DTPMPA: polyamino polyphosphonic acid and its use in paper related processes

*Part 2: paper production from silicate-free pulp bleached with DTPMPA as a stabilizer

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ABSTRACT *Paper was produced from silicate-free pulp bleached with DTPMPA as the peroxide stabilizer on the pilot plant of CTP, Grenoble, France. Using such pulp, the efficiency of retention aids on both fines and fillers is greatly enhanced. Evaporation of water from the paper sheet is accelerated and can lead either to substantial energy savings or faster throughput on the machine. The quality of the finished product is unchanged, but some improvement in the final sizing quality can be seen.*

KEYWORDS
Bleaching
Phosphonic acids
Pretreatment
Retention aids
Silicates
Stabilizers

One can easily demonstrate in a laboratory experiment that DTPMPA can replace silicates as a peroxide stabilizer to yield silicate-free pulp with high brightness. On a laboratory scale, it is also possible to show that this silicate-free bleached pulp leads to enhanced efficiency of different types of retention aids.

While laboratory bleaching data may be extrapolated to plant conditions without great risk, retention results obtained in the Britt dynamic drainage jar only reflect general trends. Other variables controlling the general runnability of paper pulp on the paper machine cannot be measured by noncontinuous tests in the lab.

Therefore, a semi-industrial trial was run on the paper machine of the Centre Technique du Papier (CTP) at Grenoble, France, starting from DTPMPA-bleached stock.

This trial allowed a more comprehensive assessment of the implications of DTPMPA bleaching on all aspects of paper runnability and on finished product quality.

Results and discussion

Bleaching of the mechanical pulp

Although bleaching performance *per se* was not the ultimate goal of the test, it was measured for both systems. The CTP mill does not have a bleaching tower, so the bleaching was carried out at lower consistencies than those practiced in industry. **Table I** lists the results obtained.

Under the bleaching conditions used, brightness was about equivalent when silicates were replaced by DTPMPA. However, the percentage of residual peroxide was substantially higher. This residual peroxide can lead to savings when the white waters are recycled.

Retention of fines and fillers

The interference of the anionic silicate colloids with cationic retention aids is a common problem encountered in paper mills. The retention of both fines and fillers can be negatively affected. On the pilot paper machine, the retention of fines and fillers was measured at regular intervals. The results are shown in **Fig. 1**, while the run numbers are given in **Table II**.

This figure shows the strong increase of total retention when silicates are replaced by DTPMPA. This increase is particularly noticeable on the retention of the kaolin filler (**Fig. 2**) but is substantial on the retention of fines as well. The total impact of retention agents depends on the type of retention aid used and is particularly strong on the cationic polyethyleneimine-based agent.

With the concentration of DTPMPA being 10 times lower, this lack of compatibility practically disappears.

Response to drying

Samples of paper were taken after the post dryer, and the residual water was the same (within experimental error) for all runs, because the speed of the machine was not varied. Therefore, only the differences in water evaporation rate in the pre-drying stage

