

THE EFFECT OF COATING COMPONENTS AND FILLERS IN THE DEINKING OF PAPER

Per Stenius and Jukka Heimonen

Laboratory of Forest Products Chemistry
Department of Forest Products Technology, Helsinki University of Technology,
Vuorimiehentie 1 A, 02150 Espoo, Finland

ABSTRACT

The effect of titanium dioxide, kaolin, calcium carbonate and talc on the properties of foams formed by sodium oleate/sodium stearate solutions and the flotation yield of these pigments in the presence of the same soaps have been investigated. In addition, the flotation of dispersed model coatings prepared from these pigments with styrene-butadiene and polyacrylate latexes was studied. The influence of coating colour composition and flotation chemicals (including silicate) was investigated using factorial experiments. The latexes strongly increase pigment floatability, but the effects are interrelated with the effects of other components in the coatings in a complex way. The flotation yield of the different pigments depend quite differently on the amounts of calcium and silicate added. This indicates that it may be possible to achieve flotation selectivity by proper design of flotation strategies. The factorial experiments also make it possible to draw some tentative conclusions with regard to mechanisms giving rise to the observed effects.

INTRODUCTION

Several investigations have shown that it is easier to remove printing ink from coated paper than from paper without coating (1-3). This effect is obviously partly due to the detachment of ink from the fibres together with the coating. However, there are several other effects of coatings in the flotation process:

- (i) It is well established that the inclusion of inorganic pigments (*viz.*, coated paper) has a positive effect on the efficiency of ink removal by flotation (4, 5) and possibly also on the removal of sticky contaminants (6).
- (ii) In the manufacture of deinked pulp for tissue, the pigments have to be fairly completely removed. This is usually achieved by a combination of flotation and washing, but it is clearly advantageous to carry out the flotation so that the yield of pigments in the reject is maximised and the amount of fibres is kept as low as possible (7)
- (iii) Pigments may contribute to the brightness of paper. On the other hand, calcium dissolved from carbonate pigments may cause runnability problems. It may therefore be of interest to achieve selective flotation, i.e. so that pigments that may cause runnability problems are selectively removed from the pulp (8).
- (iv) The large amounts of ash resulting from the burning of waste from recycling plants may be a problem. In some cases, it may be useful to consider recycling of the fibre in new products rather than using them as a landfill. Again, an

understanding of the selectivity of the flotation process may be of interest as a means of controlling the pigment composition in the waste.

In this paper, we report on studies of the effect of the most commonly used flotation system, calcium oleate/stearate, several pigments and full coating formulations on foam stability and flotation. The discussion is limited to aspect on the possibilities indicated of achieving selective flotation. Fuller considerations of the surface chemical aspects on the flotation systems and the observed effects, as well as studies of flotation of pigments and coatings in the presence of printing ink and fibres will be reported in forthcoming papers.

EXPERIMENTAL

Pigments

Kaolin. The kaolin was type SPS delivered by ECC International. According to the manufacturer, this pigment, which is specially designed for coatings, contains no additives. It has a specific surface area of 9.4 m²/g, with 80% of the particles < 2 μm and max 0.2% > 10 μm.

Talc. Talc was Finntalc P05 delivered by Finnminerals. This quality is mainly used as pitch talc. It was chosen because it contains no additives. The specific surface area is 10-11 m²/g (according to the manufacturer). 50% of particles are < 2 μm and 2% > 10 μm, implying that the particles are somewhat smaller than the sizes generally used for coatings.

Precipitated calcium carbonate (PCC). This synthetic calcium carbonate was of type Social P2, mainly used in the production of high quality disperse paints, and delivered by Solvay Alkali GmbH. According to the manufacturer its crystalline structure is predominantly aragonite. The specific surface area 7 m²/g, 90% of the particles are < 2 μm and 0.5 % > 10 μm. The pigment contains no additives.

Ground calcium carbonate. This mineral was of type Hydrocarb Filler L (Partek Minerals). This pigment is used as a filler pigment and it contains dispersants (polyacrylate). The pigment was delivered as a slurry containing 65 % (by weight) of pigment. According to the manufacturer, 52 % of particles are < 2 μm and less than 0.02 % are > 24 μm.

Titanium dioxide. An anatase-type special coating pigment (Finntitan AN, Kemira Oy) was used. The specific surface area is 8-10 m²/g (according to the manufacturer). The product contains no additives.

Flotation chemicals

Sodium oleate and sodium stearate was technical quality from Riedel de Haen. They were used without further purification. Sodium silicate (technical grade) was used as delivered from the manufacturer (Zeofinn Oy, Finland).

Coating chemicals

Sodium polyacrylate (dispersion agent) was Polysalz S from BASF.

Binder latexes. The styrene-butadiene latex (SB) was type DL 950 from Dow. This is an anionic, carboxylated styrene-butadiene latex with a minimum film-forming temperature (MFFT) of 5 °C and a glass transition temperature of 8°C. The acrylate latex (AL) was Acronal S360D from BASF. This is an anionic copolymer based on acrylate ester, acrylonitril and styrene with MFFT < 10°C. Both latexes contain dispersants and were developed for use in coatings.

Carboxymethylcellulose (CMC). The quality used was Finnfix 5 from Metsä-Serla Chemicals Oy, Äänekoski, Finland, with $M_w \approx 40000$ ($DP \approx 180$) and the degree of substitution ≈ 0.7 .

Starch. The starch was Raisamyl 302 E (Raisio Chemicals Oy, Raisio, Finland). This is an anionic, strongly oxidised potato starch. The starch was cooked according to the recommendations by the manufacturer and then diluted to 3% concentration. New batches were prepared weekly.

Hardener and lubricant. The hardener was ethanediol, CHOCHO (Glyoxal T, 40 % solution, BASF). The lubricant was a 50% Ca stearate dispersion (Nopcote C-104 from Diamond Shamrock).

Other chemicals.

All other chemicals were of analytical grade and used as delivered from the manufacturer. The water was ion exchanged and distilled.

Surface tension

Surface tension was measured using a computer controlled ring tensiometer (Sigma 70, KSV Instruments, Helsinki, Finland).

Preparation of coatings

The purpose in the preparation of coating colours was, rather than to prepare 'real' coatings, to use all possible coating colour components and to find out how these affect flotation after redispersion. However, the concentrations of the components were chosen to be on an average level compared to real coating colours. The recipes used are given in table 1. Coating colours were prepared using the following procedure. Deionised water, 0.1 part sodium hydroxide, dispersion agent and pigment were mixed together with effective laboratory propeller mixer. The suspensions were mixed for 0.5 h. The dispersion concentration was 65 % except for talc for which it was 35 %. The talc suspension had to be diluted because the viscosity was too high at higher concentrations. Coatings free of dispersion agent could be tested only for titanium dioxide-based coating colours. Preparation of the other colours required addition of sodium polyacrylate.

Following mixing, latex and other components were added. In colours containing both starch and AL, the starch was added before the AL. pH was adjusted to 8.5 with sodium hydroxide. The final concentration was 60 % except for talc for which it was 30 %. The coating colour was then spread on large foil plate, dried 5 min in an oven at 105°C and 24 h at room temperature, except the colours containing starch which were dried at room temperature only. The dry coatings were broken into smaller pieces and kept in a refrigerator in plastic bags until used in further experiments.

Foam formation and stability.

Foam formation and stability were studied with a modified Bikerman-type foam column (fig. 1). This column makes it possible to measure both dynamic and static foam stability. The weakness of the equipment is that the hydrodynamic conditions are restricted. Thus, higher soap concentrations than those corresponding to real flotation concentrations had to be used in order to obtain foams on which measurement could be made. The sodium oleate and sodium stearate concentrations were 3.93 mmol/l (1.196 g/l and 1.204 g/l). The added calcium concentrations were 0, 0.357, 0.893 and 1.786 mmol/l, corresponding to 0, 2, 5 and 10 °dH, respectively. The ionic strength was adjusted to 0.02 M with sodium chloride. Sodium silicate concentrations were 0.2, 1 and 3 g/l. In all experiments, the pigment concentration was 10 g/l. The nitrogen gas flow was adjusted with a calibrated rotameter to 14 ml/min, which made it possible to use the same flow rate at all calcium concentrations.

Table 1. Coating colour compositions (in parts by weight of pigment). Latexes SB=DL 950 and AL = Acronal S 360 D. Values in brackets are those used for titanium dioxide; for all other pigments the recipes were the same, except that no polyacrylate was added to ground CaCO₃ which already had some added when delivered.

