Original Research Article

Treatments of Recycled Pulps from Old Corrugated Containers. Part II. The Effects of Boron Compounds on Strength Properties

8 ABSTRACT

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9 The selected boron compounds used in this study exhibit a more moderate reduction 10 on burst strength, even though they may only limited improvements in other properties. 11 However, at the fifth recycled stage, guite high burst strength values observed with at both 12 selected boron treatment conditions that approximately 32.31% and 35.94% higher burst strengths at 5.0% level while 20.32% and 14.06% higher burst strengths at 10% boric acid 13 and sodium borohydride level compare to control sample at similar recycling phase. The more 14 15 less similar trend was also observed for tensile strength properties of test papers. The highest 16 tensile strength (index) of 19.74 Nm/g and tensile stiffness value of 386 kN/m was observed at 17 second recycling phase with boric acid. For tensile energy absorption (TEA) properties, only 10% sodium borohydride treated test papers showed higher TEA of 23.25 j/m² compared to 18 19 counterpart control samples (C₂: 20.60 j/m²).

20 The paper from secondary fibers has generally considered to be used in corrugated 21 cardboard production. For this purpose, Sack Corrugated Test (SCT) and Corrugated Medium Tests were used to determine the strength resistance behaviors. The highest CMT value of 22 23 73.5kN/m was found with first recycling stage of control samples. For boron treated pulps, the 24 highest CMT of 63.3 N was found at 10% boric acid treatment at second recycling phase 25 followed by 5.0% boric acid treatment at second recycling phase, respectively. However, some level improvement of SCT properties was observed at certain level both boric acid and 26 sodium borohydride treatment conditions, the highest improvements of SCT of test papers 27 28 was found with 5.0% boric acid treatment at forth recycling phase that show approximately 39.74% improvement compared to control. 29

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Keywords: Old Corrugated Container, recycling, boron compounds, tensile strength, burst
 strength, corrugated medium test,

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35 INTRODUCTION

36 The multi-stage paper production stages affect the structure of cellulose by both 37 chemically and physically [1]. To manufacture paper products from recovered cellulosic fibers 38 (secondary fibers/pulps), the secondary pulp needs to have intrinsic strength and some certain 39 properties. However, it was noted that some of the fillers have removed during recycling, 40 which indicates that papermaking from secondary pulps requires higher fillers [2]. Moreover, 41 the cellulose fiber undergoes mechanical and drying cycles during papermaking and causing a 42 very complex phenomenon and has not fully explained yet. These changes have usually 43 called hornification that irreversible hydrogen bonding potantial and hydrophilic nature of 44 cellulose fibers [3-7]. In addition, the removing of hemicellulose and lignin from the cell wall 45 during recycling also causes the collapse and negative impact on cellulose structure. In 46 hornificated fibers, the amorphous region has typically reduced to some extent resulting 47 increasing crystalline index with lowering re-wetting propeties of fibers [7-11].

48 Since environmental concern and protection of natural forestslands for 49 papermaking industry, the recycling of post-consumer paper products has become an Comment [Š1]: potential

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50 important issue in worldwide. Hence many technologies and alternative approaches have 51 become established regarding waste paper recycling.

A typical paper sheet is a composite material that contains cellulosic fibers, air, fillers and some extraneous materials. However, fiber-fiber bonding is closely associated with fibers contact areas and important parameter for paper strengths [12]. Certain chemicals have been reported to be promote fibre bonding and improve paper properties some level [3, 13-16]. It was proposed by Wistara and Young (1999) that the microstructure of cellulose must be modified to establishing further swelling capacity. Moreover, hemicelluloses have also important influences in regulating the physical properties of the pulps during recycling [15].

