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

Part III: A Comparison Between ASAM-Pulps and Soda-AQ pulp

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ABSTRACT

Bleaching of different ASAM pulps and a soda-AQ bagasse pulp was compared. All pulp types showed highest brightness and lowest kappa number when 0.05% phenanthroline and 0.05 or 0.1% DTPMPA were added to the peroxide stage. The highest brightness for ASAM pulps was 85.8—87.2% ISO and 80.9% ISO in the case of soda -AQ pulp. During bleaching of the ASAM pulps H_2O_2 was more stable against degradation and the drop in viscosity was smaller than for the soda - AQ pulp. The papermaking properties of ASAM pulps were superior to those of soda - AQ pulp.

INTRODUCTION:

During the last two decades the pulp and paper industry has intensified its efforts to minimize pollution arising from pulping and bleaching processes. Substantial improvements were achieved for the already established delignification processes. Moreover, new pulping methods were developed in order to produce pulps which are more easily bleachable using only chlorine free bleaching agents.

The ASAM pulping process (alkaline sulfite pulping with addition of anthraquinone and methanol) is a promising approach to pollution free pulp production. Unbleached ASAM pulps have very low kappa numbers, excellent papermaking properties and can be bleached in totally chlorine - free sequences(1-5). In this pulping process NaOH (ASAM I) or Na_2CO_3 (ASAM II) or a mixture of both alkali sources (ASAM III) can be used(6). By changing the alkali source and varying the alkali ratio (sodium sulfite : total alkali) very different pulp properties can be attained(7-8). In previous studies single stage peroxide bleaching of ASAM I pulp was investigated. The effects of a chelation stage prior to bleaching as well as some bleaching parameters, such as H_2O_2, NaOH, $MgSO_4$ charges and type of chelant used within the P stage were studied(9). Furthermore activated or catalyzed P stages were examined(10). The present study deals with the bleaching response of different ASAM pulps produced with different alkali sources (NaOH, Na_2CO_3, NaOH + Na_2CO_3) in comparison to a soda - AQ reference pulp. The aim was to find out, if the pulping procedure and type of the alkali used during pulping affect the efficiency of peroxide bleaching.

EXPERIMENTAL

The procedures for pulping and bleaching and for testing of the pulp properties are given in details elsewhere (9). Papermaking properties are measured according to the German Zellcheming standards.

RESULTS AND DISCUSSION

Behaviour of the Different Pulps Towards the Q Stage

Table-1 shows some properties of the different pulps before and after the Q stage with DTPA. For all pulps the Q stage resulted in a remarkable increase of the brightness (44.5%) and a reduction of the kappa number (0.5-1.3 units). The viscosity decreased in the case of ASAM I and soda - AQ pulps.

Peroxide bleaching of the different pulps

The peroxide bleaching conditions are based on the results of former investigations on bleaching of

Table-1

Some properties of the bagasse pulps unbleached (unbl.) and after chelation in a Q stage with 0.2% DTPA

Pulp type	Brightness (% ISO)	Kappa number	Viscosity (ml/g)
ASAM I unbl.	56.8	5.2	856
ASAM I Q	61.8	4.6	819
ASAM II unbl.	53.8	6.4	825
ASAM II Q	58.5	5.1	821
ASAM III unbl.	56.4	5.7	833
ASAM III Q	61.2	5.2	823
Soda-AQ unbl.	43.8	7.6	714
Soda-AQ Q	48.2	6.9	693

ASAM I bagasse pulp :

- A charge of 0.1% DTPMPA provides the best peroxide stabilization effect(9) at a $MgSO_4$ addition of 0.1%.
- The addition of phenanthroline in a small charge of 0.05% results in very high brightness over 85% without excessive degradation of the carbohydrates(10), if the $MgSO_4$ is increased to 0.3%.

As there is a strong interference between the Mg ions and the complexing agent, the DTPMPA addition has to be optimized at the higher $MgSO_4$ charge which is beneficial for the P stage activated by phenanthroline. Different amounts of DTPMPA (0.025-0.2%) were applied at 0.3% $MgSO_4$. Tables 2-5 show the results for the different pulp samples.

It was found for all pulps that highest brightness and lowest kappa number could be achieved when 0.05% phenanthroline and lowest kappa number could be achieved when 0.05% phenanthroline and 0.05 or 0.1% DTPMPA are added. The results confirm that phenanthroline is a powerful activator for hydrogen peroxide which affects a significant brightness gain. For the ASAM pulps 85.8-87.2% ISO brightness was attained, whereas in the case of the soda-AQ pulp a maximum brightness of 80.9% ISO could be reached.

