Pitch detackification with natural and modified talcs

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SUMMARY

Pitch deposition in the 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. Tackiness is the property of pitch which related to the deposit formation. One of the methods to control pitch deposition in the pulp and paper industry is the use of the talc. The talc acts primarily by a detackification mechanism and hence must be part of the deposit to control further deposition. The effectiveness of talc as control agent depends on its structural and surface characteristics, e.g. specific surface, surface energy, surface charge and ratio lypophilic/hydrophilic surface, being these related to its mineral composition and the thermal and surface treatments it has undergone. Five commercial talcs, corresponding to two groups of different mineralogical compositions, have been tested to determine their detackification capacity using the deposition tester developed by the Complutense University of Madrid. In this method, the quantification of the deposits is carried out by an image analysis (IA) of stainless steel collectors on which the deposit has formed. After IA a qualitative analysis to determine the deposit organic fraction is carried out by gas chromatography (CG) 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 surface properties of mineral, as for example chlorite proportion, surface area and surface treatment and to the adsorption capacity of pitch on talcs. The general conclusions are that the talc having the highest quantity of mineral talc presents the best detackification capability and

1 that all talcs studied have an appreciable detackification reduction at low proportion of

2 addition.

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4 **Keywords** Detackiness; deposit formation; dissolved and colloidal material; papermaking; paper

5 recycling; pitch, pitch control; pulp; talc; wood extractives

6

7 **INTRODUCTION**

8 Wood pitch is released from fibres into process water during the production of

9 thermomechanical pulp (TMP). The dispersion of pitch takes the form of colloidal droplets

10 with a hydrophopic core, composed mainly of steryl esters and triglycerides, and a thin

11 surface layer of sterols, fatty acids and resins acids (1-3). The changes of pH and salt

12 concentration (ionic force) produced during bleaching, the oxidant treatment stages and the

13 extraction stages produce the destabilization of dissolved and colloidal matter from the pulp

14 extractive, forming sticky deposits called õpitchö (4). The characteristics of the wood pitch

15 including hidrophobicity, deformability, tackiness, low surface energy, can cause deposition

16 problems, decreasing the final product quality and the efficiency of papermaking process (5).

17 The tendency of organic material to form deposits is related to its nature, and therefore to its

18 tackiness. Tack is defined as the stickiness of a particle, qualitatively determined by touch.

19 More specifically, tack is the energy required to separate two particles no permanently bound

20 together. Nowadays, one of the technologies commonly used to control pitch deposition is the

21 detackification. The detackification technology involves eliminating the tackiness associates

22 with the pitch, but also may stabilize pitch particles preventing their agglomeration (6, 7).

23 Talc is one of the additives used traditionally for pitch control (7). Guerá (8) propose that, in

24 the mechanism of detackification, the talc become incorporate in pitch deposits, which cause a

25 decrease in tackiness and inhibits further deposition. Guerá theorized the existence of a

26 second step after the adsorption of pitch onto talc (8). This second step occurs when talc

27 particles with adsorbed resins form õsandwich structuresö with very thin intercalates

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1 constituting a sort of nano-composite material. The dectakification occurs firstly through

2 immobilization of the sticky materials (9).

3 The term õtalcö only describes a mineral on generic way while in the market it is possible to

4 find talc products with different mineralogical compositions and surface properties. Talc is a

5 mineral composed of hydrated magnesium silicate with the chemical formula

6 $Mg_3Si_4O_{10}(OH)_2$. The main or basal surfaces of this elementary sheet do not contain hydroxyl

7 groups or active ions, which explains talc hydrophobicity and inertness. Highly lamellar talcs

8 have large individual platelets whereas in a compact (microcrystalline) talc platelets are much

9 smaller. The elementary sheets are stacked on top of one another, like flaky pastry, and

10 because of the binding forces (Van der Waal's forces) linking one elementary sheet to its

11 neighbors are very weak, the platelets slide apart at the slightest touch, giving talc its

12 characteristic softness (10, 11, 12). In various studies, the water contact angle has been found

13 to be 66́90º (7).

