Studies on the Bleaching Efficiency in Newsprint Using Formamidine Sulfinic Acid

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ABSTRACT

Many different types of bleaching chemicals and processes have been globally used for deinked pulp. Besides chlorine-free bleaching chemicals, hydrogen peroxide, and sodium dithionite that could be used without restriction for almost all types of fibers, chlorine-containing chemicals such as chlorine dioxide and sodium hypochlorite have also used throughout the world. Even though hydrogen peroxide is commonly used in newsprint, it could not effectively increase brightness. Experimental evaluation on the possibility of using formamidine sulfinic acid (FAS), a reducing agent, for bleaching a wood-containing deinked pulp has been carried out in this study. The effect of bleaching efficiency for FAS on operational conditions and chemical concentrations compaired to hydrogen peroxide in one and two stages was studied. FAS bleaching showed higher brightness at high temperature and low consistency, and vice versa for peroxide one. Bleaching with sodium silicate and DTPA in FAS and peroxide stage showed better results than cases without them. Sodium silicate and chelant seemed minimize the influence of transition metal ions, including manganese and iron ions, which induce both bleaching agents to decompose. As a result, FAS as a reducing agent seems more effective than hydrogen peroxide for increasing brightness and reducing yellowness. FAS and FAS sequence seemed more efficient than the other two stages of bleaching sequences with regard to the best brightness level obtained. When bleaching was conducted with FAS, COD load was just about one-third compared to peroxide, and brightness stability of the bleached pulp appeared better than peroxide after UV light irradiation.

INTRODUCTION

Chlorine has been widely used to bleach wasted pulps in the past. Due to the ever increasing environmental concern, bleaching agents that produces AOX compound, such as dioxin has been rarely used. ECF (elementally chlorine free) using only part of Chlorine dioxide or Sodium hypochlorite and TCF (totally chlorine free) using hydrogen peroxide, sodium dithionite, and no chlorine became dominant bleaching agents (1-10).

Hydrogen peroxide is widely used in the newsprint paper making mill that uses old newsprint paper as a main fiber resource. Hydrogen peroxide bleaching is advantageous in that it has not produced environmental pollutants. However, hydrogen peroxide usually has low efficiency and extra amount of hydrogen peroxide inevitably has to be added to achieve a certain degree of brightness. In summer season, extra biocide should be added to control slime induced by catalase that decompose hydrogen peroxide at high temperature, increasing COD load.

Hartler *et al.* reported that an optimum pH was 11 in the hydrogen peroxide bleaching on kraft pulp and higher efficiency was achieved at high consistency and high temperature (15). Kappel *et al.* suggested that brightness was increased as sodium hydroxide increased and brightness was also increased as sodium silicate increased up to 2% in the hydrogen peroxide bleaching on ground wood pulping at high temperature(16).

The interest of synthetic FAS has been increased when Barnett studied the reaction of thiocarbamide and peroxide at early 1910(17). Many researchers have studied FAS bleaching efficiency on deink pulp and mechanical pulps. Daneault *et al.* evaluated the bleaching efficiency of FAS on mechanical bleaching with one stage and suggested a statistical model that takes into account of FAS amount, stock consistency, and reaction temperature (18-19). Kang *et al.* reported that in the FAS bleaching on deink pulps, sodium silicate showed better results than sodium hydroxide as a pH controller, suggesting the roll of sodium silicate in minimizing manganese and iron ions that decompose FAS in the bleaching stage(20). Hache *et al.* reported that two or three stages of bleaching showed better bleaching efficiency and decreased yellow tint more effectively than one stage of bleaching that used large quantity of bleaching agent at one time in mechanical deinked pulps(21).

The objective of this study is to investigate the characteristics of FAS bleaching on ONP and OMG pulps and the application in the newsprint paper making process. Optimum dosage of bleaching agents including FAS, sodium hydroxide, sodium silicate, chelants at different temperature and reaction time were experimentally determined in this study. Bleaching characteristics of two stages, COD load behaviors, and physical strengths of bleached pulp were evaluated.

