IMPARTING FLAME-RETARDANT PROPERTIES TO COMMERCIAL PAPERS USING THE IMMERSION METHOD

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The objective of this study was to develop fire-resistant paper by immersing commercial paper samples into various fire-retardant chemical solutions. In the experimental work, untreated commercial papers were treated with fire-retardant chemicals boric acid (BA), borax (BX), and aluminum hydroxide (AH) at different concentrations. The papers were impregnated for a fixed duration using the impregnation method, and following drying under controlled conditions, their weight, thickness, thermal stability (TGA), limiting oxygen index (LOI), and printability were evaluated in accordance with relevant standards. The results revealed that impregnation increased both paper weight and thickness, whereas the liquid-penetration behavior was strongly dependent on the flame-retardant type, concentration, and immersion frequency, with low-concentration BA and BX treatments and repeated AH treatments generally providing improved resistance to water penetration. However, the TGA analysis indicated an increase in residual mass. Furthermore, the LOI test demonstrated that papers treated with BA and BX could be classified as fire-resistant, and the printing tests confirmed an improvement in print quality.

Keywords: commercial papers, fire-resistant chemicals, impregnation method, thermal stability, LOI test

INTRODUCTION

Cellulose-based paper, composed of cellulose, hemicelluloses and lignin, is one of the most abundant renewable biomaterials. Due to its lightweight structure, low cost, recyclability, and versatility, paper is extensively employed in packaging, construction, interior decoration, agriculture, and everyday life.[1,2,3] Despite these advantages, paper is inherently flammable and can easily ignite, thereby acting as a trigger for fire accidents that pose significant risks to human life, property, and the environment.[4,5] Consequently, imparting flame-retardant properties to paper has become an important research objective to both reduce fire hazards and broaden its range of applications.

Various flame-retardant modification methods have been proposed, including the direct surface application of flame-retardant chemicals,[6] the incorporation of flame-retardant additives into pulp during papermaking[1,2,3] and immersion techniques.[4] Several studies have demonstrated the effectiveness of such strategies. For instance, Katović *et al*.[7] applied N-hydroxymethyl-3-dimethylphosphonopropionamide solutions with melamine-formaldehyde or citric acid as binders, achieving significant improvements in flame retardancy of office paper. Similarly, Jindasuwan *et al*.[8] employed a coating mixture of monoammonium phosphate (MAP), poly(methylhydrogen siloxane) (PMHS), and poly(dimethyl siloxane) (PDMS) on mulberry paper via immersion, reporting enhanced self-extinguishing behavior and higher char residue in thermogravimetric analysis (TGA). Xu *et al*.[4] further synthesized a halogen- and formaldehyde-free ammonium phosphite and demonstrated that kraft paper immersed in this solution exhibited a substantial increase in the limiting oxygen index (LOI) from 19.1% to 48.2%. Likewise, Boran *et al*.[9] reported improvements in the burning properties of kraft paper treated with flame-retardant paints.

Among the available modification approaches, impregnation treatment represents a practical route for introducing flame-retardant agents into cellulosic paper. Previous studies have primarily focused on the type and concentration of the applied flame-retardant formulation. For example, Chen *et al*.[10] prepared flame-retardant cellulosic paper by impregnation using modified phytic acid at different concentrations and reported that increasing the treatment concentration substantially enhanced flame

retardancy, with the LOI increasing from 19.6% for untreated paper to 41.5% at an optimized treatment concentration. However, compared with the effects of flame-retardant type and concentration, the influence of repeated impregnation cycles as an independent processing parameter has received considerably less attention. In particular, the combined effects of treatment concentration and repeated impregnation on chemical retention and the subsequent flame-retardant, thermal, liquid-penetration, and printing properties of paper have not been comprehensively addressed. Therefore, systematic evaluation of both treatment concentration and immersion frequency may provide further insight into the relationship between chemical uptake and the resulting functional properties of flame-retardant papers.

Boron-based compounds, such as boric acid and borax, are well known for their flame-retardant activity and have been successfully applied to cellulose-based materials.[9,6,11] They act primarily through dehydration catalysis, glassy barrier formation, and synergistic interactions with other flame-retardant additives. In particular, Wang *et al*.[11] demonstrated that borate treatment can substantially improve the flame retardancy of kraft paper by promoting char formation and generating a protective B_2O_3-rich glassy layer during thermal decomposition. Borate-containing surface coatings have also been reported to act as effective flame-retardant barriers on paper substrates.[12] More recently, the development of multifunctional flame-retardant paper systems has further demonstrated the potential of material modification strategies to improve fire safety while maintaining other functional properties of paper-based materials.[13] Aluminum hydroxide, on the other hand, is widely recognized as an environmentally friendly, halogen-free flame retardant that decomposes endothermically, releasing water vapor and diluting flammable gases.

Based on this research gap, the present study aimed to systematically investigate the effects of both flame-retardant concentration and immersion frequency on the performance of commercial fluting paper. Boric acid (BA), borax (BX), and aluminum hydroxide (AH) were applied at different concentrations and immersion cycles, and their effects on chemical uptake, thickness, liquid-penetration behavior, flame retardancy, thermal stability, and printability were evaluated. By considering treatment concentration and repeated immersion simultaneously, this study seeks to establish relationships between flame-retardant retention and the resulting functional properties of paper and to identify treatment conditions capable of providing improved flame retardancy, without substantially compromising other properties relevant to practical paper applications.

EXPERIMENTAL

Materials

Commercial fluting papers, without any prior treatment, were supplied by Kahramanmaraş Kağıt Sanayi ve Ticaret A.Ş. These papers were selected as the substrate material for the experiments. As determined prior to the impregnation process, the initial average basis weight and average thickness of the control paper were 148.82 ± 4.37 g/m² and 0.230 ± 0.007 mm (230 ± 7 µm), respectively. The initial surface color of the control paper was characterized according to the CIE Lab* color system. The mean color coordinates were determined as L* = 70.40 ± 0.39, a* = 3.36 ± 0.34, and b* = 9.39 ± 0.50, based on three replicate measurements. Fire-retardant solutions were prepared using boric acid (BA, H_3BO_3), borax (BX, $Na_2B_4O_7 \cdot 10H_2O$), and aluminum hydroxide (AH, $Al(OH)_3$). The BA and BX chemicals were obtained from Balmumcu Kimya Sanayi ve Ticaret Ltd. Şti. (Balmumcu, Technical Grade), while AH was purchased from Merck Chemicals. All chemicals were of technical or analytical grade and were used without further purification.

