Original Research Article

Treatments of Recycled Pulps from Old Corrugated Containers. Part I. The Effects of Boron Compounds on Optical and Physical Properties

ABSTRACT

Aims: It was aimed to to provide understanding of the properties of recycled fibers from Old Corrugated Container (OCC) and to explore boric acid and sodium borohydride effects for improvement of the properties of secondary OCC pulps.
Study design: In order to control past and the stages of the recovered fibers, repeatedly five recycling phases were applied on the same sheets. In each recycling phase, repulped OCC fibers were treated with 5.0% and 10% concentration (w/w) of sodium borohydride and boric acid at least 12 hours (overnight).
Methodology: The test sheets were prepared as 120 g/m^2. The test papers were dried in conditioned room for one day. Standard paper tests were applied according to Tappi Test Methods. This involves determination of water absorption (Cobb test) (Tappi T-441), color and optical properties (Tappi T-220 and T-525, ASTM E313, D523 and D1925, CIE L*a*b*) strandard methods, respecitvely. A number of combinations was utilized during recycling procedure of cellulose fibers.
Results: It has been found that the bulkiness of paper produced from sodium borohydride treated secondary pulps show higher bulk values than that of the control and boric acid process in the same phase. The highest bulk value of 3.41 cm^3/gr was found with 10% sodium borohydride treated pulps at the fifth recycle phase. However, both boron compounds positively effect on Old Corrugated Container (OCC) secondary fibers regarding water absorption properties (Cobb value) of test papers. The highest water absorption value of 135 g/m^2, was observed in 10% boric acid treatment conditions at fifth recycling stage that was approximately 8.0% and 26.16% higher than the former recycled papers and control at the same recycling phase, respectively.
Conclusion: Test papers treated with both compounds have showed in marginal limits for total color differences (ΔE) regardless of chemical tretament and recycling phase. It was realized that the selected boron compounds used for treatment of OCC secondary fibers did not cause significant changes in the color and optical values. However, need further work to validate reliability.

Keywords: Old Corrugated Container, recycling, boric acid, sodium borohydride, water absortion, paper color, brightness

INTRODUCTION

Prior to the invention of paper, people utilized clay tablets, tree barks, animal skins, and papyrus plant for communication and writing purposes. However, one of the first cellulose based writing material produced from papyrus plants, which naturally grew up in Egypt since pre-historic times. Thereby, the English name of paper has belived to derive from that plant [1,2]. The paper that we have used in modern time was invented by Ts'ai Lun at 105 A.D, in China. Since the invention of paper, it has become one of the most important communication and social tools. [1-3].

However, the needs of paper based products increased every year. But the main cellulose source of forest lands has become important and very valuable sources for human beings. In this sense, the idea of preservation of those sources have become an important issue that they should be carefully utilized and if possible not much consumed for forest products and paper industry. For that reason, the alternative cellulose sources for paper industry have become emerging topic. In this regard, the post consumer waste paper products could be an alternative raw material source for paper industry due to cellulose fibers readily available in their structure [1,2].

The physical and strength properties of paper based products are important for its aesthetic value and end use places. However, paper made from recycled fibers (i.e. post consumer papers or OCC) has a characteristic gray appearance without deinking process. In this sense, a chemical compound that utilized in recycling of paper products is important considering improving not only strengths but also optical properties and aesthetic values.

It has already well established that the high yield pulps (mechanical) shrink less than that of low yield or bleached pulp (chemical) upon drying [4-6]. This is most due to the fact that the presence of lignin between cellulose microfibrils prevents direct contact among fibrils when bound water is evaporated. However, lignin also prevents the formation of hydrogen bond cross-linking between cellulose microfibrils [7]. But, the cracking of dried fibers and formation of further intra-hydrogen bonds that partially irreversible are the effects on strength loss of sheets. Thereby, these irreversible intra-hydrogen bonds should need to be broken during recycling in order to regain fiber bonding potential [8].

Chemical treatment of pulp is a common way to increase and regain the bonding potential of dried pulps. Numerous chemical treatments have been evaluated for various type of secondary pulps (recycling). But, the most common chemical used for improving bonding potential of pulp was reported to be alkaline based chemicals [9-11]. It was proposed that the sodium hydroxide treatment improves the swelling capacity of dried Thermo Mechanical Pulp (TMP), but does not affect those of chemical pulps properly [12]. Freeland and Hrutfiord (1993) treated old corrugated containers (OCC) with alkali soaking during recycling. They found that the 2% sodium hydroxide at 52 ^{o}C and 14% consistency in four hours treatment conditions were effective for strength improvement of recycled pulps [11].

