

# Single Stage Peroxide Bleaching of Alkaline Sulphite Anthraquinone Methanol (ASAM) Bagasse Pulp.

## Part 2: Effect of a Mn-complex (catalyst) and phenanthroline (activator) on the bleach performance of $H_2O_2$

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### ABSTRACT

*By adding 10 or 20 ppm of a Mn-complex to the peroxide bleaching system the brightness of an ASAM bagasse pulp increased from 80.9% ISO to 82.2 and 83.9% ISO, the kappa number decreased from 2.3 to 2 and 1.8, respectively. The Mn-catalyst did not cause degradation of the carbohydrates. Addition of 0.025-0.1% phenanthroline to the bleaching system raised the brightness to 82.9-84.0% ISO, but the use of this peroxide activator was accompanied by a pronounced drop in the viscosity. The degradation action of the activator could be overcome by increasing the charge of  $MgSO_4$  in the bleaching system from 0.1 to 0.3%. In this case, an increased brightness of 84.7% ISO and very low kappa number of 0.5 were obtained.*

### Key words

*$H_2O_2$  bleaching, Mn-complex, Phenanthroline, Brightness, Viscosity*

### INTRODUCTION

Hydrogen peroxide is an ecologically safe bleaching chemical, which can be used as principal reagent [1, 2]. Under optimal condition,  $H_2O_2$  can provide high pulp brightness and adequate quality. To reach optimum results the important bleaching parameters that affect the reaction of  $H_2O_2$ , such as pH, temperature, and reaction time have to be controlled [3, 4]. Transition metal ions have to be removed as far as possible, because they catalyze peroxide degradation, whereby unselectively acting OH-radicals are generated [5].

The bleach performance of  $H_2O_2$  can further be improved by using  $H_2O_2$  catalysts or activators. Among catalysts, bi-nuclear Mn-complexes have been considered very effective, where Mn has a high oxidation state ( $3^+$ ,  $4^+$ ). Such catalysts considerably reduce the activation energy of lignin oxidation by  $H_2O_2$ , thus lower temperature and shorter retention

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time can be applied [6, 7]. Activators such as cyanamide [8, 9] dicyandiamine [10] and heterocyclic nitrogen compounds such as poly-pyridines [11] increase the reactivity of H<sub>2</sub>O<sub>2</sub> towards lignin so that less peroxide charges can be used and a higher brightness can be obtained.

In a previous paper [12] the effects of a chelation stage prior to peroxide stage as well as some bleaching parameters, such as H<sub>2</sub>O<sub>2</sub>, NaOH, MgSO<sub>4</sub> charges, and the type of chelant and within the P stage were examined. The present study aims at investigating the effect of adding an H<sub>2</sub>O<sub>2</sub> catalyst (Mn complex) and an activator (1, 10- phenanthroline) on the properties of ASAM bagasse pulp.

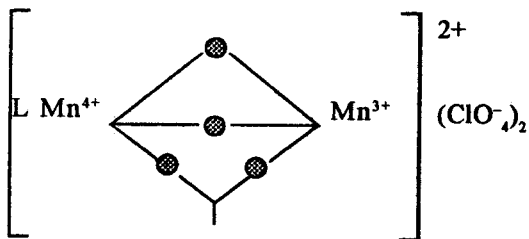
**EXPERIMENTAL**

The procedures of pulping, bleaching and determination of pulp properties are given in details in the previous part [12]. The charges of bleach chemicals are given in the corresponding tables.

**RESULTS AND DISCUSSION**

**EFFECT OF CATALYZING THE BLEACHING PROCESS BY A Mn-COMPLEX**

The bleaching experiments were carried out by adding 10 or 20 ppm of a catalyst with the following structure :