The prepared fire-retardant solutions were applied to the fluting papers using the dipping (impregnation) method under controlled laboratory conditions. The general physicochemical properties of BA, BX, and AH are summarised in Table 1.

Method

Immersion of commercial papers in fire-resistant chemical solutions

Commercial fluting papers obtained from Kahramanmaraş Paper Factory, without any further processing, were cut into sheets of 27 × 36 cm. The papers were immersed in aqueous fire-retardant solutions prepared at six different concentrations (0%, 1%, 2.5%, 5%, 10%, and 15%). Borax (BX) was completely soluble in distilled water, whereas aluminum hydroxide (AH) exhibited solubility limitations at higher concentrations (10% and 15%), resulting in highly concentrated mixtures that were not applicable. Solutions containing up to 5% AH showed no dissolution problems. Boric acid (BA) could not be dissolved in distilled water alone; therefore, ammonia was added to adjust the pH to neutral conditions (pH 8.00), which enabled complete dissolution. The immersion process was performed for 10 s.

Table 1
General features of BA, BX and AH

Chemical properties	Boric acid (BA)	Borax (BX)	Aluminum hydroxide (AH)
Chemical formula	H_3BO_3	$Na_2[B_4O_5(OH)_4]•8H_2O$	$Al(OH)_3$ * x H_2O
Molar mass (g/mol)	61.83	381.38	78
Density (g/cm^3) (20 °C)	1.44	1.73	2.42
Melting point (°C)	171	75	300*
Solubility in water	46.5 g/L (20 °C)	51.4 g/L (20 °C)	0.0015 (20 °C)

*Elimination of water of crystallization

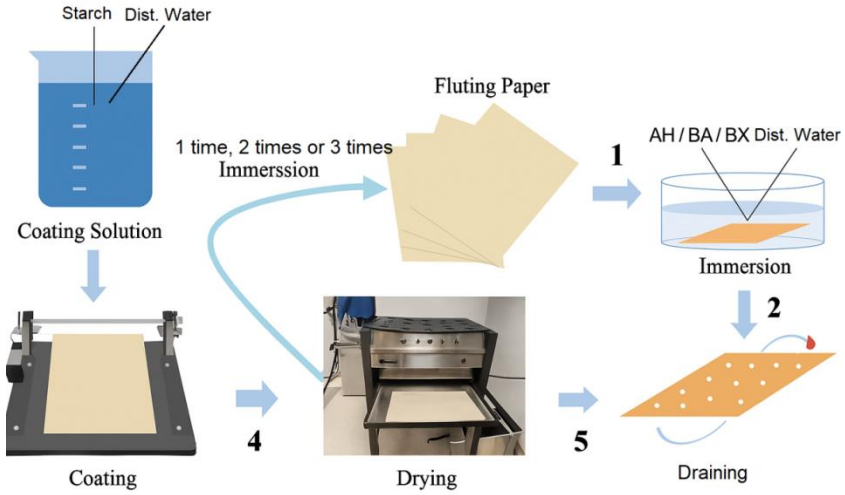


Figure 1: Application stages of flame retardant chemicals using the immersion method

After immersion, the wet papers were first drained on a mesh under ambient conditions to prevent adhesion to the dryer surface. Once dripping had ceased, the samples were dried in a cylinder dryer for one full rotation. Subsequently, a starch coating containing 15% starch was applied. For its preparation, a distilled water–starch mixture was cooked at 85–90 °C for 30 min using a magnetic stirrer. The temperature of the starch solution was then adjusted to 50–55 °C, and the coating was applied to the previously treated and dried papers using a laboratory-scale coating machine (K-coater). Finally, the coated papers were dried again by one full rotation in the cylinder dryer. The production stages are schematized in Figure 1.

Determination of weight changes

After immersion in each fire-retardant chemical at different frequencies, the papers were coated with starch solution. The initial weights of the papers prior to immersion were considered as the control group. In the single-immersion group, the papers were dried after the first immersion, coated with starch solution (15% starch), dried again, and their final weights were recorded. In the double-immersion group, the same procedure was repeated after the second immersion, and the final weights were determined. In the triple-immersion group, the papers were dried after the third immersion, coated with starch solution, dried again, and weighed. In this way, weight changes after each immersion were determined, and the amount of chemicals deposited on the paper surface was quantified.

Determination of thickness changes

The thicknesses of the commercial fluting papers obtained from Kahramanmaraş Paper Factory, without any processing, were measured in accordance with the TAPPI T 411 om-89 standard. The thickness of the papers prior to immersion in the fire-retardant solutions was compared with their thickness after immersion. Following immersion in different numbers of cycles for each fire-retardant chemical, the papers were coated with starch solution, and the starch-coated thickness measurements were also included in the evaluation.

Determination of water absorption properties

After the immersion process, the water resistance of the commercial fluting papers obtained from Kahramanmaraş Paper Factory was evaluated using an Emtec EST Surface and Sizing Tester device (Leipzig, Germany 2002). When a paper specimen initially comes into contact with water, a thin air layer is formed at the

paper–liquid interface, causing a fraction of the ultrasonic signal to be reflected. As wetting progresses, this interfacial air layer gradually disappears, thereby reducing signal reflection and increasing the intensity of the ultrasonic signal transmitted through the paper. Surface sizing restricts the immediate penetration of water into the surface fiber network, resulting in a gradual wetting process. Furthermore, when the reverse side of the specimen is sealed, air may become entrapped within the porous structure of the paper. As water progressively penetrates the paper structure and the wetted fraction increases, the transmission of ultrasonic waves through the specimen increases accordingly. This phenomenon constitutes the fundamental operating principle of the Emtec Surface & Sizing Tester (EST).[14]

The EST employs an ultrasonic liquid penetration technique in which ultrasonic waves are transmitted through the thickness of the paper specimen immediately after contact with the test liquid, while the transmitted ultrasonic signal intensity is continuously recorded as a function of time.[15] In the present study, the MAX-related parameter was evaluated and reported as ultrasound transmission time. This parameter represents the time required for the transmitted ultrasonic signal to reach its maximum level and is associated with the resistance of the paper surface to liquid penetration. Longer ultrasound transmission times indicate slower liquid penetration and, consequently, greater surface hydrophobicity and a higher degree of surface sizing. In surface-sized papers, this parameter can therefore provide an indirect indication of differences associated with the presence and distribution of sizing agents, such as starch, at the paper surface. Accordingly, ultrasound transmission time was used in this study to evaluate the effects of the treatments on the surface sizing and liquid-penetration behavior of the paper specimens.

