

Adsorption of anionic dissolved and colloidal substances onto calcium carbonate fillers

TAKANORI MIYANISHI, YASUYUKI KAMIJO, AND HIROSHI ONO

SYNTHETIC OR NATURAL POLYMERS are used in papermaking systems as retention and drainage aids. Cationic retention aids interact with anionic substances. These anionic substances are called *pitch* or *anionic trash*, whose sources are shown in **Table I** (1). These substances decrease the efficacy of wet-end chemicals. Dissolved and colloidal substances (DCS) of mechanical pulp are carbohydrate, hemicellulose, and wood extractives such as resin acid and fatty acid. Wood extractives in particular lower the retention of pulp furnishes and have a detrimental influence on paper machine performance.

There are two approaches to pitch control. The first one employs a chemical treatment to retain the pitch in the paper sheet and remove it from the white water system. The second is to use anionic dispersants to prevent the pitch molecules from adhering to the machine equipment. In the chemical treatments, pitch control by talc or surface-modified clay was reported (2, 3). Many substances were studied relative to their adsorption behavior on precipitated calcium carbonate (PCC), such as copper (II) ions, calcium (II) ions (4, 5), surfactants (6), cationic starch, and alkyd resin (7–9). However, the pitch-controlling ability of PCC has not been well documented. The purpose of this study is to investigate the mechanism of pitch adsorption onto PCC.

EXPERIMENTAL

Sample preparation

Lignosulfonate, which is generally considered to be a dispersant, is used as a pitch model for the adsorption experiment in Jones's study (10) because this compound has an anionic character and its content in water is easy to determine. Hence, in addition to oleic acid and abietic acid, lignosulfonate was selected as the pitch model in our experiments.

The dissociation of the carboxyl group of oleic acid and abietic acid increases the water solubility of pitch models. But at high consistency, both oleic acid and abietic acid have low water solubility. Converting to a sodium salt can increase solubility. Ten percent of sodium oleate can be dissolved in water, and 20% of sodium oleate can be dissolved in ethanol. The pitch models used potassium salts of oleic acid and abietic acid. These acids were converted to potassium salts in a KOH ethanol solution according to Farley's method (11). Ethanol stock solutions were diluted for the adsorption experiments.

Two PCCs with different particle sizes were used. PCC has a low solubility in water; it dissolves by only 0.013 g/L in pure water. As a result, we considered that oleate molecules that were solubilized in water could be "adsorbed" on PCC particles. Talc was also examined to compare its pitch-controlling ability with PCCs. **Table II** shows the physical properties of fillers used in this experiment.

ABSTRACT

The proliferation of on-site precipitated calcium carbonate (PCC) filler plants allows substitution of an inexpensive material for fibers and a reduction in raw material cost, while at the same time enabling an increase in brightness and opacity. In neutral papermaking with wood-containing pulp grades, anionic trash derived from mechanical pulp has a tendency to cause pitch problems. The purpose of this study is to evaluate the pitch-controlling ability of PCC, which has not been well documented in the literature.

The key to pitch adsorption on PCC was the surface area and charge of PCC. Oleic acid was adsorbed on PCC ten times more than was abietic acid. This is explained by the different equilibrium constant to form calcium salt of oleic acid vs. abietic acid. The zeta potential of PCC changed from positive to negative with the adsorption of pitch model compounds. Anionic dissolved and colloidal substances in BTMP filtrate were adsorbed on PCC. Measurement of the total organic carbon (TOC) and colloid titration revealed that they were adsorbed on PCC until the anionic demand of PCC was neutralized. Colloidal substances were adsorbed on PCC more preferentially than were dissolved substances.

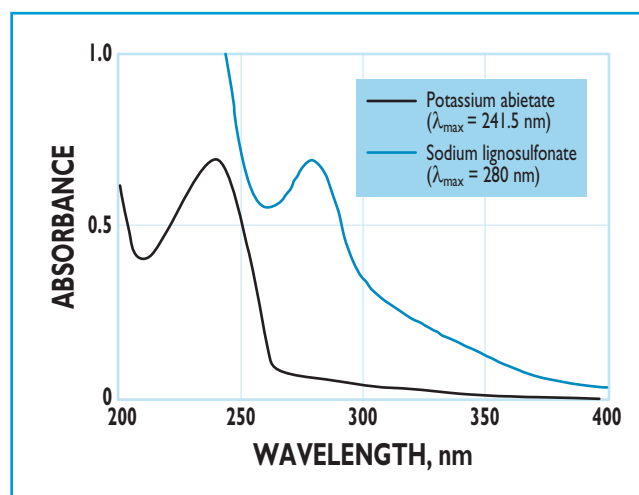
Application:

To avoid pitch problems when converting from acid to alkaline papermaking, we recommend using PCC from the beginning of the trial and maintaining the first-pass retention of PCC at a high level.