Fig.-1 shows the effect of varied DTPMPA charges on the brighness of the different pulps. All these P stages were carried out with addition of 0.3% $MgSO_4$, but without phenanthroline. The highest brightness for all pulps was obtained at a DTPMPA charge of 0.05%. With increasing the charge of the complexing agent the brightness was significantly lowered. This result shows that an overdosing of

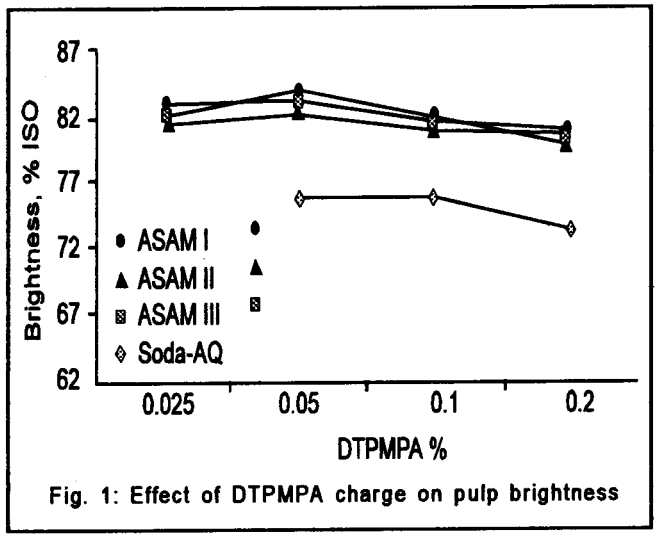

Fig. 1: Effect of DTPMPA charge on pulp brightness

DTPMPA within the peroxide treatment must be avoided, because otherwise greater amount of the Mg ions are bound into complexes and lose their beneficial effect.

Soda-AQ pulp is also easy to bleach like pulp from alkaline sulfite process, inspite of the lower initial brightness. However, it must be considered that the manganese content of the soda AQ pulp in the P step was much higher than for the ASAM pulps (7.1 ppm in the soda -AQ and 2.6-4.9 ppm in the ASAM pulps) as shown in tables 2-5. The high content of manganese is an explanation, that even at a high $MgSO_4$ charge of 0.3%, the peroxide (applied in a high amount of 4%) was almost completely consumed in case of soda pulp) (cf. the residual peroxide of the ASAM pulps and soda AQ pulp). The excessive catalytic decomposition of the peroxide is reflected by more drastic losses in pulp viscosity of soda AQ compared to the ASAM pulps (172 ml/g in the soda - AQ pulp and 115-146 ml/g in the ASAM pulps). The viscosity of the unbleached soda - AQ pulp was 693 ml/g and dropped to 521 ml/g. For the ASAM I pulp the viscosity was 819 and decreased to 704 ml/g at the highest brightness, for ASAM II the visocsity decreased from 821 to 675 ml/g and for ASAM III from 823 to 682 ml/g. It is also known that Mn ions have a very harmful effect on the peroxide stability during bleaching[11] and contribute significantly to high peroxide consumption[12].

From these results it can be concluded that soda AQ pulp showed better bleachability compared to ASAM bagasse pulps. It is the high initial brightness and viscosity of the ASAM bagasse pulps, because of which these pulps could be bleached to a higher brightness level and showed better viscosity compared to the bleached soda AQ pulp. Among the ASAM cooking alternatives ASAM I is preferred because it

Table-2

Bleaching of ASAM I pulp

Sample	DTPMPA (%)	Activator (%) (% charge)	Residual peroxide (%) ISO)	Brightness (% ISO)	Brightness gain	Kappa number	Viscosity (ml/g)
Unbl.				56.8		5.2	856
Q				61.8	5	4.6	819
P_{39}	0.025	0.00	7.7	82.9	21.1	2.0	732
P_{40}	0.050	0.00	10	83.1	21.3	2.5	721
P_{41}	0.100	0.00	17.4	82.1	20.3	2.3	748
P_{42}	0.200	0.00	13.8	80.3	18.5	2.2	675
*P_{43}	0.050	0.05	17.0	87.2	25.4	1.4	704
P_{38}	0.100	0.05	15.9	84.7	22.9	0.5	716

Unbl. = unbleached pulp, Q = after chelation step

Bleaching conditions : $MgSO_4$ = 0.3%, NaOH = 2.5%. H_2O_2 =4%, Temp. = 80°C, Time = 2 hr

*Mn = 3.4 ppm, Mg = 176 ppm, Cu = 2.6 ppm, Fe = 85.ppm

Table-3

Bleaching experiments carried out on ASAM II pulp

Sample	DTPMPA (%)	Activator (%)	Residual peroxide (% charge)	Brightness (% ISO)	Brightness gain (%) ISO)	Kappa number	Viscosity (ml/g)
Unbl.				53.8		6.4	825
Q				58.5	4.7	5.1	821
P_{44}	0.025	0.00	4.7	81.3	22.8	2.3	717
P_{45}	0.050	0.00	15.9	82.8	24.3	2.4	710
P_{46}	0.100	0.00	23.4	81.2	22.7	2.8	729
P_{47}	0.200	0.00	16.6	80.0	21.5	3.1	656
*P_{48}	0.050	0.05	20.4	85.8	27.3	1.7	675
P_{49}	0.100	0.05	22.7	85.4	26.9	1.7	696

Unbl. = unbleached pulp, Q = after chelation step

Bleaching conditions : $MgSO_4$ = 0.3%, NaOH = 2.5%. H_2O_2 =4%, Temp. = 80°C, Time = 2 hr

*Mn = 4.9 ppm, Mg = 197 ppm, Cu = 3 ppm, Fe = 78 ppm

allows delignification to very low kappa number and the bleached pulp has the highest brightness and viscosity.

