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Influence of pulp colour on bleachability. Ways to improve the bleaching response of alkaline pulp.

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Abstract

Chemical pulps were produced by the conventional kraft process and by alternative alkaline sulphur-free processes. They were bleached by ClO_2-based ECF sequences. The kraft pulps were easier to bleach. However all the kraft pulps were not equal and some were harder to bleach than others. It was observed that the pulps which were more difficult to bleach were richer in quinone groups. They were also more coloured, with a more pronounced reddish hue (a*coordinate of the L* a* b* values) which must be given by the quinone groups. Since quinones are not easily degraded by ClO_2 it was proposed that pulp bleachability would be related to the amount of quinone groups, or to the level of a* coordinate.

The origin of quinone groups is not known. When AQ was used in the process, some of the detected quinones could be adsorbed residual AQ or AQ derivatives and possibly AQ condensation products with lignin. However since the simple NaOH cooking gave rise also to high contents of quinones, other origins have to be looked for. In the case of kraft cooking the reducing character of HS- might hinder the formation of quinones.

Ways to deal with the problem caused by the presence of quinones are proposed.

Introduction

During the last decade numerous studies have been devoted to the problem of bleachability differences between chemical pulps (1-6). One reason was the development of ECF bleaching, which led to a dramatic increase in the chemical cost related to bleaching, because of the substitution of chlorine dioxide for chlorine (Cl_2). Any change in the bleaching chemical requirement for any reason had sud-

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denly a significant impact on the bleaching cost, which was not so much the case with the use of the cheap chlorine. A second factor was the renewed interest for non-sulphur pulping, for various reasons such as the potential yield benefit, the most efficient recovery of the cooking chemicals, and the reduction of the smell problem. New processes were proposed and some are still under investigation, like IDE (7, 8) and Novacell (9), which were in fact improved versions of the former NaOH-Anthraquinone (AQ) cooking process. It appeared that the pulps obtained by these new sulphur-free processes were more difficult to bleach. A third reason was the imperious necessity to improve the profitability of pulp production, which imposed drastic cuts in operating cost, including bleaching cost (10). These reasons explain why bleachability has become an important issue. Understanding what makes a pulp more difficult to bleach than another one would pave the way to valuable process adjustment or modification.

One must admit that after 10 years of intensive research the reasons for differences in bleachability among alkaline pulps are still unknown. The focus has been put on possible variation in lignin structure which would influence the response to bleaching in one way or another. It was claimed for example that a lower amount of free phenolic groups would affect bleachability positively (11). An opposite trend was observed with the amount of residual _O4 linkages (12, 13). Possible adverse effect of condensed structures (14), lignin-carbohydrates linkages (4) and chromophores issued from carbohydrates (4) was also suggested. However the responsibility of these structures could not be confirmed by others. As an example the chromophores present on the carbohydrates matrix were found to be easily degraded by the bleaching chemicals. Therefore, they would not interfere with the degradation of the main chromophores which must be located on the lignin molecules (15).

In a recent study we showed that the residual lignins in unbleached alkaline pulps differed in their content in quinones groups (16, 17). Although there exists no entirely reliable quantitative method to measure quinones in lignin we have shown by two independent analytical techniques (^{19}F NMR spectroscopy and voltametry) that the content in quinones was significantly higher in the sulphur-free pulps than in kraft pulps and that its level depended on the cooking conditions for a given process. Quinone groups are coloured species by themselves and must contribute to pulp colour. The fact that chlorine dioxide is not a reagent of choice to transform quinones groups into colourless structures (18,19) suggests that the pulp content in quinones groups might be related to its bleachability by ECF sequences.
The purpose of this paper is to elaborate more on this hypothesis and to draw some practical consequences.