Bleached thermomechanical pulp (BTMP) was sampled from a mill. A 1% BTMP slurry was passed through No. 5B filter paper (ADVANTEC) to prepare the filtrate. The cationic demand of this solution was 443

Chemical nature	Origin
Sodium silicates	Peroxide bleaching, deinking, wasteboard
Polyphosphate	Filler dispersant
Polyacrylate	Filler dispersant
Organic acids	Pitch dispersant
Carboxymethylcellulose	Broke (coated)
Starch	Recovered paper, broke, strengthening agents
Humic acids	Fresh water
Lignin derivatives	Kraft pulp, wood pulp
Ligninosulfonates	Sulfite pulp
Hemicellulose	Wood pulp
Fatty acids	Wood pulp

I. The chemical nature and origins of detrimental substances (1)



I. UV spectra of pitch models

Sample	Dry brightness, %	Moisture, %	+325 mesh residue	Charge density, $\mu\text{eq/g}$	Particle size, μm	Specific surface area, m^2/g
PCC-A	>98	1.0	<0.1	41.0	2.64	5.8
PCC-B	97	0.5	<0.01	86.0	1.30	11.9
Talc	-	0.2	-	-4.2	10.60	5.9

II. Physical properties of fillers used in this experiment

$\mu\text{eq/L}$, and the amount of total organic carbon (TOC) was 376 mg/L. Cationic demand was determined by colloid titration using a streaming current detector (Charge Analyzer II, Rank Brothers). The colloid titration was performed by adding 0.001N potassium polyvinyl sulfate solution (PVSK) in an excess presence of polydiallyl dimethyl ammonium chloride (polyDADMAC) at $\text{pH } 9.0 \pm 0.1$. The reagents used in the colloid titration were products of Wako Pure Chemical Industries, Ltd.

Measurement of adsorbed pitch

The suspension, containing 1 g/L of PCC and 100 mg/L of the pitch model, was prepared, and its pH was adjusted to 9.0 with an HCl or NaOH solution. The samples were stirred for 30 min in a 500-mL Erlenmeyer flask. After stirring, fillers were removed from the sample suspension by suction filtration with a membrane filter (pore size = 0.22 μm). The pH of the filtrate was adjusted below pH 2.0 with an HCl

solution. The pitch model compounds that remained in the filtrate were extracted with dichloromethane. These compounds were converted to ethyl ester with diethyl acetate in dimethylformamide, and a quantitative analysis of the pitch model compounds was performed by gas chromatography (GC-14A, Shimadzu).

The zeta potential of the PCC filler was measured with a Zeta Sizer 2C (Malvern). When sodium lignosulfate (SLS) and abietic acid were used, the adsorbed amount of pitch on the filler was determined by measuring the residual pitch left in solution at equilibrium (11). The amount adsorbed was calculated by subtracting the amount remaining in solution from the amount added. The concentration of abietic acid and SLS in solution was determined using ultraviolet-visible spectroscopy (UV-265Fs, Shimadzu). The absorbance of the filtrate, which passed through a 0.22- μm membrane filter, was also measured.

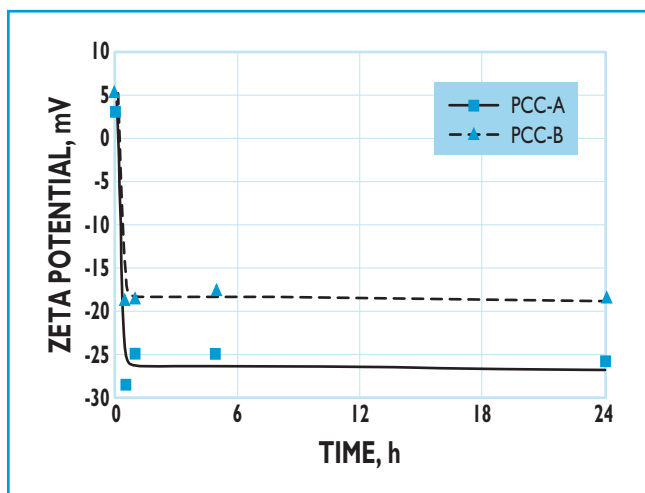
Figure 1 shows the maximum absorbance peaks: SLS reached 280 nm and abietic acid attained 241.5 nm. The absorption coefficient was determined by a calibration curve; the SLS coefficient was 6.67 $\text{L} \cdot \text{g}^{-1} \cdot \text{cm}^{-1}$ and the abietic acid coefficient was 10,700 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