Material and Methods

Materials

Sample

All samples of wasted newsprint papers were provided from a Korean Newsprinting company. Stock was consisted of 95% of ONP and 5% of OMG.

Methods

Repulping and flotation

All samples of wasted newsprint papers were repulped, disintegrated, and stored at water bath having 45 ℃ for 30 minutes to simulate a dumping chest effect. Repulping and flotation conditions are listed in Table 1.

Table 1. Repulping and flotation conditions

	Repulping	Flotation
Temp. (℃)	50	50
Time (min)	10	10
Consistency (%)	5	0.5
H_2O_2 (%)	1.0	-
Surfactant (%)	0.5	-
NaOH (%)	1.0	-
Na_2SiO_3 (%)	1.5	-
DTPA (%)	0.03	-

Reagents

Hydroperoxide, sodium silicate, sodium hydroxide, chelants were provided from Korean chemical suppliers. FAS were powder type provided from Donghae Junwha Inc.

Bleaching conditions

Tables 2-3 show the experimental conditions for FAS bleaching (one stage) and second stage.

CODcr measurements

After bleaching stock was filtered using Whatman GF/C filter paper. Filtered solution was used to measure COD using reactor digestion methods with Odyssey DR/2500.

Dranage curve

0.3%, 1000 ml stock was put into dewatering measurement device and dewatered and dranage curve was obtained in an automatic fashion.

Table 2. FAS bleaching conditions in first stage

pulp cons. (%)	Temp. (℃)	Reaction Time (min)	Chemicals (%)			
			FAS	Sodium silicate	Sodium hydroxide	DTPA
10	50	30, 60, 90, 120	1.0	-	0.5	-
10	60		1.0	-	0.5	-
10	70		1.0	-	0.5	-
10	80		1.0	-	0.5	-
5	80	30	1.0	-	0.5	-
10	80	30	1.0	-	0.5	-
15	80	30	1.0	-	0.5	-
20	80	30	1.0	-	0.5	-
25	80	30	1.0	-	0.5	-
10	80	30	0.2	-	0.5	-
10	80	30	0.4	-	0.5	-
10	80	30	0.6	-	0.5	-
10	80	30	0.8	-	0.5	-
10	80	30	1.0	-	0.5	-
10	80	30	1.2	-	0.5	-
10	80	30	0.2	-	0.1	-
10	80	30	0.4	-	0.2	-
10	80	30	0.6	-	0.3	-
10	80	30	0.8	-	0.4	-
10	80	30	1.0	-	0.5	-
10	80	30	1.2	-	0.6	-
10	80	30	1.0	-	0.2	-
10	80	30	1.0	-	0.4	-
10	80	30	1.0	-	0.6	-
10	80	30	1.0	-	0.8	-
10	80	30	1.0	-	1.0	-
10	80	30	1.0	0.5	0.5	-
10	80	30	1.0	1.0	0.5	-
10	80	30	1.0	1.5	0.5	-
10	80	30	1.0	2.0	0.5	-
10	80	30	1.0	2.5	0.5	-
10	80	30	1.0	1.0	0.5	0.1
10	80	30	1.0	1.0	0.5	0.2
10	80	30	1.0	1.0	0.5	0.3
10	80	30	1.0	1.0	0.5	0.4
10	80	30	1.0	1.0	0.5	0.5

Table 3. Bleaching conditions in second stage

Bleaching Sequence	Stage	Temp. (℃)	Time (min)	Chemicals (%)				
				Peroxide	FAS	Sodium hydroxide	Sodium Silicate	DTPA
P-P	First	80	120	2.0	-	0.6	7.0	0.3
	Second	80	120	2.0	-	0.6	7.0	-
P-FAS	First	80	120	2.0	-	0.6	7.0	0.3
	Second	80	30	-	1.0	0.5	1.0	-
FAS-P	First	80	30	-	1.0	0.5	1.0	0.3
	Second	80	120	2.0	-	0.6	7.0	-
FAS-FAS	First	80	30	-	1.0	0.5	1.0	0.3
	Second	80	30	-	1.0	0.5	1.0	-

Handsheet making

50 g/m^2 handsheet was made to evaluate bleaching efficiency according to Tappi test method T205 sp-95.

