Comparing colloidal pitch adsorption on different talcs

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KEYWORDS: Talc, Pitch, Stickies, Deposition, Agglomeration, Papermaking

SUMMARY: In the paper industry talc is frequently used to prevent deposition of pitch, consisting of a variety of organic compounds derived from tree resins forming colloidal microspheric droplets or particles in the wet circuit of a paper mill. This work quantifies experimentally the degree of pitch adsorption on different talc qualities, as defined by source, physical parameters, such as particle size (major dimension) and specific surface area, and additional chemical factors in the form of surface treatment, such as cationising, and mineralogy. A pitch-containing suspension was produced by pressure dewatering fresh thermomechanical pulp to create a dilute liquor. To samples of this suspension, the various talcs were added individually under continuous agitation. After a given time the mix was centrifuged to separate the talc from the colloidal suspension, and the amount of pitch adsorbed onto the talc surface was determined and compared with the amount of free colloidal pitch remaining in the liquid phase. A clear correlation of pitch adsorption with the free surface area of the talc was observed, thus acting as the predominant parameter. Variations in mineralogy and particle major dimension, although important, were of less influence than the especially high surface area achieved in this study.

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In the papermaking process it is well known that “pitch problems” may occur, reported mainly as a deposition of organic sticky material coming out of water suspension either onto the papermaking equipment or as spots in the paper web itself.

Pitch refers mainly to the release of natural resin contained in the wood, which, during the grinding and further treatment of the wood to create individual fibres, is released into the water in the form of microscopic droplets/particles. Naturally occurring surfactants like glucomannans help to stabilise the colloidal droplets in an oil-in-water colloidal suspension. Problems arise when the droplets deposit onto surfaces in the paper mill’s wet-end circuit, form agglomerates and eventually break loose appearing as visible spots in the paper, ranging from yellow to black in colour. In the last few decades the increased use of recycled paper added to the problem by way of additional so-called white pitch and stickies. The sources of these additional extraneous nuisance materials are binders and additives from coated broke, hotmelts and other thermoplastics, respectively. Furthermore, the use of silicone-based defoamers etc. provide an additional source of hydrophobic material.

Talc is known to act in preventing deposition of these hydrophobes but little literature can be found comparing different talcs, and virtually no known detailed studies exist relating mineral properties and their particulate morphological parameters to efficiency in pitch adsorption or detachification. It is the aim of this paper to fill that gap with a study comparing typically applied talc grades in their ability to remove organic species from an aqueous system. One specially produced high surface area talc is included for comparison. Of most interest for the industry is the effectiveness in terms of controllable talc characteristics like particle size distribution, surface chemical treatment and specific surface area. After testing different deposition methods, as proposed in the literature (Gustafsson et al. 1952, Allen, Filion 1996, Reynolds, Yordan 2002), none was found to be adequate for a quantitative study involving thermomechanical pulp. Instead we developed a direct laboratory adsorption method quantifying the pitch adsorbed on the talc and the remaining free pitch in the aqueous phase. The analytical technique is described fully later in this paper, and involved detection using a number of methods including chemical oxygen demand (COD), turbidity, gravimetry, thermogravimetry (TGA) and microscopic analysis.

Background

Pitch and adsorption

The standard reference concerning pitch composition is the book of Back and Allen (2000) who compiled hundreds of publications. The chemical composition of wood resin is characterised by four classes of lipophilic components:

1) fats and fatty acids,
2) steryl esters and sterols,
3) terpenoids, and
4) waxes, i.e. fatty alcohols and esters.

Colloidal stabilisation of these compounds may occur through ligno-sulphonates and polysaccharides. Traditionally, in a paper mill, Alum (K₂Al(SO₄)₂·24 H₂O) is used to bring the pH into the acidic domain where colloidal resin coagulates onto fibres. This procedure enabled the invisible colloidal material to be removed harmlessly from the circuit and carried out with the product. According to microscopic analyses (Parmentier 1973) there are three kinds of pitch. The first is called “filmy”. It appears as an organic film of material of transparent or translucent colouring. Its thickness varies according to its concentration and nuclei are required to form an initial coalescence. The second type of pitch is called “globular“ (of typical size, d = 0.1-1.0 μm). In this globular state, the pitch is readily able to coagulate. The last type of pitch is characterised as having an agglomerate or pitch ball form (having a wide particle size range, d = 1-120 μm), and is often found in those systems exhibiting the worst problems of pitch deposits. His study has revealed that pitch does not cause
problems until the free pitch has agglomerated.

