DTPMPA: polyamino polyphosphonic acid and its use in paper processes

Part 1: The chemistry of pulp bleaching with DTPMPA and its impact on fines retention

Krzysztof Kuczynski, Hubert Nijs, and Bronislav Henri May

Research chemist, research leader, and development manager, respectively, Monsanto Europe SA, Technical Center Europe-Africa, rue Laid Burniat, 1348 Louvain La Neuve, Belgium

ABSTRACT *The performance of DTPMPA (diethylene triamine penta-methylene phosphonic acid) has been evaluated in different pulp bleaching processes. As a result of the effective peroxide stabilization, high brightness can be achieved, and a great amount of residual peroxide can be maintained.*

The selective complexation of metal ions which catalyze the decomposition of hydrogen peroxide means that DTPMPA can be efficiently used in pretreatment. The advantage of silicate-free formulations extends beyond the bleaching stage and can be perceived in other stages of the papermaking process. Some specific problems caused by silicates are identified. Examples of incompatibility with cationic retention aids are given.

KEYWORDS
Bleaching
Deinking
Phosphonic acids
Pretreatment
Retention aids
Silicates
Stabilizers

A number of pulp bleaching operations are carried out using hydrogen peroxide. A loss of bleaching efficiency takes place, however, when this expensive chemical is wasted by decomposition reactions. Because transition metal ions catalyze this reaction, they must be removed from the bleaching operation.

By pretreating the pulp and bleach liquor, stabilization with a sequestrant, efficient peroxide bleaching is achieved. The stabilizer need not necessarily be a sequestrant. Sodium silicate, for example, performs well in many cases, though it can be a source of specific problems in downstream processes. For this reason, some organic sequestrants represent an interesting alternative. DTPMPA is one of the best peroxide stabilizers known and is used in several other applications (*1*). **Figure 1** shows its chemical structure. Its chemical properties are maintained in alkaline and oxidizing media.

The same compound can also be effectively applied in pretreatment. Polyamino polyphosphonic acids could represent an opportunity for papermakers who are facing specific production problems.

Results and discussion

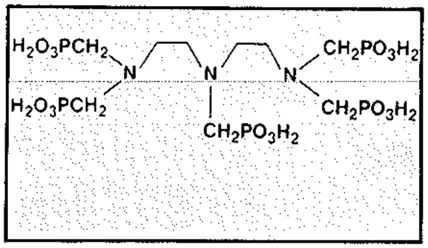
Pretreatment

The benefits resulting from efficient pulp washing prior to bleaching are generally recognized. The bulk of transition metal ions is chelated and removed by this process, together with some water-soluble impurities (*2*). Iron, manganese, and copper are the main contaminants that catalyze peroxide decomposition (*3*). Iron and manganese are usually the predominant species.

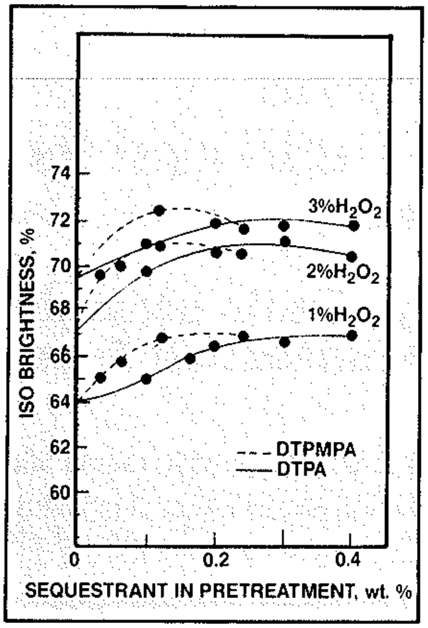
The efficiency of pretreatment can be evaluated either by the decrease in ion content after washing or by bleaching tests run with pretreated pulps (*4*). Our results were obtained from bleaching tests because this method should better reflect the effective deactivation of metal residuals that remain in the pulp after pretreatment.