Material and Methods

Kraft, IDE, Novacell and caustic soda pulps have been used in this study. Two mixed hardwood kraft pulps of kappa number around 13 were provided by a French pulp mill. Although the operating conditions should have been the same during cooking for the 2 pulps, one of them (kappa number 12.9, Kraft 2) appeared to be more difficult to bleach than the other one (kraft 1). The Novacell pulp (kappa number 53.3) was produced from Nordic softwoods and was provided by one partner in the Novacell European project. Novacell (9) is basically a NaOH-AQ process (0.2%AQ) consisting of an impregnation step followed by a cooking stage stopped at higher kappa number than usual. Delignification is completed by an oxygen treatment. Reference kraft pulps of kappa numbers 46.6 and 25.0 were produced for comparison. Birch IDE pulp (kappa number 19.8) was prepared according to the procedure described in (8). IDE stands for impregnation (I), delignification (D) and extraction (E). The cooking liquor was a mixture of ethanol and water (EtOH/H$_2$O 60:40) containing AQ (0.05% on wood). Impregnation was carried out at 100°C during 60min.; delignification was performed at 140°C for 4 hours and the extraction stage was carried out at 100°C for 60 min.. The total NaOH charge was close to 25% on wood. This pulp was prepared by one partner in the EFPRO European project. In one experiment no AQ was added to the IDE liquor. The other cooking conditions were adjusted so as to give a pulp of similar kappa number (18.3). The same birch chips were used to produce one reference kraft pulp (kappa number 18.7). Effective alkali was 22%, sulphidity 40% and cooking temperature 154°C for 60min. A NaOH birch pulp of kappa number 18.1 was also prepared. NaOH charge was 25% and cooking temperature was 170°C.

Standard bleaching procedures were followed. Operating conditions are given in the text. ISO standards were applied to measure brightness and kappa number. CIELAB colour values, L*a*b*, which are of current usage with recycled fibres contaminated with dyes, were measured with a Color Touch spectrophotometer (Technidyne). The T 524 om-86 Tappi standard was followed.
Lignin extraction and analysis for quinone was described in (17, 20). ^{19}F NMR spectroscopy (20) and voltametry (17, 21) were used to estimate the content in quinone groups.

Results and Discussion

1. Bleachability differences between chemical pulps

Bleachability of NaOH-AQ pulp has been found to be worse than that of corresponding kraft pulp (22). In this

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study comparison was made between kraft and the new sulphur-free pulps (IDE and Novacell). Table 1 compares the bleaching response of kraft and IDE birch pulps to ODEDD sequence. In table 2 the comparison is given bet-

		Kraft	IDE
Unbleached	Kappa no	18.7	19.8
	Brightness, %	37.2	33.7
O	Kappa no	12.1	12.7
	Brightness, %	50.8	49.1
Do	ClO_2 consumed, %	1.08	1.30
E	Kappa no	4.40	4.20
	Brightness, %	70.0	70.0
D1	ClO_2 consumed, %	1.1	1.1
	Brightness, %	86.5	85.7
D2	ClO_2 consumed, %	0.60	0.56
	Brighness, %	89.5	88.5

O: 100°C, 60 min., 1% NaOH, 5 bar O2, 0.3% MgSO4 7H2O
D0: 50°C, 60 min.; E: 1.5% NaOH, 60°C, 1h; D1: 80°C, 2h; D2: 80°C, 3h.
All stages at 10% consistency.

Table 1 : Response of kraft and IDE birch pulps to $OD_0ED_1D_2$ Bleaching.

		Kraft	Novacell
Unbleached	Kappa no	46.6	53.3
	Brightness, %	23.0	19.8
O	Kappa no	20.3	22.8
	Brightness, %	30.0	25.4
DEDED	Total ClO_2 charge, %	3.55	4.65
	Total ClO_2 consumed, %	3.40	4.20
	Brightness, %	88.7	88.1

O: 100°C, 60 min., 4% NaOH, 0.3% MgSO4,7H2O
All stages at 10% consistency.

Table 2 : Response of kraft and Novacell softwood pulps ODEDED Bleaching.

		Kraft 1	Kraft 2
Unbleached	Kappa no	13.3	12.9
	Brightness, %	33.0	29.5
D_0	ClO_2 consumed, %	1.23	1.20
	Brightness, %	48.7	42.3
EO	Kappa no	2.6	2.7
	Brightness, %	60.0	56.0
D_1	ClO_2 consumed, %	1.0	1.0
	Brightness, %	85.4	82.5
D_2	ClO_2 consumed, %	0.60	0.60
	Brightness, %	88.9	87.2

D_0: chlorine multiple 0.25, 50°C, 1h; D_1: 80°C, 2h; EO: 80°C, 2% NaOH, 2 bar O2; D_2: 80°C, 3h.
All stages at 10% consistency.

Table 3 : Response of mixed hardwood kraft pulps from the same mill to $D_0(EO)D_1D_2$ bleaching.

ween kraft and Novacell softwood pulps, bleached with an ODEDED sequence. Both IDE and Novacell pulps exhibited a lower final brightness (and/or a higher ClO_2 consumption) when bleached under the same conditions as the control kraft pulps.

