Interaction Forces between Talc and Pitch Probed by Atomic Force Microscopy

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Colloidal wood resin components present in pulp are collectively called “pitch”. The presence of pitch may cause severe problems due to deposits in and on the paper machine. There is thus a need for controlling pitch aggregation and adsorption. To be able to develop more efficient pitch control systems, one needs to develop the understanding of pitch—pitch interactions and of the interactions between pitch and other materials. With this general goal in mind, we present methods for preparing geometrically well-defined pitch particles attached to atomic force microscopy tips. This has enabled us to investigate the interactions between pitch and talc, an additive commonly used for pitch control. We have used model pitch particles consisting of one component only (abietic acid), a mixture of components (collophonium), and particles prepared from real pitch deposits. We show that the forces acting between pitch and talc are attractive and, once the initial approach is made, exert this attraction out to large distances of separation. We present evidence that the formation of bridging air bubbles or cavities is responsible for this interaction.

1. Introduction

Talc is a naturally occurring mineral with the chemical formula Mg₃Si₄O₁₀(OH)₂. The pure talc mineral has hydrophobic properties due to its preferred cleavage along the planar layers that are connected by weak van der Waals forces (Figure 1), which exposes the nonpolar and inert basal plane. However, because the transplanar edges contain exposed OH groups, the measured hydrophobicity of pure talc is normally varying depending on particle size, comminution method, and exposure time to air after cleavage. Talc is also known to contain impurities of other minerals, giving it a wide range of colors in addition to the white color of pure talc. Water contact angles of 66°–90° (e.g., see refs 1 and 2) have been mentioned in the literature, the wide span being due to the above-mentioned differences between talc samples.

Talc is used in the paper industry mainly as a filler but also as a coating pigment. Because of its hydrophobic properties, it has also been shown to be efficient as a pitch adsorber. The term “pitch” describes colloidal resin components present in pulp, which may agglomerate and deposit in and on the paper machine (Figure 2). These deposits may sometimes cause plugged washer screens or breaks, holes, and spots on the paper. Chemically, pitch covers a wide range of substances: fats and fatty acids, steryl esters and sterols, terpenoids, including terpenes, as well as compounds from adhesives contained in recycled paper, such as polyisoprenes and waxes. Process problems during pulp and paper manufacturing due to pitch vary a lot depending on the wood species used, the type of pulping process, and the conditions during papermaking. The solvent extractable resins from softwood species can typically contain 50% fatty acids, 40% resin acids, and 10% neutral components (glycerides, terpenoids, sterols, etc.) whereas hardwood species have a higher amount of neutral components and no resin acids. In chemical kraft pulping, at high temperature and pH, acid components will be saponified to form liquid crystalline sodium soaps or calcium soaps at lower

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temperatures.5 Soaps formed during pulping can be more or less sticky depending on, for example, pH, electrolyte concentration, and temperature, and detackifiers such as talc find use in chemical pulp mills. During thermomechanical pulping (TMP), a mechanical action is used and the resinous components are not saponified but may instead be dispersed in the aqueous phase and receive a high colloidal stability due to steric stabilization from wood carbohydrates or lignin compounds. In closed process streams, the dissolved and colloidal substances will build up, tend to aggregate, and form pitch problems.6 The pitch-adsorbing properties of talc have been investigated by a number of authors.7–11 Talc is believed to act in pitch control mainly as a detackifier;9 that is, it reduces the stickiness of pitch, but the detailed mechanisms involved in pitch control by talc are not known.

In an earlier study, we have shown that the attraction between talc and hydrophobic model surfaces is stronger than that expected from the van der Waals force alone at large separations.12 The mechanism was suggested to be due to gas/vapor cavities bridging the surfaces once the surfaces are brought sufficiently close together. This mechanism has earlier been suggested as a cause for the “hydrophobic” long-range attraction between nonpolar macroscopic surfaces immersed in aqueous solutions,13–16 but this topic is still frequently debated.17–21 In the present study, the interaction forces between cleaved talc surfaces and colloidal pitch particles produced from pulp, abietic acid, colophonium, or pitch deposits from paper machines are investigated with atomic force microscopy (AFM). The presence of long-range attractive interactions will be demonstrated, and the origin of this interaction will be discussed. The paper starts with a description of the preparation of the colloidal probe particles made from pitch and their characterization. Thereafter, the measured forces are reported and discussed.