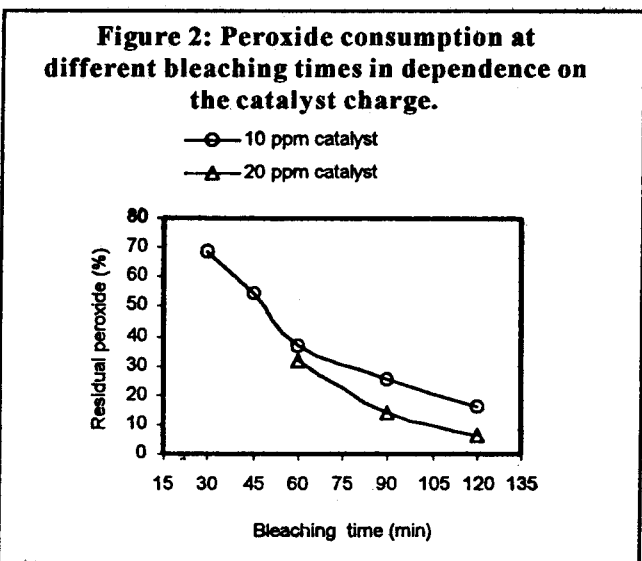
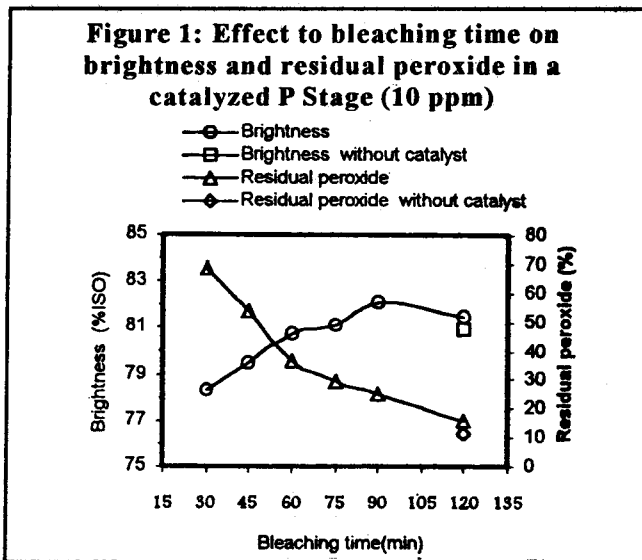


where L = 1, 2 - bis - (4, 7 - dimethyl - 1, 4, 7 - triazacyclonon - 1, yl) - ethane.

Table-1 and figures 1-3 show the bleaching results obtained at different reaction times.

The brightness of the reference pulp bleached without catalyst addition was 80.9% ISO after 120 min retention time (no. 22). The same brightness level at higher residual peroxide could be reached after

only 60-75 min when 10 ppm of the catalyst was added (no. 25, 26 and Fig. 1) The brightness could be increased to 82.2% by extending the treatment to 90 min (no. 27). A higher peroxide consumption and thus a further improvement of the brightness could be achieved with addition of 20 ppm of the catalyst (Fig. 2, 3). After 60 min retention time a brightness of 82.5% was attained. An extension of the reaction time up to 120 min led to further improvement. The brightness gain attained by addition of the catalyst can be explained by more intense lignin degradation.



Without catalyst addition a kappa number of 2.3 was reached, while with addition of 20 ppm catalyst the kappa numbers dropped below 2. The catalyst did not affect the DP of the cellulose. The cun-viscosity of all pulp samples bleached with catalyst addition

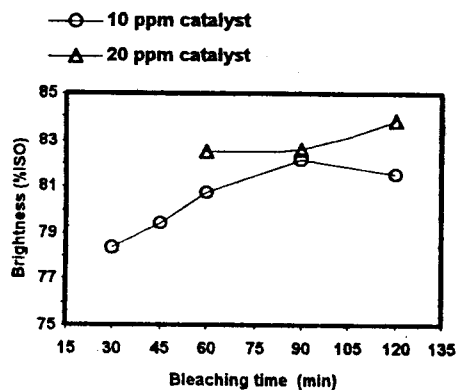
**Table-1 : Bleaching of ASAM bagasse pulp in a peroxide stage with catalyst addition**

Experiment No.	Bleaching time (min)	Catalyst (ppm)	Brightness (% ISO)	Kappa number	Residual H <sub>2</sub> O <sub>2</sub> (% of charge)	Viscosity, (ml/g)	pH	
							Initial	Final
unbl.			48.7	4.9		795		
Q			53.2	4.4		797		
P <sub>22</sub>	120	0	80.9	2.3	11.7	722	11.3	11.9
P <sub>23</sub>	30	10	78.3		68.7		11.4	11.5
P <sub>24</sub>	45	10	79.5		54.2		11.3	11.6
P <sub>25</sub>	60	10	80.8		36.7		11.4	11.9
P <sub>26</sub>	75	10	81.2		29.2		11.4	11.9
P <sub>27</sub>	90	10	82.2	2.0	25.3	726	11.3	11.8
P <sub>28</sub>	120	10	81.5		16.2		11.4	11.9
P <sub>29</sub>	60	20	82.5	1.9	31.6	731	11.4	11.8
P <sub>30</sub>	90	20	82.6	1.9	14.1	718	11.4	12.1
P <sub>31</sub>	120	20	83.9	1.8	6.6	715	11.4	12.2