Determination of fire resistance properties of papers

The fire resistance of the produced paper groups was evaluated by thermogravimetric analysis (TGA) and Limiting Oxygen Index (LOI) tests.

Thermogravimetric analyses were conducted using a Shimadzu TGA-50 thermal analyzer at a heating rate of 10 °C/min and a nitrogen flow rate of 20 mL/min. For each analysis, 10 mg of paper sample was used. The samples were heated from room temperature up to 600 °C under nitrogen atmosphere.

The Limiting Oxygen Index (LOI) test was performed in accordance with ASTM D2863-10 (2000) using an LOI apparatus (Dynisco, Heilbronn, Germany). Paper samples were vertically positioned inside a glass column with the aid of a holder. During testing, controlled mixtures of oxygen and nitrogen were introduced into the column. Combustion was initiated from the top edge of the paper samples, and the minimum oxygen concentration required to sustain burning was determined as a percentage. Three replicates were tested for each immersion group.

Determination of printing properties

The printing properties were evaluated according to the DIN ISO 2846-1 standard using mineral oil-based sheet-fed offset magenta ink with an IGT-C1 device under a pressure of 350 N. The total inked area was 720 cm^2. The device was equipped with two aluminum inking disks and one main roller, and the printing speed was set at 0.3 m/s. The test prints were left to dry under laboratory conditions. Once fully dried, the solid tone density and gloss of the printed samples were measured. Colorimetric measurements of the printed ink films (L*, a*, b*) were performed using an X-Rite eXact™ spectrophotometer.

RESULTS AND DISCUSSION

Weight change results

After the immersion cycles, a 15% starch coating slurry was applied to the paper surfaces. Following drying, the weight changes were measured. Figure 2 shows the results for the papers treated with BA as the flame-retardant chemical. Figure 2 shows the percentage weight changes of the papers treated with BA as flame-retardant chemical. Papers that were not subjected to flame-retardant immersion, but received the same starch coating as the treated samples, were used as the control (reference) group for calculating the percentage weight changes. Since the starch formulation and application conditions were kept constant for all groups, the differences in weight relative to the control can primarily be attributed to the retention of the flame-retardant chemicals.

The BA group showed a clear increase in paper weight with higher BA content and repeated immersion. Even at 1% BA, gradual increases were observed, while the largest gain occurred in the 15% BA group subjected to three immersions. Comparable results have been reported earlier.[4]

Figure 3 presents the weight changes of the BX group. The BX group exhibited similar behavior to the BA one. Weight increased with higher BX content and immersion frequency, with the most pronounced effect in the 15% BX group after three immersions. At lower concentrations (particularly 1% BX), the change was minimal, and the weight remained close to the control. In contrast, high BX

levels produced more distinct increases. The findings confirm that BX, like BA, remained in the paper matrix, in agreement with earlier studies.[4]

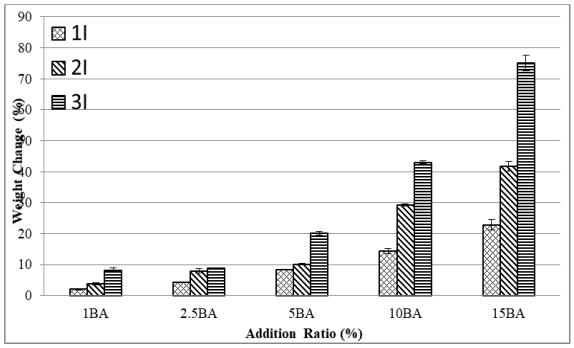


Figure 2: Weight changes of BA group papers

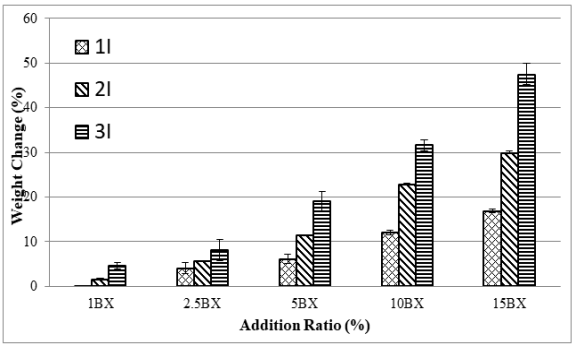


Figure 3: Weight changes of BX group papers

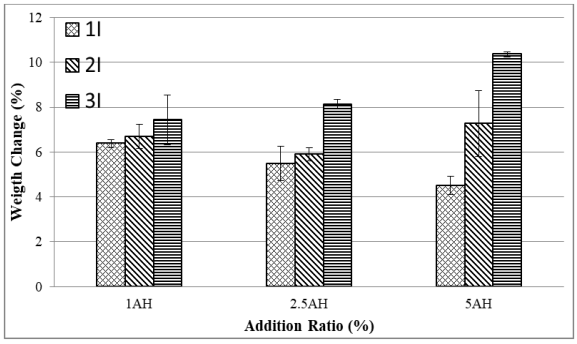


Figure 4: Weight changes of AH group papers

Comparison of the two groups showed that the maximum weight gain in the BA group (15BA3I) corresponded to ~75% relative to the control, whereas the BX group (15BX3I) showed ~47.5%. This represents a 27.5-percentage-point difference, with the BA treatment yielding approximately 57.9% greater chemical uptake than the BX treatment. Consistent with this finding, the BA-treated specimens exhibited higher fire-retardant retention than the BX-treated specimens across all treatment concentrations and immersion cycles.