Figure 2 presents the results of bleaching tests carried out with *Pinus radiata* samples, pretreated separately with increasing amounts of DTPMPA and DTPA. The experimental conditions are summarized in **Table I.**

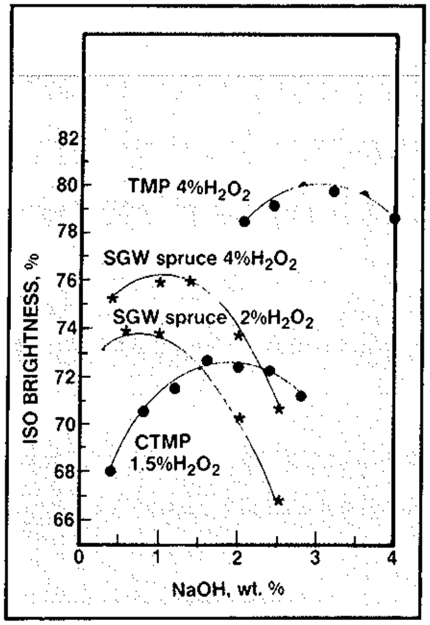
The optimum dosages applied in pretreatment (0.12% DTPMPA, 0.20% DTPA) did not depend on the concentration of hydrogen peroxide. In some cases, the effect of pretreatment with DTPMPA can result in a brightness increase of 1 ISO point over pretreatment with DTPA (*4*). Alternatively,



1. Molecular structure of DTPMPA



2. The influence of sequestrant dosage in pretreatment on bleaching performance of stone groundwood



3. Bleaching performance as a function of caustic dosage for several pulp samples

I. Conditions for bleaching for pretreatment evaluation

Initial metal content, ppm			
Iron	7		
Manganese	130		
Copper	2		
Composition of bleaching liquors, %			
H_2O_2, %	1	2	3
NaOH, %	1.00	1.50	2.00
DTPMPA, %	0.3	0.3	0.3

50% DTPMPA can be used to achieve a performance equal to 100% DTPA.

Overdosage of DTPMPA is not useful, because it results in a slight brightness decrease, as shown in Fig. 2 (*4*). However, no clear explanation for this phenomenon can be given.

Bleaching

DTPMPA can be applied either as the main stabilizer (silicate free formulation) or as a complimentary peroxide protection in bleach liquors with low silicate content.

The bleaching efficiency depends mainly on three parameters:

1. Efficiency of pretreatment
2. Ratio of caustic to hydrogen peroxide in the bleaching formulation
3. Efficiency and concentration of stabilizer.

The second parameter is critical for any type of stabilizer. Perhydroxyl ions, HO^{-2}, are the active bleaching species generated in alkaline solutions. They are not formed when the alkalinity is too low. On the other hand, an excess of alkalinity gives rise to hydrogen peroxide decomposition and to pulp yellowing.

Both situations are illustrated in **Fig. 3**, which presents brightness results for several pulp samples as a function of NaOH dosages. Bleaching conditions are detailed in **Table II**. Each curve presented in Fig. 3 has a maximum, corresponding to the optimum dosage of NaOH, which is specific for the type of pulp and for the concentration of hydrogen peroxide applied.

II. Bleaching conditions of the pulp samples studied

	Pretreatment	*Stabilizer*	*H_2O_2, %*	*Temp., °C*	*Time, min*	*Consistency, %*
SGW spruce*	0.3% DTPMPA	0.3% DTPMPA	2	60	90	16
SGW spruce*	0.3% DTPMPA	0.3% DTPMPA	4	60	90	16
CTMP	0.2% DTPA	5.0% silica	1.5	50	180	17
TMP pine	0.4% DTPA	0.5% silica and 0.6% DTPMPA	4	50	120	13

*The process water was contaminated with 1.7 ppm Mn and 1.3 ppm Fe.