14 In this paper the capacity of different talcs, modified or not, used as a pitch dectackification

15 agents has been studied by the measurement of the deposition tendency of water containing

16 extractives. For this, $CaCl_2$ has been added in order to get an approach to the real

17 destabilization conditions that occur as consequence of the presence of Ca^{2+} in process waters

18 in papermaking. The deposits have been measurement by means of the deposition tester

19 developed by the UCM research group. On the other hand, the efficiency of the talcs on the

20 extractives reduction was measurement by GC analysis.

21 **EXPERIMENTAL**
22 *Characterization of talcs*
23 Five commercial talcs have been used. The talcs correspond to two groups of different

24 mineralogical compositions: A, with high concentration of talc and some dolomite; and B,

25 with medium concentrations of talc and chlorite. The A group is formed by a natural talc (A)

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1 and anionic (A-T) and cationic (A-K) talcs modified superficially. The B group is formed by a

2 natural anionic talc (B) and modified cationic talc (B-K). Theses talcs have been characterized

3 by X Ray Diffraction, Scanning Electron Microscopy and Analysis by Dispersive Energies,

4 Zeta Potential and surface area measurements. The analysis showed that the type of chlorite

5 present in the talc B was Clinochlore. The Zeta Potential was determined with the Mütek PCD

6 03 device (at pH 7) and particle size distribution was determined by Sedigraph 5100 (13). The

7 mineralogical composition measured by X Ray Diffraction of both talc groups is shown in

8 table 1. The physic properties are summarized in table 2.

9

10

Table 1.- Mineralogical composition of talcs (%)

	GROUP A			GROUP B	
	A	**A-T**	**A-K**	**B**	**B-K**
Talc (1), $Mg_3Si_4O_{10}(OH)_2$	85,4	82,4	94,3	61,7	55,7
Talc (2), $Mg_3Si_4O_{11}nH_2O$	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
Clinochlore, $Mg_5Al(Si_3Al)O_{10}(OH)_8$	-	-	-	37,0	42,1
Ferrous and calcium oxide, $Ca_2Fe_7O_{11}$	-	-	-	0,9	1,8

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Table 2.- Physic properties of talcs

	GROUP A			GROUP B	
Talc	**A**	**A-T**	**A-K**	**B**	**B-K**
Specific area BET (m^2/g)	12	14	12	8,5	8,5
Density (g/cm^3)	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_2O adsorbed (%)	15 at 120ºC	<1	1 at 120ºC	>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

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15 From point of view of mineralogy, the majority component in all of them is talc although the

4

group B talcs are composed by 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 (30L), evaporation of the solvent and re-extraction with hexane in order to increase the selectivity of lypophillic compound extraction, according to standard SCAN-CN 50:93 (14). Subsequently, the solvent was evaporated in a rotary evaporator. Colloidal dispersions were obtained after alkaline hydrolysis with KOH solution and a new extraction of lipophilic compounds with hexane. A concentrated solution of pitch in acetone was obtained by evaporation until a 3000 mg/L concentration. The 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 Milli-Q water and stirred overnight at the natural pH in order to be used as slurry.

Deposition experiments

The depositions experiments were carried out with the deposition tester developed by the UCM Research Group and described in more detail in previous researches (15, 16, 17). It 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 sticky material is transferred to the outer cylinder surface due to the flow mechanism. On the inner cylinder surface, depositions occur via an impact mechanism.

The experiments were carried out at 50 ºC for 2 h and the rotation speed of the rotor was 250 rpm. The beaker was filled with 1.8 L of pitch dispersion contained about 50 mg/L of extractives. The experiments were carried out at pH 8. The talc concentrations used during the experimentation were 50, 100, and 200 mg/L. In order to know the performance of the

1 different talcs, a blank trial without talc addition was carried out. CaCl$_2$ was added 1 min after

2 the talc addition to obtain the maximum amount of pitch aggregates to study in the deposition.