As mentioned above briefly, numerous chemical formulations have shown promising results on recycled pulps, and valuable improving effects reported on recycled pulps. Although some boron compunds have been utilized for Kraft pulping approaches on lignocellulosics **[13-17],** there is not much information available on boron based treatments on recycled OCC pulps. Thereby, this study was aimed to to provide more fundamental understanding of the properties of recycled fibers from OCC and to explore selected boron compound treatment (sodium borohydride and boric acid) effects for improvement of the properties of recycled OCC pulps.

MATERIALS AND METHODS

The additive and treatment free recycled pulps from old corrugated containers (OCC) were supplied from a commercially operated paper recycling plant, located in Istanbul, Turkey. It was reported that the knowledge of the stages during the recycling was important for better understanding of cellulose properties and restoring/improving effects [10]. In this regard, the same OCC pulps were used as received, in all recycling and treatment procedures. Boric acid and sodium borohydride have chosen to be treat OCC secondary OCC fibers during recycling process in order to study restoring effects on selected pulp properties. However, it has been possible to investigate the effect of selected boron compounds more closely on the recycled fibers that have been known since the past and have been subjected to successive drying and wetting processes. Although boric acid and sodium borohydride have been utilized in some industries, these has not yet found a common use in the paper industry. The purity level of the boron compounds (boric acid and sodium borohydride) used is above 95%. The chemicals were supplied directly from the Etibank Borax plant, located in Bandırma, Turkey. The chemical characteristics of selected boron compounds are given in Table 1.

Before the secondary OCC pulps were being used for test papermaking, it was first subjected to mixing procedure at room temperature (23 °C) in a laboratory-type standard disintegrator. The laboratory type standard British Sheet Former was used to prepare test papers from those pulps **[18].** In order to close control and understand the past and the stages of the recovered fibers, repeatedly five recycling phases were applied on the same sheets. Thereby, 50 sheets were prepared in first recycling phase, 10 sheets were reserved and 40 sheets were repulped for second recycling stage. This procedure had followed up to fifth recycling stage in similar order. In each recycling phase, disintegrated/repulped OCC fibers were treated with 5.0% and 10% concentration (w/w) of sodium borohydride and boric acid at least 12 hours (overnight). In this sense, the effects of those chemicals on secondary cellulose fibers were investigated at specific recycling phase.

The test sheets were prepared as 120 g/m^2 (typical level for OCC manufactured papers) accordance with Tappi Standards T-205 **[18].** The test papers were dried in specific conditioned room for 1 day, without being subjected to any stress or temperature effects. This procedure has been applied to all processes within the scope of the study. Hence, it was possible to investigate the effect of certain selected chemicals on the fibers more closely and correctly. Standard paper tests were then applied. This involves determination of water absorption (Cobb test) was carried out in accordance with the Tappi T-441 standard by weighing 100 ml of water for 60 second [19]. The Cobb value refers to the percentage of the amount of water absorbed by paper during a certain period of time relative to paper.

The color and optical properties of handsheets were measured according to Tappi T-220 [20], ASTM E313 [21], and D1925 [22], (whiteness and yellowness), Brightness (Tappi T-525) [23] and CIE L*a*b* (1976) standard methods, respecitvely. The color and optical characteristics of the papers were measured with the X-Rite 938 color spectrophotometer.

In the paper industry, the gloss most frequently measured is specular reflectance. It is the intensity ratio of specularly reflected light to the incident light. The specular reflection occurs in the surface layer of paper because light that enters the paper undergoes many reflections. Paper gloss at 60° was measured according to **ASTM D523 [22],** using a Glossgard Glossmeter from (Gardner/Neotec Company, Michigan, USA).

While many combinations was utilized during recycling procedure of cellulose fibers, some code number and abbreviations were established throughout the study given in Figures and Tables. These are: C: Control, Ba: Boric acid; NaB: Sodium borohydride; 5 and 10: chemical concentration %, weight/weight; 1, 2,3,4, and 5: recycling number.