The weight changes for the AH group are shown in Figure 4. The AH group followed the same general trend as BA and BX, with higher chemical concentrations and immersion cycles resulting in greater weight gain. This indicates retention of the flame-retardant within the paper, consistent with Xu *et al.*[4] However, unlike BA and BX, experiments with 10% and 15% AH were not possible due to its insolubility in water. After immersion, AH particles detached from the surface, and drying led to severe dusting, which made high concentrations impractical. As seen in Figure 4, gradual increases occurred in the 1% and 2.5% AH groups, while the 5% AH group showed the most evident weight gain.

Thickness change results

The thicknesses of the fluting papers prior to exposure to the flame-retardant chemicals were compared with those measured after the impregnation treatments. Following a predetermined number of impregnation cycles with each flame-retardant formulation, a starch-based surface coating was applied. The reported thickness values therefore incorporate the contribution of the starch-coated layer.

Figure 5 presents the dimensional changes in thickness of the paper groups treated with the BA chemical, both after the impregnation process and subsequent surface coating application.

The analysis of post-coating thickness values in the paper groups treated with the BA flame-retardant chemical via immersion revealed an overall increase in thickness across all groups. However, as shown in Figure 2, while the weight gain ratios were more pronounced in the groups treated with higher BA concentrations, a corresponding increase in thickness was not observed. This discrepancy is likely due to the homogeneous dissolution of BA in water, which facilitates its penetration into the

paper matrix. As a result, a substantial increase in paper weight was achieved, whereas thickness changes followed a more gradual trend. In particular, paper groups immersed three times in 5%, 10%, and 15% BA solutions exhibited more distinct weight gains compared to those immersed three times in the 2.5% solution. In terms of thickness, the percentage increases for the groups immersed three times in 1%, 2.5%, 5%, 10%, and 15% BA solutions were determined to be 10%, 23.9%, 12.6%, 16.2%, and 20.4%, respectively. Considering that the starch coating applied to the paper surface was evenly distributed and yielded consistent thickness values, the group immersed three times in the 2.5% BA solution exhibited the highest increase. These findings suggest that the papers were still capable of absorbing BA, even after the third immersion cycle. Furthermore, in the third immersion of the 15% BA group, the papers continued to absorb the chemical, with thickness values comparable to those of the papers immersed twice.

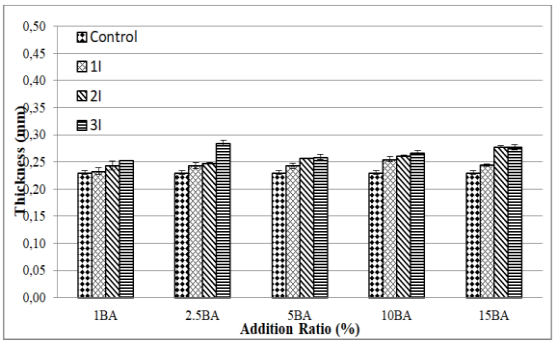


Figure 5: Thickness variations in BA group papers following impregnation and coating treatments

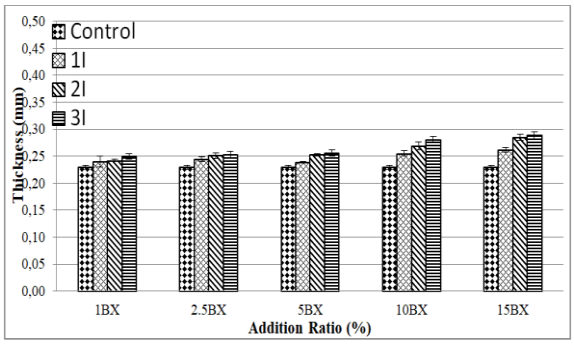


Figure 6: Thickness variations in BX group papers following impregnation and coating treatments

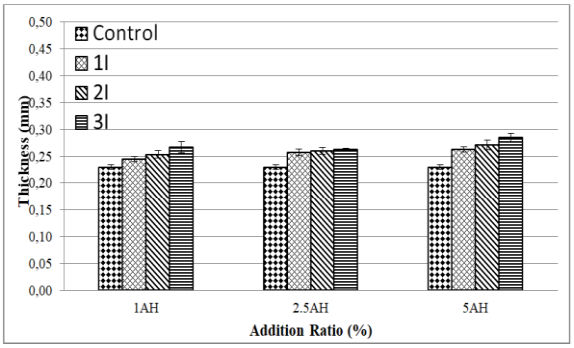


Figure 7: Thickness variations in AH group papers following impregnation and coating treatments

Figure 6 illustrates the thickness values of papers treated with BX following immersion and coating. In the groups treated with 1%, 2.5%, and 5% BX solutions and subjected to three immersion cycles, thickness increases were relatively close, measured at 8.5%, 9.9%, and 11.4%, respectively. In contrast, the groups treated with 10% and 15% BX solutions and immersed three times showed thickness increases of 21.9% and 25.6%, respectively. Taken together, these results indicate that BA penetrates the paper structure more effectively than BX.

The thickness variations of the papers treated with the AH chemical by immersion, followed by surface coating, are presented in Figure 7. In the groups treated with AH as the flame-retardant chemical, progressive increases in thickness values were observed relative to the control groups with increasing chemical concentration and number of immersion cycles. Specifically, the paper groups immersed once in 1%, 2.5%, and 5% AH solutions exhibited thickness increases of 6.4%, 12.0%, and 14.3%, respectively. For the groups subjected to two immersion cycles, the thickness increments were 10.2%, 13.0%, and 17.9%, while for those immersed three times, the corresponding increases were 16.0%, 14.3%, and 23.8%. These results clearly demonstrate the cumulative effect of both concentration and immersion frequency on the dimensional response of the papers.

