Addition of sodium silicate and chelant to the FAS stage to bleach recycled fibers

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ABSTRACT

Formamidine sulfinic acid (FAS) is more effective than sodium hydrosulfite as a reducing agent for removing dyes in the bleaching of recycled fibers. When sodium silicate instead of sodium hydroxide is used for pH control during treatment with FAS, bleaching results are better. Sodium silicate minimizes the influence of transition metal ions, including manganese and iron ions, which induce FAS to decompose. When both chelant and sodium silicate are added to an FAS stage that is followed by a peroxide stage, the final brightness of the pulp is higher than it would be otherwise. Bleaching improves in the peroxide stage since less hydrogen peroxide is consumed by transition metal ions and pigments, some of which have already been removed in the FAS stage.

Application:

Sodium silicate and chelant can improve both the bleaching of recycled fibers with formamidine sulfinic acid and further bleaching in a subsequent peroxide stage.

THE QUALITY AND BRIGHTNESS OF the recycled fiber furnish dictates how it will be used. Dyes, ink, and stickies have to be removed for the mill to produce recycled pulp with good properties, including good optical properties.

Chemicals used in a totally chlorine-free process for bleaching recycled fibers include oxidative and reductive chemicals. The oxidative chemicals commonly used are oxygen, ozone, and hydrogen peroxide, and the reductive chemicals are sodium hydrosulfite and formamidine sulfinic acid (FAS) (*1*). Both oxidative and reductive chemicals are required for the recycled fibers to reach a high brightness (*2*, *3*).

Between the two reducing chemicals, formamidine sulfinic acid is more effective than sodium hydrosulfite in terms of color stripping (*1*, *4*). However, FAS is much more expensive, so it would be beneficial to be able to use it more effectively. Therefore, we studied ways to improve the effectiveness of FAS as the reducing agent in bleaching recycled fibers.

BACKGROUND

The use of FAS in bleaching recycled fibers has been studied extensively. The most important parameter is its pH profile, with the pH usually starting at about 10 and ending at a neutral pH (*4*, *5*). Sodium hydroxide is commonly used as the source of alkalinity for bringing the pulp to the desired initial pH. A ratio of FAS to NaOH of 2:1 has been shown to be effective (*4*–*7*).

The removal of transition metal ions from a TMP pulp is enhanced when a small amount of sodium hydrosulfite is added to a DTPA chelation stage (*8*). This stage is the so-called "reducing-agent-assisted" chelation, or the Q_y process. Consequently, the subsequent peroxide bleaching is improved. Implementation of the Q_y process has resulted in significant savings in bleaching costs (*9*).

In pulp fibers, at least some of the transition metal ions are present in their high oxidation states. Unfortunately, transition metal ions with high oxidation states form stable complexes with pulp constituents, which hinders their removal during chelation with DTPA. However, the complexes formed between the same pulp constituent and the same transition metal ion at a lower oxidation state are much less stable. Therefore, by reducing transition metal ions from their higher to their lower oxidation states during chelation, we can improve the removal of transition metal ions from pulp fibers.

Here, we have adopted this concept of reduction and chelation in bleaching recycled fibers. Since FAS is more efficient for recycled fibers, we used FAS as the reducing agent instead of sodium hydrosulfite.

RESULTS AND DISCUSSION

FAS reduction and DTPA chelation

First we studied the effect of a simultaneous action of reduction by FAS and chelation by DTPA on the residual manganese and iron contents and on the pulp brightness of recycled pulp. The results are shown in **Table I**.

The three processes studied are designated as the Q, F, and F_Q processes. The Q process consisted of 0.2% DTPA at 70°C for 30 min at pH 5 and at a pulp consistency of 5%. The F process consisted of 0.5% FAS and 0.25% NaOH at 90°C for 60 min. The F_Q process was the same as the F process but with 0.2% DTPA added. The control pulp was not treated with DTPA.