Table 1. The general characteristics of boric acid and sodium borohydride compounds

Particulars	**Boric acid**	**Sodium borohydride**
Chemical formula	H_3BO_3	$NaBH_4$

Composition	56.30% B_2O_3; 43.70% H_2O	60.77% Na; 10.66% H; 28.57% B
Molecular weight	61.84 g/mol	37.83 g/mol
Specific weight	1.435 g/cm^3	1.07 g/cm^3
Melting point	171 ^0C	400 ^0C
IUPAC name	Trihydrooxidoboron	Sodium tetrahydridoborate

RESULTS AND DISCUSSIONS

The sheet density (presented as bulk) properties are shown in **Table 2.** In general, the bulk values of the control test papers were increased at a certain level until the first three recycling processes, and then decreased. A similar trend was also observed on test papers produced from boric acid treated secondary OCC pulps. However, in the treatment with sodium borohydride, only 5.0% concentration and fourth recycle stage ($5NaB_4$) showed a continuous increase. Moreover, the highest bulk value of 3.41 cm^3/gr was found with 10% sodium borohydride treated pulps at the fifth recycle phase ($10NaB_5$). This value is approximately 15.98% and 24.0%, higher than the previous recycling and the control sample at the same recycling stage, respectively. In general, it has been understood the papers produced from sodium borohydride treated secondary pulps show higher bulkiness than that of the control and boric acid process in the same recycling phase. In this sense, it could be suggested that sodium borohydride looks like more effective on density of sheets than boric acid. In general, changes in bulk (density) values of paper reproduced from secondary fibers are consistent with the literature reports [2, 25].

Table 2. Bulk properties of papers made from recycled OCC pulps

Samples	Bulk (cm^3/gr)	Change (%, from former stage)	Change (%, from control)
C_1	2.80	0.0	0.0
C_2	2.82	0.71	0.0
C_3	2.89	2.48	0.0
C_4	2.82	-2.42	0.0
C_5	2.75	-2.48	0.0
$5NaB_1$	2.72	0.0	-2.86
$5NaB_2$	2.91	6.98	3.19
$5NaB_3$	2.91	0,0	0.71
$5NaB_4$	2.73	-6.18	- 3.19
$5NaB_5$	2.94	7.69	6.91
$10NaB_1$	2.72	0.0	-2.85
$10NaB_2$	2,82	3,68	0.0
$10NaB_3$	2.96	4.97	2.42
$10NaB_4$	2.94	-0.68	4.25

10NaB5	3.41	15.98	24.0
5Bx1	2.80	0.0	0.0
5Bx2	2.91	3.9	0.32
5Bx3	2.54	-12.7	-12.1
5Bx4	2.87	12.9	1.77
5Bx5	2.86	-0.34	4.0
10Bx1	2.88	0.0	2.90
10Bx2	2.91	1.0	3.19
10Bx3	2.82	-3.80	-2.40
10Bx4	2.55	-9.60	-9.57
10Bx5	2.97	16.91	8.0

Table 3 shows comparable water absorption (Cobb) properties of test papers. It can be seen that both boron compounds positively effects on OCC secondary fibers regarding water absorption properties. The highest water absorption value of 135 g/m^2 was observed in 10% boric acid treatment conditions at fifth recycling stage (10Bx$_5$). However, this value is approximately 8.0% and 26.16% higher than the former recycled and control sample at the same recycling phase, respectively. Moreover, the lowest water absorption value of 100 g/m^2 was found in 5.0% sodium borohydride conditions at fifth recycling stage (5NaB$_5$) and this indicates 16.66% and 6.54% lower water absorption properties than the previous and control sample at the same recycling phase, respectively. As a general conclusion from Table 3, it could be said that both sodium borohydride and boric acid treatment of secondary OCC pulps have an increase trend regarding water absorption (Cobb) properties. Similar results have already been reported by numerous researchers for other type pulps and treatment chemicals **[25,26].**

Table 3. Water absorption (Cobb) properties of papers made from recycled OCC pulps

Samples	Water absorption (Cobb) (gr/m^2)	Change (%, from former stage)	Change (%, from control)
C1	126	0.0	0.0
C2	108	-14.28	0.0
C3	108	0.0	0.0
C4	108	0.0	0.0
C5	107	-0.93	0.0
5NaB1	128	0.0	1.59
5NaB2	116	-9.37	7.41
5NaB3	108	-6.89	0.0
5NaB4	120	11.11	11.1
5NaB5	100	-16.66	-6.54
10NaB1	124	0.0	-1.59
10NaB2	104	-16.12	-3.70
10NaB3	116	11.53	7.41
10NaB4	104	-10.34	-3.70
10NaB5	116	11.53	8.41