The bleaching response of two mixed hardwood kraft pulps produced at the same mill and which, for unknown reasons, differed in bleachability, is given in Table 3.
All these results illustrated the fact that pulps obtained by sulphur- free processes were more difficult to bleach by ECF sequences than kraft pulps, and also that some differences did exist between kraft pulps themselves.

2. Quinone content of residual lignin from chemical pulps of different bleachability.

Residual lignin in the previous pulps was extracted by mild acidolysis and analysed for quinones content. Two methods were used depending on the samples: 19F NMR spectroscopy and voltametry. As detailed in (17) a fairly good correlation was found between these two analytical techniques. Some other pulps were analysed as well, to enrich the discussion. Results are given in table 4 and show that the sulphur-free pulps contained more quinone groups than the corresponding kraft pulps. Moreover between the two mixed hardwood kraft pulps of different bleachability, the one which was more difficult to bleach had also the higher content in quinone groups. Therefore it appeared that, at least in this study, the pulp quinones content correlated with bleachability.

Simple quinones absorb visible light at wavelengths between 400 to 450 nm. Absorption can extend to higher wavelengths when conjugations to other groups are added. The higher quantity of quinones in sulphur-free pulps would be in accordance with the visual observation that those pulps turned reddish when they were put into contact with air at the outlet of the reactor. It was then interesting to measure the L* a* b* values as commonly practiced with coloured paper. Results in table 4 show that a* and b* values (which quantified the red and yellow contribution to the pulp colour, respectively) were higher for sulphur-free pulps. The a* value was likely linked to the amount of red conjugated quinones. It is then proposed that the measurement of a*and b*, which is quite simple, would give an indication on the bleachability of the pulp by ECF sequence. However this would need to be confirmed by further experiments.

3. Formation of quinone groups during pulping.

The presence of quinone groups in residual lignin of chemical pulp has already been discussed by several authors

	Kappa no	Quinone mole/200g	L*	a*	b*
Novacell (softwood)	53.3	0.053*	65.9	7.12	21.0
Kraft (softwood)	46.6	0.016*	68.1	5.87	19.8
Kraft (softwood)	25.0	0.012	71.7	5.00	16.8
IDE (birch)	19.8	0.062	78.3	6.25	13.8
Kraft (birch)	18.7	0.021	77.4	4.76	6.20
IDE without AQ (birch)	18.3	0.059	76.1	5.30	14.7
NaOH (birch)	18.1	0.037	75.1	5.10	12.0
Kraft (mixed hardwood)	13.3	0.030	70.8	4.28	12.6
Kraft (mixed hardwood)	12.9	0.037	68.2	5.00	14.2

*measured by voltametry

Table 4 : Quinone content (17) and L* a* b* values of the unbleached pulps used in the study.

(11, 23-25). There were very few methods available to quantify the amount of quinones in pulp. Quinone groups in unbleached kraft pulps could be measured by ^{31}P NMR spectroscopy (25) and ^{19}F NMR spectroscopy (20). These two methods gave similar results. However it was doubtful that all the quinones present could be detected by these NMR techniques, which required the formation of appropriate lignin derivatives. A voltametric analytical technique, presented in (17), made it possible to rank the unbleached pulp according to their content in quinone groups. The ranking was the same as for the ^{19}F NMR spectroscopy. Therefore, there is some confidence that these analytical techniques gave, at least, some kind of quinone index.

The exact nature of these quinones is not known. As previously proposed (17), one possible way would be the air oxidation of catechols in the alkaline environment (Figure 1). Catechols are known to be produced by demethylation of the guaiacyl and syringyl lignin units during kraft cooking (26). It cannot be excluded that some of the detected qui-
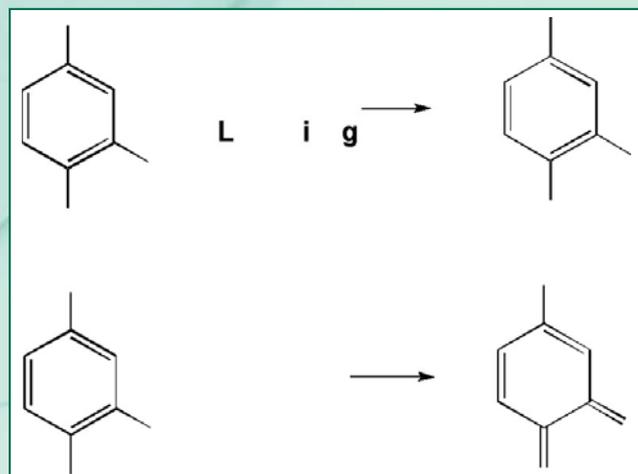

Figure 1. Possible formation of ortho-quinone in residual lignin of alkaline pulp.

nones in sulphur-free pulps were adsorbed residual AQ or condensed AQ or AQ derivatives. This would explain partly the higher quantity found in these pulps compared to kraft pulps. However higher values were also observed in the absence of AQ, which suggested that in kraft cooking the presence of HS- or the lower effective akali charge would minimize the generation of quinones.