3 The pitch droplets are susceptible to an electrolyte-induced aggregation with Ca^{2+} that led to

4 the formation of deposits. The concentration of Ca^{2+} added was 10 mmol/L of Ca^{2+} (18; 19).

5 When the deposition experiment was finished, the stainless steel foils with the deposits were

6 withdrawn from the cylinder support and dried at room temperature before scanning with a

7 commercial computer flatbed scanner (HP Scanjet 6100C) at 600 dpi. The resulting scanned

8 images were analysed using the image analysis system õStickies Measurement Systemö,

9 developed by the British Research Centre PIRA International and the UCM. The results are

10 expressed as follows: covered area of deposits expressed as mm^2, mm^2 of deposits per m^2 of

11 surface (ppm) and percentage of covered area of deposits (%). In this paper, the sum of the

12 internal and external deposits, expressed in mm^2, (total deposits) are shown, representing the

13 deposition on the entire collector. Therefore the reduction of the depositability by IA is

14 obtained by the equation 1.

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$$\mathrm{Re}\,duction\ (\%) = \frac{Total\ deposits\ without\ talc\ \left(mm^2\right) - Total\ deposits\ with\ talc\left(mm^2\right)}{Total\ deposits\ without\ talc\ \left(mm^2\right)} \times 100 \qquad (1)$$

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17 *GC analysis*
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19 The analysis of extractives was carried out by a chromatograph Varian 3800 GC with a

20 detector FID, coupled with a Varian 8200 Autosampler and with injector for liquids 1079

21 Universal Capillary Injector. The capillary column has a 15 m length and a 0,53 mm diameter

22 and a film thickness 0,15 m. The chromatograph was programmed from 100ºC (0,5 min) to

23 340ºC at a rate of 12ºC/min. The injector was programmed from 100ºC (0,5 min) to 340 ºC at

24 200ºC/min. After the experiment, the steel foils were removed and extracted with a solution

25 of MBTE (40 mL) and acetic acid (1 mL) in an ultrasonic bath. Lypophilic extractives were

26 silylated and determined by GC (20).

1 Lypophylic extractives in water were determined by extraction with MBTE and analysis by

2 CG.

3 In other to correlate the deposits obtained by the deposition rotor with their composition the

4 results of the analyses by GC were referred to the deposits obtained in the foils, from the

5 corresponding blank values and according to the following relation:

6 $$SCG\left(mm^2\right) = \frac{BSI\left(mm^2\right)}{BSG\left(mg\right)} xSMG\left(mg\right) \qquad (2)$$

7 *Where*
8 *SCG: Total deposits measured by GC in mm².*
9 *BSI: Total deposits without talc measured by IA*
10 *BSG: Total deposits without talc measured by GC*
11 *SMG: Total deposits with talc measured by GC*

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13 The blank surface measured by IA (BSI), corresponds to the measures of the foils surface

14 covered with pitch, in absence of talc. These values are the most reliable ones due to their

15 reproducibility, two tests per talc series, and the lack of interferences by talc deposition.

16 The blank mass measured by GC (BSG) was obtained from the analysis of the blank by GC.

17 The sample mass by CG (SMG) was obtained by means of the CG analysis of each of the

18 samples studied.

19 From equation 2, it may be assumed that the pitch deposits measured by IA are proportional

20 to the mass of pitch measured by GC. This hypothesis is exact when the average thickness of

21 the layer deposited is constant in all the foils analysed. Therefore, if the surface covered by

22 pitch is proportional to the mass, the relation between blank covered surface and pitch mass of

23 the blank can be expressed by the following proportionality constant:

24 $$K = \frac{BSI\left(mm^2\right)}{BSG\left(mg\right)} \qquad (3)$$

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2 According to this hypothesis, equation 2 can be formulated as:

3 $SCG = K \ x \ SMG$ (4)

4

5 With this mathematical treatment, the total deposits measured by GC are expressed as square
6 millimeters. On the other hand, the reduction of the depositability measured by GC is
7 obtained from equation 5.