2. Experimental Section

2.1. Materials. A cleavable talc sample giving smooth talc surfaces was obtained from the Swedish Museum of Natural History (Figure 3). The sample originated from Tarrekaise in Lapland, Sweden, and consisted of pure natural talc (verified by X-ray diffraction). Colloidal probes were prepared by water extraction from a softwood thermomechanical (TMP) pulp taken closely after the mechanical refiner but before the pulp was in contact with process water from the paper machine (SCA, Sweden) and by using abietic acid (Fluka, Switzerland), colophonium (Omya, Switzerland), or pitch deposits from a newspaper mill using softwood mechanical pulp (Stora Enso, Sweden). The chemical composition of the different pitch samples will be reported in the Results.

Inc., United States) glued to a cantilever using a very small amount of a solvent-resistant epoxy glue [Araldite Rapid from Casco, Sweden, containing 2,2-bis(p-2,3-epoxypropoxy)phenyl]propane]. The deposition was performed by pouring one droplet of the overphase onto the silica probe attached to the cantilever. The liquid was allowed to evaporate, and as a result, a pitch film formed on the silica probe. Colloidal probes from abietic acid (Fluka), collophonium (Omya), or pitch deposits (Stora Enso) were prepared using two methods. In each case, the manipulation of the pitch aggregates was performed using a clean, electrochemically etched tungsten fiber attached to a micromanipulator (Eppendorf AG, Germany).

The first method used for preparing pitch colloidal probes was started by placing a piece of the material on the cantilever, heating it to its softening temperature, and letting the material spontaneously form a hemisphere due to surface tension forces. It was attached to the cantilever by molecular forces only. This method, which worked for all pitch samples, is hereafter called the melt method.

The second method started by dissolving the pitch substance in acetone, followed by precipitation in water. Next, drops of the liquid containing dispersed pitch particles were placed on a clean object glass and allowed to dry. These pitch particles were attached to the cantilevers by the Araldite glue. This method will be referred to as the precipitation method. The precipitation method worked only for abietic acid, whereas the other materials gave too soft or irregular probes for later use in AFM studies.

After the attachment of the probes to the cantilevers, each of them was imaged from the side using ESEM (environmental scanning electron microscopy, Philips XL30). The curvature of the probe was measured, and the corresponding radius was used when normalizing the measured force, i.e., to obtain $F/R$ (force/radius) values. ESEM images of some of the probes used for obtaining the force curves presented in this article are shown in Figure 4.

The talc substrates were prepared according to the following procedure: A circular magnetic stub with a diameter of 1 cm was covered with double-sided adhesive tape on which a mica sheet was placed. A very small amount of a thermosetting resin (Epikote 1004, Resolution Europe B.V., The Netherlands) was placed in the middle of the mica surface and heated to 100 °C. A sheet (platelet) of talc, with the approximate dimensions of 5 mm × 5 mm × 0.2 mm, was pulled away from the talc ore and placed with its center on the resin spot, covering it completely. After some cooling at 20–22 °C (at least 30 min), the substrate was introduced into the AFM. A light microscope was used to locate a smooth and even area on the talc surface, where the force measurements were conducted. A tapping mode AFM image (taken in air) of a talc surface prepared in this way is displayed in Figure 5. The roughness characteristics over the line scan, shown in Figure 5, are defined by $R_s = 0.477$ nm and $R_k = 0.337$ nm (see Appendix), which is typical for the talc samples prepared this way. We note that each measurement series was performed on a freshly prepared talc sample.