4. Fate of the quinone groups during ECF bleaching.

Since quinones are coloured substances it is of interest to discuss the reactivity of ClO_2 with them. Very few studies have been devoted to this subject. It was shown (18) that a white pulp impregnated with *p*-benzoquinone could be bleached by application of ClO_2 but that other bleaching chemicals were more efficient, like hydrogen peroxide and ozone. In fact, considering the known chemistry of ClO_2 with lignin, one must say that ClO_2 should not be a reagent of choice for quinones degradation. This statement is confirmed by the results of table 5 which compares the content of quinones in the kraft pulp of kappa number 25 before and after a D stage. The fact that more quinones were found in residual lignin after D suggested that not only they were not reacting well with ClO_2, but also that new quinones were formed. Formation of quinones in residual lignin during ClO_2 delignification has been shown by others (27) and the corresponding mechanism is well understood (28).

	Unbleached	D-treated
Kappa no	25	12
Quinone, Mole/200 g	0.012	0.032

Table 5 : Quinone groups in kraft softwood residual lignin (kappa no 25) before and after a D stage.

5. Practical relevance of the results.

The results of this work suggest that pulp bleachability would be affected by the presence of quinones in residual lignin. All the pulps presenting bleachability problems in our study were also the richer in quinones groups. This hypothesis could be supported by the fact that these groups are coloured and not easily degraded by ClO_2. Moreover ClO_2 does form new quinones groups when it reacts with residual lignin.

Based on that, several actions can be proposed. Their assessment is under investigation:

- introduce in ECF bleaching sequence some reagents which do degrade quinones in an efficient way. H_2O_2 is one of the best candidates. O_3 is another one. They will

complement the action of ClO_2 on lignin and contribute to cost reduction.

- transform the quinones groups into phenols which will react with ClO_2. This should be possible by applying a reducing agent (dithionite for example) directly on the unbleached pulp and/or at the end of each D stage. The best way to implement this reducing phase has to be found.
- transform the quinones groups into polyphenols by an alkaline treatment (24,29) for the same purpose as before. These polyphenols will be then taken care of by ClO_2. One may ask why some quinones have not been transformed into polyphenols under the alkaline cooking conditions. The explanation could be that the quinones which are still present in the lignin of the unbleached pulp have been formed at the end of the cook when the pulp was put in contact with air.
- minimize the formation of quinones during cooking. Unfortunately, since the mechanism by which they are formed is not known, it is not possible to suggest any operating procedure. A systematic study on the effect of the operating conditions on the quinones content in pulp has still to be performed. The only suggestion which could be made at this point would be to reinforce the reducing character of the cooking liquor.

An example of application of the previous principles is given in Table 6. The two mixed hardwood kraft pulps of different bleachability were treated by a new sequence which should minimize the effect of quinones. The two pulps showed equivalent response. Whether or not the improvement is related to quinones destruction has still to be demonstrated.

	Kraft 1	Kraft 2
Brightness, %	33.0	29.5
Kappa no	13.3	12.9
E kappa no	11.1	10.9
D_0 brightness, %	53.0	53.0
E/P brightness, %	68.8	68.5
D_1 brightness, %	89.0	89.0

E conditions: 2% NaOH, 95°C, 2h
D_0 (E/P) D_0: same conditions as in table 3 except 0.25% H_2O_2 in E ((E/P) instead of EO).

Table 6 :. Improvement of the bleaching response of mixed hardwood kraft pulp by performing the $ED_0(E/P)D_1$ sequence.

Conclusion

The residual lignin in unbleached chemical pulps contains quinone groups. It is proposed that these quinones affect pulp bleachbility adversely when ClO2-based ECF sequences are used.

Since ClO2 in not an efficient degrading agent for quinones and does create new quinones itself modification to the ECF sequence must be performed to make the bleaching process cheaper. Some of the possible improvements such as the systematic use of hydrogen peroxide at appropriate locations in the sequence or the degradation of quinones by alkali at high temperature (95°C) are proposed and are very easy to implement.

Acknowledgements

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