Although some research conducted for pulping of lignocellulosics with boron 59 60 compunds, and valuable restoring effects on pulp properties [17-20], there has not much 61 information available in literature regarding certain boron compounds treatments of secondary 62 pulps and their effects on paper properties. A systematic approach have carried out with boric acid and sodium borohydride on recycled old orrugated containers (OCC) substrate to 63 determine clear effects on recycling approach and chosen methods. In the first part of this 64 65 study, 'Treatments of Recycled Pulps from Old Corrugated Containers. Part I. The Effects of 66 Boron Compounds on Optical and Physical Properties' has already send to "submitted for 67 publication". In the second part of this study, it is aimed to study for providing more fundamental understanding of the strength development of recycled fibres from old corrugated 68 69 container (OCC) fibers.

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71 MATERIALS AND METHODS

The additive and treatment free recycled pulps from old corrugated containers were 72 73 supplied from a commercially operated paper recycling plant, located in Istanbul, Turkey. The 74 purity level of the boron compounds (boric acid and sodium borohydride) used is above 95%. 75 The chemicals were supplied directly from the Etibank Borax plant, located in Bandırma, Turkey. The test papers were prepared as 120 g/m² (typical level for OCC manufactured 76 77 papers) accordance with Tappi Standards (T-202 and T-205). The detailed information on 78 boron compounds, experimental recycling procedures for treatment of OCC substrate and 79 related similar informations have already given in first part of this study.

The standard paper strength tests were applied. These involves determination of 80 tensile (T-494) and burst (T-403), strengths. Sack Crushing Strength Test or Short 81 82 Compression Test (SCT) that is is indicates internal compression resistance of paper fibres and suitable for fluting in the middle layer of the cardboards, was applied on sheets 83 accordance with ISO 9895 standard. The SCT properties of papers are expressed in 84 85 Kilonewtons/Meter (kN/m). The Corrugating Medium Test (CMT) was also conducted on hand 86 sheets followed DIN EN ISO 7263 standard. The CMT determines the flat crush resistance of 87 corrugating papers and made on laboratory corrugated samples for describing the usability for 88 fluting. CMT is a way of estimating the crush resistance of corrugated board manufactured 89 with those papers. The CMT is expressed in Newtons (N). Both SCT and CMT tests have 90 used after forming corrugated paper forms, and usually applied on corrugated papers 91 alternatively to each other.

While many combinations were 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, Bx: Boric acid; NaB: Sodium borohydride; 5 and
 10: chemical concentration %, weight/weight; 1, 2,3,4, and 5: recycling number.

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100 **RESULTS AND DISCUSSION**

101 The burst strength values of the test papers produced from the control and treated 102 pulps are given comparatively in Table 1. It has realized that the burst strengths of control 103 papers have increased in the first two recycling steps. Then, it has showed a downward trend 104 in further recycling operations. The similar results have also been observed with sodium 105 borohydride and boric acid treated pulps.

However, in general, the burst strength values of sodium borohydride and boric acid 106 treated pulps show about 3.22% to 20.43% lower than the control samples up to fourth 107 recycling steps. Interestingly, at the fifth recycled phase, quite high burst strength values 108 observed that approximately 32.31% and 35.94% higher at 5.0% concentration while 20.32% 109 and 14.06% higher burst strengths at 10% concentration in comparison to control sample at 110 111 similar recycling phase. It is important to note that selected boron compounds used in this study exhibit a more moderate reduction on burst strength, even though they may only limited 112 113 improvements in other recycling phases.

Sample	Burst strength (kPa)	Burst index (kPa m²/g)	% Change (from former treatment)	% Change (from control)
C 1	119	0.95	0.0	0.0
C ₂	118	1.07	8.42	0.0
C₃	98	0.88	-17.75	0.0
C ₄	102	0.93	5.68	0.0
C ₅	70	0.64	-31.18	0.0
5NaB ₁	95	0.86	0.0	-9.47
5NaB₂	115	0.92	6.97	-14.10
5NaB₃	92	0.84	-8.69	-4.54
5NaB ₄	99	0.90	0.71	-3.22
5NaB₅	87	0.85	-5.56	32.31
10NaB ₁	101	0.81	0.0	-14.73
10NaB ₂	98	0.89	9.87	-16.82
10NaB₃	84	0.78	-12.36	-11.36
10NaB ₄	85	0.83	6.41	-10.80
10NaB₅	68	0.77	-16.87	20.32
5Bx1	104	0.83	0,.0	-12.63
5Bx ₂	119	1.08	30.12	0.93
5Bx₃	93	0.82	-24.07	-6.81
5Bx4	93	0.86	4.87	-7.53
5Bx₅	104	0.87	1.16	35.94
10Bx1	114	0.91	0.0	-4.21
10Bx ₂	110	1.0	9.89	-5.61
10Bx₃	88	0.80	-20.0	-9.09
10Bx ₄	81	0.74	-7.50	-20.43
10Bx₅	66	0.73	-1.35	14.06