N	Pigment	Latex	Na poly-acrylate	CMC	Starch	Glyoxal	Ca stearate
1	100	8 (SB)	0.3 (0)	0 (0)	0 (0)	0 (0.1)	1 (1)
2	100	8 (SB)	0.3 (0.3)	1 (0)	0 (0)	0 (0)	0 (0)
3	100	8 (SB)	0.3 (0)	0 (1)	4 (0)	0 (0)	0 (1)
4	100	8 (SB)	0.3 (0.3)	1 (1)	4 (0)	0 (0.1)	1 (0)
5	100	8 (SB)	0.3 (0)	0 (0)	0 (4)	0.1 (0.1)	1 (0)
6	100	8 (SB)	0.3 (0.3)	1 (0)	0 (4)	0.1 (0)	0 (1)
7	100	8 (SB)	0.3 (0)	0 (1)	4 (4)	0.1 (0)	0 (0)
8	100	8 (SB)	0.3 (0.3)	1 (1)	4 (4)	0.1(0.1)	1 (1)
9	100	8 (AL)	0.3 (0.3)	1 (1)	4 (4)	0.1(0.1)	1 (1)
10	100	8 (SB)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
11	100	8 (AL)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)

Measurements were made according to following procedure. Appropriate amounts of pigment, NaCl, soap, and sodium silicate were mixed and the mixture was heated to the foam test temperature (55 °C). Suspensions containing sodium stearate were heated to 70 °C and cooled to test temperature. Calcium chloride was added and the pH was adjusted. The suspensions were then mixed for 15 min. The foam column was carefully cleaned with water and a 1:10 diethyleter: methanol solution and rinsed carefully with a small amount of test solution immediately before measurement.

Foamability. The dispersion was flowed into the column along the column wall. Nitrogen was flowed through the dispersion until the foam height had reached a stable level. This level was taken a measure of the foamability of the suspension.

Foam stability. The nitrogen flow was stopped, and the decrease in foam height was recorded for 20 min. The time taken for the foam height to decrease to half of its initial value or the height after 20 min (whichever was the higher) was taken as a measure of the stability of the foam.

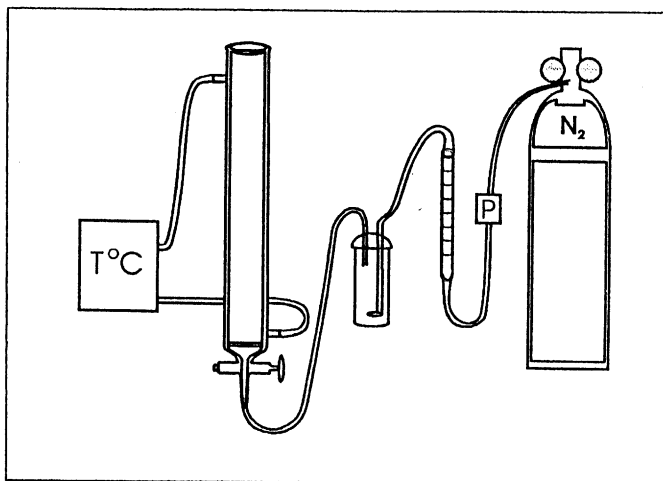


Figure 1. Modified Bikerman test apparatus used in the investigation of foam stability.

The effect of coatings on foam properties. 5 g/dm³ of dry titanium dioxide or kaolin coating was dispersed by stirring the coating for 1h in distilled water at 55 °C. The suspension was cooled. After one day it was filtered through a 0.2 μm membrane filter. 1.5 g/l sodium oleate was added to the filtrate and the ionic strength was adjusted with NaCl. The solution was heated to 55°C, 1.786 mmol/l calcium chloride was added and pH was adjusted with NaOH to 9.5. The final ionic strength was 0.02 M. After 15 min stirring the foam properties were measured. The nitrogen flow was 27 cm³/min.

Flotation.

A pilot scale Outokumpu flotation machine was used. This machine is equipped with a rotating air injector submerged in a half-cylindrical flotation vessel. The volume of the flotation vessel is 3.5 dm³. The rate of stirring was 1600 min⁻¹. Air was injected at a rate of 9 dm³/min.

Many variables could affect the flotation result. In order to evaluate the main effects in a reasonably limited number of flotation experiments a 2^k factorial design was used. In such a design it is important that the levels of the different variables can be chosen independently of each other. Another problem is how to choose levels for variables in such a way that very strong deviations from linearity in the response of the system are avoided. General experience of the flotation behaviour of systems such as these gives a guideline for the choice of levels but it should be stressed that

the conclusions drawn from the factorial designs should be checked in more detailed experiments. Such experiments will be reported in forthcoming papers.

Flotation of pigments. The experimental design used in the study of the effect of flotation chemistry on the flotation of pigments is given in table 2. The sodium oleate concentration was constant ($0.164 \text{ mM} = 50 \text{ mg/dm}^3$) and the ionic strength was adjusted to 0.02 M with NaCl. The following procedure was used. Appropriate amounts of NaCl, soaps, pigment and sodium silicate were mixed with deionised water. pH was adjusted with NaOH and the mixture was heated to 55°C . Then CaCl_2 was added and the pH was checked. Stirring was continued for 15 minutes. The mixture was poured into the flotation vessel and the flotation stirrer and air flow was started. Foam was collected from the surface for five minutes. In practice, additional foam was not formed after 2-3 minutes so the flotation time is not of importance to our results.

Flotation of coatings. The flotation conditions used in the investigation of coatings are given in table 3.

Table 2. Experimental design used in the study of the influence of flotation chemicals and conditions on the flotation of pigments.

N.	pH	$[\text{CaCl}_2]$ mmol/l	Sodium stearate mmol/l	Sodium silicate mg/l
1	8	1.786	0	0
2	9.5	1.786	0	250
3	8	5.358	0	250
4	9.5	5.358	0	0
5	8	1.786	0.163	250
6	9.5	1.786	0.163	0
7	8	5.358	0.163	0
8	9.5	5.358	0.163	250

Table 3. Standard flotation conditions in coating flotations.

Flotation volume	3.5 dm^3
Coating	5 g/l
Sodium oleate	0.164 mmol/l
Sodium stearate	0.163 mmol/l
Sodium silicate	250 mg/l
pH	9.5
added CaCl_2	1.786 mmol/l

The coatings were dispersed in the following way. A 10 % suspension of small coating pieces was stirred for 30 min and heated to 55°C with the flotation chemicals (except NaCl and CaCl_2). Then suspension was dispersed in a

laboratory mixer for 30 min and diluted to the final concentration with a NaCl solution at 55 °C. CaCl_2 was added, pH was adjusted and the suspension was stirred for 15 min. Flotation was done in the same way as for the pigments.

Note that samples 8 to 11 (table 1) were designed so that the effect of latexes only on pigment floatability can be compared with the combined effect of soluble coating polymers and latexes

Evaluation of flotation The foam collected in the flotation was dried at 105 °C and weighed. The ash content was determined by weighing samples before and after incineration ($T=925$ °C, 2 h). The yield of pigment was calculated from the weight of the ash as % of total initial amount of pigment. Appropriate corrections were made to account for the decomposition of calcium carbonate in the incineration.

The size distribution of the pure pigments and particles (from coatings) before and after flotation was measured with a Coulter Multisizer II after dispersion the sample in 0.1 mol/l NaCl solution. The 100 μm aperture (measuring range 2-60 μm) was used. Electrophoretic mobilities of pigments and coating particles were measured from the Doppler shift in scattered light using a Coulter Delsa 440 instrument. The dispersion medium was either 0.02 M NaCl or filtrated flotation solution at room temperature.

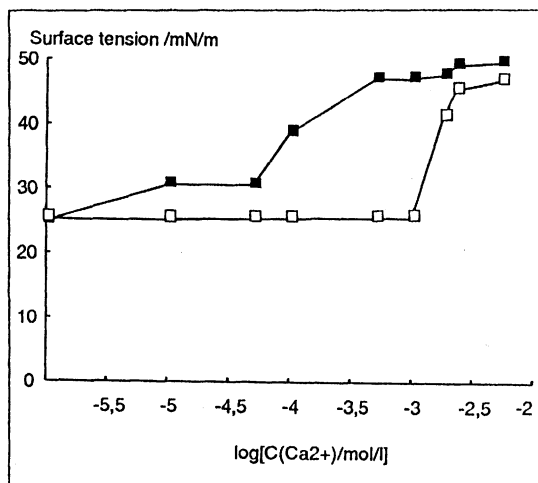


Figure 2. The surface tension of sodium oleate solutions as a function of the concentration of added calcium chloride. $T = 25^\circ\text{C}$. □ 3.93 mM oleate, ■ 0.16 mM oleate.