Today, increasingly, papermaking pH is either neutral or slightly alkaline, such that the removal of pitch is no longer an automatic corollary of the use of Alum, and talc is playing an ever more important role in its control. The increase in pH to pseudo-neutral is a growing trend in mechanical papers and so the study of pitch removal under these conditions is also of growing importance. Moreover, in the literature (Holmbom, Sundberg 2003) it is stated that mechanical pulps carry over much more dissolved and colloidal matter than chemical pulps and recycled pulps. The need to consider these aspects of pitch under pseudo-neutral and alkaline conditions for mechanical papers becomes a matter of increasing focus for research activity.

**Talc properties and parameters**

Talc is an hydrated magnesium silicate, separated into layers, an octahedral brucite layer situated between two tetrahedral sheets of silica, with the chemical formula Mg₃(OH)₂Si₄O₁₀. The particles are platelets reflecting the sheet structure of the mineral, where the planar particle surface constitutes approximately 90% of the talc surface, i.e. the platelets have a very high aspect ratio. Talc is naturally hydrophobic in that it cannot normally be wetted by the addition of water without the use of surfactant. The definition of hydrophilicity is therefore understood as the opposite to this non-wetting tendency, and the literature more than adequately describes the role of the talc crystal structure in relation to these properties. Hydrophobicity is an apparent property of the planar face, while the exposed particle edges are hydrophilic due to the presence of pH-influenced MgOH⁺ groups (Yildirim 2001, Morris et al. 2002, Charnay et al. 2001)

Parmentier (1979) states that the properties of talc are unaffected by pH, temperature or chemical balance and the adsorption process continues as long as the sorption potential of organophilic surfaces is unsatisfied. More so, due to Biza (2001), the advantage of talc is that it is chemically inert; it will not take part in any chemical interactions with the other papermaking chemicals and no toxic, dangerous or harmful products can be formed by talc.

**Action of talc against pitch deposition:**

*Previous observations and models*

Most existing literature, though dealing extensively with the topic of pitch, as found in both mechanical (Holmbom, Sundberg 2003, Otero et al. 2000, Sihvonen et al. 1998) and chemical pulps, reference to pitch in combination with talcum appears mostly limited to the case of chemical pulps or the use of synthetic pitch preparations.

Wilför et al. (2000) study the interaction of different mineral particles with colloidal and dissolved matter present in pulp liquors. Talc is shown to adsorb substantial amounts of neutral carbohydrates, mainly glucomannans, from water taken from unbleached TMP, while kaolin adsorbs both much of the glucomannans, from peroxyde-bleached TMP water, as well as pectins. Calcium carbonate removes much of the lipophilic extractives from unbleached TMP water at pH 8. Kaolin and talc are shown to remove substantial amounts of lipophilic extractives from both unbleached and bleached TMP waters.

Rogan (1994) presents a systematic investigation of the adsorption of oleic acid (as lab-prepared aqueous emulsions) onto various minerals and surface treated minerals, viz. kaolinite, treated kaolinites, montmorillonites, talcs, gibbites, calcites and a treated calcite. Among others, adsorption onto talc is well correlated in this work to the Langmuir model. Adsorption mechanisms for the other minerals are explained by proposing different models, but without discussing hydrophobic forces. Oleic acid adsorption is furthermore compared with triolein adsorption on one of the talcs. Triolein adsorption on the talc is well correlated with the Langmuir model, too. The triolein adsorption by the talc is greater than its oleic acid adsorption. Application of these findings to practical pitch in relation to the properties of the talc, however, remains to be investigated due to the idealised model character of the adsorbates.