A comparison of the thickness variations in the paper groups treated with BA, BX, and AH revealed noticeable differences between the chemicals. In the BA-treated samples, thickness increased in all groups after immersion and coating; however, the increments were not as proportional as the

corresponding weight gains. This outcome is likely related to the ability of BA to dissolve uniformly in water and penetrate the paper structure, which results in a marked increase in weight, while producing only gradual changes in thickness. In the BX-treated groups, thickness changes were relatively small at lower concentrations (1%, 2.5%, and 5%), but became more significant at higher concentrations (10% and 15%) and with repeated immersions. This pattern suggests that BX penetrates the paper to a lesser extent than BA. In the case of AH, increases in thickness were observed with higher concentrations and immersion cycles, particularly at 5%, although the trend was less consistent than for BA and BX. The irregular behavior of AH can be explained by its limited solubility in water, which leads to uneven deposition on the paper surface. Overall, the results indicate that BA shows the greatest penetration into the paper matrix, followed by BX, whereas AH demonstrates a more restricted and less uniform effect.

Water resistance results

Following the application of the flame-retardant chemicals by immersion in aqueous solutions, a starch coating was applied to the paper surfaces at a fixed concentration of 15%. The water repellency of the papers was then evaluated using the ultrasonic liquid penetration method. Figure 8 presents the bar charts of ultrasound transmission times for the paper groups subjected to different numbers of immersions in the BA solution.

The ultrasound transmission times presented in the graphs provide insights into the hydrophobicity and surface adhesion properties of the paper samples. Longer transmission times indicate improved adhesion and enhanced hydrophobicity of the paper surfaces. As illustrated in Figure 8, the immersion of the papers in BA solutions up to a concentration of 5% resulted in extended transmission times compared to the control group, suggesting an increase in surface hydrophobicity and stronger surface adhesion. However, when the BA concentration exceeded 5%, the transmission times progressively decreased, indicating faster water penetration into the paper matrix.

Furthermore, in paper groups treated with BA concentrations up to 5%, increasing the number of immersion cycles led to shorter transmission times, reflecting a decline in the physical performance of the papers. Nevertheless, when compared with the control samples, all groups produced with BA concentrations up to 5%, regardless of the number of immersions, exhibited superior results. The most favorable outcome was obtained in the group treated with 5% BA through a single immersion, while papers treated with 10% BA and a single immersion also demonstrated better performance than the control. In contrast, papers treated with multiple immersions at 10% BA, as well as all groups containing 15% BA, showed transmission times considerably shorter than those of the control samples. This reduction is likely due to the increasing amount of chemical deposited on the paper, which hindered the uniform application of the starch coating. As a result, the starch film layer was disrupted, diminishing the intended water-repellent effect of the coating.

Figure 9 presents the bar charts of ultrasound transmission times for the paper groups treated with BX solutions at varying immersion frequencies.

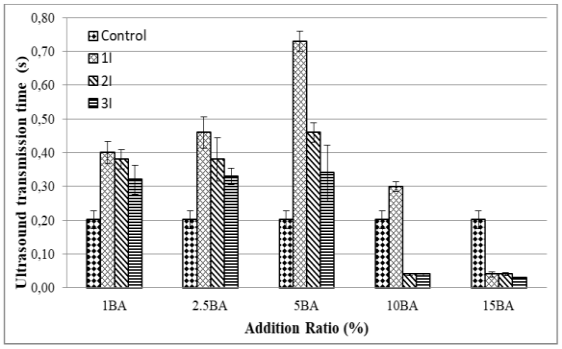


Figure 8: Ultrasound transmission times in BA group papers following impregnation and coating treatments

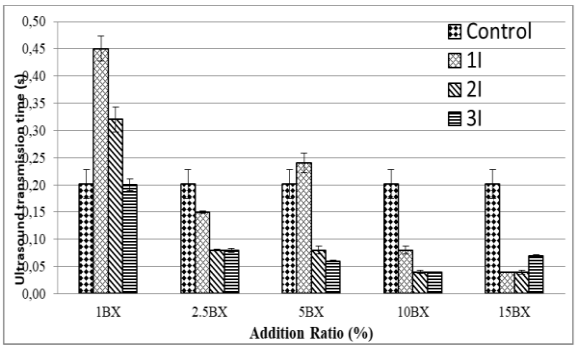


Figure 9: Ultrasound transmission times in BX group papers following impregnation and coating treatments

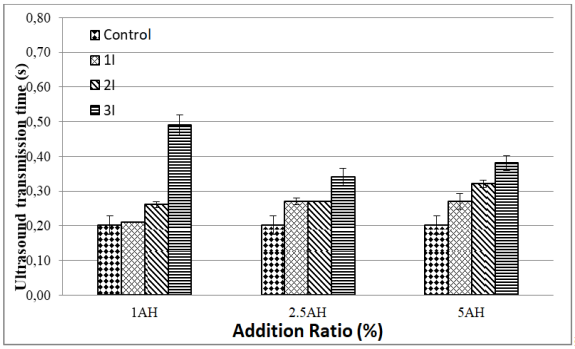


Figure 10: Ultrasound transmission times in AH group papers following impregnation and coating treatments

The examination of the ultrasonic transmission times in Figure 9 indicates that the most favorable results were obtained in the groups treated with 1% BX through a single immersion. Papers immersed twice in the 1% BX solution also performed better than the control group. However, with additional immersion cycles, the transmission times decreased, reflecting shorter water uptake times and increased surface hydrophilicity. For all groups produced with BX concentrations above 1% (with the exception of the single-immersion 5% BX group), the results were inferior to those of the control samples. This outcome is attributed to the residual fire-retardant chemicals left on the surface after immersion, which hindered the even distribution of the starch coating. The resulting disruption of the film layer reduced the intended water-repellent properties. Increasing the number of immersion cycles further elevated the chemical residue on the paper surface, leading to a substantial decline in hydrophobicity. The results also suggest that with higher BX concentrations, the chemical increasingly occupied the surface area, leaving little to no starch layer on the paper. The changes observed in the liquid-penetration behavior of borate-treated papers are also consistent with previous observations that borate-containing surface treatments can alter paper–liquid interactions. Çölük *et al*.,[12] for example, reported that the incorporation of barium borate into starch-based paper coatings decreased the contact angle, indicating that borate-containing formulations can substantially influence the wetting characteristics of the paper surface.