RESULTS

Stabilisation of foam by flotation agent

Surface tension. Figure 2 shows the surface tension of sodium oleate solutions. The cmc of pure sodium oleate is ≈ 1 mM or $\approx 0,3$ g/dm³ at room temperature (9). Measurements on the rather impure sample used by us indicate a cmc around 1-3 mM, with a minimum in the surface tension below this value. The solubility of

calcium oleate is 0.013 mM at 27 °C and 0.2 μM at 60 °C(10). No measurements were made for stearate; 25°C is well below the Krafft point of sodium stearate and the solubility of calcium stearate is 2.7 μM at 27,5°C and 1.1 μM at 60°C (10).

As expected, the surface tension of 0.16 mM oleate increases already at $[Ca^{++}] \approx 0.01$ mM as calcium oleate precipitates. For 3.93 mM oleate (well above cmc) the surface tension remains almost constant until precipitation of calcium oleate decreases the solution concentration below the cmc (≈ 1 mM $[Ca^{++}]$).

The effect of pH on foam stability. The effect of pH and calcium concentration on the properties of foams formed by sodium oleate solutions is shown in figure 3. Three effects can be observed: (i) Both foamability and foam stability decreases with increasing calcium concentration, (ii) without any added calcium, foamability and foam stability are both high; at intermediate concentrations foam stability is relative independent of calcium concentration and at high calcium concentrations the foam is virtually completely suppressed; (iii) both foamability and foam stability appear to have a maximum at pH 9.5

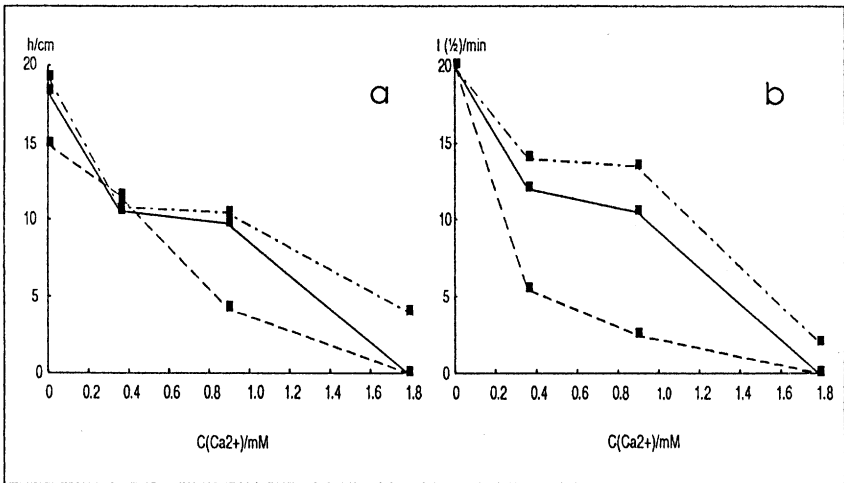


Figure 3. (a) The maximum foam height (foamability) (b) the half-life (foam stability) of sodium oleate foams as a function of the concentration of calcium in the foaming solution. $T = 55^\circ\text{C}$, ionic strength 0.02 M (adjusted with NaCl), oleate concentration 3.93 mM. — pH 9, - - - pH 9.5, . . . pH 10.5.

Figure 4 shows the results of similar experiments with sodium stearate. The foamability of the sodium stearate dispersion is much higher than that of the oleate solution; the height 550 mm in the figures represents the height of the foaming tube so that the real height could not be observed. The foam also broke down quite slowly and instead of a foam half-life the volume of the foam remaining after 20 min was recorded. As for oleate, foamability and foam stability is at a maximum for pH 9.5, but the dependence on calcium concentration is different. Calcium can be

added to a concentration of about 0.5 mM; then foamability and foam stability suddenly drops to much lower values. It is notable that the sodium stearate foam also dries out much more markedly than the oleate foam.

Effect of temperature on foam stability. Table 4 shows the effect of temperature on the foam characteristics of sodium soaps. Changing the temperature did not affect the optimum pH. The stability and foamability of both stearate and oleate increases with decreasing temperature. The sodium oleate foams become more sensitive and the sodium stearate foams become less sensitive to additions of calcium at the lower temperature.

Table 4. Effect of temperature on foamability and stability of sodium oleate and sodium stearate at different Ca^{++} concentrations. Foamability = steady state foam height in mm. Foam stability = percent of initial foam height after 20 minutes. pH = 9.5.

[Ca] mM	Sodium oleate				Sodium stearate			
	Foamability		Foam stability		Foamability		Foam stability	
	55°C	40 °C	55°C	40 °C	55°C	40 °C	55°C	40 °C
0	192	230	53	57	550	550	100	100
0.867	104	169	34	57	285	550	78	100
1.786	40	0	7.5	0	118	215	17	68

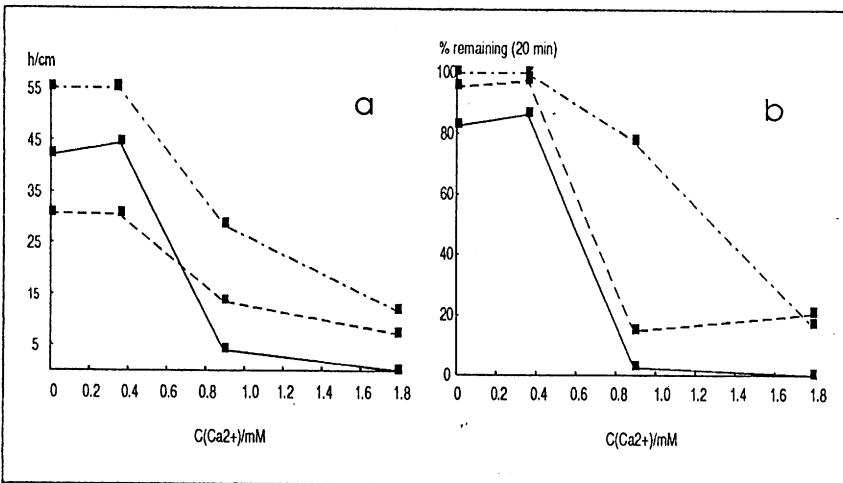


Figure 4. (a) The maximum foam height (foamability) of sodium stearate foam as a function of the concentration of calcium in the foaming solution. Note that 550 mm is the height of the foam tube. (b) The % of the sodium stearate foam remaining after 20 min. $T = 55^\circ\text{C}$, ionic strength 0.02 M, adjusted with NaCl, stearate concentration 3.93 mM. — pH 9, - - - pH 9.5, . . . pH 10.5

The effect of calcium soaps on foam properties. The precipitated calcium oleate forms a colloidal dispersion of very small particles (9). Figure 5 shows the effect of these particles on foamability (fig 5a) and foam stability (fig 5b). In these experiments the oleate concentration is somewhat higher than in fig. 3. Before the second series of measurements, the solution was filtered through a 0.2 μm membrane filter. The foamability of the solution is considerably reduced when the calcium soap particles are removed. At Ca concentrations lower than 1.8 mM, foamability does not depend on the concentration of oleate remaining in solution, as also seen in figure 3a. The foam stability does not (within experimental error) depend on whether the foam contains calcium oleate particles or not.

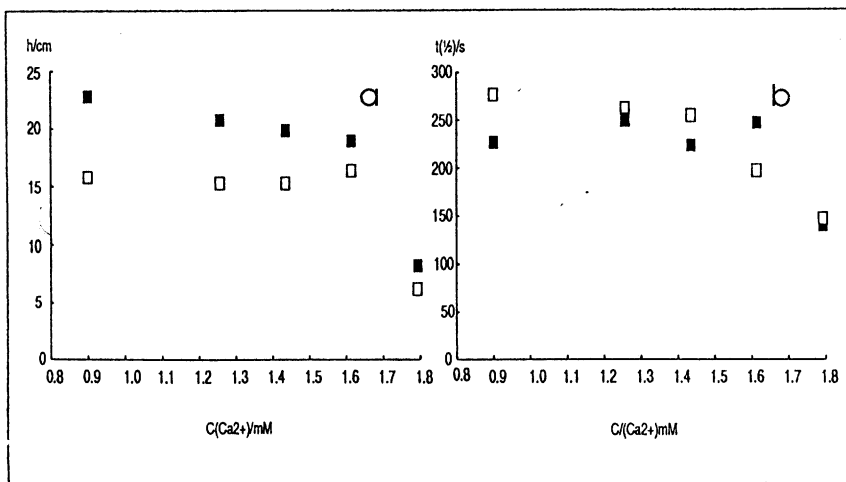


Figure 5. (a) The effect of filtering off the calcium soap on the foamability of oleate foams. (b) The effect of filtering off the calcium soap on the foam stability of oleate foams. $T = 55^\circ\text{C}$, $\text{pH} = 9.5$, initial sodium oleate concentration 4.93 mM = 1.5 g/l. Open symbols: filtered. closed symbols: not filtered solutions.