$5Bx_1$	119	0.0	-5.56
$5Bx_2$	120	0.84	11.1
$5Bx_3$	120	0.0	11.1
$5Bx_4$	123	2.50	13.89
$5Bx_5$	132	7.32	23.36
$10Bx_1$	118	0.0	-6.34
$10Bx_2$	120	1.70	11.1
$10Bx_3$	120	0.0	11.1
$10Bx_4$	125	0.0	17.74
$10Bx_5$	135	8.0	26.16

The basic color values of test papers that produced from control and selected boron treated pulps are prensented in Table 4. It is very difficult to explain all these parameters and correlate to each other while it is also not intent to do in this study. However, it is clearly seen that the color changes of test papers treated with both compounds have very limited changes and mostly in marginal limits (ΔE), in most cases lower than 1.0%. But, it is important to note that these boron compounds have some level positive effects on yellowness values that lowering yellowness values indication less yellow paper.

It can be seen that the sodium borohydride and boric acid has not cause significant changes in both brightness and gloss values. There are even only less than 1.0 degree changes of brightness value depending on the recycling phase (Table 4). However, the gloss of a paper can be greatly influenced by a number of factors, particularly surface properties (i.e. smothness). The highest gloss value of 5.2 was found in the fifth recycling stage of 5.0% boric acid treated sheets ($5Bx_5$) while the lowest gloss of 3.5 found in 10% boric acid treatment at first recycling phase ($10Bx_1$). It can be understood that the selected chemical substances used for treatemnt OCC secondary fibers do not cause significant changes in the color values of the papers and do not cause important level color reduction.

Table 4. The color properties of papers made from recycled OCC pulps

	CIE L*,a*, b*				**Yellowness Index**		**Brightness**	**Gloss (60^o)**
Samples	**ΔL**	**Δa**	**Δb**	**ΔE**	**ASTM E313**	**ASTM D1925**	**Tappi T525**	**ASTM D2457**
C_1	0	0	0	0	0	0	24.51	3.8
C_2	0.49	0.06	-0.14	0.36	-0.37	-0.43	24.76	4.4
C_3	0.94	0.002	0.006	0.30	-0.21	-0.29	25.52	4.2
C_4	0.71	0.03	0.02	0.28	-0.17	-0.21	25.58	4.3
C_5	1.09	0.014	0.09	0.28	-0.57	-0.76	25.96	4.2
$5NaB_1$	1.09	0.06	0.39	0.52	0.37	-0.32	23.57	3.6
$5NaB_2$	0.69	-0.03	-0.56	0.61	-0.77	-0.87	24.54	4.0
$5NaB_3$	0.32	0.03	-0.27	0.66	-0.37	-0.43	24.31	4.4
$5NaB_4$	0.05	0.25	0.38	0.65	-0.64	-0.52	24.49	4.3
$5NaB_5$	0.23	0.04	0.39	0.49	-0.75	-0.90	24.39	4.6
$10NaB_1$	-1.11	0.08	0.38	0.50	0.33	-0.31	23.73	3.8
$10NaB_2$	-0.83	0.09	-0.61	0.72	-0.81	-0.91	23.83	3.7

10NaB$_3$	0.31	0.02	0.26	0.61	-0.67	-0.82	24.44	4.3
10NaB$_4$	0.23	0.15	0.29	0.62	-0.42	-0.37	24.46	4.0
10NaB$_5$	0.14	0.09	0.33	0.52	-0.60	-0.67	24.45	4.5
5Bx$_1$	0.02	0.20	0.22	0.37	-0.39	-0.72	24.30	4.1
5Bx$_2$	0.83	0.29	0.35	0.75	-0.84	-1.40	24.68	4.3
5Bx$_3$	1.08	0.36	0.11	0.80	-0.46	-1.02	24.33	4.4
5Bx$_4$	1.24	0.24	0.13	0.74	-0.58	-1.02	23.65	4.2
5Bx$_5$	1.21	0.22	0.15	0.76	-0.03	-0.39	24.55	**5.2**
10Bx$_1$	0.69	0,06	0.65	0.66	-0.77	-1,16	24.11	3.5
10Bx$_2$	-0.09	0.24	0.78	0.75	-1.34	-1,07	24.64	3.7
10Bx$_3$	0.14	0.08	0.46	0.66	-0,08	-1,14	24.01	3.8
10Bx$_4$	0.22	0.06	0.45	0.69	0.85	-1,08	24.95	4.1
10Bx$_5$	0.60	0.03	0.40	0.54	-0.74	-0,99	24.61	4.1