Figure 10 presents the bar charts of ultrasonic transmission times for the paper groups treated with AH at different immersion frequencies. In contrast to the trends observed with BA and BX, the use of AH as a flame retardant led to increased hydrophobicity with rising immersion cycles. Higher concentrations of AH also contributed to extended ultrasonic transmission times, indicating improvements in the physical performance of the papers. The only exception was observed in the three-immersion groups, where a slight decrease occurred when moving from 1% to 2.5% AH. This may be explained by the relatively lower solubility of AH in water compared to BA and BX, which allowed BA and BX to penetrate more effectively into the paper matrix. In the case of AH, incomplete solubilization likely limited penetration, causing the chemical to remain primarily on the paper surface and form a protective barrier against water ingress. Thus, AH appears to act as a surface-layer retardant, blocking water penetration rather than being absorbed into the paper structure.

Compared with the untreated control samples, the AH-treated papers generally exhibited increased resistance to water penetration, with the highest resistance observed in the group subjected to three immersion cycles in the 1% AH solution. Interestingly, the lowest resistance after the control was also recorded in the single-immersion 1% AH group. Unlike the BA- and BX-treated papers, the AH-treated samples exhibited improved water repellency with increasing numbers of immersion cycles. Furthermore, in contrast to the other flame-retardant chemicals, the gradual increase in AH concentration contributed positively to enhancing the hydrophobic behavior of the paper surfaces.

Fire resistance property results

Limiting oxygen index (LOI) results

To evaluate the flame resistance of the immersed paper samples, the limiting oxygen index (LOI) test was carried out in accordance with ASTM D2863-10 (2000). The LOI and weight change rate results for the boric acid (BA) groups are presented in Table 2.

The examination of these values shows that the control group papers fall within the B2 flammability class, indicating that they are easily flammable under normal atmospheric conditions.

Since atmospheric air contains approximately 21% oxygen, ignition trials were conducted at 17% oxygen, where the control papers burned rapidly. Attempts at even lower oxygen levels were unsuccessful, as the ignition source was extinguished before sustained combustion could occur.

In contrast, papers treated once with 5% BA shifted from the easily flammable class to the "difficultly flammable" category. For instance, the 5BA1I samples ignited at 29% oxygen, but extinguished shortly afterward; complete burning was only observed at 30% oxygen. Increasing the number of immersions led to further improvements in flame resistance, although the overall flammability classification remained unchanged. In the case of the 5BA2I samples, no ignition occurred at 32% oxygen, but localized smoldering was observed at 33%, and full combustion occurred at 34%. Similarly, the 5BA3I samples displayed smoldering at 34% oxygen and complete burning at 35%.

When the BA concentration was increased from 5% to 15%, all paper groups achieved the B0 classification, which corresponds to non-inflammable materials. The LOI values of the single- and double-immersion groups were similar, whereas a substantial increase was observed in the triple-immersion groups. In fact, the 15% BA samples subjected to three immersion cycles withstood oxygen levels as high as 47% without burning, representing the highest resistance recorded in the system.

The LOI results for the borax (BX) groups are presented in Table 3.

Table 2
LOI results for BA group papers

Weight changes (%)	Sample group	LOI (% O_2)	Flammability rating[a]
-	Control	20.00	B2
8.3	5BA1I	30.00 (0.00)*	B1
10.1	5BA2I	34.00 (0.00)	B1
20.1	5BA3I	34.00 (1.00)	B1
22.9	15BA1I	37.00 (1.73)	B0
41.7	15BA2I	36.67 (0.58)	B0
75.2	15BA3I	47.00 (0.00)	B0

*Numbers in parentheses represent standard deviation; [a] (B0: non-inflammable, LOI > 35; B1: difficultly flammable, 25 < LOI ≤ 35; B2: flammable, 20 < LOI ≤ 25)[4,16]

Table 3
LOI results for BX group papers

Weight changes (%)	Sample group	LOI (% O_2)	Flammability rating[a]
-	Control	20.00	B2
6.1	5BX1I	28.00 (0.00)*	B1
11.5	5BX2I	28.67 (0.58)	B1
19.1	5BX3I	38.67 (0.58)	B0
16.9	15BX1I	39.67 (0.00)	B0
30.0	15BX2I	46.00 (0.00)	B0
47.5	15BX3I	45.33 (0.58)	B0

*Numbers in parentheses represent standard deviation; [a] (B0: non-inflammable, LOI > 35; B1: difficultly flammable, 25 < LOI ≤ 35; B2: flammable, 20 < LOI ≤ 25)[4,16]

The limiting oxygen index (LOI) values of the groups treated with borax (BX) were examined to assess improvements in the flame resistance of the papers. The control samples were classified in the B2 flammability class, indicating that they are easily combustible under normal atmospheric conditions. Similarly to the BA-treated groups, the use of 5% BX led to noticeable improvements in flame resistance. Papers treated with a single immersion in 5% BX (5BX1I) were elevated to the "difficult-to-burn" category. While little difference was observed between single and double immersions, a significant enhancement in resistance was recorded in the samples subjected to three immersions at the same concentration. In fact, the 5BX3I samples advanced to the B0 classification, corresponding to non-inflammable materials. Within this group, some specimens exhibited slow, smoldering, flameless combustion at 39% oxygen, which self-extinguished after a period without further propagation. The mean LOI value for these samples was determined to be 38.67%. All groups

prepared with 15% BX were classified as B0, regardless of immersion frequency. While a clear difference was found between the single- and double-immersion groups, the LOI values of the double- and triple-immersion groups did not differ significantly.

In general, for both BA- and BX-treated papers, the LOI test identified the oxygen concentration required to sustain combustion, while the next lower concentration (at which no ignition occurred) was reported as the LOI value. At oxygen levels just above the LOI threshold, samples typically exhibited smoldering, flameless combustion. At concentrations approximately 2% higher, combustion proceeded more rapidly, resulting in accelerated charring of the papers.

The substantial increase in LOI observed for both BA- and BX-treated papers can be attributed to the characteristic condensed-phase flame-retardant mechanism of boron compounds. Wang *et al.*[11] reported that the thermal decomposition of boric acid and borates promotes the formation of a porous B_2O_3-rich glassy layer on the paper surface. This layer acts as a physical barrier that restricts heat and oxygen transfer and suppresses the release of combustible degradation products, while simultaneously promoting the formation of a more stable carbonaceous char. The pronounced increases in LOI obtained in the present study, particularly for the highly retained BA and BX treatments, are therefore consistent with the protective barrier and char-promoting mechanisms reported for borate-treated cellulosic materials.