Sodium oleate/sodium stearate mixtures. Figure 6 shows how mixtures of sodium oleate and stearate in different ratios affect foamability at constant total concentration of soap and calcium. Foamability is at a maximum when the two soaps are mixed in about equal amounts. Foam stability could not be measured because foam drainage was cut off by the appearance of big holes at the lower part of the foam. This indicates that different types of foam stabilisation occurs in different parts of the foam.

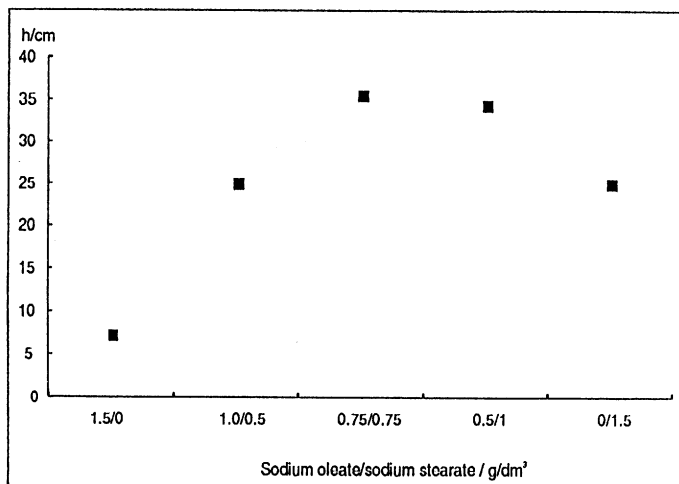


Figure 6. The foamability of sodium oleate/sodium stearate mixtures. $T = 55^{\circ}\text{C}$, total soap concentration ≈ 4.9 mM, $[\text{Ca}^{2+}] = 1.8$ mM, $\text{pH} = 9.5$, flow rate 27 cm^3/min .

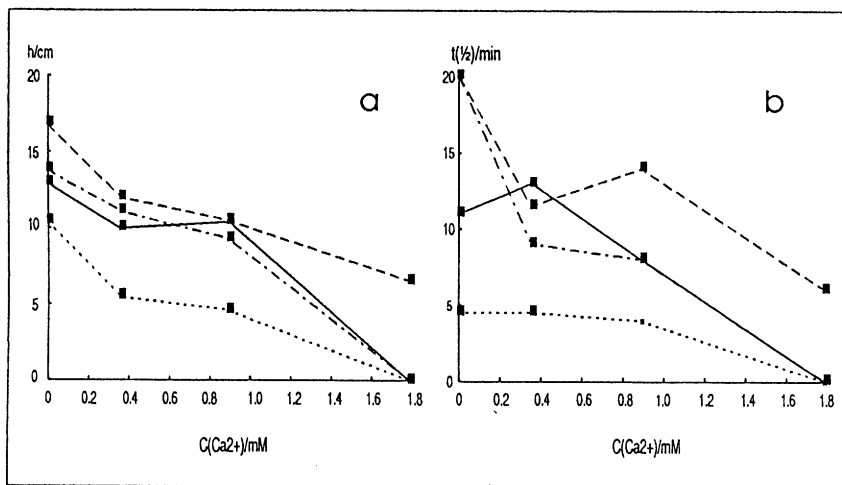


Figure 7. The effect of pigments on (a) foamability b) foam stability of sodium oleate solutions (3.93 mM). $\text{pH} = 9.5$, pigment concentration 5 g/l. — kaolin, --- TiO_2 , ··· talc, - · - CaCO_3 .

Stabilization of foam by pigments.

Figure 7 shows the effect of titanium dioxide, kaolin, talc and PCC on the foam characteristics of sodium oleate foam as a function of added calcium. The general shape of the curves is the same as for pure soap (fig. 3). While TiO_2 has very little effect on foamability, it is somewhat reduced by talc and kaolin. The effect of PCC is more marked. TiO_2 somewhat stabilizes the foam. Without any calcium added, kaolin reduces foam stability, but in calcium-containing solutions, neither kaolin nor talc has any marked effect on foam stability. PCC strongly reduces foam stability. Thus, the pigments stabilise the foam in the order: titanium dioxide > talc \approx kaolin > PCC.

Figure 8 shows the effects of pigments on sodium stearate foam. In the presence of TiO_2 , foamability is even stronger than for pure stearate. Kaolin does not markedly affect foamability, while it is clearly reduced by talc. When PCC is added, no foam is formed at all. The effects on foam stability follow the same trend. Thus both stability and foamability of stearate foams is affected by pigments in the order titanium dioxide (increases) > kaolin (no effect) > talc (decreases).

Stabilization of foam by sodium silicate.

Sodium silicate had no effect at all on sodium oleate foams. Figure 9 shows the foamability and foam stability of sodium stearate in 1.786 mM CaCl_2 . Sodium silicate increases the foamability of pigment-containing foams except for PCC. The stability of talc and kaolin foams is also increased (with TiO_2 , the foam is already quite stable without any silicate). Silicate does not have any effect on pure sodium stearate foams.

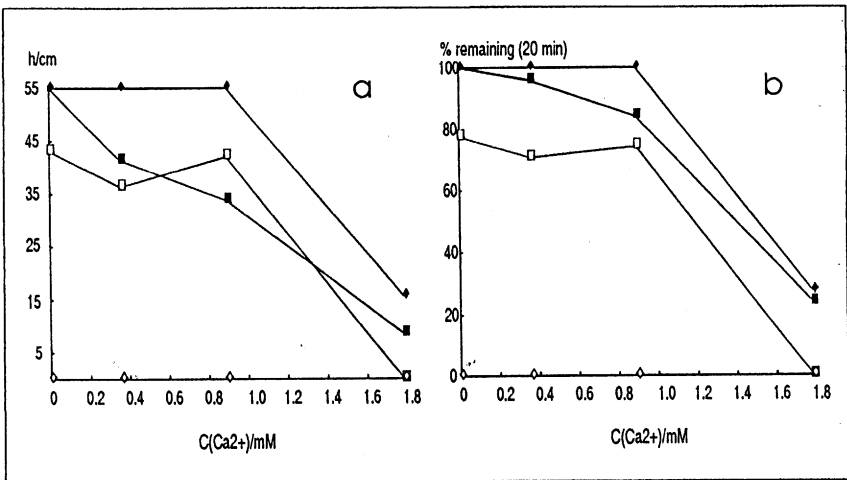


Figure 8. The effect of pigments on (a) foamability b) foam stability of sodium stearate solutions (3.93 mM). pH = 9.5, pigment concentration 10 g/l. □ talc, ■ kaolin, ◆ TiO_2 , ◇ CaCO_3 .

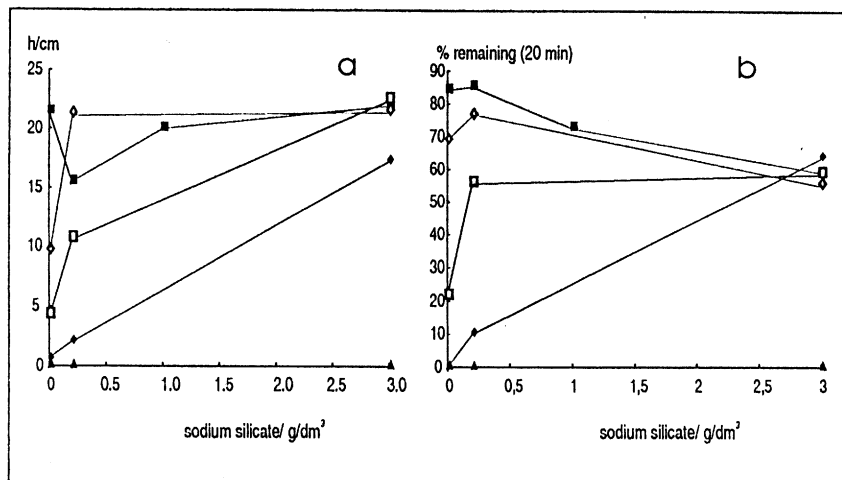


Figure 9 The effect of added sodium silicate and pigments on (a) foamability (b) foam stability of calcium stearate dispersions (3.93 mM). pH = 9.5, pigment concentration 10 g/l. □ kaolin, ■ stearate, ◆ talc ◇ TiO₂, ▲ CaCO₃.