Another study (Lee, Sumimoto 1991) well demonstrates the effect of talc for the control of pitch on more than 24 pulps obtained from different eastern species of trees. On only one species, Shorea Kunstleri, containing polymers of α- and β- resin, does talc fail to be effective.

Gill (1974) affirms that white water from a paper mill, containing pitch, acts to form nuclei for even larger agglomerates (dirt) when it is subsequently recirculated to a pulp mill. It is found that by adding a further quantity of talc, following the first caustic extraction stage in the bleaching sequence, it is possible to reduce the dirt count by approximately 66% while consuming less than 0.5% talc.

Hamilton et al. (1984) use extractives (acetone) from newsprint pulp to quantify adsorption on different talcs but without giving details about talc parameters. They find a strong dependence on the chemical “type” of extract.

Yordan et al. (1997) use a stickies deposition device, an FT-Infrared imaging system and a scanner-based image analyser to evaluate the efficiency of talc as a pitch/stickies control agent. To collect stickies they take 60 g of an oven-dried (OD) pulp, re-pulp it in a Tappi disintegrator at 3% by weight consistency using 2000 cm² of deionised water for 10 minutes at 25°C. After repulping, the pulp is screened by adding all of the pulp to the screening device in one charge. The quantification for the dirt/stickies collected with the screen is conducted with the image analyser. The unit used to quantify dirt/stickies is the equivalent black area (EBA) of dirt/stickies in square millimetres per kilogram (mm²kg⁻¹) of dry pulp. They find that the addition of talc did not help reduce the level of contaminants present in an old newsprint pulp (ONP). They say that the talc should be added in the process at a point where the microstickies are still present and not after they have agglomerated to form macrostickies. Although such definitions are difficult to apply rigorously, their conceptual value in
respect to particle/agglomerate size is considered useful in qualitatively describing the action of individual talc particles in respect to the control of pitch.

A new observation is made by Morris et al. (2002). They claim that the adsorption on talc of anionically charged polymers, in their case carboxymethylcellulose and polyacrylamide, resulting in depression of talc effectiveness, is greatest when conditions of electrostatic repulsion are minimized. Talc depression is largely influenced by variations in solution conditions. Thus the adsorption density of the two anionic polymers, CMC and PAM-A, on talc increases either at high ionic strength or low pH. On the contrary, at high pH values and low ionic strength, the pitch adsorption density increases.

The oft quoted positive mechanism preventing pitch deposition, is the sorption of the pitch resin onto talc. For example, Kiser (1976) explains that the organophilic planar surface of the talc particle is wetted by the pitch particle, such that the pitch particle is thus prevented from linking itself to other pitch particles. This attachment to talc is irreversible and the pitch goes out of the wet end circuit retained in the finished product bound on the talc particle.

Controversially, Allen et al. (1993), besides discussing many practical issues of talc addition in a pulping mill, calculate that only < 10% of the pitch material is adsorbed on talc. How then does talc control deposition? Typically, pitch deposits found in mills where talc is used contain up to 40% talc. Evidently, the attraction between talc and deposited pitch is sufficient for a relatively large amount of talc to become part of the deposit. Based on this, it has been hypothesised that talc works by a detackification mechanism; that is, talc becomes incorporated in pitch deposits, which causes a decrease in tackiness and inhibits further deposition.

We propose that the two mechanisms are not theoretically contradictory. The adsorption of pitch and other organic species onto talc is observed in many experiments including our own. The proposed detackification process we see as a second step 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 immobilisation of the sticky materials. A sufficiently mobile surface is the first attribute a glue needs for proper adhesion. Secondly, the intercalation of the polymers between the talc platelets shields the polymers from further adhering action and the non-stick properties of the talc/resin nano-composite renders it harmless in the paper making process.

We have not found any discussion in the literature about hydrophobic interaction in relation to talc and pitch adsorption. Hydrophobic interactions are seen to occur between hydrophobic species surrounded by a polar medium like water. In other fields of science the discussion is ongoing about the nature and cause of these attraction forces, (van Oss et al. 1985, Hato 1996, Ederth et al. 2001, Pashley et al. 1985). Adsorbed layers of gas (very hydrophobic) seem to play an important role in respect to hydrophobic attractive forces, and may well do so also in the case of talc.