8

9 $$\text{Reduction (\%)} = \frac{\text{Deposited pitch without talc} \left(mg \, m^{-2}\right) - \text{Deposited pitch with talc} \left(mg \, m^{-2}\right)}{\text{Deposited pitch without talc} \left(mg \, m^{-2}\right)} \times 100 \quad (5)$$

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11 As a summary, the figure 1 shows the schematic representation of the experiments carried out.
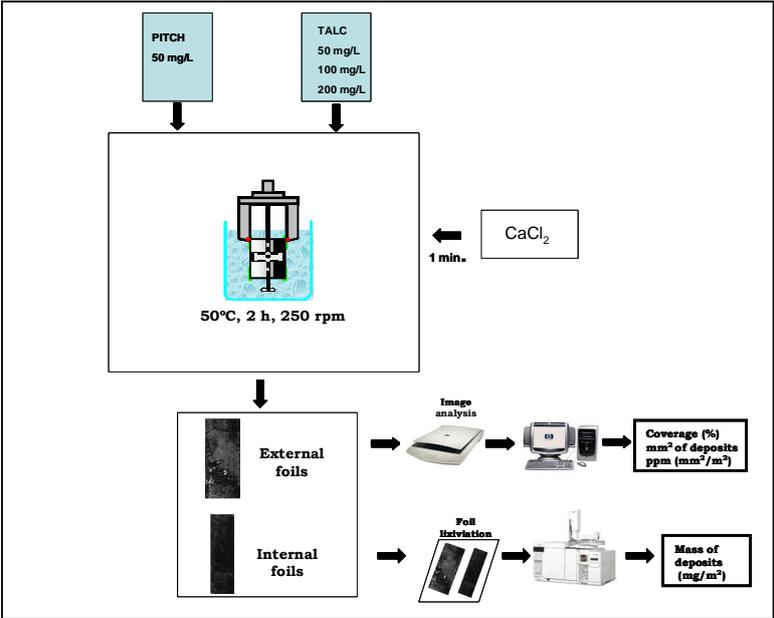

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13 **Figure 1. Experimental protocol**

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15 **RESULTS AND DISCUSSION**

16 The results of the extractive characterization and the composition of the lypophilic fraction

17 determined by GC are shown in table 3. The extractive content of the *Eucalyptus globulus*

18 wood used in this experimentation is very low comparing with other genus species. This

19 justifies the need to use a pilot plant extractor.

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5   **Table 3. Composition of *Eucalyptus globulus* extractives**.

Total extractives (%)	Total lypophilic fraction (%)	Lypophilic fraction on total extractives (%)
0,75±0,5	0,10	13,50

6

7 The composition of the lypophilic fraction was 33% of sterol esters, 8 % of triglycerides, 17%

8 of fatty acids and 42% of sterols (13). The figure 2 shows the total deposit obtained with the

9 addition of different talc concentrations of the A group, by IA and by GC, respectively. In all

10 cases, the amount of deposits decreases with respect to the blanks when talc was added.