Flat macroscopic surfaces coated with collophonium used in the collophonium–collophonium force measurements were prepared by melting a layer of collophonium onto a mica surface. A tapping mode AFM image (taken in air) of a collophonium surface prepared in this way is displayed in Figure 6. The roughness characteristics over the line scan shown in Figure 6 are $R_s = 0.331$ nm and $R_k = 0.224$ nm.

2.4. Theoretical Considerations. The measured forces were compared with theoretically calculated van der Waals and electrostatic double-layer forces. To calculate the expected van der Waals force, the dielectric properties of the interacting surfaces and the intervening medium must be known. Thus, the dielectric properties for the different materials used in this investigation are summarized in Table 1.23

\[ A = \frac{3}{4} kT \left( \frac{e_1 - e_2}{e_1 + e_2} \right) \left( \frac{e_2 - e_3}{e_2 + e_3} \right) \left( n_1^2 - n_3^2 \right) \left( n_2^2 - n_3^2 \right) \]

\[ \frac{3h\nu^2}{8\sqrt{2} \left( n_1^2 + n_3^2 \right) \left( n_2^2 + n_3^2 \right) \left( n_1^2 + n_3^2 \right) \left( n_2^2 + n_3^2 \right) + \left( n_1^2 + n_3^2 \right) \left( n_2^2 + n_3^2 \right)} \]  \tag{1}

where $e_i$ is the static dielectric constant for medium $i$, $\nu$ is the main electronic absorption frequency in the UV region assumed to be the same for all three media, $n_i$ is the refractive index of medium $i$ in the visible region, $k$ is the Boltzmann constant, and $\hbar$ is Planck’s constant.

In these calculations, the dielectric properties of the materials, as given in Table 1, were used together with an absorption frequency of $3 \times 10^{15}$ s$^{-1}$. The results (where the second term in the formula was found to be dominating) are summarized in Table 2.

The theoretical van der Waals force curves were calculated using these values and the formula valid for a flat surface interacting with

3. Results and Discussion

3.1. Pitch Composition. The chemical composition of pitch can vary widely, and it is thus of interest to carry out chemical analysis of the samples. This was done by employing gas chromatography with flame ionization detection (GC-FID) using a method described by Örsä and Holmbom. The sample extracted from pulp has a chemical composition of 0.8% fatty acids, 9.8% resin acids, 29% alkanoles, 27% sterylesters, and 34% triglycerides. For the collophonium sample, the composition was found to be 1% fatty acids, 98% resin acids, and 1% steryl esters. For the pitch deposits, the composition was 60% fatty acids, 40% resin acids, and a negligible amount of neutral substances. This is consistent with the observation that resin and fatty acids are primarily found in deposits, even though extractives from softwood contain a significant amount of neutral fatty substances. There is, however, some contradiction in the literature, and Hassler finds the same components in the deposit as in the pulp extractive. Moreover, in the review paper by Hubbe et al., it is noted that triglycerides can indeed be a major factor in sticky deposits. In colloidal wood resin dispersions formed in a mechanical wood pulp, pitch particles show remarkable colloidal stability. This finding was attributed to steric stabilization by water-soluble or precipitated wood carbohydrates or lignins and is a factor that can influence the formation of sticky deposits. When a large amount of the pulp is chemical pulp from hardwood species, it can be even more complicated due to the high amount of natural substances.

\[ F/R = - \frac{A}{6D^2} \]  

quoting in units of N m\(^{-1}\).

Table 1. Dielectric Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive index, (n)</th>
<th>Dielectric constant, (\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc</td>
<td>1.57(^{23})</td>
<td>3.25</td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td>1.411</td>
<td>2.01</td>
</tr>
<tr>
<td>Abietic acid</td>
<td>1.546</td>
<td>2.75(^{a})</td>
</tr>
<tr>
<td>Water</td>
<td>1.333</td>
<td>80</td>
</tr>
<tr>
<td>Air</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^{a}\) No value was found for abietic acid; the value given is for a fatty acid.