A further increase in brightness can be achieved through the optimization of pretreatment. The evolution of brightness for two stone groundwood (SGW) samples as a function of DTPMPA dosage in pretreatment is plotted in **Fig. 4**. In the example, an efficient pretreatment could increase the brightness by 8 ISO points.

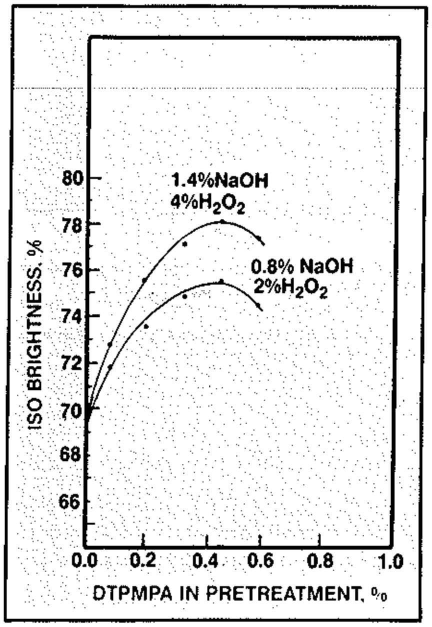
The optimum dosage of DTPMPA is unusually high (0.58%) in the example presented and is related to the contamination of process water with 1.7 ppm of manganese and 1.3 ppm of iron.

The total quantity of DTPMPA consumed in pretreating and bleaching the sample amounts to 0.88%, relative to dry pulp. Would this quantity be equally efficient if used in a pretreatment and bleaching amounts other than 0.58% and 0.3% DTPMPA? The results in **Table III** show that only one distribution of sequestrant over pretreatment and bleaching allows the maximum brightness to be achieved and that dosages applied were optimized. The amount of hydrogen peroxide used did not affect the defined dosages.

The performance of DTPMPA in bleach liquor stabilization has already been reported, and advantages over DTPA were demonstrated (*4-5*).

As to the relative performance of formulations containing different type of stabilizers, **Table IV** presents bleaching results of SGW (A) and CTMP (B) samples, run separately with silicates, DTPMPA, and with their blends.

4. Bleaching of stone groundwood from spruce as a function of DTPMPA dosages in pretreatment



III. Final brightness as a function of DTPMPA distribution over pretreatment and bleaching

DTPMPA, %		*Brightness achievable with*	
Pretreatment	*Bleaching*	*4% H_2O_2*	*2% H_2O_2*
0	0.88	75.8	73.7
0.12	0.76	75.4	74.2
0.30	0.58	76.1	74.5
0.58	0.30	77.4	76.0
0.76	0.12	76.8	74.8
0.88	0.00	75.5	74.4

IV. Brightness achieved after bleaching with different stabilizer formulations

No.	*Silicate, %*	*DTPMPA, %*	*H_2O_2, %*	*Brightness, %*	*Residual peroxide, %*
A1	0.5	0	4.0	74.9	14.5
A2	0.5	0.2	4.0	77.5	15.9
A3	0.5	0.4	4.0	78.8	16.8
A4	0.5	0.6	4.0	80.5	16.5
A5	0.5	0.8	4.0	80.6	17.9
A6	1.0	0	4.0	76.4	10.1
A7	1.0	0.2	4.0	78.6	18.8
A8	1.0	0.4	4.0	79.3	19.6
A9	1.0	0.6	4.0	80.4	18.0
A10	1.0	0.8	4.0	80.7	18.5
A11	5.0	0	4.0	80.8	17.5
B12	4.0	0	1.5	72.0	13.2
B13	1.0	0	1.5	70.3	10.4
B14	0.0	0.6	1.5	69.8	18.7
B15	0.0	0.4*	1.5	71.8	14.2
B16	0.0	0.6*	1.5	71.8	16.9
B17	0.5	0.6	1.5	71.8	17.0

*Sodium carbonate was used as a buffer.
A = SGW, B = CTMP.

Low-silicate and silicate-free formulations, completed with DTPMPA, can be as efficient as 4% silicates (A4, A9, A11).