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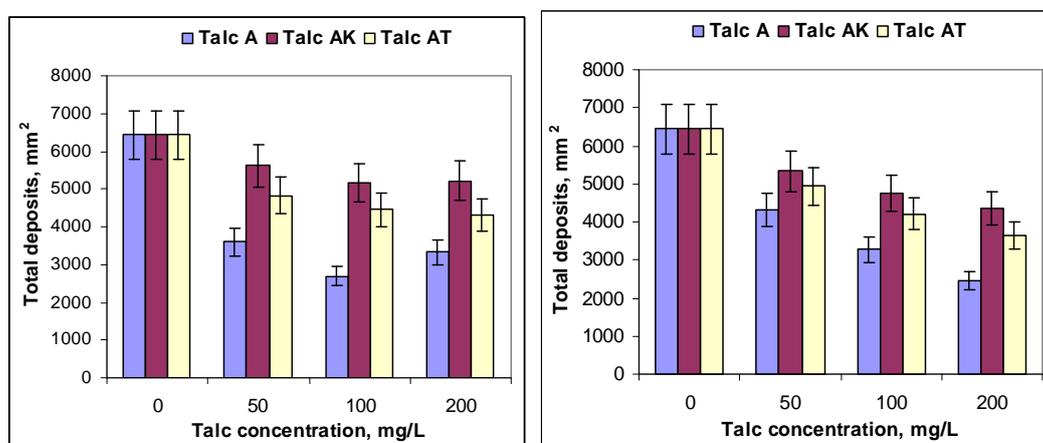
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14   **Figure 2. Total deposits obtained with the addition of group A talcs by IA and GC.**.
15

16 The results obtained with the two deposits determination techniques employed in the study

17 showed slightly different trends. The deposits obtained by the deposition rotor and analysed

18 by IA show a slightly higher degree of deposition than the obtained by GC analysis. The

19 results measured by GC shown a regular decrease of the deposits with the addition of talcs.

20 Both IA and CG analysis show that the lowest amount the deposits was achieved with talc A.

9

1   The best performance obtained with this talc was at 100 mg/L according to the measurements

2   performed with IA, and 200 mg/L when using CG. Figures 3 shows the difference between

3   the reduction results obtained by IA and by GC for the talcs A studied. The ordinate axis

4   represents the decrease of the property considered as a reduction percentage of the formed

5   deposits or as a percentage of pitch retained by adsorption on talc.

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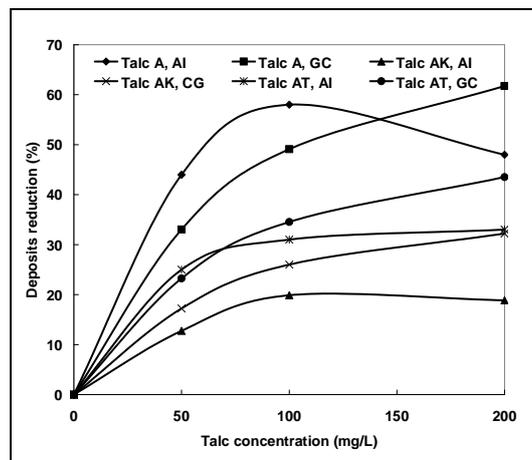
9   **Figure 3. Deposition reduction versus talc concentration by IA and by GC for A group talcs.**

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11 The talc A depositions reductions measured by IA present a maximum of 57 % at 100 mg/L

12 of talc concentration and decrease at 200 mg/L. A similar tendency was shown in all talcs

13 when depositability reduction was determined with IA except with talc AT, which shows a

14 slight increase in the reduction of deposit at 200 mg/L

15 These results indicate that the initial hypothesis that the mass of extractives are proportional

16 to the covered surface is only an approximation; the main deviation from this hypothesis

17 could be due to talc deposition.

18 The highest detackification capacity was shown by talc A, high talc mineral grade, with a

19 deposits reduction effectiveness obtained by GC of 62%. This reduction of deposits, with

20 initial pitch concentration of 50 mg/L and talc addition of 200 mg/L, is significant since it

21 reduces the accumulative effect of pitch in the recirculation water.