Table 2. Hamaker Constants for the Different Systems

<table>
<thead>
<tr>
<th>Material 1</th>
<th>Medium</th>
<th>Material 2</th>
<th>Hamaker constant, (A) (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon</td>
<td>Water</td>
<td>Talc</td>
<td>7.58 \times 10^{-21}</td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td>Air</td>
<td>Talc</td>
<td>6.67 \times 10^{-20}</td>
</tr>
<tr>
<td>Abietic acid</td>
<td>Water</td>
<td>Talc</td>
<td>1.56 \times 10^{-20}</td>
</tr>
<tr>
<td>Abietic acid</td>
<td>Air</td>
<td>Talc</td>
<td>8.53 \times 10^{-20}</td>
</tr>
</tbody>
</table>

References:
of neutral substances that cannot be solubilized. However, the present study is focused to develop an experimental technique using model pitch but with examples both from dispersed colloidal resin from a softwood TMP pulp and from a pitch deposit.

The chemically simplest probe that we have used is thus abietic acid, which is a typical resin acid. Collophonium contains mainly a mixture of resin acids with a small amount of fatty acids and neutral fatty compounds. In comparison, the pitch deposits contain significantly more fatty acids, and the deposit is highly enriched in fatty acids and depleted in neutral fatty substances (triglycerides, sterylesters, and alkanols) as compared with the pitch extracted from pulp.

3.2. Water Contact Angles. The static contact angle of water, i.e., the contact angle obtained for a given drop volume, on freshly cleaved talc surfaces from the Tarrekaise source was found earlier to be in the range of 75°–86°. Surfaces made from abietic acid and collophonium were prepared by dissolving the material in acetone and letting the solution dry on a clean object glass forming a film. For both abietic acid and collophonium, we obtain initial water contact angles (pH 5.5–5.7) of around 90°. Figure 7 illustrates how the contact angles for abietic acid and collophonium change over time. We note in Du Nouy ring tensiometer measurements on pure water and water containing pieces of abietic acid or collophonium that the surface tension of the water in contact with the surfaces did not change markedly with time, which indicates that the decrease in water contact angle with time is primarily due to rearrangements in the surface layer leading to exposure of a larger number of polar groups toward the solution.

3.3. Force Measurements. 3.3.1. First Contact. The forces acting between an abietic acid particle prepared by the precipitation method and a talc surface across an aqueous 6 mM NaCl solution are displayed in Figure 8, which shows the results for the first five measurements. It should be noted that the approach force curve measured when the surfaces are brought together for the very first time is purely repulsive. The repulsion reaches a measurable strength at a separation of 10 nm. The distance dependence of the force is not consistent with that of an electrical double-layer force suggesting a steric origin due to compression of some asperities. On separation, a relatively strong attractive force amounting to 45 mN m⁻¹ was observed. The attraction measured on separation did not change significantly during the five measurements reported in Figure 8, all falling within the range 44–49 mN m⁻¹. Except for the very first time, the forces acting on approach were attractive. The jump-in distance increases with the number of approaches until it becomes saturated after about five measurements. We note that already at the second approach the measured attraction is larger than the theoretical van der Waals force.

The force curves measured on approach between a talc surface and a glass surface carrying a layer of pitch extracted from pulp were found to change with the number of measurements in the same manner as described above. Thus, for both model pitch and for the real pitch a long-range attraction develops as the pitch probe is brought into contact with the talc surface repeatedly.

A spontaneous cavitation (or dewetting) is expected to occur when two smooth and chemically homogeneous surfaces having...
water contact angles larger than 90° are brought together to sufficiently small separations,31 and this has been confirmed by experiments.32 Such a mechanism is, however, not operative when the contact angle is below 90°,31,33 which is the case for our systems. The larger than expected attractive force between hydrophobic surfaces has earlier also been suggested to be due to bridging of submicroscopic bubbles already existing on the surfaces before they approach each other.13 The stability of such bubbles on molecularly smooth hydrophobic surfaces has been questioned due to the high pressure inside such bubbles, which should result in very fast dissolution of the air into bulk water.34 Nevertheless, a range of reports supports the notion that submicroscopic air bubbles bridging between two surfaces in many cases are the reason for the long-range and strong attraction observed between nonpolar surfaces in aqueous media.19-21,34,37-41 This has recently been rationalized by the finding that the contact angle of the nanobubbles, as measured through the denser phase, is significantly larger than that of the corresponding macroscopic bubbles.13,44 This results in a lower Laplace pressure and thus a slower evaporation.