As Table I shows, the F_Q process has the lowest content of residual transition metal ions among the three stages studied. The explanation follows that of the Q_y process,

	Mn, ppm	Fe, ppm	Brightness, % ISO
Control	2.5	85	55.0
Q pulp	1.3	50	55.5
QF pulp	0.9	38	61.6
F_Q pulp	0.5	27	62.3

Q: 0.2% DTPA at 70°C for 30 min at pH 5 and 5% pulp consistency.
F: 0.5% FAS , 0.25% NaOH at 90°C for 60 min.
F_Q: 0.5% FAS, 0.2% DTPA, and 0.25% NaOH at 90°C for 60 min.

I. Comparison of the brightness and the residual Mn and Fe contents of the Q-, QF-, and F_Q-treated pulps

	Brightness, % ISO	*b** value	Residual H_2O_2, % on pulp
QP	75.1	5.9	0.30
QFP	76.5	5.8	0.40
F_QP	78.1	5.3	0.32

P: 1.5% H_2O_2, 0.2% $MgSO_4$, 2% Na_2SiO_3, and 1% NaOH, for 150 min at 95°C and 12% pulp consistency.

II. Bleaching performances of the QP, QFP, and F_QP processes

	Brightness, % ISO	*b** value	Residual H_2O_2, % on pulp
PF	73.2	7.8	0.00
PF_{Si}	73.8	7.8	0.00
FP	76.0	5.7	0.12
$F_{Si}P$	77.5	5.7	0.18

III. Replacement of NaOH with Na_2SiO_3 in the FAS stage

except that FAS is the reducing agent instead of sodium hydrosulfite. Apparently, the F_Q stage serves the purpose of reduction and chelation very well. As a result, more transition metal ions are removed.

Table I shows the brightness of F_Q-treated pulp to be higher than that of the QF-treated pulp. There are two possible explanations that can account for this difference.

First, the complexes formed between transition metal ions and pulp constituents can be highly colored. The presence of such complexes suppresses the brightness (*10–13*). Furthermore, for the same transition metal ions, such as iron, the high oxidation state (Fe^{3+}) has a more pronounced negative effect on pulp brightness than its low oxidation state (Fe^{2+}) (*13*). Therefore, the reduction–chelation effect caused by the F_Q stage decreases not only the occurrence of the colored metallic complexes arising from enhanced removal of transition metal ions but also the color intensity of the residual metallic complexes.

The second possible explanation is that some of the FAS charged in the process may be consumed in the FAS decomposition induced by transition metal ions. The presence of DTPA in the F_Q stage could then stabilize the transition metal ions, thus reducing the wasteful FAS consumption caused by decomposition.

To determine which of these two is the dominant mechanism, we studied the effect of DTPA on the FAS decomposition induced by transition metal ions. We carried out the control run at 70°C using 2 g/L FAS and 5 ppm manganese(II), with an initial pH of 9.9 reached by the addition of NaOH. The other run was conducted under the same conditions except that 0.8 g/L DTPA was added. By following the FAS concentration at various reaction times, we found that DTPA has a negligible effect on the stability of FAS solution. Therefore, we concluded that the first mechanism is mainly responsible for the higher brightness observed for the F_Q process.

Alkaline peroxide bleaching

Subsequently, the three samples obtained were subjected to an alkaline peroxide bleaching. The results are shown in **Table II**. [In the table, the *b** value is one of the *L** *a** *b** color scales in the CIELAB system of CIE (International Commission on Illumination).]

The pulp slurry was always washed thoroughly between stages. An F stage in a QFP sequence produced pulp with a brightness of 76.5% ISO. In contrast, the pulp from an F_QP sequence had a brightness of 78.1% ISO. The improvement in bleaching for the F_QP sequence over the QFP sequence was apparently caused by the enhanced removal of transition metal ions. As discussed, removal is enhanced by the simultaneous addition of reduction and chelation agents and the decreased occurrence of the colored metallic complexes.