Table 1. Burst strength properties of papers made from recycled OCC pulps

Figures 1 and 2 show the effects of boron compounds concentration in recycling stages on 114 burst strength properties of hand sheets. It has been observed that the increasing sodium 115 borohydride concentration at higher recycling phase has no positive effects while at lower 116 117 recycling number (up to two) and sodium borohydride concentration shown to improving burst strengths of sheets (Figure 3). Like sodium borohydride treatments, lower recycling phase 118 (up to two) but in both level boric acid concentration have increasing effects on burst strengths 119 of sheets (Figure 4). increasing recycling phase beyond second recycling phase have not 120 121 effective for improving burst strengths of papers made from selectec boron treated recycled OCC pulps. 122 123

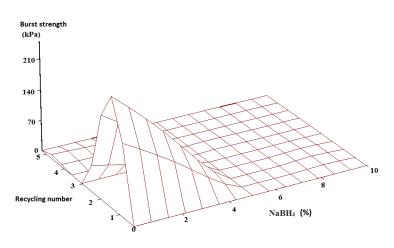
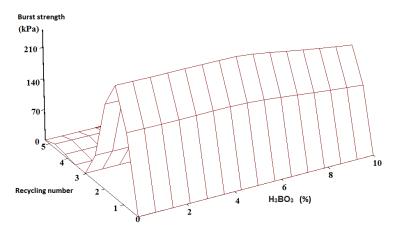


Figure 1. The effects of sodium borohydride concentration and recycling phase on burst

125 strengths of papers



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Figure 2. The effects of boric acid concentration and recycling phase on burst strengths of papers

In Table 2 the tensile strengths properties of the test papers are given comparatively.
In general, the tensile properties (index) of control samples did not change much and even
decreased only by 1.20% to 5.79%, continuously recycling procedure. It is important to note

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that no any improvements was observed with sodium borohydride treated pulps regardsless of
 concentration and recycling phase, except 10% treatment conditions at second recycling
 stage (10NaB₂) that shows only 3.23% improvement in comparison to control samples.

For boric acid treatments, except in 5.0% conditions at first recycling stage (5Bx₁), 2.69 to 8.34% improvements of tensile strengths were observed compare to counterpart control samples. The highest tensile index of 19.74 Nm/g was observed at second recycling stage (5Bx₂).

140 Stretch is usually reported percentage of elongation. As seen in Table 2, marginally changes were observed regarding stretchs of papers. The changes occurs only in marginal 141 limits. However, tensile stiffness is the ratio of tensile force per unit width to tensile strain 142 within the elastic region of the tensile-strain relations. The highest tensile stiffness value of 143 144 386 kN/m was observed with 5.0% boric acid treatment at fifth recycling phase that is the only higher value for boron treated pulps regardless of recycling phase, than counterpart control 145 146 samples. Tensile energy absorption (TEA) is the work done when a specimen is stressed to rupture in tension under prescribed conditions. It is expressed as energy per unit area (test 147 148 span x width) of test specimen. For sodium borohydride treatments of secondary pulps, only 149 10% treated pulps at second recycling phase (10NaB2) show higher TEA of 23.25 J/m2 150 compared to counterpart control samples (C2: 20.60 J/m2). It is important to note that boric 151 acid seems to be effective only at 5.0% concentration phase (except first recycling stage).