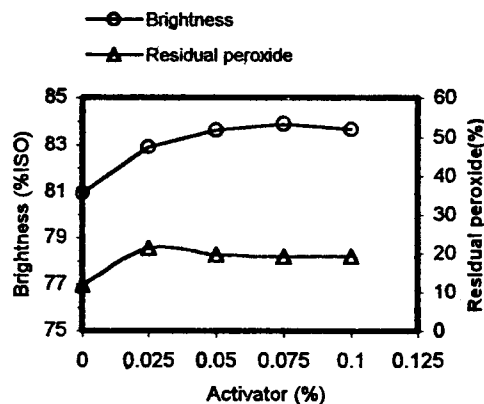
unbl. = unbleached pulp, Q = after chelation step.

Bleaching conditions : Temperature = 80°C, H<sub>2</sub>O<sub>2</sub> = 4%, NaOH = 2.5%, MgSO<sub>4</sub> = 0.1%, DTPMPA = 0.1%

**Figure 3: Brightness at different bleaching times in dependence on the catalyst charge**



**Figure 4: Effect to increasing the activator charge in a P stage on brightness and residual peroxide.**



was on the same level as for the reference.

### EFFECT OF ACTIVATING THE PEROXIDE TREATMENT BY 1, 10-PHENANTHROLINE

Table-2 and Fig. 4 show the results attained by

adding different charges of 1, 10-phenanthroline in peroxide bleaching of the same ASAM bagasse pulp applied in the bleaching series with catalyst addition. It was found that 0.025% activator improved both the brightening and the delignifying action H<sub>2</sub>O<sub>2</sub> at lower peroxide consumption. Increasing the concentration of the activator to 0.05% further improved the

Table-2 : Bleaching of ASAM bagasse pulp in a P stage activated by phenanthroline

Experiment No.	MgSO <sub>4</sub> , %	DTPMA, %	Activator, %	Brightness (% ISO)	Kappa number	Residual H <sub>2</sub> O <sub>2</sub> (% of charge)	Viscosity, (ml/g)	pH	
								Initial	Final
P <sub>22</sub>	0.1	0.1	0.000	80.9	2.3	11.7	722	11.3	11.9
P <sub>32</sub>	0.1	0.1	0.025	82.9	1.9	21.3	683	11.3	11.9
P <sub>33</sub>	0.1	0.1	0.050	83.6	1.7	19.6	667	11.3	11.8
P <sub>34</sub>	0.1	0.1	0.075	84.0	1.6	19.2	637	11.3	11.8
P <sub>35</sub>	0.1	0.1	0.100	83.7	1.5	19.2	630	11.3	11.7
P <sub>36</sub>	0.1	0.0	0.050	79.8	1.8	13.5	675	11.3	11.9
P <sub>37</sub>	0.0	0.1	0.050	83.0	1.7	6.1	638	11.3	11.9
P <sub>38</sub>	0.3	0.1	0.050	84.7	0.5	15.9	716	11.3	11.8

Bleaching conditions : Temperature = 80°C, Time = 120 min, H<sub>2</sub>O<sub>2</sub> = 4%, NaOH = 2.5%

brightness and kappa number. The higher amount of residual peroxide indicates that less peroxide was consumed to achieve this improvement. An increase of the activator charge to 0.075 or 0.1% resulted in a further reduction of the kappa number, but no essential brightness gain was obtained. Our results are in accordance with those from Patt et al. [11]. They also found that phenanthroline activates the delignifying action of hydrogen peroxide at low peroxide consumption. It was also noticed that the viscosity is considerably lowered when the activator charge is increased. At a charge of 0.1% activator the viscosity dropped by 90 ml/g. Therefore, charging only 0.05% of the activator can be considered as the best option, since the loss in viscosity was restricted at 55 ml/g.

