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RETENTION AND ZETA POTENTIAL: TRIALS ON A PILOT PAPER MACHINE WITH VARIOUS RETENTION AIDS

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1—*Objectives*

THIS investigation was initiated with the intention of defining the mode of action of the chemical retention agents used, especially with regard to their ionic nature and chain length. The efficiency of these agents is often explained in the literature as being due to their action on the electrical charge on the surface of the various substances present in papermaking suspensions.(1 - 12) After numerous laboratory studies carried out in media with well defined ionic strengths and on simple mixtures, we tried to see if a relationship existed between retention and zeta potential for a medium as complex as the papermaking water system.

Trials were carried out on the pilot papermachine at the Centre Technique du Papier.

2—*Experiments*

2.1—*The furnish*

As the problems associated with retention arise particularly during the production of filled papers, such as printings and writings, we chose a furnish of this type as a basis for our trials.

A 50/50 mixture of Bleached Laponin Kraft and a Bleached Hardwood sulphate pulp plus filler was beaten to a wetness of 43°SR.

Since the nature of the medium has a great influence on the properties of the surface of the suspended particles, trials were carried out in an acid medium and also in a neutral medium. For the acid medium sizing was achieved with a reinforced rosin at an addition level of 1·5 per cent (as received). The pH was adjusted to 4·5 by the addition of 2·2 per cent $Al_2(SO_4)_3$.

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18 H_2O. For these trials the filler used was china clay added at a rate of 20 per cent on fibre. For the neutral medium sizing was carried out by adding 2·5 per cent alkyl ketenedimer in the form of an emulsion. The introduction was made continuously, by a dosing pump to the dilution chest, using a solution diluted ten times with demineralised water. For these trials, in a neutral medium, the filler used was calcium carbonate (chalk) also at 20 per cent addition level on fibre. The target grammage for these trials was 65 g/m^2. Grammage was not controlled. The flow and consistency of the thick stock and the backwater flow used for dilution were constant. Variations in grammage were only due to variations in retention.

2.2—*Retention aids*

The following retention aids were used:

Cationic starch—cooked by steam injection as a 3·5 suspension
(Starch$^+$)
Polyethylene imine—an aqueous solution (20 per cent active material) of modified
(PEI) polyethylene imine of high molecular weight
Cationic polyacrylamide—mean molecular mass: 2 million
(PAA$^+$) Ionic nature: 10 per cent of unit groups made cationic
Non-ionic polyacrylamide—mean molecular mass: 6 million
(PAA^0)
Anionic polyacrylamide—mean molecular mass: 10 million
(PAA$^-$) Ionic nature: 10 per cent of unit groups made anionic.

These retention aids were added in quantities such that the cost of the treatment at maximum addition level was identical for each trial. This was equivalent to a treatment cost of approximately 13F per tonne. Although this figure may seem high we thought it of interest to exceed the amounts normally introduced.

The additions of the retention aids used are summarised in Table 1.

In all cases additions were made into the stock inlet pipe of the headbox to avoid disturbances due to possible shearing effects during passage through the pump.

2.3—*Measurements*

Filler concentration and ash content were determined on all stock samples and on the finished paper. The turbidity of the white water was also measured. Measurements were made of the conductivity and hardness of the water (complexion method) throughout the trials. The pH of the stock was measured from samples taken from the headbox and from the white water. During the trials carried out in an acid medium the acidity of these samples was quantified as the volume of caustic soda (N/50) necessary to neutralise 100 cm^3 of water after filtration.

TABLE 1

Products	*Condition*	*Machine Test in medium*	*Amount incorporated % on paper (active material)* Test I	Test II	Test III	Test IV
Cationic starch	Powder	Acid	0·15	0·30	0·45	0·60
		Neutral	0·15	0·30	0·45	0·60
PEI	Liquid 20% active material	Acid	0·02	0·04	0·06	0·08
		Neutral	0·015	0·03	0·045	0·06
PAA^+	Powder	Acid	0·01	0·02	0·04	
		Neutral	0·02	0·04	0·06	
PAA^0	Powder	Acid	0·015	0·030	0·060	0·090
		Neutral	0·025	0·05	0·075	0·1
PAA^-	Powder	Acid	0·010	0·03	0·09	0·115
		Neutral	0·025	0·05	0·075	0·1

COMMENT: Different amounts were used between the test in neutral medium because modifications in the price took place for certain products.