The main focus of our work here is based on the claim (Gill 1974), that when the talc is delaminated it exposes more adsorptive surface for pitch adsorption. The claim was hitherto not supported by experimental data. It has also been mentioned previously that the action of talc is more beneficial if the pitch is treated when it is still in the colloidal state, the treatment of agglomerated pitch being much more inefficient. This is why in this paper we assess the effect of talc on colloidal pitch from TMP.

Materials and Characterisation

The TMP used for the tests consists of 70% spruce, the rest being composed of fir and a small part of pine. Some 6.0 kg of the fresh wet pulp (3.7 wt% solids content) were taken from the accept of the screen at a temperature of 90°C before the bleaching step at a paper mill in Switzerland. This pulp is used for the production of LWC papers and has a fineness of 63° Schopper-Riegler which equates to 120 Canadian Standard Freeness (CSF). The experiments have been performed using repetitive pulp samples taken in February and March 2004. Each test was submitted to a duplicate analysis. The pH of the three pulp samples remained consistently between 5.6-5.7 at 25°C.

The pulp samples were wet pressed through a filter of 2 µm pore size (membrane filter, circular 602 EH). A sample of the 5.0 dm³ of filtrate/liquor obtained was examined under a light microscope to check for the presence of fibrils which might have distorted the adsorption results. Pitch was clearly seen in the liquor. Membrane filtration was found to be advantageous compared with centrifugation due to the lack of density differentiation between pitch and micro-fibrils. The filtration method adopted avoided the compaction of fibres at the filter interface by employing continuous stirring. It may well have been the case that the filtration process limited the pitch to the finer colloidal fraction, but it was this that was of primary interest. It was found that significant quantities of pitch could be collected in this way for the following experimentation, and the subsequent studies were focused on quantitative adsorption of pitch independent of any pitch selectivity as a result of the preparation process.

The zeta potential of the suspension was measured with a PenKem 500 device (PenKem, Inc., Bedford Hills, N.Y) giving a value of -15 mV. The total charge was determined by a streaming current detector titration (SCD), (Mütek PCD-02, BTG Mütek GmbH, Arzbergerstrasse 10 82211 Herrsching / Germany) and was found to be 0.56 µEqg⁻¹ and the polyelectrolyte titration of the pulp filtrate gave -2.6 µEqg⁻¹, where 1 Eq (equivalent) is the weight in grams of that substance which would react with or replace one gram of hydrogen. Ion chromatography ( Dionex DX 120 Ion-Chromatograph, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94085, USA) of the TMP sample of March 04 reported the following anions present in the
 TMP filtrate: $\text{SO}_4^{2-} = 256 \text{ ppm}, \text{PO}_4^{3-} = 33 \text{ ppm}, \text{Cl} = 20 \text{ ppm} \text{ and } \text{NO}_3^{-} = 2 \text{ ppm}$.

The talc samples examined are all typically available grades, except for one experimental product with exceptionally high surface area. The sample abbreviations used are based on their mineralogical properties and/or provenance and are shown in Table 1. For the X-ray diffraction analysis a Philips (Philips Analytical, Lelyweg 1, 7602 EA Almelo, Netherlands) PW series X-ray diffractometer with X'menu / PC-APD software was used ($2\theta$ ranging 5 – 35°, Cu anode) and the area between the Bragg d-spacing values of 17.65 – 2.56 Å was analysed. X-ray diffraction is only a semiquantitative method in respect to crystallite concentrations, so the characterisation of mineralogical composition was made by comparing the talcs relative to one another. To evaluate the total charge of the talc, an electrolytic titration against N-methylglycol-chitosan, concentration 0.0025 mol dm$^{-3}$, as anionic agent (both from W ACO-chemicals), was made using streaming current detection. Particle size distribution was also determined with two different devices, namely a laser light scattering-based method (Malvern Master Sizer, Malvern Instruments Ltd., Enigma Business Park, Grovewood Road, Malvern, Worcestershire WR14 1XZ, UK) and a sedimentation method (Mütek PCD-02), was used between the Bragg d-spacing values.