Brightness measurement

Using L&W Elrepho 070R brightness tester, L, a, and b values of each handsheet were measured.

Physical strength measurement

Tensile, tearing, and burst strength were measured according to Tappi T 494 om-96, Tappi T414 om-98, and Tappi T403 om-97 respectively.

UV deterioration

After 1,2,3,6, and 24 hours irradiated at deterioration tester having 365nm UV lamp, L, a, b, and R457 values were obtained for each sample.

RESULT AND DISCUSSION

Figs 1-4 represent bleaching efficiencies with different temperatures and reaction times.

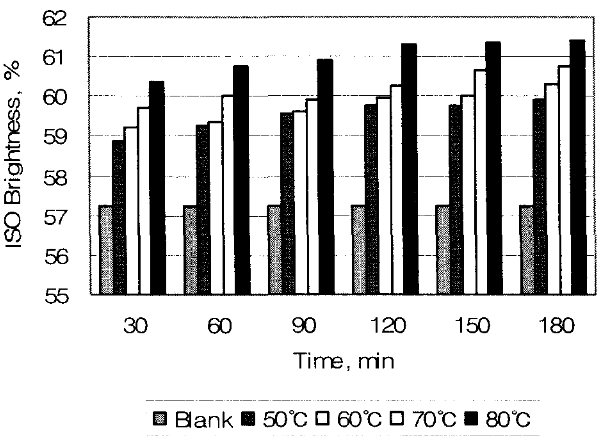


Figure 1. The effect of reaction time and temperature for peroxide bleaching on ISO brightness.

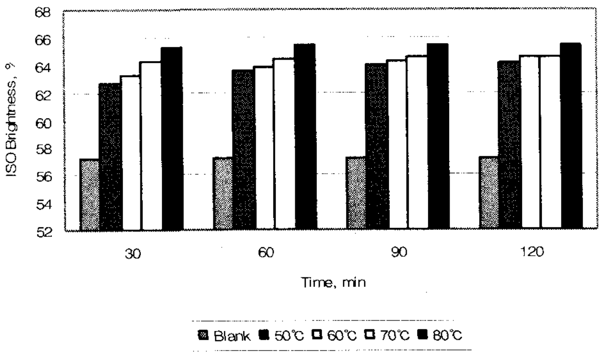


Figure 2. The effect of reaction time and temperature for FAS bleaching on ISO brightness.

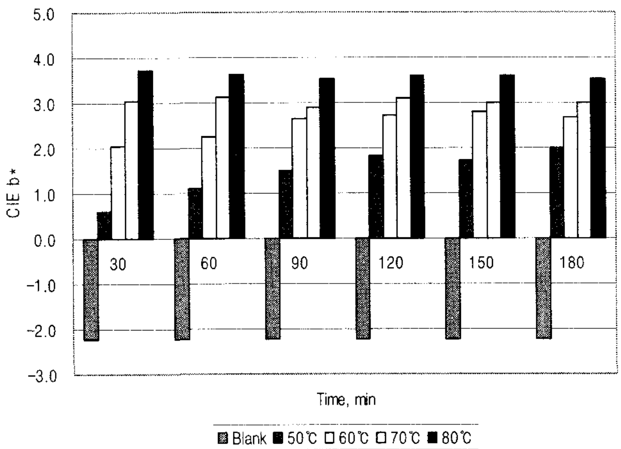


Figure 3. The effect of reaction time and temperature for peroxide bleaching on CIE b value.