10

1 Talc AK (high mineral grade cationized talc) presents a similar mineralogical composition to

2 A talc, although it differs in its surface properties. The superficial nature of this cationic talc is

3 the result of a treatment by adsorption with a cationic polyelectrolyte such as poly-diallyl-di

4 methyl ammonium chloride (polydadmac). The reduction of deposits reached using talc AK

5 was only 32% by CG. The lower detackificacion capacity of cationized talc AK could be

6 explained assuming that the presence of cationic charges does not increase the affinity of talc

7 to lipophilic compounds. The presence of cationic groups, such as quaternary ammonium salts

8 of polydadmac, would form a layer of water molecules attached to the polyelectrolyte though

9 their negative polar charges that it partially occupies along with the adsorbed molecules of

10 polyelectrolyte.

11 The superficial nature of talc can be modified by heat treatment, as in the talc AT, keeping its

12 mineral composition similar to talc A. These treatments increase its strong affinity for many

13 types of organic molecules and its strongly hydrophobic and low influence on the overall

14 distribution of micropores and mesopores in the particles of talc. However the inner surfaces

15 created with these treatments are not accessible to the micelles of colloidal pitch. The

16 formation of deposits reduction effectiveness obtained by GC dropped from 62% in the talc A

17 to 44% with the AT. This latter talc is best for other applications as rheological control agent

18 in liquid, resins, plastisols and adhesives and whitening reinforcing filer and processing aids

19 in elastomers and plastics. The adsorption capacity of colloidal pitch over the talc AT is

20 comparable to that of talc A.

21 The figure 4 shows the results obtained with the addition of different talc concentrations of
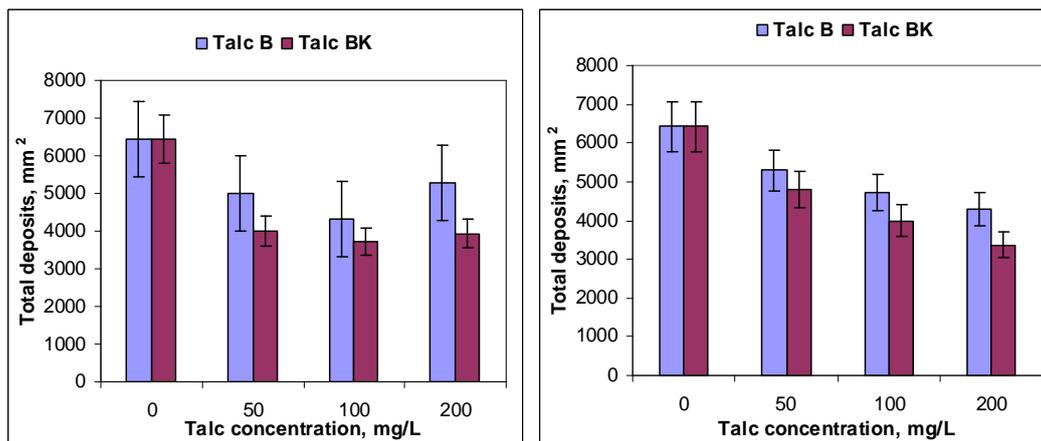
22 the B group.

23

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

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 IA, and 200 mg/L when using CG. In IA the deposits obtained at 200 mg/L show an increase of the deposits detected. At high talc concentration, a part of the deposits detected by IA seems to be formed by talc, whereas with GC, only pitch deposits were detected, that is the reason for the increase of the deposits at talc concentration of 200 mg/L. This increase of the deposits was not detectable by gas chromatography. Figure 5 shows the difference between the results obtained by IA and by GC for B talcs studied.
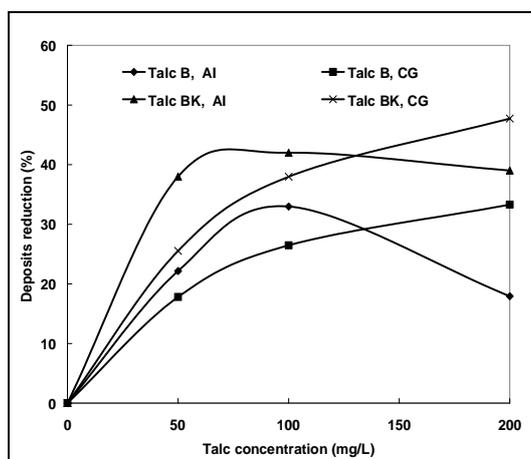

Figure 5. Deposition reduction versus talc concentration by A and by GC for B group talcs.