The tests were made in duplicate for each sample talc. A reference sample without talc, also measured twice, was used as a sample talc. A reference sample without talc, also measured twice, was used as a reference sample.

### Experimental

The tests were made in duplicate for each sample talc. A reference sample without talc, also measured twice, was used as a reference sample to determine the effectiveness of the talc in removing colloidal species from the suspension.

The filtrate from the pulp was distributed into glass bottles; 200 g of filtrate in each bottle and 1% (w/w) of talc was added. The bottles were closed and agitated for 2 hours. After 2 hours, the suspension was centrifuged for 15 minutes in a Jouan C312 centrifuge at a speed of 3 000 min$^{-1}$.

A liquid upper phase is obtained after the centrifugation of the TMP filtrate treated with talc. Evaporation and gravimetric analysis expresses the quantity of total remaining solved or colloidal material. However, these results reflect also salts in solution. If the talc is efficient, it should reduce the residue in this liquid upper phase. The upper and the lower phases after centrifugation were carefully separated and analysed as follows.

### Table 1. Mineralogical evaluation of talc samples.

<table>
<thead>
<tr>
<th>Description</th>
<th>Sample abbreviation</th>
<th>Source</th>
<th>X-ray diffraction (XRD) characterisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>High chlorine talc cationised</td>
<td>HCTC</td>
<td>Austria</td>
<td>Talc, relatively high amount of chlorine, probable quartz, some carbonates (dolomite &amp; magnesite), trace of possible amphibole mineral, some weak unidentified XRD peaks.</td>
</tr>
<tr>
<td>High chlorine talc</td>
<td>HCT</td>
<td>Austria</td>
<td>Talc, relatively high amount of chlorine, probable quartz, some carbonates (dolomite &amp; magnesite), some weak unidentified XRD peaks.</td>
</tr>
<tr>
<td>Finnish talc</td>
<td>FT</td>
<td>Finland</td>
<td>Talc, relatively small amounts of chloride and magnesite.</td>
</tr>
<tr>
<td>High dolomite-containing talc</td>
<td>HDT</td>
<td>South of France</td>
<td>Talc, dolomite, small amount of calcium carbonate and chloride, possible traces of quartz, some weak unidentified XRD peaks.</td>
</tr>
<tr>
<td>Australian talc</td>
<td>AT</td>
<td>Australia</td>
<td>Talc, small amounts of chloride and dolomite.</td>
</tr>
<tr>
<td>Turkish talc</td>
<td>TT</td>
<td>Turkey (Production, - provenance: near East)</td>
<td>Talc, calcite, chlorite, probably small amount of quartz, trace of possible amphibole mineral, probably small amount of dolomite, some small unidentified XRD peaks.</td>
</tr>
<tr>
<td>Pure Turkish talc</td>
<td>PTT</td>
<td>Turkey (Production, - provenance: near East)</td>
<td>Talc (no other clear XRD peaks in analysed area).</td>
</tr>
<tr>
<td>Special high surface area talc</td>
<td>SHSAT</td>
<td>Finland</td>
<td>(Same as FT)</td>
</tr>
</tbody>
</table>