Pulp wetness and resistance to filtration were determined for the thick stock at the beginning of each trial and also at the headbox for each sampling.

The zeta potential was calculated from measurements of particle mobility obtained by electrophoresis. Particle suspensions were obtained after samples taken from the headbox and white water had been passed through a 200 mesh screen. In such a strongly ionised medium, no account was taken of the different mobilities of fillers and fines. Calculations of the zeta potential (ζ) were made using the Smoluchowski approximation (assuming that the radius of the particles is very much greater than the thickness of the double layer),

$$\zeta = \frac{4\pi\eta\mu}{\varepsilon},$$

where μ = mobility of particles
η = viscosity of solution
ε = dielectric constant.

An SCD (Streaming Current Detector), whose measuring principle is based on the streaming potential, was placed in the white water line.(1)

3—*Results*

SINCE the nature of the sizing, acid or neutral, strongly modifies the physico-chemical properties of the medium, the results obtained from these two sets of trials are presented separately.

3.1—*Acid medium*

Control runs, in this medium, without the addition of retention aids, gave residual filler contents of 12·3 ± 0·2 per cent. The addition of retention aids raised this figure to between 14·4 and 15·6 per cent, a gain of 2·3 to 3·1 per cent. All of the products used were shown to be effectively equivalent. The determination of retention, including total retention and filler retention allowed us to rank the additives in order of efficiency, see Figs. 1–5, curves A. The ranking order was

1. PAA^+
2. $Starch^+ = PAA^0$
4. PEI
5. PAA^-

Analysis of the concentration and turbidity of the white water produced the same rank order, Figs. 1–5, curves C.

If the level of retention required is chosen to be 80 per cent, the ranking of the additives in terms of their cost effectiveness is shown in Table 2. The additives PAA^- and PEI did not reach the 80 per cent retention level.

TABLE 2

Additive	*Amount for 80% retention*	*Treatment cost in F/t of paper*
PAA^+	0·017	2·50
PAA^0	0·045	5·30
Cationic starch	0·33	9·90

The two other products (PAA^- and PEI) did not reach the desired retention value of 80 per cent.

The hardness of the water used was practically constant at 18°TH. Its resistivity was 1300 Ω cm and its pH 7·3. Checks carried out on the white water during the trials did not show up any great variation in hardness (average 19°TH) whereas the resistivity fell to around 800 Ω cm. Acidity measured in the headbox remained practically constant at 6 cm^3 N/50 caustic soda whilst values measured in the white water varied as a function of the amount of retention aid used. Values ranged from 5 cm^3 for the control to 3 cm^3 for the highest retention aid addition level.

The presence of retention aid led to a lowering of the specific filtration resistance, its value almost halved except for the anionic polyacrylamide for which it did not vary. The °SR of the stock, taken from the head box was lowered by 3 to 10° depending on the retention aid used.

The presence of aluminium sulphate resulted in a positive electrokinetic potential for the control runs. This varied from +8 to +10 mV for the five