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1   The depositability reduction achieved with talc B reached 33% at the highest concentration of

2   talc studied, i.e. 200 mg / L measured by GC, a significantly lower value than that obtained

3   with talc A. The reduction of the deposits with the cationized talc BK reaches higher values,

4   up to 48% with the BK talc concentration of 200 mg /L by IA. These results imply that

5   detackificacion is not only based on the adsorption on talc, but also on other phenomena such

6   as the degree of readiness of talc to disperse in water. Talcs with a high content of chlorite can

7   be dispersed better in aqueous medium than talcs having a higher mineral talc concentration;

8   cationized talcs can be dispersed better in aqueous medium than unmodified talcs and these

9   latter better than heat-treated talcs. Dectakification increases with the proportion of colloidal

10   pitch fixed on the surface of talc and with the capacity of talc to maintain this dispersion. Due

11   to its larger hydrophilic surface and the polar water adsorption to the positive charges of

12   polyelectrolyte talc BK is the one having the highest capacity to disperse of the talcs studied.

13   As summary, figure 6 shows the deposits reduction capacity of 200 mg/L of talcs in 50 mg/L

14   of pitch dispersion, calculated by GC and IA.

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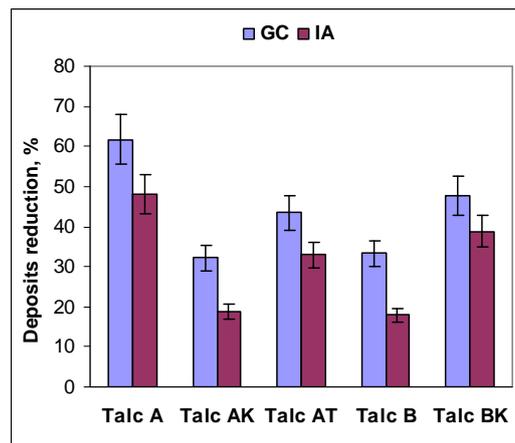
16
17   **Figure 6. Deposited reduction capacity with 200 mg/l of every studied talc.**
18

19
20   The highest deposition reduction was obtained by GC analysis. The tendency of the reduction

21   of deposits at this concentration is the same by both of the system analysis. The talc A show

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the highest deposition reduction with both analysis techniques. The second best de position

reduction was obtained with the talc B-K, surface modified talc with high contents in chlorite.

CONCLUSIONS

The talcs studied have a high dectackification capacity in the paper and pulp mills waters even

to low pitch concentrations. The detackification capacity of talcs can be attributed to two

effects:

- The capacity to retain pitch on the lipophilic surface of talcs resulting in colloidal
  adsorption phenomena.

- The capacity of talcs to disperse in water.

Talc A was found to be the most effective talc to achieve the passivation of pitch due to its

high lipophilic surface. Talcs having a higher content in chlorite show a lower surface

lipophilic character, but a better dispersion capacity in water due to the higher proportion of

polar surface. The use of these talcs may be more effective if the goal is the passivation of

pitch to prevent pitch deposition on equipment surfaces. Cationic talc BK, with low mineral

talc composition and positively charged surface, is the second best talc in detackiness

capacity. Its high detackiness capacity is due to its dispersion capacity. Talc AT, with the high

composition of mineral talc, has relatively less detackiness capacity, possibly due to its lower

dispersion capacity.

At high talc concentrations, a low amount of talc was deposited in low turbulence areas (rotor

outer foil deposition). This talc deposit, which is easily removed by flowing water shear

forces, was obtained by AI analysis and was not detected by GC analysis.

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