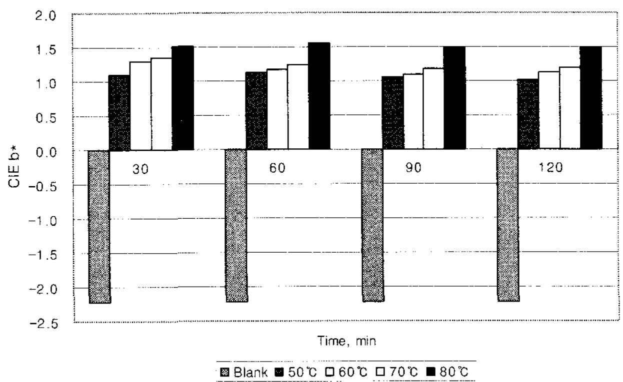
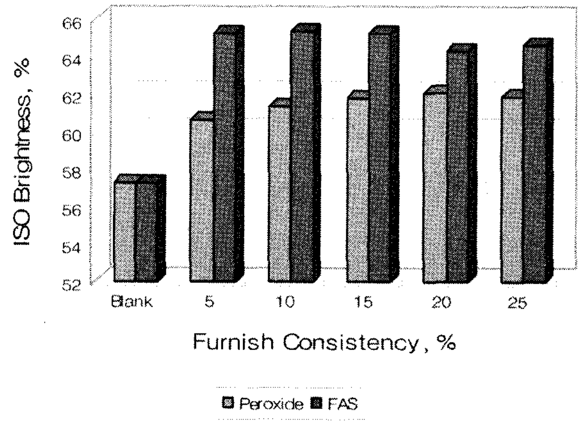


Figure 4. The effect of reaction time and temperature for FAS bleaching on CIE b value.

Figs 5-6 represent bleaching efficiencies with different pulp consistencies.



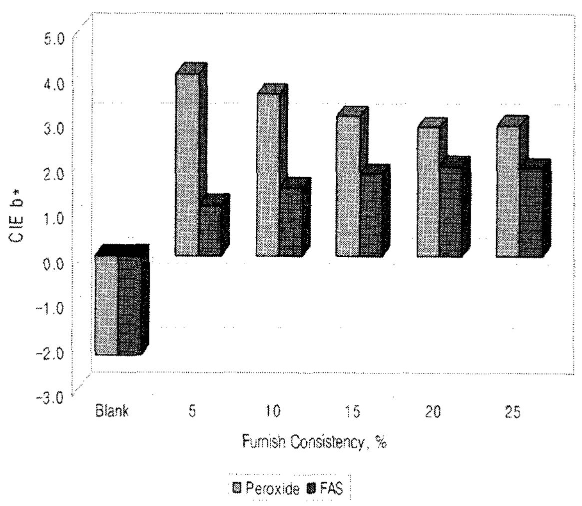


Figure 6. The effect of furnish consistency on CIE b value.

Tables 4-7 represent bleaching efficiencies with different experimental conditions. Experimental results showed that 5-10% of furnish consistency come up with optimum brightness. Brightness was even decreased as the furnish consistency increased over 10%. Brightness was proportionally increased as FAS concentration increased up to 1.0 % and gradually increased over 1.0 %. COD load was not nearly increased up to 0.6 % FAS concentration. Brightness was increased as sodium hydroxide increased up to 0.5 %. However, brightness was decreased over 0.5% sodium hydroxide concentration. It might be that sodium hydroxide can react with FAS to bleach pulp up to 0.5% concentration and extra sodium hydroxide over 0.5% concentration can cause alkali darkening and increase yellowness value, lowering brightness of the pulp.

Table 4. The effect of FAS concentration on bleaching efficiency.

Concentration (%)	L	a	b	Brightness (%)	COD Load (ppm)
Blank	79.72	0.45	-2.22	57.22	-
0.2	82.75	-0.85	3.35	60.15	396
0.4	83.02	-0.86	2.96	62.43	405
0.6	83.64	-0.64	2.26	63.77	399
0.8	83.84	-0.55	1.98	64.58	454
1.0	84.21	-0.38	1.51	65.26	468
1.2	84.36	-0.41	1.74	65.53	509

Table 5. The effect of sodium hydroxide concentration on FAS bleaching efficiency.