*The talc SHSAT was produced by delamination in a laboratory media mill*

### Table 2. Physical properties of the various talcs.

<table>
<thead>
<tr>
<th>Sample abbreviation</th>
<th>Specific surface area / m$^2$g$^{-1}$</th>
<th>Median particle diameter / µm</th>
<th>Density - (streaming current detector) / (SCD) / µg g$^{-1}$ (Müttek PCD-02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCTC</td>
<td>6.3</td>
<td>7.74</td>
<td>3.60 (Master Sizer S) 3.60 (Sedigraph 5100) 3.60 (Philips) 3.60 (MÜtek)</td>
</tr>
<tr>
<td>HCT</td>
<td>7.2</td>
<td>7.23</td>
<td>3.05 (Master Sizer S) 3.05 (Sedigraph 5100) 3.05 (Philips) 3.05 (MÜtek)</td>
</tr>
<tr>
<td>FT</td>
<td>8.6</td>
<td>5.87</td>
<td>2.30 (Master Sizer S) 2.30 (Sedigraph 5100) 2.30 (Philips) 2.30 (MÜtek)</td>
</tr>
<tr>
<td>HDT</td>
<td>10.8</td>
<td>6.06</td>
<td>3.00 (Master Sizer S) 3.00 (Sedigraph 5100) 3.00 (Philips) 3.00 (MÜtek)</td>
</tr>
<tr>
<td>AT</td>
<td>13.1</td>
<td>4.94</td>
<td>2.62 (Master Sizer S) 2.62 (Sedigraph 5100) 2.62 (Philips) 2.62 (MÜtek)</td>
</tr>
<tr>
<td>TT</td>
<td>19.5</td>
<td>5.93</td>
<td>2.42 (Master Sizer S) 2.42 (Sedigraph 5100) 2.42 (Philips) 2.42 (MÜtek)</td>
</tr>
<tr>
<td>PTT</td>
<td>24.5</td>
<td>6.33</td>
<td>2.21 (Master Sizer S) 2.21 (Sedigraph 5100) 2.21 (Philips) 2.21 (MÜtek)</td>
</tr>
<tr>
<td>SHSAT</td>
<td>51.0</td>
<td>10.53</td>
<td>0.79 (Master Sizer S) 0.79 (Sedigraph 5100) 0.79 (Philips) 0.79 (MÜtek)</td>
</tr>
</tbody>
</table>

*The value is determined with streaming current detector (SCD) / µg g$^{-1}$ (Müttek PCD-02)*

**Upper phase - aqueous phase - chemical oxygen demand, turbidity and gravimetry**

The aqueous upper phase was divided into further samplings for testing.

A 2 cm$^3$ sample was taken to make a chemical oxygen demand (COD) analysis, which gives a value for the total organic content. The COD analysis expresses the quantity of oxygen necessary for the oxidation of organic materials into CO$_2$, and was measured using a Lange CSB LCK 014, range 1000-10 000 mg dm$^{-3}$ with a LASA 1 / Plus cuvette.

A 45 cm$^3$ sample was taken to make an analysis of the Turbidity; by means of a Novasina 155 (NOVASINA is a division of Axair Ltd., Talstrasse 35-37, CH-8808 Pfäffikon) model NTM-S (152). This instrument transmits light in the near infrared spectrum through an optical fibre probe where the emerging beam is scattered by particles in...
suspension. Light scattered back at 180° is received by parallel optical fibres in the probe and focused onto a photo-diode. The resulting signal is amplified and displayed directly in Nephelometric Turbidity Units (NTU), defined as the intensity of light at a specified wavelength scattered, attenuated or absorbed by suspended particles at a method-specified angle, usually 90°, from the path of the incident light compared to a synthetic chemically prepared standard. Interference from ambient light is eliminated using a modulated transmitting signal, removing the need for light-tight sample handling systems.

A further 100 cm³ was placed into a pre-weighed aluminium beaker and dried in an oven (90°C, 24 hours) to get a total amount of non-volatile residue in the aqueous phase.

**Lower phase - sediments talc phase - thermogravimetric analysis (TGA)**

There is a fundamental problem when considering the thermal capacity and evaporation of adsorbed materials, in that the adsorbed material probably does not have the same vapour pressure as that of the chemically equivalent freely suspended material, such that a false absolute balance of material in upper and lower phase might occur due to the (latent) heating effect. This issue is not addressed here as it is assumed to be minimal and the test is designed for comparative purposes only and not directed at an absolute determination.

Thermogravimetric analysis was made on an SDTA 851e, from Mettler-Toledo (Mettler-Toledo Schweiz AG, Im Langacher, CH-8606 Greifensee), using a continuous heating rate of 20°C min⁻¹ from 30°C up to a possible maximum of 1 000 °C.

Initial study of tree resin showed that no volatiles could be found up to 90°C. The talcs were then measured to form subtractive blank runs to determine any volatiles, e.g. chemical agents used in the manufacturing of the talcs. The corresponding blank value is subtracted from the value subsequently obtained from the sediment.