From the results observed in Table 2, it can be summarized that treatment of OCC secondary fibers with both boron compounds at 5.0% treatment levels have some restoring/improving effects on the tensile strength values at certain treatment phases.

Tensile Tensile Tensile Stretch stiffness TEA Sample strength index (J/m^2) (kN/m)(%) (kN/m) (Nm/g) C₁ 2.40 1.69 31.20 356 19.34 C₂ 2.15 1.34 20.60 18.22 341 2.09 1.28 19.15 313 18.0 C₃ 2.08 255 **C**₄ 1.27 16.10 18.26 C₅ 2.24 1.21 18.15 328 18.98 5NaB₁ 2.02 1.88 26.75 269 16.10 5NaB₂ 1.85 1.52 20.40 273 16.67 1.25 17.05 272 17.79 5NaB₃ 1.93 5NaB₄ 1.87 1.27 16.10 254 17.32 2.02 1.29 17.85 291 5NaB₅ 18.53 10NaB1 1.77 1.96 25.0 212 14.71 10NaB₂ 2.05 1.59 23.25 274 18.81 10NaB₃ 1.72 1.20 14.10 259 17.73 10NaB₄ 1.80 1.80 16.20 257 17.39 10NaB₅ 1.54 0.95 10.33 266 17.50 23.25 5Bx1 1.93 1.72 254 16.69 2.23 22.90 19.74 5Bx₂ 1.45 302 1.32 5Bx₃ 2.13 19.50 290 18.85

Table 2. Tensile strength properties of papers made from recycled OCC pulps

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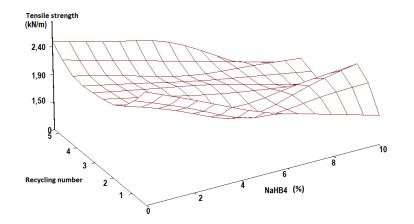
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5 Bx 4	2.16	1.29	19.80	296	18.94
5Bx₅	2.30	1.14	19.15	386	19.49
10Bx1	1.96	1.71	24.0	253	15.68
10Bx ₂	1.93	1.09	14.83	289	17.31
10Bx₃	1.97	1.42	19.25	267	18.41
10Bx4	1.74	1.20	14.20	253	16.57
10Bx₅	1.42	1.10	10.71	228	13.40

Figures 3 and 4 show the combine effects of sodium borohydride and boric acid concentration during recycling phases on tensile strength properties of test papers. It has been observed that the increasing sodium borohydride concentration at low recycling phase marginally improving effects (Figure 3). In contrast to sodium borohydride, low level of boric acid concentration and higher recycling phase positive affects tensile strengths of sheets (Figure 4). In this sense, increasing boric acid contcentration to 10% up to third recycling

162 phase not effective for improving tensile strengths of papers.



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Figure 3. The effects of sodium borohydride concentration and recycling phase on tensile strengths of papers

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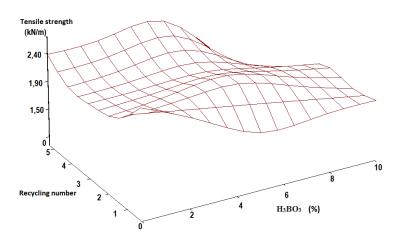


Figure 4. The effects of boric acid concentration and recycling phase on tensile strengths of papers

The Corrugate Medium Test (CMT) values of the test papers are given in Table 3. It can be seen that there is not certain restoring trend realized for the CMT values of test papers. It seems to selected boron compounds have not positively affected the CMT of papers. The highest CMT value of 73.5 N was found after first recycling stage of control samples. However, for boron treated pulps, the highest CMT of 63.3 N was found at 10% boric acid treatment at second recycling phase ($10Bx_2$) followed by 5.0% boric acid treatment at second recycling phase ($5Bx_2$), respectively.