The LOI results for the aluminum hydroxide (AH) groups are presented in Table 4.

Table 4
LOI results for AH group papers

Weight changes (%)	Sample group	LOI (% O_2)	Flammability rating[a]
	Control	20.00	B2
5.5	2.5AH1I	20.00	B2
4.5	5AH1I	20.00 (0.00)*	B2

*Numbers in parentheses represent standard deviation; [a](B0: non-inflammable, LOI > 35; B1: difficultly flammable, 25 < LOI ≤ 35; B2: flammable, 20 < LOI ≤ 25)[4,16]

The examination of the LOI values presented in Table 4 for the AH-treated groups revealed that the addition of 2.5% AH had little influence on flame resistance, whereas an increase to 5% resulted in improved resistance values. Similarly to the control samples, papers containing 2.5% AH ignited at a minimum oxygen concentration of 17%. At lower oxygen concentrations, the ignition source was extinguished, preventing reliable measurement of the LOI. Furthermore, the combustion classifications of all paper groups produced with AH remained unchanged, falling within the B2 category (flammable materials). The limited solubility of AH in water posed difficulties during sample preparation, and in many cases, paper specimens could not be successfully manufactured. In the groups where AH incorporation was possible, multiple immersions resulted in poor surface adhesion and significant powdering, with the deposited particles detaching after drying. Consequently, the AH groups did not achieve meaningful flame-retardant performance.

Thermogravimetric analysis results

To evaluate the thermal stability of the immersed paper samples, thermogravimetric analyses (TGA) were conducted, and the results were compared across the groups. Since in the AH series only the 5% concentration with a single immersion could be successfully prepared, TGA tests were limited to these samples alongside the control and the corresponding 5% single-immersion groups of the other flame retardants to allow for reliable comparison. The TGA and DTG data for the tested samples are summarized in Table 5.

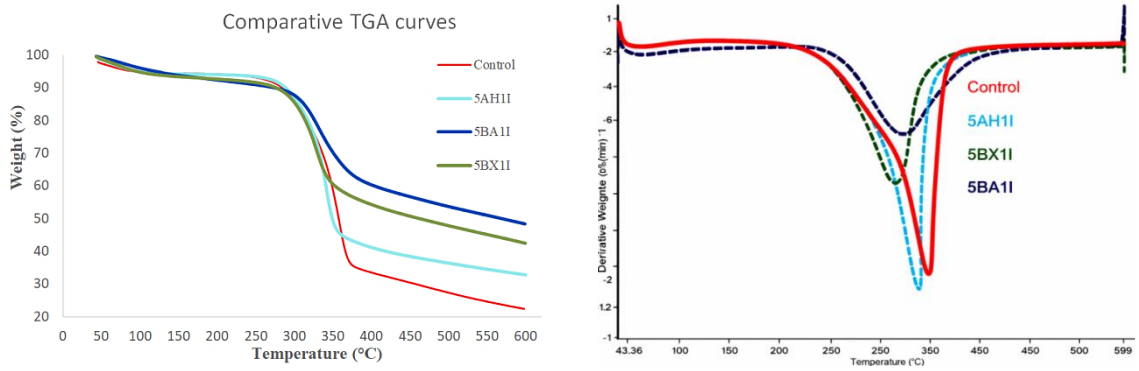
Comparative TGA and DTG curves of the control sample and the 5BA1I, 5BX1I, and 5AH1I specimens are presented in Figure 11. The examination of the DTG curves in Figure 11 (b) indicates that all groups exhibited a single thermal degradation stage. As shown in the comparative TGA curves in Figure 11 (a), no significant weight loss was observed in the control paper samples up to 163.40 °C. The minor changes occurring below this temperature are attributed to the release of moisture retained within the paper structure. The initial decomposition temperature for the control samples was determined to be approximately 200 °C. The main degradation occurred between 220 and 380 °C, accounting for about 68.18% weight loss, with the maximum decomposition rate observed at 355 °C.

This major decomposition stage is likely associated with the breakdown of hemicelluloses, cellulose, and lignin components.

Table 5
TGA and DTG data of paper samples immersed in flame-retardant solutions under a nitrogen atmosphere

Sample group	T_{in} (°C)	T_{max} (°C)	T_{end} (°C)	MD (%)	Residue at 520 °C (%)
Control	200.00	355.55	380.00	68.18	26.28
5BA1I	255.00	333.10	435.60	39.34	52.70
5BX1I	230.00	327.60	430.00	50.62	46.30
5AH1I	220.00	339.50	445.00	57.47	35.72

T_{in}: Initial decomposition temperature; T_{max}: Maximum decomposition temperature; MD: Maximum decomposition amount; T_{end}: Final decomposition temperature



a) b)

Figure 11: Comparative thermographics of immersion group samples: a) TG graphs, b) DTG graphs

In the literature, TG analyses of untreated wood components have reported a sharp weight loss between 231 and 350 °C, which has been attributed to the onset of wood degradation.[17,18] Hemicelluloses are known to decompose within the range of 224–325 °C, whereas cellulose degradation occurs between 324–407 °C.[19,20] Furthermore, previous studies have indicated that the cleavage of carbon–carbon (C–C) bonds in lignin occurs between 370 and 400 °C.[21] According to LeVan,[22] lignin retains approximately 50% of its initial mass even at 720 °C, while Burhenne *et al.*[20] reported lignin decomposition between 416–607 °C, with the maximum degradation observed at 557 °C. In addition, the starch present in the coating composition is also believed to contribute to the weight loss observed within the aforementioned temperature range, accounting for part of the 68.18% total degradation. Earlier research has shown that starch decomposition begins at around 237 °C and reaches its maximum at approximately 290 °C.[23] For the control samples, the residual mass at 520 °C was determined to be 26.28%. Üner *et al.*[18] reported a 33% residue for Oriental beech wood at 600 °C, while Sulaiman *et al.*[24] found 19.50% residue in particleboards at 800 °C. These findings confirm that the thermal behavior of the control samples is consistent with that of lignocellulosic materials reported in the literature.