DCS of BTMP

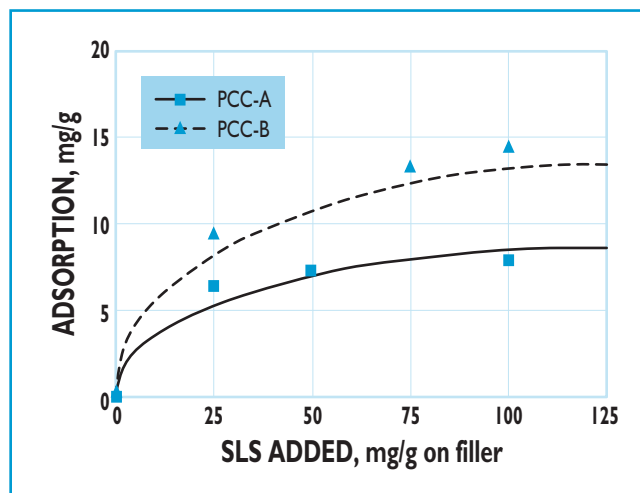
The PCC slurry, whose concentration was 2 g/L, was added to DCS at various levels. The BTMP/DCS ratio was changed from 0.25 to 5.0 on an oven-dry basis. The weight of BTMP was calculated by measuring the amount of DCS and BTMP concentration before filtration. For example, when 1 L of DCS (BTMP: 1% or 10 g/L) and 1 L of PCC slurry (2 g/L) were mixed, the weight of BTMP was 10 g and that of PCC was 2 g. Thus the BTMP/PCC ratio was calculated as $10/2 = 5$. The pH of the filtrate passing through a 0.65- μm membrane filter was adjusted to 11.0 after stirring for 2 hours. Cationic demand of the filtrate was determined by a streaming current detector.

Effects of DCS molecular weight

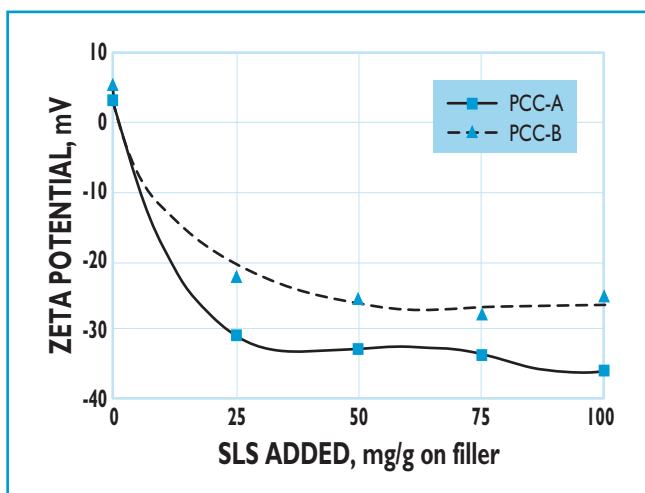
PCC-B was added to 500 mL of DCS, and the ratio of BTMP to PCC-B was varied from 1 to 5 on an oven-dry basis. The sample was stirred for 2 hours. Total organic carbon (TOC) concentration of filtrate that passed through a 0.65- μm membrane filter was measured by a TOC-5000 (Shi-



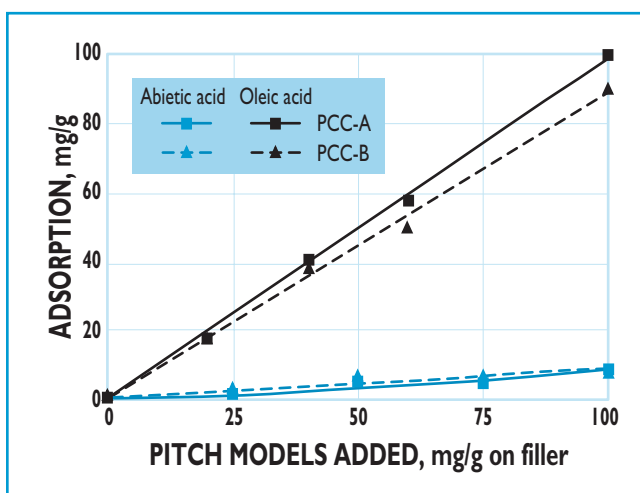
2. Change of zeta potential of PCC by oleic acid adsorption



3. Adsorption isotherm of SLS on PCC



4. Change of zeta potential of PCC



5. Adsorption isotherm of pitch models on PCC

madzu). The TOC concentration of the filtrate that passed through a 0.10- μm membrane filter was also measured. In this study, we defined colloidal substances as having a particle distribution of 0.10–0.65 μm , and dissolved substances were smaller than 0.10 μm . The concentration of colloidal substances was calculated by subtracting the amount remaining in solution from the concentration of dissolved and colloidal substances.