Papermaking properties of ASAM alternatives and soda-aq pulps

Some papermaking properties of unbleached and bleached ASAM and soda - AQ pulps are given in table 6. The unbleached ASAM pulps are superior to the soda - AQ pulp, especially in breaking length and burst strength. The strength properties of the ASAM pulps were not or only slightly affected during bleaching whereas the strength of the soda pulp was substantially lowered. Therefore, the advantage in strength of the ASAM pulps are even more pronounced after bleaching.

CONCLUSION

Hydrogen peroxide can delignify and brighten ASAM and soda - AQ bagasse pulps successfully, especially if this stage was activated by addition of

Table-4

Bleaching of ASAM III pulp

Sample	DTPMPA (%)	Activator (%) (% charge)	Residual peroxide (%) ISO)	Brightness (% ISO)	Brightness gain	Kappa number	Viscosity (ml/g)
Unbl.				56.4		5.7	833
Q				61.2	4.8	5.2	823
P_{50}	0.025	0.00	5.7	82.2	21.0	2.4	776
P_{51}	0.050	0.00	15.5	83.5	22.3	2.5	723
P_{52}	0.100	0.00	25.9	81.9	20.7	2.2	749
P_{53}	0.200	0.00	23.0	79.8	18.6	2.5	701
*P_{54}	0.050	0.05	21.3	85.9	24.7	1.9	682
P_{55}	0.100	0.05	25.7	82.9	21.7	2.3	685

Unbl. = unbleached pulp, Q = after chelation step

Bleaching conditions : $MgSO_4$ = 0.3%, NaOH = 2.5%. H_2O_2 =4%, Temp. = 80°C, Time = 2 hr

*Mn = 2.6 ppm, Mg = 216 ppm, Cu = 3 ppm, Fe = 74 ppm

Table-5

Bleaching of Soda-AQ pulp

Sample	DTPMPA (%)	Activator (%) (% charge)	Residual peroxide (%) ISO)	Brightness (% ISO)	Brightness gain	Kappa number	Viscosity (ml/g)
Unbl.				43.8		7.6	714
Q				48.2	4.4	6.9	693
P_{56}	0.050	0.00	8.7	75.8	27.6	2.6	566
P_{57}	0.100	0.00	6.8	75.9	27.7	2.3	550
P_{58}	0.200	0.00	3.2	73.7	25.0	2.5	509
P_{59}	0.050	0.05	6.4	79.3	31.1	2.6	519
*P_{60}	0.100	0.05	5.1	80.9	32.7	2.2	521

Unbl. = unbleached pulp, Q = after chelation step

Bleaching conditions : $MgSO_4$ = 0.3%, NaOH = 2.5%. H_2O_2 =4%, Temp. = 80°C, Time = 2 hr

*Mn = 7.1 ppm, Mg = 210 ppm, Cu = 4 ppm, Fe = 146 ppm

small amounts of phenanthroline. However, ASAM pulps are superior to the soda - AQ in final brightness, residual lignin content, pulp viscosity, and strength properties. Soda AQ pulp contains high amount of Mn ions which accelerated peroxide decomposition and led to greater viscosity losses during the P stage. Moreover, no serious losses in pulp strength occurred during bleaching of the ASAM pulps. The best results were obtained for the ASAM I pulp produced by using NaOH as supporting alkali.

ACKNOWLEDGEMENT

Part of this work was carried out at the Institute of Wood Chemistry and Chemical Technology of Wood, University of Hamburg, Germany. The authors thank Prof. Dr. R. Patt for his encouragement and helpful advises.

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Table-6

Papermaking properties of ASAM and Soda-AQ pulps

Sample	Beating Time (min)	°SR	Breaking length (m)	Burst factor	Tear factor
ASAM I, unbl.	3.5	53	6530	46.5	52.4
Q	3.5	54	6851	48.5	52.6
P_{40}	3	52	6637	44.6	47.3
P_{43}	3	53	6443	42.3	43.8
P_{38}	3	52	6451	41.1	50.8
ASAM II, unbl.	3.5	56	6531	47.7	50.6
Q	3.5	54	6753	52.1	48.6
P_{45}	3	52	6370	45.3	51.5
P_{48}	3	51	5948	41.7	50.2
ASAM III, unbl.	3.5	55	6815	42.6	43.2
Q	3.5	53	6743	42.8	42.4
P_{51}	3	52	6849	43.1	50.5
P_{54}	3	53	6628	42.8	44.0
Soda-AQ, unbl.	3.5	48	6320	37.8	43.4
Q	3.5	49	5933	34.9	47.8
P_{56}	3	52	5778	33.2	49.7
P_{59}	3	49	5645	32.9	45.3
P_{60}	3	52	5979	34.8	41.8

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

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