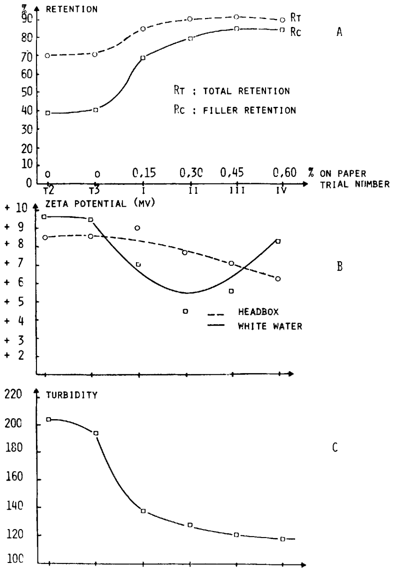

Fig. 1

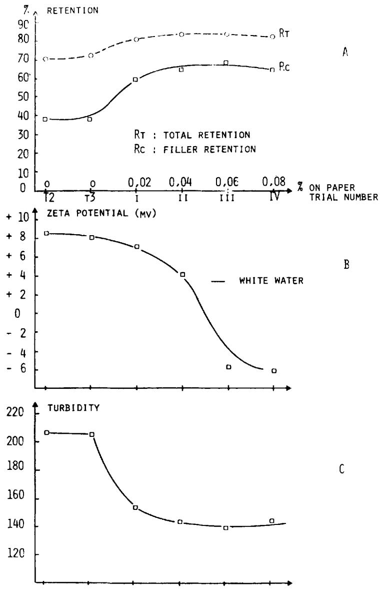

Fig. 2

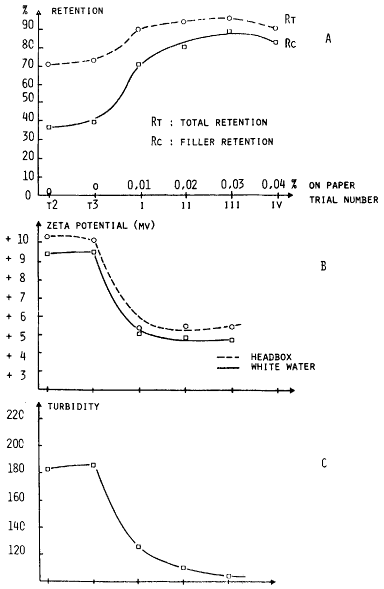

Fig. 3

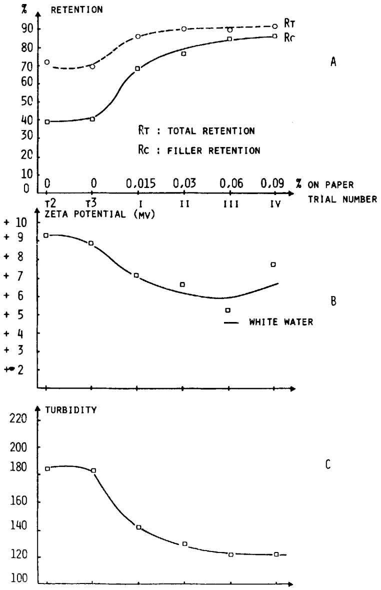

Fig. 4

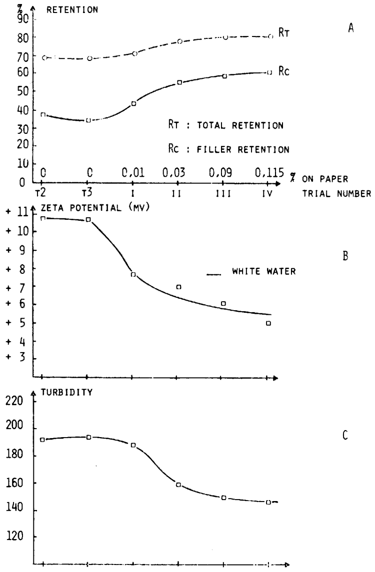

Fig. 5

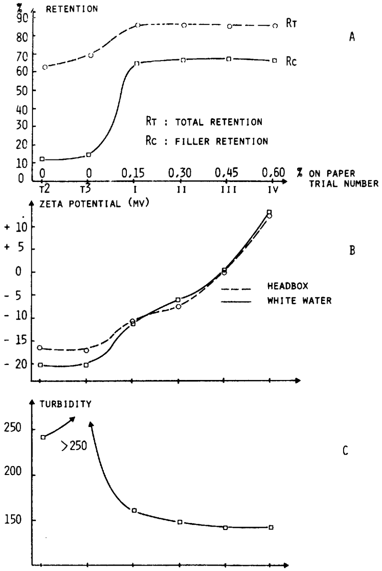

Fig. 6

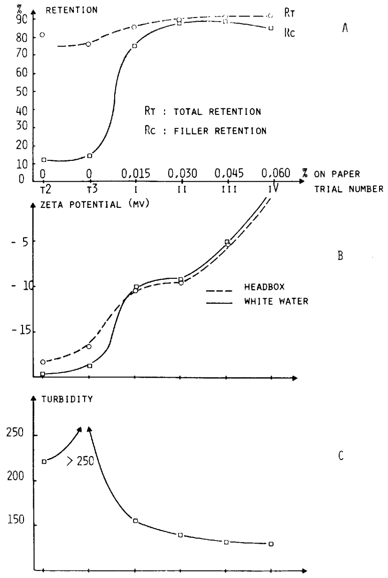

Fig. 7

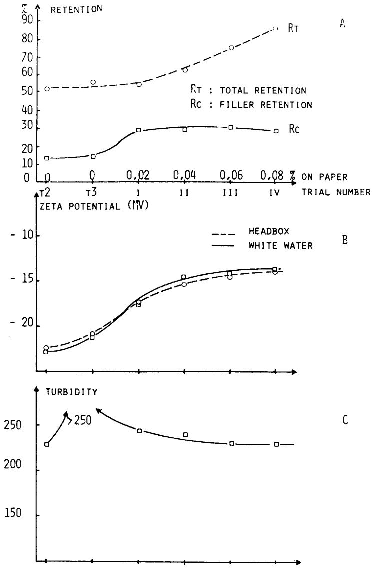

Fig. 8

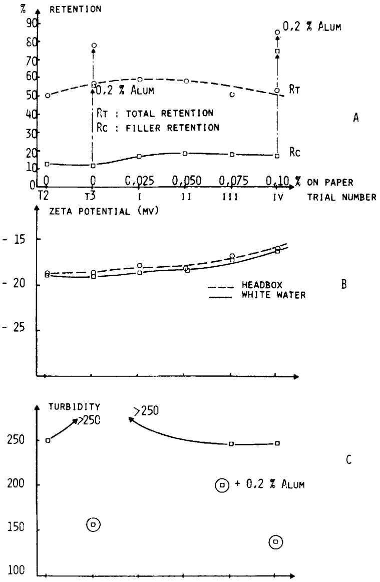

Fig. 9

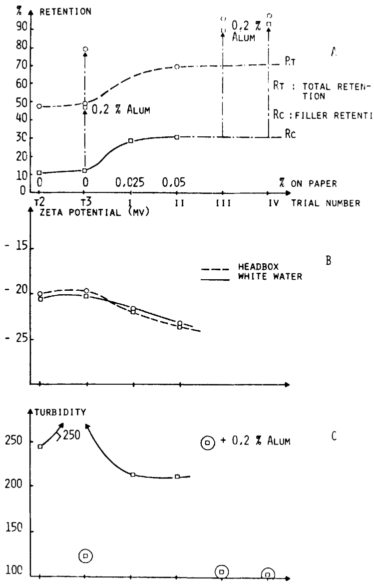

Fig. 10

runs. The addition of the various retention aids decreased these values slightly to +4 mV. In the case of polyethylene imine the zeta potential became negative at −6 mV. Zeta potential results are plotted in Figs 1–5, curves B. The apparent lack of sensitivity of the zeta potential to the different types and quantities of retention aid added was surprising. It seems difficult to correlate these slight variations of the potential with the variations of the retention.

3.3—*Neutral medium*

The control runs, in a neutral medium, had residual filler contents of 6·7 ± 0·8 per cent. Thus the filler contents of these reference papers were lower than those obtained from papers made in an acid medium. Allowing for the fact that the fillers were different, this could be attributed to the presence of aluminium sulphate in the trials carried out in an acid medium.

The maximum filler contents after the addition of retention aids ranged from 8·5 to 13·9 per cent. Only the non-ionic polyacrylamide had a distinctly lower efficiency than the others improving retention by only 2·1 per cent. The addition of very small quantities of aluminium sulphate proved to be an effective remedy in this case.

The determination of retention, again allowed us to rank the retention aids in order of performance, see Figs 6–10, curves A. The rank order was

1. PEI
2. Starch$^+$
3. PAA$^+$ = PAA$^-$
5. PAA^0

Analysis of the concentrations and turbidity of the white water led to a similar conclusion, see Table 3, and Figs 6–10, curves C. Since a level of 80 per cent retention was only achieved by PEI we have shown the cost effectiveness of PEI and cationic starch for a 70 per cent retention level, see Table 4. The other retention aids did not provide 70 per cent retention.

TABLE 3

Retention agent	*Minimum concentration in backwater in g/l*
PEI	0·39
Cationic starch	0·54
PAA$^+$	0·79
PAA$^-$	1·29
PAA^0	2·27

TABLE 4

Additive	*Amount for 70% retention*	*Treatment cost in F/t of paper*
PEI	0·01	2·20
Cationic starch	0·30	9·00

The other retention agents did not reach the 70 per cent value.