 Table 3. Corrugated Medium (CMT) strength properties of papers made from recycled OCC pulps

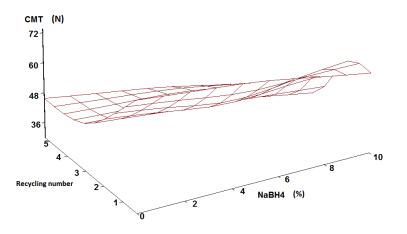
Sample	СМТ	Change	Change
-	(N)	(%, from former stage)	(%, from control)
C ₁	73.5	0.0	0.0
C ₂	60.7	-17.41	0.0
C₃	50.0	-17.62	0.0
C ₄	46.0	-8.0	0.0
C₅	45.7	-0.06	0.0
5NaB ₁	69.3	0.0	-5.71
5NaB ₂	54.3	-21.64	-10.54
5NaB₃	46.7	-13.99	-6.60
5NaB ₄	43.7	-6.2	-5.00
5NaB₅	39.0	-10.76	-14.66
10NaB ₁	61.7	0.0	-16.05
10NaB ₂	59.0	-4.38	-2.80
10NaB₃	40.1	-3.03	-19.98
10NaB ₄	37.0	-7.73	-19.56
10NaB₅	29.7	-1.72	-35.01

5 Bx 1	63.3	0.0	-13.54
5Bx ₂	62.3	-1.58	2.63
5Bx₃	43.3	-30.49	-13.40
5 Bx 4	41.7	-12.70	-7.17
5Bx₅	36.0	-21.21	-21.22
10Bx1	60.7	0.0	-17.41
10Bx ₂	63.3	5.43	4.28
10Bx₃	43.3	-31.59	-13.40
10Bx ₄	39.0	-9.90	-15.21
10Bx₅	29.7	-23.84	-35.01

Figures 5 and 6 show the effects of boron compounds of sodium borohydride and boric acid in recycling phases on CMT properties of test papers. It has been observed that the increasing sodium borohydride concentration do not influence on CMT values while increasing reycling number negatively affects the test papers. Interestingly, more less similar trend was also observed in case of boric acid treatment conditions as seen in Figure 6.

170 biserved in case of bone and treatment conditions as seen in Figure 0.

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Figure 5. The effects of sodium borohydride concentration and recycling phase on CMT properties of papers

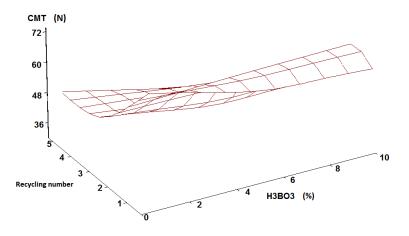


Figure 6. The effects of boric acid concentration and recycling phase on CMT properties of papers

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174 The paper from secondary fibers has generally considered to be used in corrugated 175 cardboard production. For this purpose, Sack Corrugated Test (SCT) is used to determine the 176 surface crush strength resistance behaviors. In this test, the content of paper is more sensitive 177 than fiber content as compared to conventional testing methods. In Table 4, the SCT values of 178 the test papers produced from the treated secondary fibers with the control and boron 179 compounds are given comparatively. As seen in Table 4, the SCT properties of the (control) papers showed a steady decline as the recycling stage increased. It is very complicated to 180 181 interpret the data presented in Table 4. However, some level improvement of SCT properties 182 was observed at certain level of samples treated by both boric acid and sodium 183 borohydride. However, the highest SCT value of 1.18 kN/m was found for control sample 184 (C1). The highest improvement of SCT of test papers under treatment conditions with 5% 185 boric 5.0% boric acid at forth recycling phase (5Bx₄) that shows approx. 39.74% improvement 186 as compared to control samples (C4: 0.78 kN/m vs 5Bx4: 1.09 kN/m), followed 16.44% 187 improvement by fifth recycling phase at same boric acid concentration.