The sediment itself was dried in an oven at 90°C during 24 h before TGA analysis.

**Results and Discussion**

**Analysis of the aqueous phase**

The efficiency of talc for removing material from the aqueous phase is shown in Fig 1. The quantity of residual deposit (non adsorbed pitch remaining in the water phase), as determined gravimetrically lies between 40 g dm⁻³ and 4.7 g dm⁻³.

We saw that the experimental product with especially high surface area, SHSAT, can reduce the quantity of total solved or colloidal material present in the filtrate of the TMP by 15% of the untreated pulp value. The result of the turbidimetric analysis is in good agreement with the gravimetric analysis of residue, as shown in Fig 2.

The test probably most specific for the pitch is the COD analysis of the liquid upper phase obtained after the centrifugation of the talc-treated TMP filtrate. In Fig 3 we can see that all talcs depress the remaining quantity of organic compounds in the TMP filtrate. In order of effectiveness: SHSAT > PTT > AT > HCTC > FT > HDT > TT > HCT.

The amount of chlorite present in the talcs follows, in decreasing order: HCTC, HCT > TT > FT, HDT, AT, SHSAT > PTT. The HCTC has a high proportion of chlorite and the PTT is virtually pure. There was, in this series, no apparently strong correlation between the level of chlorite and the order of effectiveness of the talc on pitch reduction.

**Analysis of the solid phase – effect of soluble Ca²⁺ ion in respect to sample pH**

Under the slightly acidic conditions of the TMP filtrate, it is possible that some carbonate mineral traces contained in the talc might become dissolved, transferring them to the upper liquid phase. This may cause some error when loss of organics is compared with the blank run of unexposed talc. To check this potential influence, two talcs containing significant levels of carbonate (HCTC, HCT) were treated in a water solution at pH 5.7 (same as TMP filtrate) as follows.

An acidic aqueous solution of pH 5.7 was obtained using dilute H₂SO₄. 1% (w/w) of each talc, HCTC and HCT, was added to 800 cm³ of this acidic water, distributed equally in four bottles of 250 cm³ capacity each. 1% (w/w) of each talc, HCTC and HCT, was
separately added into two separate bottles. The bottles were closed and agitated for 2 hours. After 2 hours, the suspension was centrifuged for 15 minutes in the Jouan C312 centrifuge at a speed of 3 000 min\(^{-1}\). The tests were then repeated using the remaining two bottles for each talc. The TGA method of gravimetric weight loss analysis was made on the solid lower phase obtained from each test after centrifugation.

For the HCTC treated with the acid water we obtained a weight loss of 9.06\% against a weight loss of 9.01\% for the same talc HCTC reference (not acid treated). For the HCT talc treated with acid water a loss of 8.27\% against a loss of weight of 8.34\% for the same talc HCT untreated reference. The results show us that no significant dissolution of carbonate from the crystal structure occurred and hence no alteration of the talc due to the acid conditions of the TMP pulp. We can therefore have confidence when considering the use of the method based on TGA analysis of the centrifuged residue.

The solid lower phase obtained after the centrifugation of the talc-treated TMP filtrate was seen to contain talc and adsorbed pitch as expected. TGA analysis expresses the progressive cumulative vaporisation of organic material present in the TMP filtrate, which had previously been adsorbed onto the talc surface. Therefore, this test provided a cross-check on the values obtained from the aqueous phase by showing the inverse proportional (opposite) trend, i.e. what was taken out of the water phase should show up on the talc surface. This is indeed shown to be the case and confirms that the drying process at 90\(^\circ\)C has not led to a loss of any volatile material in the pitch.

The reference pitch suspension was also centrifuged to see if there are solid particles that sediment out which could be confused for talc-sorbed pitch. The use of a special cone-shaped centrifuge glass revealed only a very small amount of deposit that was barely visible and could not be detected gravimetrically.

Cationic treatment of high chlorite-containing talc (HCTC vs. HCT) did not show any advantage in direct adsorption measurements.

**Time-dependent (seasonal) fluctuations of the pulp samples**

Pulp and pitch composition in practice depend on the seasonal cycle, therefore it is not surprising to find differences in the material content albeit when the sampling period covers only the winter months.