The water used in the trials had a hardness of 17·5°TH, resistivity of 2 000 Ω cm and a pH of 7·5. During the trials the resistivity fell to 1 300 Ω cm and the pH stabilised to a value of 7·8. It was not possible to measure hardness during the trials due to the presence of calcium carbonate in the white water.

In the neutral medium no systematic reduction in filtration resistance and °SR were noticed. Where there are appreciable variations in these parameters they start by increasing before decreasing in proportion to the amount of retention aid added. The zeta potential in the control samples was −19 mV. The addition of retention aid resulted in logical changes in the zeta potential, see Table 5. Although the potential varied to a greater extent in this series of

TABLE 5

Additive	*Variations in potential*
PAA^-	From -20 to -24 mV
PAA^0	From -19 to -16 mV
PAA^+	From -21 to -14 mV
PEI^+	From -18 to 0 mV
$Starch^+$	From -18 to $+13$ mV

trials it was not possible to establish a relationship between potential and retention, e.g. on increasing the addition level of cationic starch the potential increases regularly to become positive whilst the retention remains constant after an initial improvement.

3.3—*Supplementary tests*

During the trials in a neutral medium two retention aids, nonionic polyacrylamide and anionic polacrylamide, were shown to have low efficiency even at high addition levels. We considered it of interest to find out what would happen if cations were added to the suspension by the introduction of very small quantities of aluminium sulphate. In the two trials carried out the pH in the headbox or the backwater never went below 7.

For the nonionic polyacrylamide 0·2 per cent aluminium sulphate was added to the headbox at the end of a run in which PAA had been added at 0·1 per cent. A spectacular improvement in retention was apparent. The PAA addition was decreased to zero to see how much of the improvement was solely due to the presence of the aluminium sulphate. It was confirmed that the improvement was due to the combined effect of the two additives.

Similar procedures were carried out for the anionic polacrylamide. 0·2 per cent aluminium sulphate was added at the headbox and then 0·075 per cent, and later 0·1 per cent, anionic PAA was added to the stock. Total retention rose to 97 per cent, filler retention to 93 per cent and the backwater concentration was found to be 90 mg/l.

The wetness of the pulp as expressed in °SR dropped appreciably due to intense flocculation. The zeta potential rose appreciably on the introduction of aluminium sulphate.

4—*Conclusions*

THE results from these trials showed up clear differences in the performance of the five retention aids under investigation, differences which depended on the nature of the suspending medium. In acid conditions practically all the retention agents performed well. The presence of aluminium ions inducing microflocculation of the fillers. In neutral conditions, however, the ionic nature of the retention aid is of importance. Only the three cationic agents gave satisfactory results. Polyacrylamide appears inefficient under these conditions unless flocculation is primed by small addition of aluminium ions.

Polyethylene imine is more efficient in the absence of aluminium sulphate, cationic starch is efficient under both acid and neutral conditions but is slightly less cost effective, in acid conditions cationic polyacrylamides and non-ionic polyacrylamides are more efficient from a cost effectiveness point of view. Final results are summarised in Table 6. Whereas under neutral conditions variations in zeta potential appeared logical, bearing in mind the ionic nature of the additives, under acid conditions the presence of aluminium sulphate had a levelling effect.

TABLE 6

	Gain in retention of filler % of reference		
Retention agents	*Acid medium*	*Neutral medium*	*Neutral medium* $+AL_2(SO_4)$
Cationic starch	112	248	
PEI^+	82	527	
PAA^+	125	112	
PAA^0	111	63	554
PAA^-	62	151	673

The making conditions on the pilot paper machine—low speed, high headbox dilution—did not permit the observation of appreciable variations in lookthrough of the different papers made.

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Discussion

Dr U. Beck I want to make a comment from our practical experience. We must be careful with mobility measurements in practical systems. I think you may say that if you have a flocculation mechanism like charge neutralisation or a patch model then you may get a good pointer from zeta potential measurements for optimum retention. But you never get the highest retention, you can only optimise your system. You can optimise the system by mobility measurements if you have special systems such as laminating base paper for instance. With only a few components things are relatively clear and opacity, retention, ash content and wet strength can be optimised. If you have systems where bridging or hydrogen bonding occurs, then zeta potential measurements are generally not good guides, and that is the problem with non-ionic or anionic retention aids. Furthermore, problems are caused by high alum concentrations at, say, pH 5 or 6 where you get the well known complexes which are also bad for monitoring production by mobility measurements.

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