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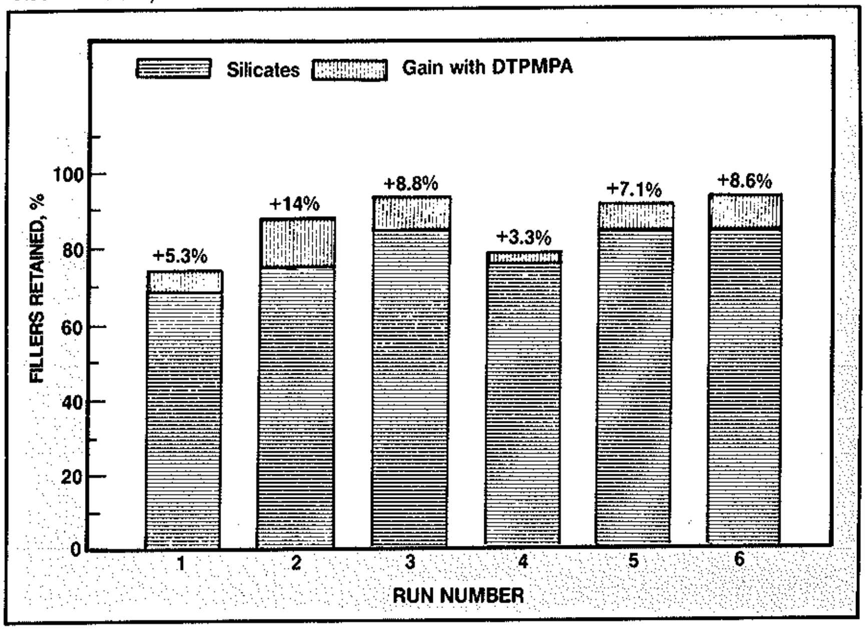
I. Brightness and residual peroxide in silicate- and DTPMPA-stabilized bleaching

	Silicate, (5%)	DTPMPA, (0.6%)
Initial brightness, %	59.7	60.8
ISO brightness, %	70.8	71.1
Residual H_2O_2, %	29.9	36.8

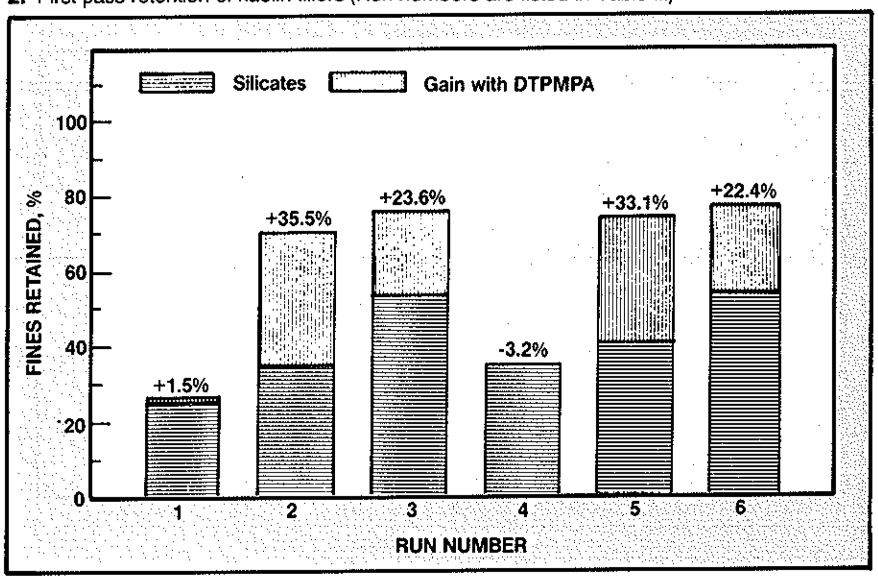
II. Identification of run rumbers

Run no.	Sizing	Retention aid
1	unsized	none
2	unsized	Aid A
3	unsized	Aid B
4	sized	none
5	sized	Aid A
6	sized	Aid B

1. First-pass retention measured at regular intervals on the pilot machine (Run numbers are listed in Table II.)



2. First pass retention of kaolin fillers (Run numbers are listed in Table II.)



were used to calculate differential drying behavior of the different stocks. Steam pressure and cylinder temperature were closely monitored during the runs and were kept constant within the accuracy of the machine.

As shown in **Fig. 3**, the gain in drying speed is high for all runs except Run 2. (The rate was increased to 17% in Run 5.) These gains in drying rate mean either that savings in steam consumption can be achieved or that the throughput of the paper machine can be increased. The true value of these benefits is dependent on paper grade and paper machine engineering. Only a full-scale industrial test on a particular pulp and piece of equipment can show the true impact of bleaching with DTPMPA on these variables.