The results presented in Table 4 has used to interpret both sodium borohydride and boric acid combine effects with recycling phase on total color differences (∆E) properties of test papers shown in Figures 1 and 2, respectively. It can be seen the use of sodium borohydride has not clear effects on total color differences but increasing concentration from 5.0% to 10% in lower recycling number somewhat negative impact on colors (Figure 1). Although boric acid has only marginal level effects on total color difference, it is important to note that increasing boric acid concentration from 5.0% to 10% and recycling number negative impact on color of test papers (Figure 2).

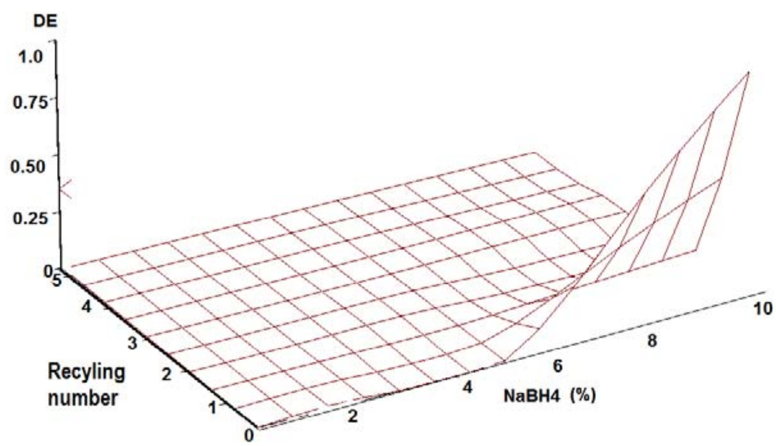

Figure 1. The effects of sodium borohydride and recycling steps on total color difference (**∆E)** of papers.

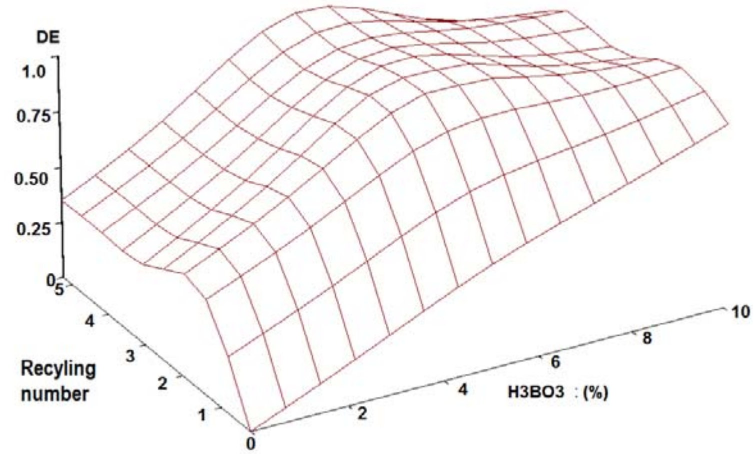

Figure 2. The effects of boric acid and recycling steps on total color difference (∆E) of papers.

CONCLUSIONS

The old corrugated containers are one of the most recycled paper based material compare to others. This is because of its recovery (recycling) easy and suitable for re-manufacturing of paper and paperboards materials primarily packaging. However, the recycling of these valuable materials has also helps decrease solid waste disposal in landfills. A number of valuable results and suggestions have reported from recycling of post consumer waste papers. But the chemical treatment approaches used in this study are new and generally compatible with the literature data. Moreover, there has not much literature on the effects of certain boron compounds on secondary OCC pulps.

However, the use of boric acid and sodium borohydride during recycling of OCC pulps as treatment agent show promising results and even restoring effects on some selected (water absoprsion and optical properties). Thereby, the results have presented in this study could be open an alternative useage of these compounds during recycling of OCC. Moreover, further studies may be appropriate to elaborate effects of those boron compounds on secondary fibers in different experimental conditions.

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