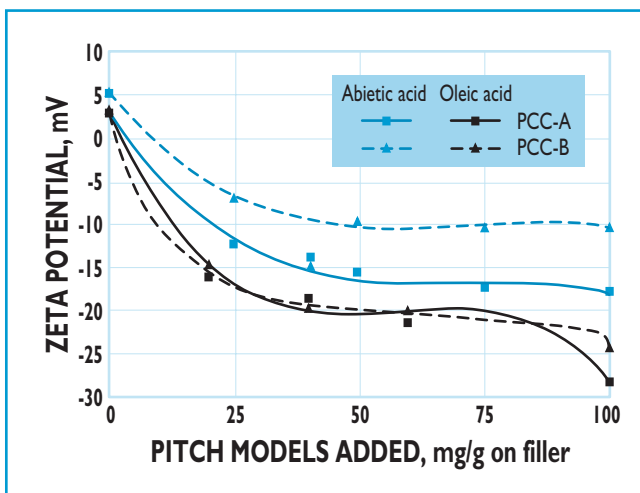
RESULTS AND DISCUSSION

Kinetic adsorption

The system reached equilibrium after 30 min. One hundred percent of the pitch model was adsorbed on PCC-A, and 90% of the model was adsorbed on PCC-B. Figure 2 shows the changes in zeta potential. The zeta potential of PCC-A changed from 3.0 mV to -25 mV, while that of PCC-B changed from 5.3 mV to -18 mV. PCC filler adsorbed oleic acid more than abietic acid.

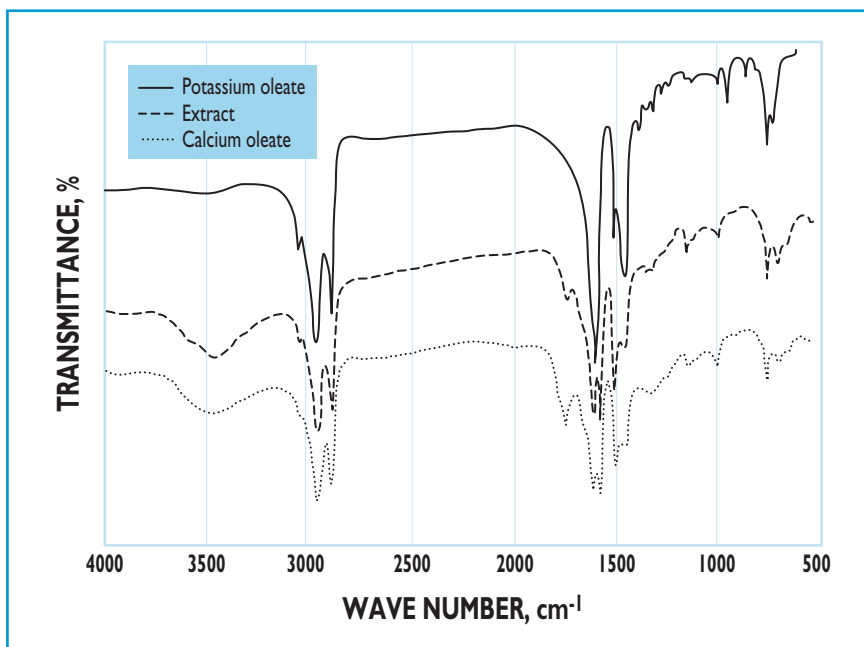
Adsorption isotherm

Adsorption isotherms of pitch model compounds and the changes of zeta potential of the PCC filler are shown



6. Change of zeta potential of PCC

in Fig. 2 and Figs. 3–6. The amount of adsorbed pitch model did not reach a plateau, except in the case of SLS. In the case of oleic acid and abietic acid, the adsorption



7. IR spectra of model samples and the extract adsorbed on PCC

Sample	100% adsorption, mg/g	GC method, mg/g	Soxhlet extraction, mg/g
PCC-A	20	16.82	7.46
	40	40.03	19.86
	60	56.80	21.94
	100	100.00	56.16
PCC-B	20	17.19	5.76
	40	37.88	20.42
	60	49.14	36.96
	100	89.83	55.62

*Gas chromatography

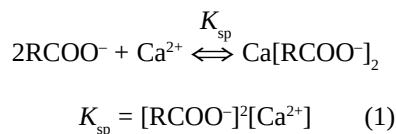
III. Difference in analytical results between GC* method and Soxhlet extraction method

increased linearly with increasing amounts of addition. Regarding fatty acids, some literature has reported that the adsorption isotherm of palmitic acid on PCC is represented by an S-shaped curve (12) and that the adsorption isotherm of heptadecanoic acid did not reach saturation (13). Our experimental results for oleic acid adsorption were similar to those obtained for the case of heptadecanoic acid. Some literature has also proposed that the interaction between filler and pitch was chemical in nature. This conclusion was based on the results of zeta potential measurements (10). We intend to further study the interaction between filler and oleic acid. Fourier transform infrared (FTIR) measurements (Nicolet, Magma-IR 850) were made for the extractive.