Paper quality

The finished paper from the different runs was subjected to the major quality tests. The paper was conditioned at 23°C and 50% RH. The results of these tests are shown in **Table III**.

No substantial differences can be observed between silicate- and DTPMPA-bleached paper for most variables. The differences between S5 and D5 suggest that better sizing efficiency can be achieved by using silicate-free pulp.

Economic aspects of the use of DTPMPA in paper pulp bleaching

Substituting silicates with DTPMPA in the bleaching stage can have major implications on the economics of the papermaking process. In spite of higher residual peroxide concentrations, the cost of bleaching alone will be increased because the cost of DTPMPA is higher than that of sodium silicate.

However, major savings can be expected downstream on the paper machine, which will more than offset the extra cost of bleaching chemicals. First, better retention will allow a higher substitution of fines by fillers, while maintaining strength requirements. Second, energy will be saved as a result of the accelerated evaporation of water from DTPMPA-bleached pulp. Faster evaporation will bring down the total steam volume and other variable costs needed per unit weight produced. Alternatively, this faster drying rate can be translated into higher machine throughput and increased income.

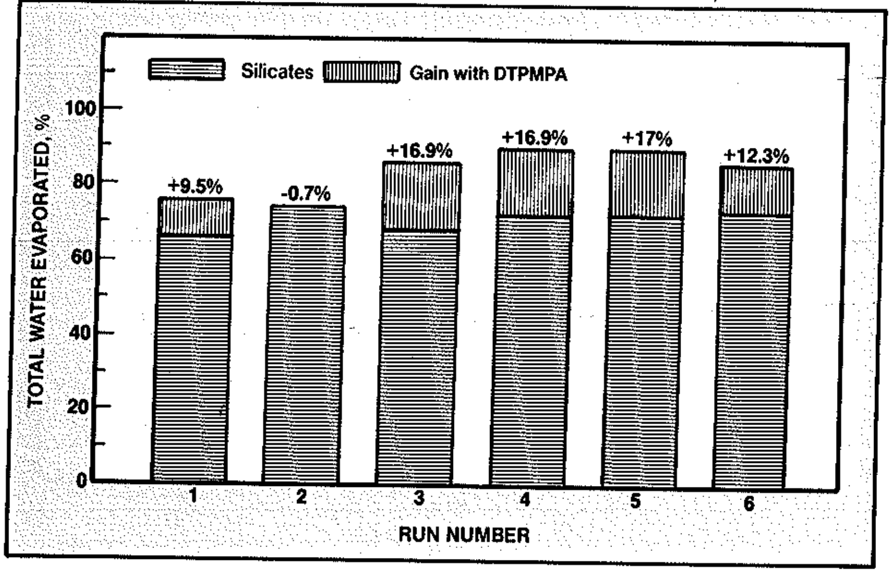
Other long-term savings can be expected by using silicate-free pulp in

III. Quality tests on finished paper

	Silicate						DTPMPA					
	S1	S2	S3	S4	S5	S6	D1	D2	D3	D4	D5	D6
Basis weight, g/m²	64.9	65.9	69.6	68.0	68.8	67.7	69.9	69.3	69.8	69.6	69.1	66.8
Moisture, %	6.8	6.8	6.6	6.8	6.6	6.7	6.9	6.6	6.7	6.9	6.8	6.7
Thickness, μm	150	148	157	153	154	151	161	155	158	158	154	148
Bulk, cm³/g	2.31	2.28	2.25	2.25	2.24	2.23	2.30	2.24	2.26	2.27	2.23	2.21
Breaking length, m												
Paper length	1980	2390	2230	2220	2410	2280	2155	2360	2310	2260	2490	2010
Paper width	1200	1360	1310	1410	1350	1330	1450	1350	1330	1350	1360	1290
Burst strength index	0.72	0.74	0.72	0.73	0.75	0.78	0.73	0.78	0.74	0.76	0.80	0.73
Tear strength index												
Paper length	280	305	313	323	291	325	346	322	383	353	324	314
Paper width	379	348	382	362	381	351	418	392	395	419	391	389
Elrepho brightness, %	75.6	75.6	76.0	75.0	75.0	75.5	76.6	76.7	77.1	75.3	75.3	75.6
Elrepho opacity, %	88.7	88.8	90.2	88.7	90.1	88.4	89.1	90.4	89.5	88.8	89.4	89.1
Sizing (Cobb method, 60 s)												
Recto	...	...	...	25.3	44.6	...*	...	...	...	31.9	35.5	34.1
Verso	...	...	...	36.9	50.4	...*	...	...	...	25	30.6	35.0
Ash (800°C)	7.4	7.0	9.0	6.9	8.9	8.0	6.6	8.9	9.0	7.1	7.8	9.3