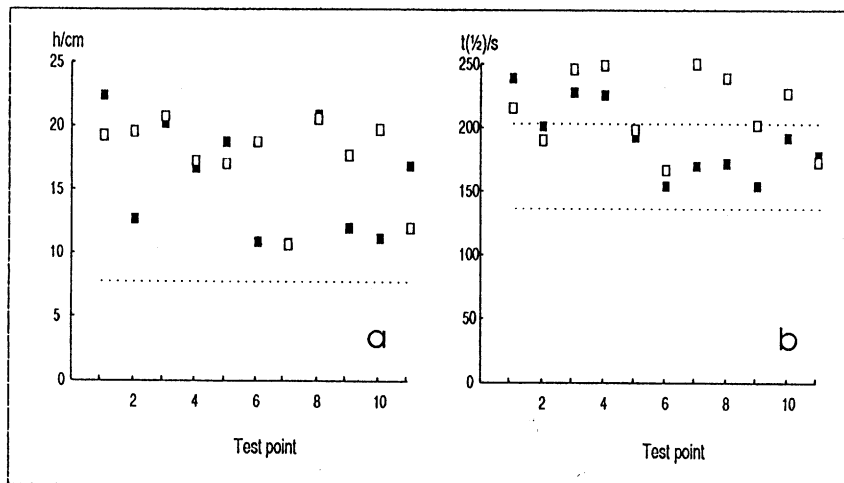


Figure 10. The effect of coatings on (a) foamability, (b) foam stability of sodium oleate foams. The drawn lines represent the values for pure sodium oleate (4.93 mM). □ kaolin, ■ TiO₂ coatings.

Table 5. Calculated effects of titanium dioxide and kaolin coating components (with SB-latex) on foamability.

	Difference in foam height mm				
	Na polyacrylate	CMC	Starch	Glyoxal	Ca stearate
TiO ₂	10	-7	-12	56	2
kaolin	not m.	-14	5	-14	30

Effect of coatings on foam stability

Figure 10 shows the effect of components dissolved from the coating on the foam. The coating components promote both foamability and foam stability; the effects are more obvious with regard to foamability.

From the factorial design (table 1), it is possible to estimate the effect of the difference between the two levels of each parameter (coating component) on foam properties. The effect (F_i) of parameter i is calculated using the equation

$$F_i = \frac{\sum y_{\text{high}} - \sum y_{\text{low}}}{N} \quad (1)$$

where the first summation is taken over the results obtained in the experiments in which the parameter is at its higher level and the second summation is over the experiments in which the level is low. N is the number of experiments in the design. These factors should be compared to experimental uncertainties, which have to be estimated from independent experiments. The effects are given for foamability in table 5 and for foam stability in table 6.

Considering the uncertainties in the determination of maximum foam height and foam half-life, it is probable that the only significant effect is the effect of calcium stearate on foamability. Note that the uncertainties in the determination of the half-life of pure stearate foams is very large (the distance between the two dotted lines in fig. 10b).

Table 6. Calculated effects of titanium dioxide and kaolin coating components (with SB-latex) on foam stability.

	Difference in foam half-life s				
	Na polyacrylate	CMC	Starch	Glyoxal	Ca stearate
TiO ₂	-16	53	-12	12	-5
kaolin	not measured.	-19	2	-51	19

Table 7. The effect of using different latexes on foamability and foam half life. Titanium dioxide and kaolin based coatings with compositions 8 - 11 (table 1). SB = styrene/butadiene and AL = polyacrylate based latex.

Pigment/composition/latex	Foamability	Foam half-life
	cm	min
Sodium oleate	8	2.2-3.5 ¹
TiO ₂ /8/SB	20	4.0
Kaolin/8/SB	21	2.8
TiO ₂ /9/AL	17.5	3.5
Kaolin/9/AL	12	2.5
TiO ₂ /10/SB	19.5	3.7
Kaolin/10/SB	11	3.2
TiO ₂ /9/AL	12	2.9
Kaolin/9/AL	17	3.0

¹ In these experiments, the foam formed by pure oleate was very dry and the uncertainties in the determination of foam stability are therefore very large

The effect of using different latexes on the foam characteristics are shown in table 7. The coating compositions are those given in rows 8 to 11 in table 1. The type of latex strongly affects the foaming: in addition to the effects of the pigments compared to sodium oleate there are also significant differences between coatings containing the same pigment but different latexes. The differences are more marked with respect to the foamability than with respect to foam stability.

Flotation of pigments

Effect of flotation conditions. Table 8 summarises the analysis of the factorial design (table 2) used to evaluate the influence of flotation parameters on the flotation yield for each pigment. From our experience of the experimental accuracy attainable, we judge that values of $|F_i| < 4-5$ (eq. 1) are probably just effects of experimental uncertainty.

Thus, most of the effects described by the numbers in table 8 are too small to be significant, but some important conclusions can be drawn.

(i) Sodium silicate reduces the yield of all pigments. The effect is particularly strong for kaolin. The flotation yield of kaolin is also reduced by sodium stearate, but this effect is offset by the addition of calcium (the AB interaction is strong)

(ii) A combination of calcium and stearate increases the yield of talc; for the other pigments this combination has a relatively small effect.

(iii) The effect of the variables on the yield is quite different for different pigments This is of course not unexpected because the surface properties of the pigments are quite different.

This conclusion is verified by the results given in table 9, which shows the variable combinations giving the maximum yield of each pigments.

(iv) The differences between the maximum and the minimum value of the yield obtained in the factorial experiment also varied significantly between the pigments: titanium dioxide 15 %, kaolin 47 %, talc 22 %, PCC 18 %, ground calcium carbonate 10 %. Thus, the sensitivity to the flotation conditions in the range of parameters studied is quite different for the different pigments.

Table 8. Calculated effects of flotation conditions on flotation yield of pigments. A=pH, B= added CaCl_2 (mmol/l), C= sodium stearate (mg/l) and D=sodium silicate (mg/l). AB, AC, BC = combined effects. The other combined effects cannot be evaluated using the design described by table 2.

Pigment	A	B	C	D	AB	AC	BC
TiO_2	1.5	-1.0	1.4	-2.9	-1.8	-0.0	-1.5
kaolin	2.1	1.0	-7.0	-13.5	6.2	-1.2	-2.2
talc	-2.4	-3.6	3.6	-1.3	1.2	0.7	4.4
PCC	-1.7	-0.5	1.5	-4.1	-2.7	-0.6	-2.0
CaCO_3	-0.7	2.7	-1.4	-0.9	-1.1	0.0	-1.7

Table 9. The maximum yield obtained for each pigment in the factorial design experiments described by table 2.

Pigment	Maximum yield %	Experiment number
PCC	93.4	6,7
TiO_2	84.0	6
Kaolin	51.3	4
Talc	45.4	1
CaCO_3	20.1	3

Effect of latexes on flotation of pigments. Table 10 shows the effect of changing from SB to AL latex on the flotation yield. In experiments where the other coating component are not used (table 1, exp. 10 and 11), changing latex from SB to AL has no effect on the yields of titanium dioxide and PCC. The change increases the yield of on talc and ground calcium carbonate. The yield of kaolin is significantly decreased. When all coating components are present (experiments 8 and 9), yield is higher with AL for all pigments except kaolin. Changing from a latex-pigment system to a complete coating system (experiments 8/10 and 9/11) decreases the yield or has no effect except for kaolin with SB-latex.

Effect of coating components of flotation of pigments The effect of different coating components on flotation was tested for each pigment using coatings described by rows 1-8 in table 1.

Table 10. Effect of latexes on flotation yield of pigments, given as percent of the initial amount of pigment in the suspension. Experiments 8 and 9: all coating components present, experiments 10 and 11: only latex+pigment. For experimental conditions, see table 1

Pigment	Experiment number			
	8 SB latex	9 AL latex	10 SB latex	11 AL latex
TiO ₂	40	82	78	82
kaolin	72	7	57	14
talc	62	76	67	90
PCC	49	58	80	77
CaCO ₃	36	40	68	75

Table 11. Calculated effects of coating components on flotation rejects (%) of pigments (experiments 1-8, table 1).

Pigment	Polyacrylic acid	CMC	Starch	Glyoxal	Calcium stearate
TiO ₂	-2.4	2.8	-10.5	-0.0	3.7
kaolin	not measured	6.6	3.3	-0.3	-5.0
talc	not measured	-1.0	-4.9	-3.0	-1.9
PCC	not measured	-1.8	-5.7	-0.5	-11.1
CaCO ₃	not measured	-6.3	-8.4	2.7	-12.0

The importance of adding a dispersion agent on floatability could not be clearly established in the case of kaolin, talc and PCC because these coating colours could not be prepared without it, nor for ground calcium carbonate which was delivered as polyacrylate-containing suspension .

Significant effects of the coating components are observed for CMC, starch and the lubricant (calcium stearate). CMC strongly increases the yield of kaolin , decreases the yield of ground CaCO₃ but has no significant effect on the other pigments. Starch decreases the yield of all pigments except kaolin. Calcium stearate decreases the yield of PCC and ground CaCO₃, increases the yield of titanium dioxide and does not significantly affect the other pigments.