The optimum initial pH for the FAS treatment is about 10 and is usually reached with the addition of sodium hydroxide. The presence of transition metal ions increases the FAS decomposition under bleaching conditions. **Figure 1** shows this effect for Mn^{2+}.

Sodium silicate is an excellent stabilizer for minimizing hydrogen peroxide decomposition induced by transition metal ions. Therefore, it may also be possible that sodium silicate can reduce the manganese-induced FAS decomposition. The results for the addition of sodium silicate are included in Fig. 1. As the graph shows, the addition of sodium silicate to an FAS solution containing Mn^{2+} can virtually eliminate the Mn-induced FAS decomposition.

Based on this experimental observation and the fact that sodium silicate is also a good source for alkalinity, one may propose that the replacement of sodium hydroxide with sodium silicate could improve the performance of an FAS treatment. We carried out experiments to test this hypothesis, and the results are shown in **Table III**.

Unchelated pulp samples were used in this set of experiments. The symbol F represents an FAS treatment with sodium hydroxide (a charge of 0.25% on pulp), and the symbol F_{Si} represents FAS treatments with sodium silicate (1% on pulp). For the two cases, the initial pH values were similar, and other conditions were identical.

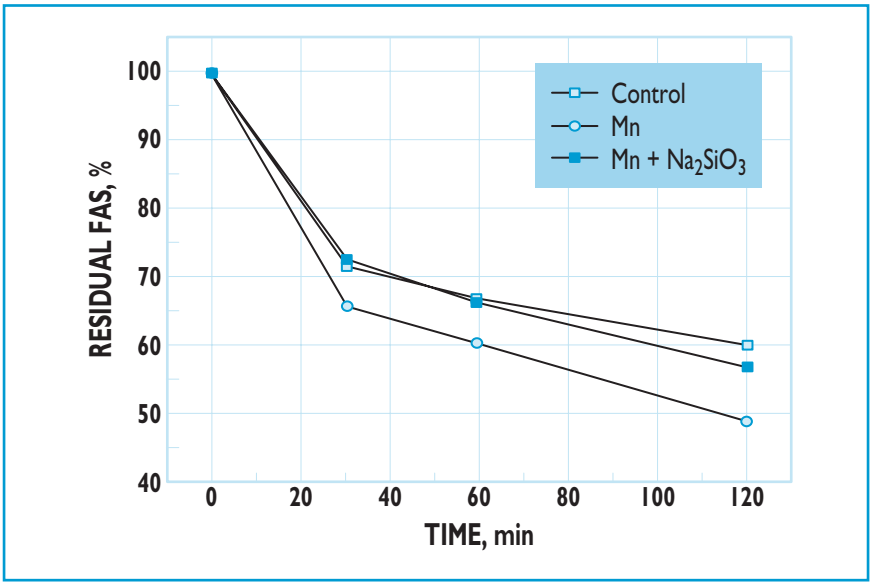
	Brightness, % ISO	*b** value
(FP)	70.3	7.89
(PF)	73.8	7.16

IV. The (FP) and (PF) sequences

	Bright-ness, % ISO	*b** value	Residual H_2O_2 of P stage, % on pulp
F	61.4	10.0	…
F_Q	62.3	10.8	…
F_{Q+Si}	62.7	10.6	…
FP	76.0	6.0	0.12
F_QP	78.1	5.3	0.32
$F_{Q+Si}P$	78.6	5.3	0.37
$F^*_{Q+Si}P$	79.4	5.1	0.42

F_{Q+Si}: 10% pulp cons., 0.2% DTPA, 1% Na_2SiO_3, 0.5% FAS, initial pH 9.6, 90°C, 1 h.
F^*_{Q+Si}: Same except that the pulp slurry was acidified to pH 5 before washing.