*Water passed through the paper.

3. Response of paper samples to drying (Run numbers are listed in Table II.)



papermaking. Problems of scale formation on the machine will be reduced, since silicates often form the basis of this scale formation. Moreover, DTPMPA is an extremely efficient threshold agent for preventing scale formation. Because of this property, it has already become the stabilizer of choice in refiner bleaching processes. We can also expect less machine maintenance and a longer lifetime for machine components such as drying felts. The total volume of discharged fines, fillers, and chemicals will also be smaller.

Some of these savings cannot be translated directly in precise numbers because they are visible only after prolonged usage of DTPMPA (e.g. reduced scaling) or because they are dependent on machine engineering or the type of paper produced. Other savings can be more realistically quantified from the results obtained on the pilot machine.

Energy savings

The experiments on the pilot plant indicated that approximately 20% less steam can be used in both the predrying and postdrying sections while maintaining a constant final consistency. Assuming a heat transfer coefficient of 0.85, a 1:1 ratio of steam to evaporated water, and a total amount of 1000 tons of water to be evaporated for 1000 tons of paper, the cost reduction per ton of paper can be calculated. Some results are shown in **Table IV**.

H_2O_2 savings

Laboratory data and the pilot plant trial indicated that residual H_2O_2 can be increased by 10% or more when DTPMPA is used. This increase allows cost savings in H_2O_2 consumption, which can be calculated as:

$$savings = cost \times amount \times RI \times PBD \quad (1)$$

where

savings = savings per kg of paper

cost = cost of hydrogen peroxide

amount = amount of hydrogen peroxide used in bleaching.

RI = increase in residual hydrogen peroxide, %

PBD = pulp bleached with DTPMPA, %

When 50% DTPMPA-bleached pulp is used with 10% more residual H_2O_2 in a bleaching process with 3% H_2O_2 at a cost of DM 2/kg (100%), the cost reduction amounts to 3 DM/ton of paper produced.

Saving of retention aids

The experimental evidence shows

IV. Results of calculations of annualized savings

Steam price, DM	Reduction in steam cost, DM/1000 kg	Annualized savings,* DM
30	7.0	700,000
40	9.4	940,000
50	11.7	1,170,000

*Plant producing 100,000 metric tons/year.

V. Bleaching conditions

	Silicate, (5%)	DTPMPA, (6.0)
Consistency, %	5.0–5.5	5.0–5.5
Active caustic, %	2.4	2.6
Active H_2O_2, %	4	4

Bleaching temperature = 50°C. Bleaching time = 90 min.

VI. Compositions of the 12 different stock suspensions

	Silicate, (5%)	DTPMPA, (6.0)
No sizing agent and no alum		
Blank	S1	D1
Retention aid A	S2	D2
Retention aid B	S3	D3
Sizing agent (1%) + alum (1%)		
Blank	S4	D4
Retention aid A	S5	D5
Retention aid B	S6	D6

that equivalent performance can readily be achieved with 20% less retention aid in the stock. Assuming a retention aid dosed at 0.2%, the savings from improved retention would amount to 0.8-3 DM per ton of paper for retention aids costing between 2-8 DM per kilogram. On a commercial scale, this can allow savings of DM 200,000 per year for a 200,000-ton plant using 50% mechanical pulp.