Table 4. SCT stre	enath properties of	papers made from	recycled OCC pulps

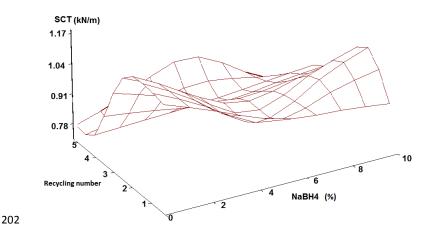
Treatme nt	SCT (kN/m)	% Change (from former treatment)	% Change (from control)
C 1	1.18	0.0	0.0
C ₂	1.16	-1.72	0.0
C ₃	1.09	-7.62	0.0
C ₄	0.78	-28.44	0.0
C₅	0.73	-0.64	0.0
5NaB₁	0.96	0,0	-17.24
5NaB₂	0.88	-9.38	-26.27
5NaB₃	0.87	-1.14	-19.27
5NaB ₄	0.78	-11.36	0.0
5NaB₅	0.92	17.94	8.00

10NaB ₁	0.90	0.0	-22.41
10NaB ₂	1.09	21.11	-7.63
10NaB ₃	0.92	-15.59	-15.59
10NaB ₄	0.84	-8.69	7.69
10NaB₅	0.67	-20.24	-8.21
5 Bx 1	0.99	0.0	-14.65
5Bx2	1.15	16.16	-2.54
5Bx₃	1.0	-13.04	-8.26
5 Bx 4	1.09	8.26	39.74
5Bx₅	0.85	-22.02	16.44
10Bx1	0.98	0.0	-15.51
10Bx ₂	1.13	15.31	-4.23
10Bx ₃	0.92	-18.58	-15.59
10Bx ₄	0.82	-10.87	-5.13
10Bx ₅	0.66	-19.51	-9.59

189 The results given in Table 4 were used to interpret selected boron compounds and 190 recycling phase effects on SCT properties of tested papers. Hence, sodium borohydride and 191 boric acid effects during recycling stages effects on SCT properties presented in Figure 7 and 192 8, respectively.

193 It can be seen that middle level of recycling (up to third) with 10% sodium 194 borohydride has some improving effects on SCT properties (Figure 7). However, treatment of 195 secondary OCC fibers with boric acid was found to have the only positive effect on the SCT 196 properties at low concentration (5.0%) and at middle level recycling stages (up to third) (Figure 197 8).

In general, it has been observed that the increase in recycle number and selected boron content concentrations have usually negative impact on the SCT properties of the test papers, but the SCT value changes were found to be within marginal levels for certain treatment conditions (see in Table 4)



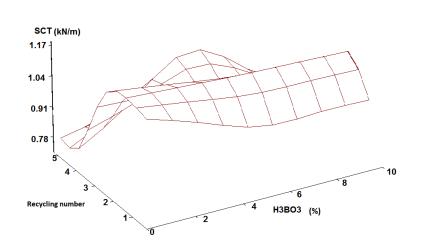


Figure 7. The effects of sodium borohydride concentration and recycling phase on SCT properties of papers

Figure 8. The effects of boric acid concentration and recycling phase on SCT properties of papers

205 Wistara et al. (1999) reported that the recycling affects lowering surface energy of 206 cellulosic fibers. This hypothesis has been suggested that the disruption of hemicelluloses 207 may occur during recycling of cellulose. They have proposed that some compounds could be capable oxidizing fiber surfaces resulting increasing carboxylic and OH groups on the surface 208 209 of the fibers during recycling. These clearly affect substitution of -OH groups and resulting 210 further swelling and, improve physical properties of sheets [15]. In our study, there has only 211 marginal improvements of paper strengths was observed while some properties have been 212 found to be restore at certain boron compounds treatment conditions.

214 CONCLUSIONS

The corrugated container manufaturing is an important sub parts of papermaking 215 216 industry. This is because of wide utilization of these products in packaging and transportation 217 needs other consumer products. Thereby, the recycling of these products has important issue 218 and to modify on similar products that they usually re-manufactured from those recycled 219 fibers. The selected boron treatments of the recovered secondary OCC pulps are aimed to 220 improve some strength propertie of sheets made. Although the use of boric acid and sodium 221 borohydride during recycling of OCC pulps as treatment agents shows some variables and 222 limited restoring/improving results on some selected strength properties, the results have 223 found in this study might be a basement for further studies.

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