Figure 7 shows the IR spectra of three compounds: potassium oleate, calcium oleate, and the methanol

extract of adsorbed material on PCC. In the extract spectra, the characteristic adsorption band of potassium oleate disappeared, and that of calcium oleate appeared at 1560 cm⁻¹. Figure 7 indicates that potassium oleate was converted to calcium oleate. Ca²⁺ ions on the PCC surface attracted the carboxyl group of oleic acid by electrostatic interaction and formed calcium salt. Table III shows that some oleic acid molecules were strongly fixed on PCC. We assumed that the adsorption of pitch models on PCC was expressed by Eq. 1 (as follows), and the solubility product was calculated by turbidimetric analysis. The solubility product (K_{sp}) of calcium abietate was 5.0×10^{-10} .

Compared to the solubility product of oleic acid (14)— 4×10^{-13} —the value of 5.0×10^{-10} reveals that abietic acid had less reactivity to form calcium salt than did oleic acid. The difference between fatty acid and resin acid came from the different solubility products of their calcium salts.



The same measurement technique was used for the extract on talc. The peak had characteristic adsorption bands at 1560 cm⁻¹ and 1720 cm⁻¹. Figure 8 shows that the methanol extract of material adsorbed on talc was a mixture of potassium oleate and oleic acid. Figure 9 shows an adsorption isotherm of pitch models on talc. PCC had the same pitch-controlling ability as talc. Some reports have indicated that talc has a hydrophobic surface with a water contact angle of 88° (2) and that the driving force for pitch adsorption on talc was van der Waals forces (15, 16). It was estimated that PCC and talc had different adsorption interactions with the model pitch.

Agglomeration of PCC

We measured the particle size of the fillers. Figure 10 shows that PCC agglomerated after adsorption of oleic acid while talc did not. We propose that this phenomenon is due to a different adsorption mechanism. Figure 11 shows a schematic of flocculated PCC particles. The zeta potential of PCC changed from positive to negative with adsorption of the model pitch. As Ca²⁺ and CO₃²⁻ ions are adsorbed on the PCC surface, giving the PCC a

surface charge, PCC can adsorb both cationic and anionic compounds (17). We hypothesized that the Ca^{2+} ions on the PCC surface attract dissociated carboxyl groups of the pitch model by electrostatic interaction, and the pitch model forms calcium salt on the PCC surface. **Figure 12** illustrates that adsorbed model pitch makes the PCC surface more hydrophobic. PCC particles agglomerate with other PCC particles by van der Waals forces.

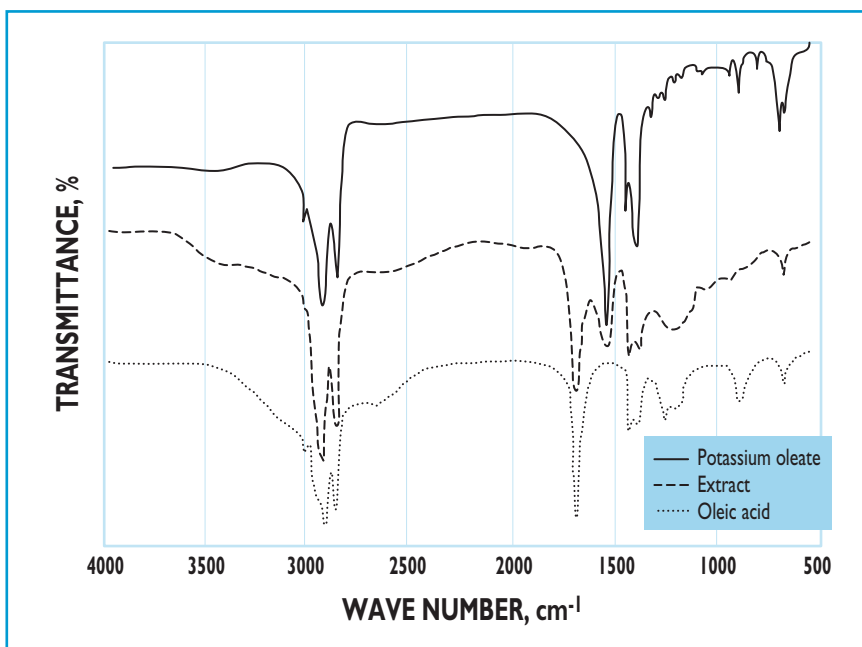
In contrast, the hydrophobic surface of talc attracts pitch model by van der Waals forces. **Figure 13** shows the changes of zeta potential by adsorption of pitch model on talc. The zeta potential of talc decreased with pitch model adsorption. Isomorphic lattice substitution and the presence of silanol and aluminol groups on the surface generally govern talc surface charge. The carboxyl group of model pitch, which faces the bulk liquid phase, provides little contribution to the surface charge. **Figure 12** illustrates that the adsorbed talc surface has a more anionic charge and repels each other by having the same electrostatic charge.