In our case, we deal with real surfaces having a certain roughness (Figures 5 and 6) and talc samples displaying a chemical heterogeneity,42,43 and this is, of course, also true for pitch particles. It is established that surface roughness and chemical heterogeneity promote contact angle hysteresis and the pinning of water droplets on surfaces in air.44,45 Similarly, air bubbles should be pinned on heterogeneous and rough surfaces immersed in water. Furthermore, some reports have previously noticed that the surface roughness and heterogeneity are of great importance for the long-range attraction between nonpolar surfaces in water.13,46,47

Thus, despite the fact that the macroscopic water contact angle is below 90°, we suggest that existence/creation of nanobubbles is the cause for the longer range (longer than van der Waals) attraction observed between pitch and talc. We suggest that each time the probe particle is separated from the talc surface an air cavity is created, as also has been observed in other systems.21,48 On further separation, the cavity collapses and some of the air attaches as nanobubbles on the surface. As the process is repeated, the amount of air attached to the surfaces in the contact region increases, which facilitates formation of more and larger nanobubbles, which serve to increase the range and magnitude of the measured attractive force.

References:


3.3.2. Difference between Probe Forming Methods for Abietic Acid. Forces measured while approaching an abietic acid probe prepared by the melt method toward a talc surface are reported in Figure 9. One force curve represents the interaction at the beginning of the measurement series, but not the very first contact, whereas the second force curve reflects the situation after contacting the probe and the surface repeatedly (about 500 times). It can be noted that, just as in the previous case, the attraction increases with the number of measurements, see Figure 10, and it is significantly larger than the predicted van der Waals force displayed in Figure 9. After repeated measurements, a repulsive force is observed at distances larger than the onset of the strong attraction. This repulsion decays exponentially with a decay length of about 10 nm, a value that is larger than the Debye length of 3.9 nm expected for a double-layer force between nondeformable surfaces at the given ionic strength (6 mM). The forces measured at this stage are very similar to those observed by Carambassis et al.\textsuperscript{14} using silanated (tridecafluoro-1,1,2,2-tetrahydrooctyl-methyldichlorosilane) silica surfaces, and our interpretation of the results is the same as theirs; that is, both the repulsion and the attraction are due to the presence of nanobubbles on the surface, where the repulsion is a combination of an electrostatic double-layer force and a force due to deformation of the air bubble. The repulsion turns into an attraction once the bubble bridges between the two surfaces.

Air bubbles have earlier been reported to have a negative charge in NaCl solution\textsuperscript{49} and also, abietic acid can bear a negative charge\textsuperscript{50,50} due to dissociation of surface-bound carboxylic acid groups. Thus, even though the force-measuring technique does not provide the sign of the charge, it seems clear that the surface potentials are negative. The jump-in distance and the adhesion force as a function of measurement number, all on the same spot on the surface, are shown in Figure 10. We note that the adhesion force, measured on separation, increases from 240 to 270 mN m\textsuperscript{-1} during the repeated measurements. At the same time, the jump-in distance, which reflects the range of the attraction, increases. The increase is large in the beginning and levels out by the same time as the repulsive force begins to show up in the approach force curve (around measurement 300). A comparison between Figures 8 and 9 shows that the attractive force is more long-range in the case where the probe is prepared using the melt method, Figure 9, as compared to when the precipitation method is used, Figure 8. Furthermore, we note that a significantly larger adhesion force is observed when a melted probe particle is used as compared to when the probe was prepared by the precipitation method. This suggests that the probe preparation method influences the hydrophobicity of the surface. Probes prepared in air, as in the melt method, expose mainly hydrophobic groups to the surface whereas probes prepared in water, as in the precipitation method, present a somewhat larger number of hydrophilic groups as the particles strive to minimize the interfacial energy toward the surrounding bulk phase. We note that, as shown by the time dependence of the contact angle, a reorientation of surface groups, leading to exposure of a larger number of hydrophilic groups, occurs when the surrounding medium is changed from air to water. However, once nanobubbles are formed on the surface, the regions covered by these bubbles will not become more hydrophilic with time.