Incompatibility of cationic retention aids with silicates

The incompatibility between cationic retention aids and silicates used in the pulp bleaching has already been reported (*6-8*). We studied further the influence of bleach liquor stabilizers on the retention of fines.

The data in **Table V** show that in the absence of retention aids (RA), pulp samples bleached with formulations containing silicates and DTPMPA retained fewer fines than unbleached pulp. The influence of two retention aids is apparent. The samples bleached with DTPMPA retained more fines in each run, and this retention was especially marked for RA1. The RA2 appeared to be less efficient and less sensitive to the presence of silicate.

A better retention of fines after silicate-free bleaching was also observed for spruce thermomechanical pulp (TMP), as shown in **Table VI**. The RA3 was more efficient than RA1 for any bleach stabilizer used.

The two examples show that bleaching with formulations that contain silicate results in lower fines retention, compared to silicate-free bleaching, although these values seem to be specific for each combination of pulp and retention aid.

Conclusions

DTPMPA is an efficient pretreatment chemical with higher efficiency per unit than DTPA. The dosing accuracy of caustic and DTPMPA is critical for optimum performance. DTPMPA can partially or totally replace silicates in bleach liquor stabilization while maintaining high bleaching efficiency. Substitution of silicates by DTPMPA helps to avoid silicate-related problems downstream on the paper machine. The main consequence is increased retention of fines on the fourdrinier wire.

V. Retention of fines as a function of bleach liquor stabilizer and retention aid

Turbulence, rpm	Unbleached, no RA, %	Bleached with DTPMPA, % no RA	0.2% RA1	0.05% RA2	Bleached with silicates, % no RA	0.2% RA1	0.05% RA2
200	87	96	99	98	92	97	96
450	67	54	86	57	42	49	54
700	58	47	50	51	32	38	47

RA = retention aid. RA1 = macromolecular polyethylenimine. RA2 = cationic polymer.
Stone groundwood *Pinus radiata*.

VI. Retention of fines as a function of bleach liquor stabilizer and retention aid

Turbulence, rpm	Unbleached, no RA, %	Bleached with DTPMPA, % no RA	0.2% RA1	0.2% RA3	Bleached with silicates, % no RA	0.2% RA1	0.2% RA3
200	96	80	99	100	92	94	100
450	53	56	62	66	41	44	58
700	40	41	45	50	34	30	33

RA1 = macromolecular polyethylenimine.
RA3 = high-molecular-weight polyelectrolite with medium cationic charge.

Experimental procedures

Disintegration

Pulp samples were disintegrated in a 2-dm^3 laboratory pulper, at a concentration of about 3% for 20-30 min, using tap water.

Pretreatment

Pretreatment was carried out after sample disintegration by adding the required quantity of sequestrant into the pulper and further agitating for 3-5 min. The pretreated pulp was dewatered to 25-30% consistency.

Bleaching

Pulp samples equivalent to 10 g of dry fibers were placed in polyethylene bags, followed by the addition of bleaching chemicals. After thorough kneading, bags were sealed and immersed in a thermostated bath.

Bleaching conditions are reported in Table I, where the dosages of sequestrants are given as a percentage relative to dry pulp.

Brightnesses, averaged from three experiments, were measured on Elrepho Datacolor 2000, using handsheets prepared from 1% pulp suspension at pH 5.5.

Retention

Tests were carried out using the Britt Dynamic Drainage Jar. Pulp samples for these tests were bleached with 5% silicates or 0.3% DTPMPA. The samples were entirely transferred into beakers. Their concentrations were adjusted to 0.1% or 0.5% for fractionation or retention measurements, respectively. The pH of the tested suspensions was adjusted to 5.5 using 1*M* sulfuric acid.

Reagents

All reagents used were commercially available grades. Retention aids and sequestrant solutions were products of Allied Colloids, BASF, and Monsanto. DTPMPA was Dequest. 2060 S (50% solution), and DTPA was Trilon. C (40% solution).

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