V. Comparison of various bleaching processes



1. Effect of Na_2SiO_3 addition on the FAS decomposition induced by manganese.

As Table III shows, substituting sodium hydroxide with sodium silicate improves the bleaching performances for the PF and FP sequences. The FP sequence is superior to the PF sequence under conditions that are the same except for the order of stages.

These results are in agreement with those obtained by Kogan *et al.* (*14*). Both sets of results show that the sequences that consist of reductive chemicals first (sodium hydrosulfite or FAS) followed by oxidative chemicals (including ozone and hydrogen peroxide) are able to produce recycled pulps with better optical properties.

Our explanation is that in the FP sequence, FAS treatment removes transition metal ions and organic and inorganic pigments that otherwise consume a substantial amount of the hydrogen peroxide charged in the subsequent P stage. Consequently, the P stage of the FP sequence is much more efficient than the P stage of the PF sequence. In support of this explanation, there was some residual H_2O_2 at the completion of the P stage for the FP sequence, whereas the charged peroxide was completely exhausted for the PF sequence.

Albertsson *et al.* (*15*) have compared the performances of (PF) and (FP) sequences on the bleaching of recycled pulp, where the parentheses indicate that stages were conducted with no washing between them (*16*). They concluded that the (PF) sequence was superior to the (FP) sequence, based on results from both lab and mill trials.

To clear up the apparent discrepancy between our results and those of Albertsson *et al.*, we repeated their runs (*i.e.*, without washing between the two stages). The results in **Table IV** confirm Albertsson's conclusion that the (PF) sequence yields a better bleaching result than does the (FP) sequence.

The explanation is quite simple. Although there was no residual FAS at the completion of the FAS treatment, the products from FAS reactions, such as bisulfite, are still oxidizable. Thus, the reaction products consume H_2O_2 in the P stage if they are not removed by washing.

Results in Table IV also show that the brightness of the (PF)-bleached pulp (73.8% ISO) is slightly better than that of the PF-treated pulp (73.2% ISO, Table III). This outcome may be explained by the presence of sodium silicate carryover in the FAS stage for the (PF) sequence, which would improve the reductive stage. These results support the following conclusions:

- The FP sequence—an FAS stage, washing, and then a peroxide stage—will produce a bleached pulp with a higher brightness than the PF sequence will produce at the same chemical charges and the same process conditions.
- If no washing is performed, the (PF) sequence is superior to the (FP) sequence.
- The PF and (PF) sequences yield similar bleaching results.

DTPA and Na_2SiO_3

We next investigated whether or not the simultaneous addition of DTPA and sodium silicate to an FAS stage, denoted as the F_{Q+Si} stage in **Table V**, would have an additive effect in improving the bleaching performance. For both the F stage itself and the FP sequence, the table shows

that the presence of both DTPA and Na_2SiO_3 improves the final brightness of the bleached pulp.

The end pH of the F_{Q+Si} stage was 7.5, and it is known that the most suitable pH for a chelation stage with DTPA is about 5. Therefore, we did another experiment in which the pH of the pulp slurry was adjusted to 5 with the addition of sulfuric acid at the completion of the F_{Q+Si} stage but before the pulp was washed. This experimental stage was denoted as F^*_{Q+Si}.

We found that the brightness of the resulting pulp was increased to 79.4% ISO as a result of this slight change. This value is 3.4 units higher than the brightness of the FP-treated pulp. The brightness of the pulp from the $F^*_{Q+Si}P$ sequence is also significantly higher than that of the QP-treated pulp (75.1% ISO, in Table I).

F^*_{Q+Si}(P+O) sequence

Peroxide bleaching at high temperature has been shown to be effective in the bleaching of deinked mixed office waste pulp (*17, 18*). Therefore, we studied the possibility of including a (P+O) stage after the F^*_{Q+Si} stage to further increase the pulp brightness.