DCS of BTMP

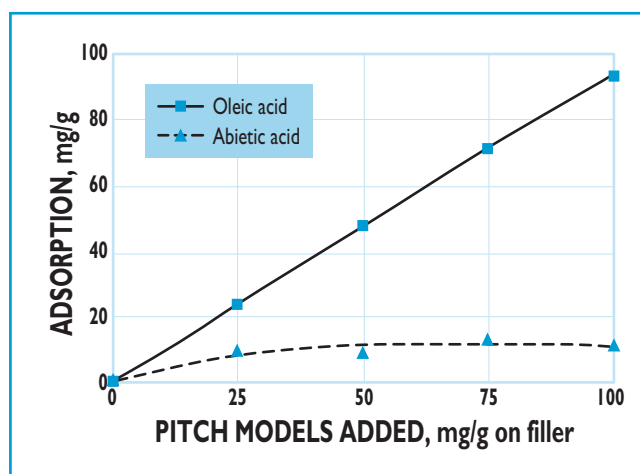
Figure 14 shows that PCC-B decreased the cationic demand of DCS two times more than did PCC-A. This was due to the different anionic demand of PCC. The anionic demand of PCC-B was 172 $\mu\text{eq/g}$, and that of PCC-A was 82 $\mu\text{eq/g}$. Both fillers adsorbed anionic substances until the anionic demand of PCC was neutralized.

Effects of DCS molecular weight

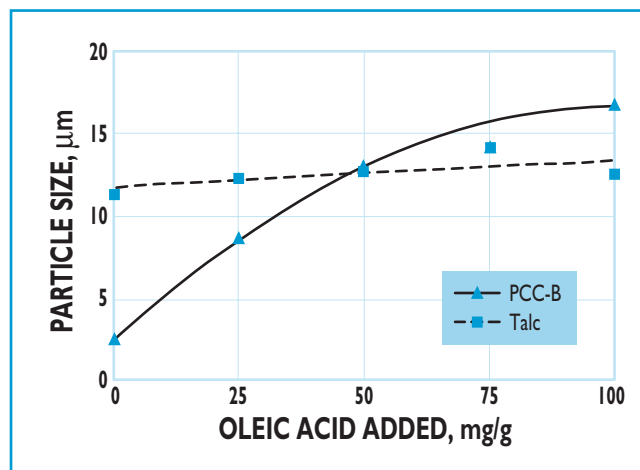
Table IV shows that BTMP colloidal substances were adsorbed on PCC more preferentially than were dissolved substances. When the ratio of BTMP to PCC was 1, colloidal substances decreased by 40%, while dissolved substances decreased by only 0.2%. This implies that colloidal substances, which have relatively high molecular weight and have many anionic binding sites to react with Ca^{2+} ions on the PCC surface, are abundant in DCS. The competitive adsorption experiment was made using abietic acid and polyacrylic acid (molecular weight=450,000). The charge density was 14.6 meq/g (pH=11.0). **Table V** shows that the presence of polyacrylic acid decreased the amount of absorbed abietic acid from 5 mg/g to 0.7 mg/g. We concluded that adsorptivity of colloidal substances depends on their molecular weight.