Some of these savings can be cumulated, such as savings from peroxide, steam, and retention aid. Others cannot, such as savings arising from a steam increase contingent on an increase in capacity.

These numbers are only indicative, since different plant conditions and different paper grades will have a strong impact on these values. They do demonstrate, however, that the cost of bleaching stabilizer alone is an insufficient basis for the calculations of the total economics of DTPMPA-assisted pulp bleaching. In addition, they show the magnitude of the potential improvement in process economics and income generated on a commercial scale by the use of DTPMPA as a replacement for silicates.

Conclusions

Excellent bleaching of paper pulp can be achieved with silicates replaced by DTPMPA as the peroxide stabilizer. Downstream, on the paper machine itself, some clear advantages of this practice can be identified.

First, the retention of fines and fillers is substantially improved by the use of DTPMPA in the bleaching stage. The relative effect depends on the type of retention aid and stock, but it was always significant in our tests.

Second, the drying of paper bleached with DTPMPA is faster than for pulp containing silicate. This faster evaporation rate of water can permit energy cost reduction or increased throughput on the paper machine.

Third, the properties of the final product are unaffected for most quality variables. The sizing quality is enhanced in DTPMPA-bleached paper.

Fourth, other long-term advantages on the process equipment such as absence of scaling and longer felt life can be expected when using silicate-free stock bleached with DTPMPA as a stabilizer.

Experimental methods

Reagents and raw materials

The following reagents and raw materials were used:

- Untreated mechanical pulp: softwood, "Egeland News"
- Bleached chemical pulp: kraft, "Pin de Tarascon"
- Hydrogen peroxide: 40.4%
- Sodium silicate: Crystal 79
- DTPMPA: Dequest 2060 S, (50% active acid solution)
- Caustic: pellets
- Sizing agent: Pexlim BR 50 rosin soap
- Retention aid A: cationic polyethyleneimine
- Retention aid B: cationic polyelectrolyte
- Filler: kaolin.

Pulp bleaching and mixing

The mechanical pulp was disintegrated and split in two portions. The first was bleached in the presence of sodium silicate, and the second was bleached in the presence of DTPMPA. The conditions were as given in **Table V**.

The two different batches were mixed with dispersed kraft pulp in a ratio of mechanical pulp to chemical pulp of 2:1. The suspension of the stock was adjusted to pH 5.5 with sulfuric acid. To these mixtures, 10% of kaolin was added. With those two different stocks, the sizing agent, alum, and different retention aids were mixed in varying proportions, yielding 12 different stock suspensions with the compositions given in **Table VI**.

With these twelve different stocks, paper was made on the CTP mill's pilot machine, which is a pilot unit with the following characteristics:

- Speed: 10-100 m/min
- Basis weight: 20–200 g/m^2
- Wire length: 650 cm
- Wire width: 56 cm
- Wire material: plastic, 21 × 27 tricot.

There are two suction boxes for each group, and there are two presses. In the drying section, the predryer has 16 cylinders of 50 cm in diameter in 8 subsections and 8 cylinders of 50 cm in diameter in 8 subsections.

Paper machine operation

The pulp was diluted to 2.0% consistency, was further diluted by white waters to 1% consistency, and was pumped to the machine headbox. The water draining through the wire was collected in a tray and was recirculated through the white water reservoir. Equilibrium was attained after about 1 h of continuous production, as indicated by the stabilized consistency of the white water.

Three samples were taken under the wire after equilibrium had been established, analyzed, and averaged to measure retention. Samples of paper were taken at the entrance to the pre-dryer section, at the exit of the pre-dryer section, and at the exit of the post-dryer section. Sampling was repeated three times per run. The samples were analyzed for moisture content, and the results were used to estimate the relative drying rates of differently treated pulps.

$US 1 = 1.699 DM

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