3.3.3. Force Measurements with Collophonium. The forces measured on approach between a collophonium probe prepared by the melt method and a talc surface across 6 mM NaCl. forces of attraction are due to the presence of nanobubbles on the surface. Probes prepared in air, as in the melt method, expose mainly hydrophobic groups to the surface whereas probes prepared in water, as in the precipitation method, present a somewhat larger number of hydrophilic groups as the particles strive to minimize the interfacial energy toward the surrounding bulk phase. We note that, as shown by the time dependence of the contact angle, a reorientation of surface groups, leading to exposure of a larger number of hydrophilic groups, occurs when the surrounding medium is changed from air to water. However, once nanobubbles are formed on the surface, the regions covered by these bubbles will not become more hydrophilic with time.

Figure 9. Statistics for the adhesion (top) and jump-in distance (bottom) for the force measurement between a collophonium particle prepared by the melt method and a talc surface in 6 mM NaCl. 

Figure 10. Adhesion force, measured on separation, increases from 240 to 270 mN m\textsuperscript{-1} during the repeated measurements. At the same time, the jump-in distance, which reflects the range of the attraction, increases. The increase is large in the beginning and levels out by the same time as the repulsive force begins to show up in the approach force curve (around measurement 300). A comparison between Figures 8 and 9 shows that the attractive force is more long-range in the case where the probe is prepared using the melt method, Figure 9, as compared to when the precipitation method is used, Figure 8. Furthermore, we note that a significantly larger adhesion force is observed when a melted probe particle is used as compared to when the probe was prepared by the precipitation method. This suggests that the probe preparation method influences the hydrophobicity of the surface. Probes prepared in air, as in the melt method, expose mainly hydrophobic groups to the surface whereas probes prepared in water, as in the precipitation method, present a somewhat larger number of hydrophilic groups as the particles strive to minimize the interfacial energy toward the surrounding bulk phase. We note that, as shown by the time dependence of the contact angle, a reorientation of surface groups, leading to exposure of a larger number of hydrophilic groups, occurs when the surrounding medium is changed from air to water. However, once nanobubbles are formed on the surface, the regions covered by these bubbles will not become more hydrophilic with time.

Figure 12. Approach and separation force curves for the interaction between a collophonium particle prepared by the melt method and a collophonium surface across 6 mM NaCl.

Figure 13. Statistics for the adhesion (top) and jump-in distance (bottom) for the force measurement between a collophonium particle prepared by the melt method and a collophonium surface across 6 mM NaCl.

Figure 13. Approach and separation force curves for the interaction between a collophonium particle prepared by the melt method and a collophonium surface across 6 mM NaCl.
The interaction forces between a collophonium probe prepared by the melt method and a talc surface were also determined. The data reported in Figure 13 illustrate a typical force curve. In particular, we note that no long-range attraction is observed on approach. Thus, these surfaces are not sufficiently hydrophobic to allow the air bubble bridging mechanism to operate. On separation, an attractive force component is present, but the magnitude of this force is significantly less than for the previous systems, again indicating the absence of any bridging bubble between two collophonium surfaces.

These results also allow an additional important conclusion to be drawn concerning the force measurements between talc and pitch. Even though we cannot disregard the possibility that some pitch material is transferred to the talc surface during measurements, it is clear that such a possible material transfer is not responsible for the long-range attraction between talc and pitch. Conversely, our data suggest that such a material transfer is expected to lower the range and magnitude of the attraction.