DISCUSSION

Our investigation, which is largely based on factorial experiments designed to emphasise the main effects, makes it possible to draw a number of general conclusions regarding effects of the calcium soap flotation chemicals on pigment flotation. Because the surface chemistry and flotation physics of the system under investigation is very complex, more detailed investigations are required to make possible a full analysis of the mechanisms involved. These will be reported in forthcoming papers.

The fundamental events taking place during flotation are (i) the collision of the solid particle with an air bubble, (ii) the attachment of the particle to the bubble; this involves drainage and breaking of the thin film of liquid formed between the particle and the bubble, (iii) the stabilisation of the bubble/particle contact and the transport of the aggregate to the froth (11-14). As suggested by Schulze (14), the overall rate of flotation (i.e. the rate of change of the particle number per unit volume, dn_p/dt) can be expressed in terms of the probability of each of these events, the frequency of particle-bubble collisions z_c and the number of bubbles per unit volume:

$$\frac{dn_p}{dt} = -z_c n_p n_b P_c P_a P_b P_s \quad (2)$$

where P_c is the probability of collision, P_a is the probability of adhesion of the particle to the bubble, P_b is the probability that adhesion leads to the formation of a stable three-phase contact (bubble/liquid/particle) and P_s is the probability of stability against the stress forces during transport to the froth. In our experiments, the dynamic conditions during flotation (and foam formation) as well as particle numbers are kept as constant as possible. Hence, we will as a first approximation assume that the observed effects mainly are due to changes in the probabilities P_a and P_b .

The effect of the calcium stearate/oleate system on foam properties

The stearate/oleate combination - in many cases modified by the addition of non-ionic surfactant - is still by far the most commonly used flotation agent in European deinking processes. The calcium ion concentrations used in practice are usually sufficiently high so that insoluble calcium soap particles will be formed (15); these will be adsorbed on the ink particles which are consequently hydrophobed and flocculate to aggregates that are large enough to float rapidly. Our investigation throws some light on the question whether, indeed, precipitation of calcium soap particles is necessary for the calcium soap flotation system to work.

The effect of this system on the floatability of pigment particles in deinking flotation has not been specifically investigated. Essentially, two mechanisms have to be considered: (i) the soaps may adsorb on the pigment particles, which would affect particle/particle and particle/bubble interactions, (ii) the soaps may adsorb at the air/liquid interface and hence affect froth stability and particle/bubble interactions. The studies of oleate and stearate foam properties give information on the latter factor.

Calcium oleate. The oleate concentrations used in the investigation of foam properties (figure 2) are well above the cmc of sodium oleate. The foamability of pure sodium oleate has a maximum around pH 9.5. The occurrence of oleate dimers $(RCOO)_2^{2-}$ or $(RCOO)_2H^-$ around this pH has been proposed by Somasundaran et al (16). Such complexes would be very surface active, but it is not clear whether they would be present when the oleate concentrations exceed the cmc, and further investigation is required to clarify the reason for the observed maximum.

When calcium chloride is added, colloiddally stable calcium oleate particles precipitate; these are stabilised by adsorption of excess oleate (9). The presence of particles increases both foamability and foam stability, but the maximum at pH 9.5 is still observed and the surface tension remains constant (fig. 2). That the particles

do participate in the formation of the foam is obvious, since foamability is decreased as the particles are filtered off (figure 5). In the range 0.8 - 1.6 mM CaCl_2 , the amount of oleate remaining in solution after addition of CaCl_2 varies from ≈ 1.7 to ≈ 3.3 mM, i.e. it remains above the cmc of sodium oleate. When the particles are filtered off, foamability is reduced to values comparable to those observed for 3.9 mM sodium oleate (fig. 3a). At the highest calcium concentrations investigated (1.8 mM), the oleate concentration is reduced below the cmc (1.8 mM Ca^{++}), the oleate forms flocculated calcium oleate particles and foamability is strongly reduced.

On the other hand, the particles do not affect foam stability very much. As shown by figure 5 b, filtering off the particles does not change the half-life of the foam. A plausible explanation is that the probability of breaking of the foam films is mainly related to electrostatic repulsion between the film surfaces. This repulsion, which is due to dissociated carboxyl groups, will be reduced by specific binding of calcium ions. However, a more detailed investigation is required in order to definitively establish the mechanism by which the particles affect foam properties.

When the concentration of oleate ions decreases below the cmc due to the precipitation of calcium soap, surface tension increases and the foam becomes much less stable.

Calcium stearate Stearate foams are much more stable than oleate foams (figures 3, 4). The stability and foamability maximum at pH 9.5 is more marked than for oleate foams. The solubility of sodium stearate is much less than the concentration of stearate used in the stability studies 55 °C is just around the Krafft point of sodium stearate (17). Therefore, by analogy with the properties of insoluble oleate particles, it can be assumed that when dispersed, stearate mainly forms electrostatically stabilised, hydrophobic particles. The importance of these is shown by the increase in foamability as temperature is decreased well below the Krafft temperature (40 °C, table 4).

A plausible explanation of the mechanism involved in foam stabilisation is the... following. Because the particles are hydrophobic, they will have a strong tendency to attach to the particle/bubble interface (i.e., P_a and P_b in eq. (2) are high). Hence, the foams are - even for pure sodium stearate - stabilised by electrostatic repulsion between the negatively charged stearate particles attached to the a/l interface. In support of this, it is observed that before breaking, the foams dry out very completely, which indicates formation of mechanically strong, particle-containing films in the foam.

Addition of small amounts of calcium ions does not affect stability, but it is very strongly reduced at higher calcium concentrations. The carboxyl groups on the particle surfaces will have a strong tendency to bind calcium ions and hence, the charge density is reduced so that the repulsion between the film surfaces decreases and the probability of breaking of the films increases.

Stearate/oleate mixtures. As shown in figure 6, a marked maximum in the foamability is observed for stearate/oleate mixtures. The dispersions from which the foams are formed contain calcium stearate and calcium oleate particles as well as free oleate and stearate ions. This combination apparently results in particularly favourable conditions for foam formation.

We conclude that the presence of calcium stearate and oleate particles enhance foamability but that high concentration of calcium do not affect the stability of oleate foams very much and strongly reduce the stability of stearate foams.

The effect of pigments on foam properties

The pigments are all of roughly the same size, so that the particle concentrations will be about the same for all systems. Hence, as a first approximation, z_c , η_p , η_b and P_c in eq. (2) will be roughly constant. On the other hand, the shape of TiO_2 and carbonate particles is quite different from the shape of kaolin and talc particles, which are rather similar. The probability of adhesion P_a and formation of a stable contact between the particles and the air bubbles P_b will depend on both the surface properties and the shape of the particles.

Calcium carbonate. In the oleate systems, foamability and foam stability are both strongly reduced by the presence of calcium carbonate particles (figure 7). The solubility of calcium carbonate is about 0.18 mM, *i.e.*, much higher than that of calcium oleate. In the pure oleate systems, the presence of calcium oleate particles (and the concomitant decrease of the amount of free oleate in solution) reduces, but does not completely suppress foam formation.

A simple explanation for the effect of calcium carbonate on foam properties is, thus, that it leads to precipitation of calcium oleate particles that participate in foam formation in the same way as in pure oleate systems. When additional calcium ions are added, the electrostatic repulsion in the foam films is reduced (as in pure calcium oleate systems) and the foam finally breaks completely.

In stearate systems, calcium carbonate completely suppresses foam formation. As shown by figure 4, stearate foam stability is quite sensitive to additions of calcium ions. The ions supplied by the dissolution of calcium carbonate are quite sufficient to reduce the electrostatic repulsion between stearate particles so that no stable foam films are formed. The concentration of free stearate ions will be very small.

Titanium dioxide. The adsorption of oleate on titanium dioxide and its effect on flotation froths was investigated by Pope *et al.* (18). They found that oleate is adsorbed already from very dilute solution and enhances flotation. The results, shown in figure 7 are consistent with this observation. One would expect titanium dioxide particles which have adsorbed oleate to become entrained in the foam and to enhance foam stability (P_a and P_b increase), while foamability would not be much affected as long as adsorption does not reduce the concentration of oleate in solution to less than the cmc.

Talc and kaolin. Neither talc nor kaolin significantly affect oleate foam stability; in the case of stearate kaolin has no effect while talc decreases formation and stability (figures 7 and 8). A simple explanation is that the free oleate ions or calcium oleate does not adsorb on these pigments. As a result, they do not attach strongly enough to the foam-forming bubbles to become entrained in the foam (P_a is low). On the other hand, the rather hydrophobic calcium stearate particles probably adsorb strongly on the relatively hydrophobic talc, which then attaches to the bubbles in the dispersion (P_a and P_b increase) but reduces foamability and stability because of hydrophobic interactions (P_s decreases).