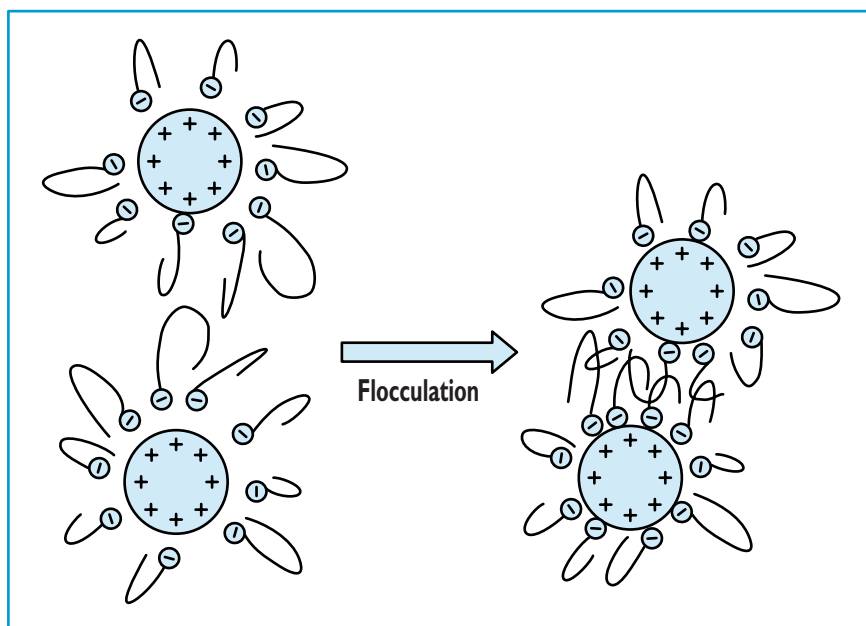
8. IR spectra of model samples the extract adsorbed on talc



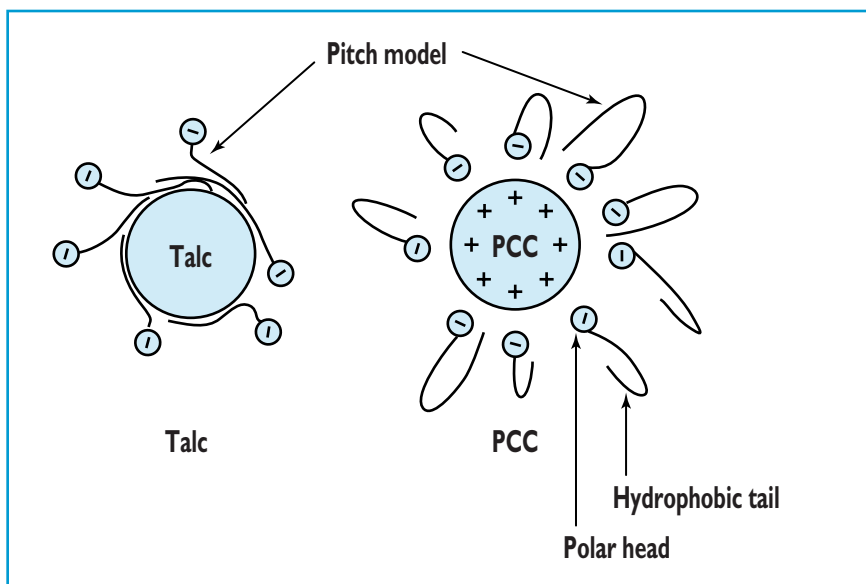
9. Adsorption isotherm of pitch models on talc



10. Oleic acid adsorption effect on particle size



10. Oleic acid adsorption effect on particle size



11. Schematic of flocculation PCC particles by adsorption of pitch model

CONCLUSIONS

We reached the following conclusions based on our experimental work:

- PCC adsorbed both oleic and abietic acids. Oleic acid was adsorbed on PCC ten times more than was abietic acid. PCC and talc adsorbed a similar amount of pitch. Thus an increase in the retention of PCC can reduce DCS in the papermaking system.
- Oleic and abietic acids were

adsorbed onto PCC by chemical adsorption, forming calcium salts. The different adsorption behaviors of oleic acid and abietic acid were most likely due to the different equilibrium constants of their calcium salts. PCC agglomerated, while talc dispersed with the addition of DCS. This difference was due to the interaction between the model pitch and filler. The surface charge of PCC was neutralized by direct contact of polar hydrophilic groups.

Hydrophobic chains, which faced toward the water phase, agglomerated PCC by van der Waals forces. In the case of talc, model pitch attached to the talc surface by physical adsorption, and free hydrophilic groups created a negative surface charge, screening the approach of other talc particles. The talc particles repelled each other by having the same electrostatic charge.

- Anionic DCS of BTMP were adsorbed on PCC until the anionic demand of PCC was neutralized.
- Colloidal substances of BTMP were adsorbed on PCC more preferentially than were dissolved substances of BTMP.

TJ

Miyanishi is a senior research manager, Kamijo is a research scientist, and Ono is a research scientist at Nippon Paper Industries Co., Ltd., Central Research Laboratory, 5-21-1 Oji Kita-ku, Tokyo 114, Japan.

