial nature of talc can be modified by heat treatment, as in talc AT, keeping its mineral composition similar to talc A. These treatments increase the talc's strong affinity for many types of organic molecules and its strongly hydrophobic and low influence on the overall distribution of micropores and mesopores in the talc particles. However, the inner surfaces created with these treatments are not accessible to the micelles of colloidal pitch. The formation of deposits reduction effectiveness obtained by GC dropped from 62% in the talc A to 44% with the AT. This latter talc is best for other applications as a rheological control agent in liquid, resins, plastisols, and adhesives, and as a whitening reinforcing filler and processing aid in elastomers and plastics. The adsorption capacity of colloidal pitch over the talc AT is comparable to that of talc A.

Figure 4 shows the results obtained with the addition of different talc concentrations of the B group. In this case, the lowest deposition was obtained with talc BK. This talc was the second best of the five talcs studied. The best performance obtained with this talc was at 100 mg/L, according to the measurements performed with image analysis, and 200 mg/L when using GC. In image analysis, the deposits obtained at 200 mg/L show an increase in the deposits detected. At high talc concentration, a part of the deposits detected by image analysis seem to be formed by talc, whereas with GC, only pitch deposits were detected, which is the reason for the increase in deposits at a talc concentration of 200 mg/L. This increase in deposits was not detectable by GC. **Figure 5** shows the difference between the results obtained by image analysis and by GC for the B talcs studied.

The depositability reduction achieved with talc B reached 33% at the highest concentration of talc studied (i.e., 200 mg/L), measured by GC, a significantly lower value than that obtained with talc A. The reduction of the deposits with the

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6. Deposited reduction capacity with 200 mg/L of all talcs studied.

cationized talc BK reached higher values, up to 48% with the BK talc concentration of 200 mg/L by image analysis. These results imply that detackification is not only based on the adsorption on talc, but also on other phenomena, such as the degree of readiness of talc to disperse in water. Talcs with a high chlorite content can be dispersed better in aqueous media than talcs having a higher mineral talc concentration. Cationized talcs can be dispersed better in aqueous media than unmodified talcs, and these latter better than heat-treated talcs. Dectackification increases with the proportion of

colloidal pitch fixed on the surface of talc and with the capacity of talc to maintain this dispersion. Because of its larger hydrophilic surface and the polar water adsorption to the positive charges of polyelectrolyte, talc BK had the highest capacity to disperse of the talcs studied. **Figure 6** shows the deposits reduction capacity of 200 mg/L of talcs in 50 mg/L of pitch dispersion, calculated by GC and image analysis.

The highest deposition reduction was obtained by GC analysis. The tendency of the reduction of deposits at this concentration is the same under either system of analysis. Talc A showed the highest deposition reduction with both analysis techniques. The second best deposition reduction was obtained with talc BK, surface-modified talc with high chlorite content.

CONCLUSIONS

The talcs studied have a high dectackification capacity in paper and pulp mill waters, even to low pitch concentrations. The detackification capacity of talcs can be attributed to two effects:

1. The capacity to retain pitch on the lipophilic surface of talcs, resulting in colloidal adsorption phenomena.
2. The capacity of talcs to disperse in water.

Talc A was the most effective talc for passivation of pitch because of its high lipophilic surface. Talcs having a higher chlorite content show a lower surface lipophilic character, but a better dispersion capacity in water because of the higher proportion of polar surface. The use of these talcs might be more effective if the goal is passivation of pitch to prevent pitch deposition on equipment surfaces. Cationic talc BK, with a low mineral talc composition and positively

ABOUT THE AUTHORS

This study was conducted as part of Ph.D. research and research is continuing on the topic at the university. Previous studies focused on pitch adsorption in different kinds of talcs by means of adsorption isotherms; this study focused on pitch dectackification with the same kinds of talcs.

Obtaining representative samples and reproducible results were the most difficult aspects of this study. Obtaining pitch also was arduous and tedious. Another difficult aspect of this research was to relate the two analysis methodologies: image analysis, a quantitative method, and gas chromatography, a qualitative method.

Among the more interesting findings of the study were the high dectackification capacity of the talcs and the relatively low detackiness capacity of thermally treated talc.

The results of this study will help mills select the



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best talc to control pitch problems. The next step will be to determine the capacity of the different talcs to control several detrimental properties of the white waters of pulp and paper mills.

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charged surface, has the second best detackiness capacity among the talcs studied. Its high detackiness capacity is the result of its dispersion capacity. Talc AT, with the high composition of mineral talc, has relatively less detackiness capacity, possibly because of its lower dispersion capacity.

At high talc concentrations, a small amount of talc was deposited in low turbulence areas (rotor outer foil deposition). This talc deposit, which was easily removed by flowing water shear forces, was obtained by image analysis and was not detected by GC analysis. **TJ**

LITERATURE CITED

1. Saarimaa, V., Vähäsalo, L., Pranovich, A., et al., *Nordic Pulp Pap. Res. J.* 21(5): 93(2006).
2. Blanco, A., Negro, C., Diaz, L., et al., *Appita J.* 62(2): 113(2009).
3. Marques, G., del Rio, J.C., and Gutierrez, A., *Bioresour. Technol.* 101(1): 260(2010).
4. Back, E.L., in *Pitch Control, Wood Resin and Deresination* (E. L. Back, and L. Allen, Eds.) TAPPI PRESS, Atlanta, Georgia, USA, 2000, Chap. 1.
5. Nguyen, D.T., *TAPPI J.* 81(6): 142(1998).
6. Hubbe, M.A., Rojas, O.J., and Venditti, R.A., *Nordic Pulp Pap. Res. J.* 21(2): 154(2006).
7. Wallqvist, V., Claesson, P.M., Swerin, A., et al., *Colloids Surf., A* 277: 183(2006).
8. Guérá, N., Shoelkopf, J., and Gane, P.A., *Nordic Pulp Pap. Res. J.* 20(2): 156(2005).
9. Benecke, F., Gantenbein, D., Gane, P.A.C., et al., *Nordic Pulp Pap. Res. J.* 24(2): 219(2009).
10. Tamura, H., Tsujimichi, K., Yamano, H., et al., *Appl. Surf. Sci.* 119(3-4): 335(1997).
11. Biza, P., *Pap. Technol.* 42(3): 22(2001).
12. Comard, M.P., Calvet, R., Balard, H., et al., *Colloids Surfaces A: Physicochem. Engin. Aspects.* 238(1-3): 37(2004).
13. Tijero, A., Monte, M.C., Blanco, A., et al., *J. Pulp Paper Sci.* 35(3-4): 130(2009).
14. SCAN-CM 50:1994, "Determination of acetone-soluble matter."
15. Blanco, A., Garcia, J., Monte, M.C., et al., *Eur. Pat. Appl. PCT/ES98/00029* (WO 98/39079.11.09.1998).
16. Blanco, A., Negro, C., Monte, M.C., et al., *J. Pulp Paper Can.* 101(9): 40(2000).
17. Monte, M.C., Blanco A., Negro C., et al., *Chem. Eng. J.* 105(1-2): 21(2004).
18. Monte, M.C., MacNeil, D., Negro, C., et al., *Holzforschung* 64: 277(2010).
19. Otero, D., Sundberg, K., Blanco, A., et al., *Nordic Pulp Pap. Res. J.* 15(5): 288(2000).
20. Nylund, J., Sundberg, A., and Sundberg, K., *Colloids Surf., A* 301(1-3): 335(2007).
21. Örsa, F. and Holmbom, B., *J. Pulp Paper Sci.* 2(12): 361(1994).