Silicate. It is well known from ordinary textile washing that sodium silicate may adsorb on surfaces, rendering them more hydrophilic and reducing the adhesion of

hydrophobic particles or bubbles to the surfaces. Indeed, such effects have been observed in deinking systems (7). Silicate may also be precipitated by calcium ions (15). In our experiments, the calcium concentrations are too small to cause precipitation, except in the presence of calcium carbonate. Since silicate is a polyanion, one does not expect significant interactions between the soaps and silicate.

Taking these properties into account, the results in figure 9 are readily understood. Silicate adsorbs on kaolin, talc and TiO_2 , thereby rendering them hydrophilic and preventing adsorption of the precipitated calcium stearate which would otherwise lead to reduced foamability and stability. Silicate does not adsorb on calcium oleate particles. Accordingly, the particle-containing systems at high silicate concentrations behave as pure stearate systems.

The effect of coatings on foam properties

Figure 10 shows that dissolved components in the coatings increase foamability, which in most cases almost doubled compared to the foamability of pure soap solutions. The coating colours contain several components (latex and pigment dispersants and stabilisers, lubricant) that may affect adsorption at the solid/liquid or gas/liquid interfaces, so that the increase in foamability is not unexpected. The lubricant is actually calcium stearate, so it is hardly surprising that it improves foamability. However, the variation between different levels of the parameters used in the experimental design is too small to make it possible to draw conclusions regarding the mechanisms by which the other components affect foamability.

The latexes significantly improve foamability and (to a lesser degree) foam stability. SB latex seems to be somewhat more effective than AL latex, which may be related to the different stabilisers used for the latexes.

The improved foamability could be one reason for the generally recognized fact that better deinking results are often obtained when coated magazine is added to recycled paper.

Effect of flotation conditions on yield of pigments

Titanium dioxide. As already noted in the discussion of foam stabilities, it is likely that calcium soaps adsorb on TiO_2 . The solubilities of calcium oleate and calcium stearate at 60 °C are 0.2 and 0.0027 mM, respectively (19). Since 1.8 mM calcium chloride was added before the flotation in the flotation experiments, the solubility of oleate ions will be ≈ 0.067 mM and that of stearate ions ≈ 0.02 μM . Assuming that the oleate adsorbs in a saturated monomolecular layer on titanium dioxide, occupying 0.33 nm²/molecule (20), the amount of oleate required to cover 5g/l titanium dioxide particles with a monolayer is ≈ 0.25 mM, i.e. considerably more than the solubility of soap used in the experiments. Thus, we may conclude that the surface may be partially covered by adsorbed oleate, but the TiO_2 surface will also be hydrophobized by the deposition of small calcium soap particles. The result is that the film formed between TiO_2 particles and air bubbles becomes unstable (P_b increases) and the particles are effectively attached to the froth without breaking it. A similar effect of calcium oleate was observed by Larsson *et al.* (15) in the flotation of printing inks with calcium soaps.

Calcium carbonate The maximum yield of PCC is quite high and is obtained for the same experimental conditions as for TiO_2 . In view of earlier studies of calcite flotation with the oleate system (20) it seems very likely that the basic reason for this efficient flotation is analogous to the reason for TiO_2 flotation: soap adsorbs and deposits as calcium soap particles on the carbonate particles, rendering them hydrophobic. Accordingly, they attach strongly to the air/liquid interface and are floated. However, with respect to stabilization of foam, the carbonate behaves quite differently from TiO_2 . As discussed above, no foam was formed in the foamability tests in the presence of calcium carbonate. The reason for this was found to be that the soaps are so completely precipitated by the calcium dissolved from the carbonate particles that their concentration in solution decreases well below the cmc.

Obviously, in the much more turbulent conditions prevailing in the flotation cell, the hydrophobed carbonate particles collide efficiently with the air bubbles (*i.e.*, P_c is much higher than in the foam experiments). Then the condition are created for formation of a large number of stable contacts between hydrophobed PCC particles and the air bubbles.

The maximum yield of ground CaCO_3 is relatively low. This actually strengthens the arguments for the flotation mechanism suggested for PCC. The type of ground CaCO_3 was delivered as a slurry stabilised by polyacrylate (see "Experimental"). Particles hydrophilized in this way will not adsorb soap, and hence their probability of attachment to air bubbles becomes very low. Precipitated CaCO_3 of course increases the solution concentration of calcium, and hence affects foam stability in the same way as PCC.

Kaolin and talc. From their effect on foam properties, the conclusion was drawn that free oleate or calcium oleate does not adsorb on these pigments. This is supported by measurements of the electrophoretic mobilities of these particles, which are not much affected by the presence of oleate ions. The flotation of kaolin is much less effective than that of PCC or TiO_2 , which is consistent with the negligible effect of this pigment on foam properties, *i.e.* the probability of formation of a stable bubble/particle contact is low and the kaolin is enriched in the foam mainly by... entrainment in the foam films. TiO_2 differs from kaolin in that the presence of calcium stearate affects its floatability. This is also consistent with the observed effect of talc particles that have adsorbed sodium stearate on foam stability.

Silicate. The foam studies show that silicate hydrophilizes the pigment particles and suppresses their effect on foam stability. As shown by column D in table 8, silicate also reduces flotation of the pigments. This depressant effect of silicate is well known to be due to the absorption of silicate on mineral particles (20 21). Silicate does not affect the floatability of ground CaCO_3 . As already noted, this pigment is stabilised by adsorbed polyacrylate, and one does not expect silicate to adsorb and further increase this stability.

We stress that the mechanisms suggested above are tentative and require confirmation by more detailed studies, which are in progress. Factorial designs of the type represented by table 2 are essentially designed to find out in which direction the process parameters should be changed in order to optimise the dependent variables, *e.g.* the yield. From a practical point of view, a very important conclusion is that the results indicate that such optima will be found for quite different parameter combinations for the different pigments, *i.e.*, conditions can probably be designed for which flotation will work quite selectively.

Effect of latex and other coating components on flotation

As shown by tables 10 and 11, the effects of latex and other coating components on pigment floatability are complex. Some general conclusions may be drawn:

(i) SB and AL latex affect floatability differently in coatings containing the same pigments. For TiO_2 and talc, AL-containing coatings give a higher flotation yield than SB-containing coatings. For the carbonates the effect is similar but less marked and the yield of kaolin coatings containing AL is much smaller than if the coatings contain SB. These trends do not depend qualitatively on whether the coatings contain other coating components, but they are affected quantitatively. SB is more hydrophobic than AL and the latexes will certainly affect the strength, and hence the mechanical dispersability, of the coatings in different ways. They may also have different effects on the wettability of the dispersed particles.

(ii) Of the other coating components, calcium stearate affects the floatability much in the same way as in the experiments with only pigments and stearate. Starch negatively affects the yield of all pigments except kaolin. This may be due to the effect starch has on the way the dried coatings are broken up in the dispersion. The other effects are difficult to interpret (for glyoxal they are probably all insignificant).

The coatings are complex systems containing pigments with different wettabilities, surfactants, water-soluble polymers and hydrophobic particles. The strength and dispersability of the dried coatings will depend on their composition. A more detailed discussion of the effects of the different components therefore will have to await more specific experiments than the simple experimental designs presented above.

Final remarks

The purpose of this investigation was to understand the factors affecting flotation of the very complex system represented by recycled fibres sufficiently well so that the amounts of different pigments in the reject and in the deinked pulp could be, at least to some extent, controlled. From the results, two quite general conclusions can be drawn:

(i) The calcium oleate/stearate flotation system interacts very differently with different pigments.

(ii) These differences are sufficiently large, even when considering complete coating compositions, so that it may be possible to design quite selective flotation processes.

The experimental designs make it possible to suggest some mechanisms that cause these differences. Thus, many results can be interpreted very simply: adsorption of oleate or hydrophobic calcium soap particles increases flotation yield of pigments (just as is the case for ink particles (15)) while the adsorption of hydrophilic polymers, such as silicate, reduces the yield. However, many of the more detailed mechanisms suggested require further experimental confirmation.

The results, so far, do not include systems containing printing inks or fibres. It is our firm belief that the complete systems cannot be properly understood without at least a reasonable understanding of mechanism that come into play in simplified model systems. In forthcoming publications we will report on the effects of adding first model printing inks and then fibres to the model systems discussed above.

ACKNOWLEDGEMENTS

This investigation was made possible through grants from the Finnish Technology Development Centre (TEKES) and the industrial group supporting the program "Uudistuva paperi" (New generation paper technology) run by TEKES. Marja Kärkkäinen, laboratory technician, is thanked for her skilful and patient experimental work. We also thank the Finish Pulp and Paper Research Institute for putting the Outokumpu flotation cell at our disposal.