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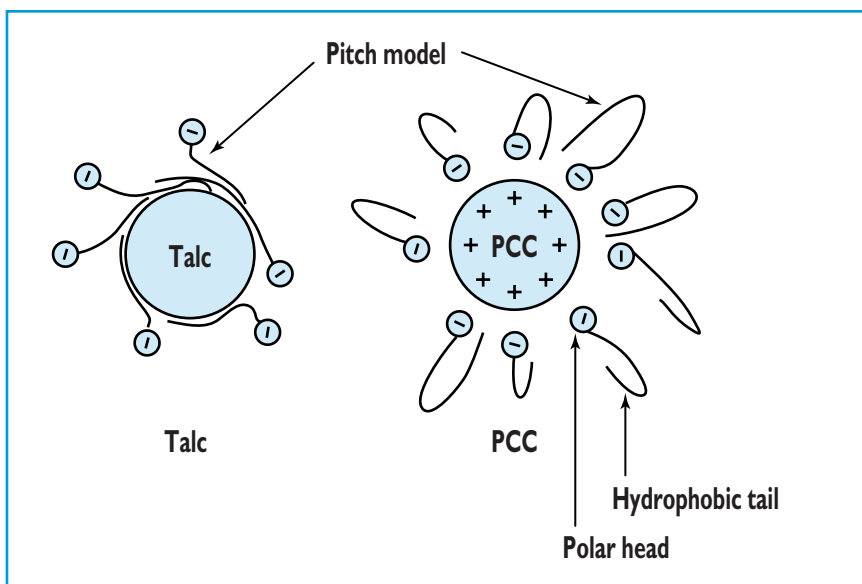
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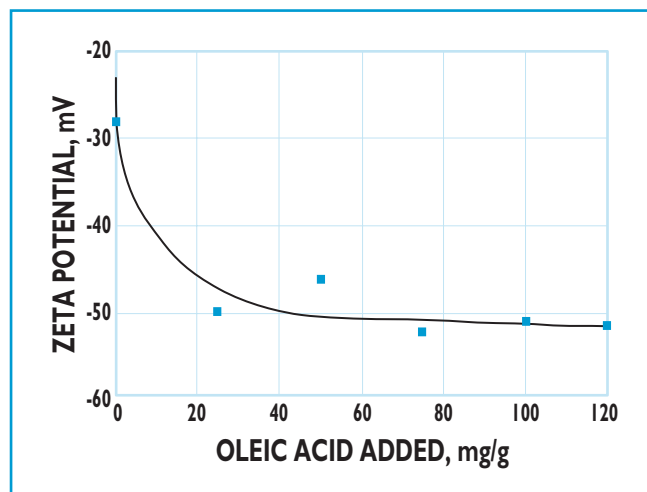
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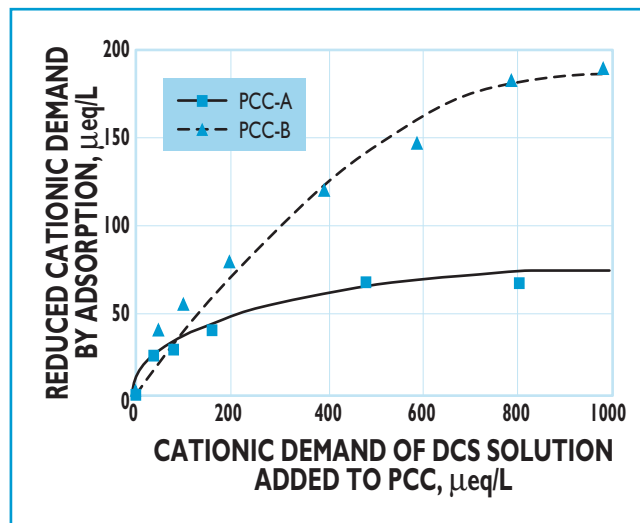
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12. Schematic of interaction between filler and pitch model



13. Change of zeta potential of talc



14. Adsorption of DCS from BTMP on PCC

BTMP/ CaCO ₃	DISSOLVED SUBSTANCE <0.1 µm		COLLOIDAL SUBSTANCE 0.1–0.65 µm	
	Conc., ppm	Reduction, %	Conc., ppm	Reduction, %
0	343.5	0	36.1	0
1	342.7	0.2	20.9	42.1
5	325.4	5.2	8.7	75.9

IV. Amount of reduction by adsorbance on PCC

AMOUNT ADDED TO PCC		Amount adsorbed, mg/g PCC
Abietic acid, mg/g PCC	Poly-A, mg/g PCC	
50	0	4.82
0	10	15.55
50	100	0.69 ^b

^apH=9.0±0.1, temp.=25±1°C
^bAbietic acid adsorbed onto PCC-B

V. Results of competitive adsorption^a