Concentration (%)	L	a	b	Brightness (%)	COD Load (ppm)
Blank	79.72	0.45	-2.22	57.22	-
0.2	84.10	-0.38	1.39	64.37	416
0.4	84.21	-0.34	1.43	64.99	461
0.6	84.21	-0.38	1.51	65.26	468
0.8	84.22	-0.39	1.59	65.06	475
1.0	84.45	-0.36	1.62	64.92	508
1.2	84.44	-0.36	1.67	64.73	708

Table 6. The effect of sodium silicate concentration on FAS bleaching efficiency.

Concentration (%)	L	a	b	Brightness (%)	COD Load (ppm)
Blank	79.72	0.45	-2.22	57.22	-
0.2	84.21	-0.38	1.51	65.26	468
0.4	84.76	-0.48	1.16	66.67	587
0.6	84.76	-0.34	0.85	67.32	607
0.8	84.69	-0.32	0.63	67.36	647
1.0	84.70	-0.28	0.63	67.37	698
1.2	84.66	-0.41	0.95	66.83	704

Table 7. The effect of chelant concentration on FAS bleaching efficiency.

Concentration (%)	L	a	b	Brightness (%)	COD Load (ppm)
Blank	79.72	0.45	-2.22	57.22	-
0.2	84.76	-0.34	0.85	67.32	607
0.4	84.69	-0.34	0.68	67.83	620
0.6	84.71	-0.34	0.78	67.54	629
0.8	84.74	-0.37	0.87	67.72	638
1.0	84.70	-0.35	0.83	67.73	637
1.2	84.68	-0.38	0.96	67.69	644

Figs 7-9 represent the effects of bleaching sequence on bleaching efficiency. Dranage curves with different bleaching agent was in Fig. 10.

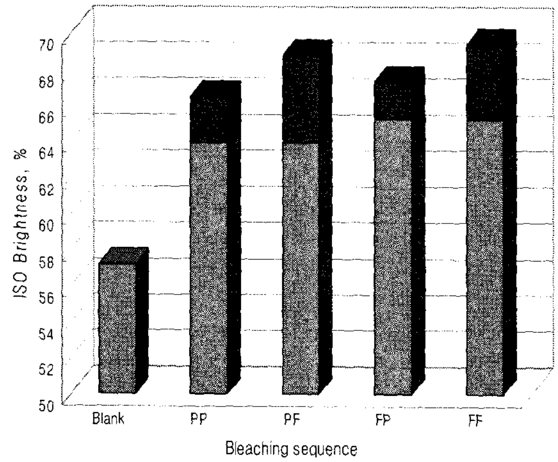


Figure 7. The effect of bleaching sequence on ISO brightness.

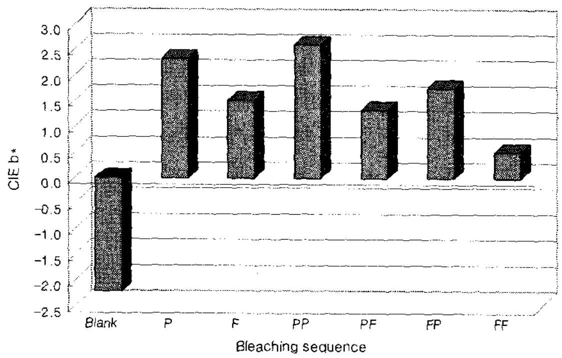


Figure 8. The effect of bleaching sequence on CIE b value.