REFERENCES

1. McCool, M. and Silveri, L.: Removal of specks and non-dispersed ink from a deinking furnish. *Proc. Tappi Pulping Conference, Washington, 1-5-11, 1987*. Tappi Publications, Atlanta, 1990.
2. Raimondo, E.F.: Deinking of printed wastepapers by flotation. *Tappi J.* **50**(9) (1967) 69A.
3. Dodson, M. and Lowell, D.: Proper deinking chemistry, Bleaching technique crucial to pulp brightness. *Pulp Paper* **64**(9) (1990) 1901.
4. Letscher, M.K. and Sutmann, F.J.: The effects of magazine and filler on the flotation deinking of newsprint. *J. Pulp Paper Sci.* **18** (1992) J225.
5. Schriver, K.E., Bingham, S.J. and Fraizer, M.W.: The function of clay in flotation deinking. *Proc. Tappi 1990 Pulping Conf., Toronto 14-17.10. 1990*. Tappi Publications, Atlanta, 1990, p. 133.
6. Galland, G., Vernac, F., Julien Saint Amand, F. and Bernard, E.: Deinking varnished paper - the removal of specs. *Paper techn.* **32**(12) (1991) 30.
7. Liphard, M., Schreck, B. and Hornfeck, K.: Surface-chemical aspects of filler flotation in wastepaper recycling. *Proc. 1st Research Forum on Recycling, Toronto, 27-29.10. 1991*, Canadian Pulp and Paper Association, 1991.
8. Süß, H.U., Nimmerfroth, N., Jakob, H., Reinold, A. and Hopf, B.: Papier-recycling: Flotation von Füllstoffen und Fasern. *Wochenbl. Papierfabr.* **120** (1992) 305.
9. Nemeth, R. and Matijevic, E., *Kolloid-Z.Z.Polymer* **254** (1971) 497.
10. Yoke, *J Phys. Chem.* **62** (1958) 753.
11. Sutherland, K. L.: Physical chemistry of flotation, *J. Phys. Chem.* **52** (1948) 394.

12. Schultze, H.J.: *Physico-Chemical Elementary Processes in Flotation*, Elsevier, Amsterdam, 1984.
13. Schultze, H.J.: Hydrodynamics of bubble-mineral particle collisions. *Mineral Processing and Extractive Metallurgy Review*, 5 (1989) 43.
14. Schulze, H.J.: The fundamentals of flotation deinking in comparison to mineral flotation. *Proc. 1st Research Forum on Recycling*, Toronto, 27-29.10. 1991, Canadian Pulp and Paper Association, 1991, p. 161.
15. Larsson, A., Stenius, P. and Ödberg, L.; Zur Oberflächenchemie des Deinking Prozesses. *Wochenbl. Papierfabr.* 14 (1982) 502.
16. Somasundaran, P., Xiao, L. and Wang, D.: Solution chemistry of flotation of sparingly soluble minerals, *Min. Met. Proc.* (1991) 115.
17. Shinoda, K., Minegishi, Y. and Arai, H., *J. Phys. Chem.* 80 (1976) 1987.
18. Pope, M.I. and Sutton, D.I., The correlation between froth flotation response and collector adsorption from aqueous solution I. Titanium dioxide and ferric oxide conditioned in oleate solutions. *Powder technology*, 7 (1973) 271.
19. Quoted from Beilstein.E IV 2 p. 1213 and 1646, where references to original publications can be found.
20. Rao, H.K., Antti, B.-M. and Forsberg, E., Mechanism of oleate interaction on salt type minerals. Part I. Adsorption and electrokinetic studies of calcite in the presence of sodium oleate and sodium metasilicate. *Colloids Surfaces* 34 (1988/89) 227.
21. Laskowski, J.S. and Pugh, R.J., Dispersions stability and dispersing agents, in "Colloid chemistry in mineral processing", ed. J. S. Laskowski and J. Ralston, Elsevier, Amsterdam, 1990.

Transcription of Discussion

THE EFFECT OF COATING COMPONENTS AND FILLERS IN THE RECYCLING OF PAPER

P Stenius

Dr J D Peel (formerly Kusters, Germany)

How important is foam stability itself? If the particles adhere to air bubbles, they will transport them to the surface where there is another air surface. So if the bubbles burst you could say that it doesn't matter. They are already there and they should stay stably at the top.

P Stenius

Yes, you are quite right. Actually mineral flotation processes are usually designed so that you do not get a very stable foam. The foam should break readily because otherwise it becomes difficult to separate the particles. We have studied foam properties because they give an indication of how the particle locates at the air/bubble interface.

Dr J Phipps, ECC International Limited, UK

I was surprised that the experiment in which you simply mixed pigment and latex particles gave the same result as the one in which you used repulped coated paper. In a paper coating you would expect the pigments to be bound up in a film of latex, and after repulping some of the pigment would remain aggregated by the latex. For the latex to influence the mineral flotation selectively suggests some interaction between latex and mineral, which one would expect to be influenced by particle size and morphology. Do you know anything about the particle size of the aggregates that are

obtained by repulping, and hence if the latex is effectively separated from the particles?

P Stenius

We did not investigate separate addition of latex to broken up paper coating. We prepared latex-containing coatings that were dispersed. The break up procedure we used results in fairly small particles ie we do not have any remaining large aggregates of latex and pigment. Usually, if you disperse coated paper a large number of small aggregates are formed of about the size we have obtained in our studies. In addition a few very large particles may remain. We have actually done some studies of the flotation of coated paper which show that so few of the very large particles are formed that it is difficult to obtain reproducible results. What really affects flotation are the smaller ones.

Prof B Lyne, Royal Institute of Technology, Sweden

There are a number of negative things that happen if surface active agents reside in the pulp once it's deinked. Interference with hydrogen bonding and sizing in the paper are examples. Can you say a few words about how much surface active material is retained in deinked pulps and whether there is a mechanism by which they can be effectively separated?

P Stenius

This was investigated at the Inst for Surface Chemistry in Stockholm years ago⁽¹⁾. Calcium soaps are deposited on the fibre surface to an extent which depends on whether you are using excess soap for flotation or not, so you have to be quite careful. The calcium naturally present in the fibres will cause precipitation of the soaps on the fibre so it is fairly difficult to avoid some transport of the

surfactant. What would be the effective means to separate the soaps I don't know, I guess it is better to know your flotation process well enough so you don't overdose - most of the flotation agent goes out with the particles into the waste and the easiest way is to avoid surfactant in the pulp is to avoid using too much of the flotation agent. It's a question of optimising each flotation plant separately.

Dr R Bown, ECC International Limited, UK

There have been several comments made relating deinking flotation to mineral flotation. There are some quite major differences and I should like to see if anyone can comment on this. In mineral flotation we normally use frothing agents which do not interact with the mineral and use collectors which differentiate between minerals but do not necessarily froth. This is a strong difference and I don't see why in the fibre flotation process you are using, what to a mineral engineer, is quite an antiquated flotation chemistry. Have you any comments on that?

P Stenius

That's a very good question and I confess that I have thought myself that you could perhaps start from the very beginning with a completely new flotation system. The reason that we have studied the calcium soap system is of course that it is very extensively used in practice. Our aim was to understand how the pigments behave in this flotation system.

R Bown

I would like to clarify things just a little bit. In most flotation processes for the minerals that you are looking at here you would use some form of polyoxy floth promoter and then you would use some kind of amine type of reagent to collect the mineral. The

'oleate alone' type systems are not that specific for the minerals you are looking at.

P Stenius

No, indeed, but you are not adding the chemical in order to float the minerals. You are adding it in order to float the printing ink. The ink forms partially hydrophilised hydrophobic particles so one should add something that renders these particles hydrophobic again and aggregates them selectively. The soap system is one that produces very fine small solid hydrophobic particles that attach fairly selectively to the printing ink. We are investigating how this system affects the pigments.

B Phillips, Shotton Paper Co plc, UK

It's not a question, but a response to Bruce Lyne's question. In practice, (and we run a deinking plant) the soap carry over, or the oleate/stearate carry over is actually quite low. We are only adding 0.8% soap in deinked pulp anyway and we are only able to detect maybe 0.2% total oleate and stearate on paper. It is difficult to detect that amount in all the rosins and other materials present.

P Stenius

There are studies however on the deposits formed in paper mills which have been run with deinked pulp that indicate that the deposits contain a lot of calcium soaps.

- 1 A Larsson, P Stenius and L Ödberg: Surface chemistry in flotation deinking 3. Deposition of ink and calcium soap particles on fibres. Svensk Papperstidn 88 (3) 1985 R2