The F^*_{Q+Si} was performed under the same conditions as before. The (P+O) stage was conducted under the conditions of 2% H_2O_2 at 70 psig O_2 pressure with a pulp consistency of 12% and with 0.2% $MgSO_4$, 2% Na_2SiO_3, and 1% NaOH at 95°C for 2.5 h. The resulting pulp had a brightness of 81.5% ISO and a *b** value of 3.52. The residual H_2O_2 at the completion of the (P+O) stage was 0.51% on pulp.

CONCLUSIONS

A chelant added to the FAS stage in an FP sequence for recycled fibers improves the bleaching performance of the FAS stage and, more importantly, that of the subsequent peroxide stage. This improvement is attributed to the enhanced removal of transition metal ions from the recycled fibers. As a result, the occurrence of the colored metallic complexes is decreased, and the peroxide decomposition induced by transition metal ions is minimized.

Also, the replacement of sodium hydroxide with sodium silicate as the source of alkali improves the FAS bleaching of recycled fibers. This outcome is explained by the reduced FAS decomposition induced by transition metal ions, arising from the fact that sodium silicate can efficiently deactivate the transition metal ions. An additive effect is observed when both chelant and sodium silicate are added to the FAS treatment in an FP sequence.

EXPERIMENTAL PROCEDURES

Material

We used a mixed office waste paper with an initial brightness of 55% ISO. Its manganese and iron contents were 2.5 ppm and 85 ppm, respectively.

FAS decomposition

The experiments on FAS decomposition were conducted in the absence of pulp. An FAS stock solution was diluted in purified water. NaOH was added. The ratio of FAS to NaOH was 2:1. The initial pH was 9.9. The solution was heated at 70°C in a water bath.

An aliquot of the solution was taken at various times for the determination of residual FAS concentration by a method obtained from Paprican.

For the runs with the addition of Mn^{2+} (as $MnSO_4$), the chemicals were charged in the order of Mn^{2+}, FAS, and then NaOH. For the runs with stabilizers present (Na_2SiO_3 or DTPA), the charging sequence was Mn^{2+}, Na_2SiO_3 or DTPA, FAS, and NaOH.

Q stage

The pulp sample was diluted in purified water and was disintegrated in a beaker. The required amount of DTPA was added to the pulp slurry, and its pH was adjusted to about 5.0. The pulp slurry was transferred to a polyethylene bag.

Fresh water was used to rinse the beaker and was then poured into the plastic bag for the pulp to reach the targeted consistency for DTPA chelation. After the specified time, the pulp sample was filtered in a Buchner funnel and was thoroughly washed with deionized water.

FAS bleaching

For the preparation of the bleach liquors, the required amount of formamidine sulfinic acid and sodium hydroxide or sodium silicate was added to a beaker containing purified water. This mixture was added to the pulp in a polyethylene bag, and its contents were thoroughly mixed. After the required retention time, the ending pH was determined.

In the case of the (FP) sequence, bleaching continued. The required chemicals were added in the order of magnesium sulfate, sodium silicate, sodium hydroxide, and hydrogen peroxide. In other cases, the pulp slurry was diluted, filtered, and washed with deionized water.

Peroxide bleaching

The required amounts of magnesium sulfate and sodium silicate were added to a polyethylene bag that contained well-disintegrated pulp slurry. The slurry was mixed well by kneading. Sodium hydroxide and hydrogen peroxide were added. The polyethylene bag with its contents was placed in a temperature bath. After the required retention time, we took a liquid sample to determine the ending pH and the residual peroxide.

In the (PF) sequence, a mixture containing the required amounts of FAS and NaOH or Na_2SiO_3 was added to the polyethylene bag to continue the bleaching. In all other cases, the pulp slurry was diluted, neutralized, and washed with deionized water.

The (P+O) bleaching was performed in a Parr reactor with Teflon® liner inside. A pulp slurry with all the required chemicals was prepared in the same manner and was transferred to the Parr reactor. **TJ**

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