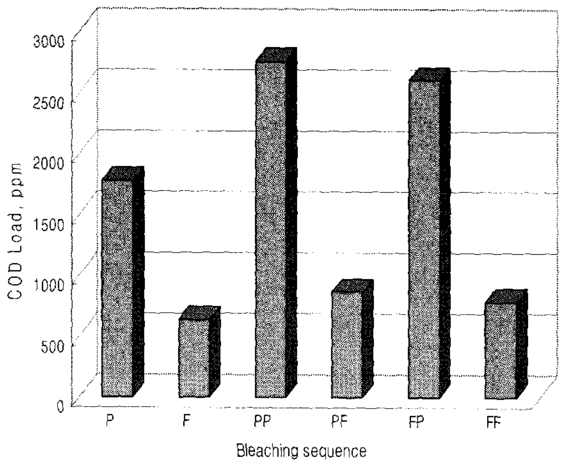


Figure 9. The effect of bleaching sequence on COD load.

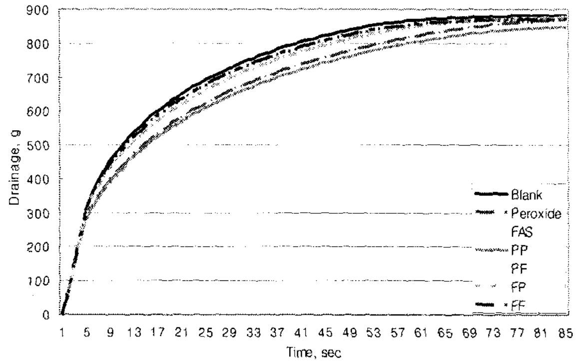


Figure 10. Dranage curves with different bleaching agent in second stage.

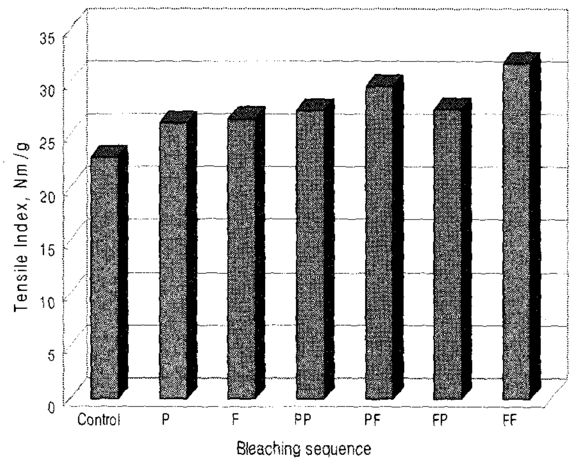


Figure 11. The change of tensile index with bleaching sequence.

CONCULSION

In order to improve bleaching efficiency and decrease environmental load (COD load), the environmental friendly FAS bleaching on ONP was carried out in this study.

1. As temperature of furnish was increased, bleaching efficiency seems improved. Two hours of reaction time in case of peroxide bleaching, 30 minutes FAS bleaching reached optimum bleaching state at 80℃.

2. As furnish consistency was increased, bleaching efficiency was increased in case of peroxide bleaching. However in case of FAS bleaching maximum bleaching efficiency was obtained at 10-15% furnish consistency and bleaching efficiency was not changed above 15% furnish consistency.
3. FAS bleaching seemed need far less bleaching agents than peroxide bleaching. In case of peroxide bleaching 2.0% hydrogen peroxide, 0.6% sodium hydroxide, 7% sodium silicate, 0.3% DTPA was the best combination for bleaching chemical composition. In case of FAS bleaching 1.0% FAS, 0.5% sodium hydroxide, 1% sodium silicate, 0.3% DTPA.

4. Two stages of bleaching using the combination of oxidative and reduced bleaching agents showed excellent bleaching efficiency with the following order (P represents peroxide bleaching and F FAS bleaching) ; PP < FP < PF < FF.

5. COD load of one stage FAS bleaching was about 0.33 times as much as peroxide bleaching. COD load of two stages were decreased with the following order; PP > FP > PF > FF.

6. Bleached furnish showed slower drange than unbleached furnish. It might come from the fact that bleaching process could oxidate and cut pulp. FAS bleaching showed faster dranage curve than peroxide bleaching.
7. Tensile, tear, and burst indices were improved through bleaching.

8. FAS bleaching showed more excellent stabilities of brightness and resistance of yellowness than peroxide bleaching.

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