### 3.3.4. Force Measurements with Pitch

A representative force curve for the interaction between a pitch particle prepared by the melt method and a talc surface across 6 mM NaCl is reported in Figure 14. The force curve has the signature of the presence of a submicroscopic bubble in the contact region. At large separations, a repulsive force with a decay length of 4.6 nm, as compared to the expected Debye length of 3.9 nm, dominates the interaction. Again, this force is suggested to be due to the combination of a repulsive double-layer force and a force due to deformation of the surface-bound bubble. The smaller decay length reported in Figure 14, as compared to in Figure 9, is suggested to be a consequence of the smaller extension of the bubble in the former case.

At a separation of about 15 nm, the repulsive force is overcome by a stronger than van der Waals predicted attraction. The adhesion between the pitch particle and the talc surface increases moderately with the number of contacts; see Figure 15. The magnitude of the adhesion observed for the different probes follows the trend abietic acid prepared by the melt method > abietic acid prepared by the precipitation method > collophonium prepared by the melt method > pitch prepared by the melt method. Because the adhesion force in water decreases with an increasing number of polar groups presented on the surface (i.e., with decreasing surface water interfacial tension), we draw the conclusion that the number of polar groups follows the same trend, and it is thus clear that collophonium is a significantly better model of pitch than abietic acid.

### 4. Conclusions

The forces between talc and pitch have been investigated using the AFM colloidal probe technique. Two methods for preparing suitable colloidal probes of pitch components and of the complex pitch deposits have been developed. The forces acting between talc and simplified pitch models differ considerably. When abietic acid is used as a pitch model, the surface of the particle is sufficiently hydrophobic to allow entrapment of submicroscopic bubbles on the surface, which results in long-range attractive forces exceeding the van der Waals force by orders of magnitude. The bubbles are not present, or too small, to give rise to this attraction during the very first approach. However, the act of repeatedly measuring the force induces bubbles on the surface that on subsequent approaches result in long-range attractive forces. When collophonium is used as a pitch model, bridging bubbles are again found to be present between the talc and the pitch model surface. However, in this case, the less hydrophobic nature of the pitch model particle prevents the bubbles from growing as a result of repeated measurements. The results for pitch probes interacting with talc are similar to those obtained for the collophonium—talc system. Thus, collophonium is a significantly better model for pitch than abietic acid. The large amount of neutral components in pitch from softwood mechanical pulp (TMP) or fatty acids from pitch deposits on a paper machine does not seem to have any large bearing on the forces acting between pitch and talc. Our results suggest that stirring and the presence of air in the aqueous phase are important for the use of talc in pitch control. The stirring facilitates the first attachment process of pitch to talc; and an increased air content in the aqueous phase facilitates bubble nucleation around the contact zone between pitch and talc.

No long-range attraction between two collophonium surfaces is observed, demonstrating that this substrate alone is not sufficiently hydrophobic to facilitate the bridging bubble mechanism. Thus, our results show that the surface nature of the pitch present is crucial for the nature of the interaction between talc and pitch. We further suggest that the topological roughness of the surfaces and their chemical heterogeneity facilitate pinning of air bubbles and this in turn facilitates attachment of pitch to talc. Thus, an efficient pitch control additive, such as talc, should be hydrophobic and present a controlled rough and heterogeneous surface layer.
Acknowledgment. Omya Development AG is thanked for funding this project and for supporting cooperation between YKI and its industrial Mineral and Surface Chemistry R&D.

Appendix

\[ R_q = \sqrt{\frac{\sum_{i=1}^{N} (Z_i - Z_{\text{ave}})^2}{N}} \]

where \( Z_{\text{ave}} \) = average \( Z \) value within the given area, \( Z_i \) = local \( Z \) value, and \( N \) = number of points within the given area.

\[ R_a = \frac{\sum_{i=1}^{N} |Z_i - Z_{\text{ave}}|}{N} \]

where \( Z_{\text{ave}} \) = \( Z \) value at the center plane, \( Z_i \) = local \( Z \) plane, and \( N \) = number of points within the given area.

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