It is not the aim of this study to give a more detailed analysis of pitch occurrence as a function of season. For example, we have no information when the trees were harvested. Furthermore, omni-present micro-organisms contribute their part to the dynamically changing chemical composition of the pulp. We notice the greatest coefficient of variation in respect to pulp from the TGA results above, which full in the interval of 3.0 - 13.6\% for the sedimented talc phase.

The trend shown by the sorptive properties of the various talcs, however, is the same across all the pulp samples, such that we can assume that the ranking tests are reproducible for a wide range of typical pulp samples.

**Correlation between the analyses**

The results from the March 04 pulp sample are used to show correlations between the various analytical methods employed. The correlations in Fig 5 show the agreement between the relevant methods for the two centrifuge product phases. Agreements between TGA for the solid phase and COD for the aqueous phase together with the turbidity versus gravimetry are good and support the observed trends, (Fig 5).

We see that the plot of turbidity against gravimetry in Fig 5 does not go through the origin. This offset was shown to be due to solved ions by correlation with the ion chromatography discussed in the experimental section, not directly influencing turbidity but showing up in the residue.

Once again we see the outlying point associated with the very high surface area experimental product. This data point is not an extrapolation but confirmed by repeated experimentation. The trend lines in Fig 5 and Fig 6 are, therefore supported by the weighting of these repeated experiments.
Specific surface area correlates with pitch-collecting efficiency

With these combined results it is obvious to see that talc, as expected, reduces the organic matter present in the TMP filtrate. By referring back to the talc properties, as shown in Table 1 and Table 2, we see that the efficiency in this reduction is proportional to the specific surface area of the talc being used, as presented in Fig 6. Again the TGA and the COD methods confirm that the specially-produced sample SHSAT, having the greatest specific surface, has the greatest effect on reducing organic material present in the TMP. These findings would confirm that it is mainly the low surface energy nature of the pure talc platelet surface, maybe in combination with the conversely more polar edges of the platelet, which gives rise to adsorption of lipophilic species dispersed in water.

The TGA/specific surface area plot in Fig 6 suggests that there might be a deviation from linear correlation at low surface area. Whether this is a systematic error or a property of talc as the theoretical lower limit of specific surface area is reached is not known. Once again, we can eliminate the possibility of some non-adsorbed sedimented organic material causing the positive offset by the tests made in the absence of talc.

Advantages/disadvantages of the different detection methods in practice

The organo-specific COD test has a drawback in that it samples also dissolved agents and bio-mass. Therefore these possibilities should be carefully considered, especially when in a mill environment and when designing a continuous monitoring technique.

The reduction of the inorganic matter present in the filtrate (seen as the difference between the explicitly organo-specific COD test and the non-specific gravimetry residue value) seems to less dependent on the specific surface than the reduction of organic material.

The turbidity is influenced by colloidal non-pitch particles such as mineral fines (including the talc itself), flocs of biomass and any other additives which may be present in colloidal form. The fibrils and any other species larger than 2 µm were eliminated in the filtration step, as checked under the microscope. The gravimetry results, in turn, contain dissolved material of both organic and inorganic nature.

In this study the thermogravimetric analysis of the sediment serves only as a double control of the adsorption behaviour of the colloidal matter as determined in the liquid phase.

Conclusion

We have shown that reliable results can be obtained by directly studying the adsorption of organics, taken from realistic thermomechanical pulp samples, onto the surface of talc, and that these results can be used to differentiate various mineralogically formed talc samples in terms of their pitch collection efficiency.

Talc pitch adsorption efficiency is seen to be primarily correlated with the specific surface area of the particles. Secondarily it is seen that the purity of the talc may also be of importance in certain contexts. Highly delaminated pure talc is therefore seen to be most advantageous for pitch adsorption. Cationic treatment of high chlorite-containing talc did not show any advantage in direct adsorption measurements.

Future work will look at the influence of increasing talc surface area on organic depositable material present in recycled or chemical pulps.

Literature


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Manuscript received June 1, 2004
Accepted November, 2004