Further experiments were carried out to check if DTPMPA or MgSO<sub>4</sub> both added in small charges of 0.1%, are really necessary for successful peroxide bleaching when 1, 10-phenanthroline is added (Table-2). the absence of DTPMPA from the bleaching system resulted in a four unit lower brightness although the peroxide was not completely consumed. The absence of MgSO<sub>4</sub> affected the brightness only marginally but due to increased peroxide degradation and formation of hydroxyl radicals the pulp viscosity was lowered. This means that both stabilizers should be applied in peroxide bleaching activated by phenanthroline.

As it is known that Mg ions efficiently retard carbohydrate degradation [13-15], the charge of

MgSO<sub>4</sub> was increased from 0.1 to 0.3% (Table-2). This resulted in a pulp with a much higher brightness of 84.7% ISO and a very low kappa number of 0.5. Furthermore, the increase of the charge of Mg ions improved the pulp viscosity from 667 to 716 ml/g.

## CONCLUSIONS

The peroxide bleaching of ASAM bagasse pulp can be considerably improved by addition of the catalyst or the activator tested in this study. By application of 20 ppm catalyst the brightness can be increased by three points without any loss in pulp viscosity. The catalyst can also be used to shorten the bleaching time. By addition of small charges of 0.05% of the activator, 1, 10-phenanthroline, at least the same brightness gain is attainable but at the expense of pulp viscosity. These serious viscosity losses could be avoided by raising the MgSO<sub>4</sub> charge from 0.1 to 0.3%. In this case, a better brightness and a lower kappa number were achieved compared to the results obtained with addition of the catalyst.

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## REFERENCES:

1. Basta J, Holtinger L, Hook J, Lundgren P. Reducing levels of adsorbable organic halogens (AOX). *Tappi J.* 1990 : 73 (4) 155-160
2. Johnson AP. Fitting together the ECF-TCF jigsaw. *Appita* 1994 : 47(3): 243-251
3. Walsh PB. Hydrogen peroxide : innovations in chemical pulp bleaching. *Tappi J.* : 41(4): 81-83
4. Johnson SE. Optimal use of hydrogen peroxide. *Tappi J.* 1994: July: 262-264
5. Sjoström E. Chemistry of delignification with oxygen, ozone and peroxides, UNI Publishers 1977 p 61.
6. Hage R, Iburg JE, Kerschner J, Koek JH, Lempers ELM, Martens RJ, Racheria US, Russell SW, Swarthoff T, van Vliet MRP, Warnaar JB, van der Wolf, Krijnen B. Efficient manganese catalysts for low-temperature bleaching. *Nature* 1994: 369: 637-639
7. Mielisch H-J, Kordsachia O, Patt R. Catalyzed Hydrogen peroxide bleaching. *Das Papier* 1996: 50 (10A), V16-V23
8. Sturm W. High-white sulfite pulps by absolutely chlorine-free bleaching - activation of peroxide by nitrilamine. 1. *Wochenblatt f. Papierfabrik* 1990: 118 (10): 423-424
9. Kuchler JG, Sturm W, Teichmann HE. High brightness and enhanced delignification in the OPMgO stage - activation of peroxide by nitrilamine. 2. *Das Papier* 1993: 47 (2): 53-56
10. Chen, J. 1996, US-Pat Appl. WO96/13634
11. Patt R, Jaschinski T, Mielisch H-J Stabilized and catalyzed peroxide bleaching. *Wochenblatt f. Papierfabrik* 1996: 124 (17): 750-755
12. Shukry N, El-Kalyoubi SF, Hassan El-barbary M. and Kordsachina O Single stage peroxide bleaching of ASAM bagasse pulp 1. Effect of some bleaching parameters on pulp properties (accepted for publication in IPPTA Journal)
13. Sjoström E, Valttila O. Inhibition of carbohydrate degradation during oxygen bleaching. 1 Comparison of various additives. *Paperi Ja Puu.* 1972: 54 (11): 695-700
14. Sjoström E, Valttila O. Inhibition of carbohydrate degradation during oxygen bleaching. 2. The catalytic activity of transition metals and the effect of magnesium and triethanolamine. *Paperi Ja Puu.* 1978: 60 (1): 37-40, 43
15. Gilbert AF, Pavlovova E, Rapson WH. Mechanism of Magnesium retardation of cellulose degradation during oxygen bleaching *Tappi J.* 1973 : 56 (6): 95-99.