The 5AH1I group displayed thermal properties similar to those of the control group, with the initial degradation starting at 220 °C. This early stage is attributed to the decomposition of hemicelluloses, starch, and aluminum hydroxide (AH). Previous studies have indicated that AH begins to decompose around 220 °C,[25] with maximum decomposition occurring at about 282 °C.[26] For the 5AH1I samples, the main decomposition was observed between 220–445 °C, with a total mass loss of 57.47% and a maximum decomposition rate at 339.5 °C. Compared with the control samples, the upper limit of the maximum decomposition temperature range shifted from 380 °C to 441 °C. Moreover, the residual mass at 520 °C was 35.72%, which is 9.44% higher than that of the control group.

The BA- and BX-modified papers exhibited similar thermal characteristics. The onset decomposition temperatures were 255 °C for the 5BA1I group and 230 °C for the 5BX1I group. The maximum decomposition temperatures were determined as 333.1 °C for 5BA1I and 327.6 °C for 5BX1I. At 520 °C, the residual masses were 52.70% for BA-modified samples and 46.30% for BX-

modified samples. Accordingly, the ranking of residual mass was BA > BX > AH > control. Üner *et al.*[18] reported that BA- and BX-modified beech wood showed increased residue at 600 °C, with BA yielding slightly higher residue values (56% for BX and 57% for BA at 4.70% loading). The results obtained in this study are consistent with those findings. A similar enhancement in char formation has been reported for borate-treated paper. Wang *et al.*[11] observed a marked increase in the residual mass of borate-modified kraft paper compared with untreated paper and attributed this behavior to the ability of boron compounds to promote the formation of a thermally stable carbonaceous residue. During heating, the decomposition products of boric acid and borates can form a glassy B_2O_3-rich phase that covers the fiber surface and limits further thermal degradation. The considerably higher residual masses obtained for the BA- and BX-treated papers in the present study therefore support a similar condensed-phase protection mechanism. This interpretation is also consistent with the LOI results, in which the BA- and BX-treated groups exhibited substantially greater resistance to sustained combustion.

Previous studies have also highlighted a direct correlation between residual mass in TG–DTA analyses of wood samples and their flame-retardant performance.[18,27,28] Based on this relationship, it can be inferred that, among the tested fluting papers produced via immersion, BA-treated groups provided the best thermal stability and flame-retardant performance, followed by BX, while AH offered the least improvement. These TGA findings are in good agreement with the LOI results.

Comparison of CIE L*a*b* color values in printed test papers

Paper, one of the most widely used substrates in printing technology, is adapted to different demands through various printing techniques. In this study, the fluting paper samples were subjected to offset printing, and the resulting colors were evaluated in terms of lightness, as well as red–green and yellow–blue coordinates.

The CIE L*a*b* color space is a three-dimensional, opponent color model based on rectangular (Cartesian) coordinates, with the L* axis representing lightness, and the a* and b* axes corresponding to red–green and yellow–blue contrasts, respectively.[29] The control paper exhibited mean CIE L*, a*, and b* values of 70.40 ± 0.39, 3.36 ± 0.34, and 9.39 ± 0.50, respectively. The positive a* and b* coordinates indicate that the paper possessed a slightly reddish and yellowish color tone, which is characteristic of unbleached or recycled fiber-based paper products. The relatively low standard deviation values observed for all color coordinates further indicate that the control paper samples had uniform and consistent surface color.

Table 6 presents the CIE L*, a*, and b* values of colors printed on fluting paper samples impregnated with BA. As shown, BA treatment resulted in a significant reduction in CIE L* values, indicating decreased brightness of the ink film. However, changes in brightness did not vary considerably with increasing BA concentration or number of immersion cycles. In contrast, CIE a* values increased markedly with BA treatment compared to the control, although further increases in BA concentration or immersion cycles produced no substantial variation. The CIE b* values, representing the yellow–blue axis, exhibited negligible differences between control and treated samples, regardless of chemical concentration or immersion number.

Table 7 presents the CIE L*, a*, and b* values of colors printed on fluting paper samples impregnated with BX. The results indicate that the color variations observed in the BX-treated paper samples after printing were comparable to those of the BA-treated groups. The most pronounced changes were recorded in the CIE a* values, followed by CIE L* and CIE b*, as summarized in tabular form.

Table 6
CIE L*, a*, b* values of color printed on papers immersed in BA chemical

Sample group	L*	a*	b*
Control	70.40	3.36	9.39
1BA1I	43.43	43.39	10.63
1BA2I	43.80	43.26	10.12
1BA3I	43.24	44.10	10.04
2.5BA1I	43.62	44.32	9.77
2.5BA2I	43.65	43.88	10.17
2.5BA3I	41.89	47.21	9.03
5BA1I	43.59	42.88	11.18
5BA2I	43.23	41.79	11.39
5BA3I	43.60	42.14	11.22
10BA1I	43.87	44.10	11.24
10BA2I	43.15	43.32	12.11
10BA3I	43.24	42.92	11.03
15BA1I	43.38	42.11	12.00
15BA2I	43.76	42.48	11.00
15BA3I	43.06	38.44	11.61

Table 7
CIE L*, a*, b* values of color printed on papers immersed in BX chemical

Sample group	L*	a*	b*
Control	70.79	3.02	8.89
1BX1I	44.32	42.36	10.56
1BX2I	43.94	43.51	10.17
1BX3I	43.65	42.85	10.64
2.5BX1I	44.42	43.48	9.73
2.5BX2I	43.85	43.46	10.34
2.5BX3I	43.17	42.98	12.25
5BX1I	43.06	43.09	11.67
5BX2I	43.76	42.49	11.58
5BX3I	42.73	42.25	11.70
10BX1I	43.25	43.43	10.95
10BX2I	42.34	44.26	12.67
10BX3I	42.71	44.05	10.35
15BX1I	43.12	43.51	10.50
15BX2I	43.37	43.11	11.43
15BX3I	42.90	40.09	12.41

Table 8
CIE L*, a*, b* values of color printed on papers immersed in AH chemical

Sample group	L*	a*	b*
Control	70.01	3.69	9.89
1AH1D	43.81	44.31	9.55
1AH2D	43.63	42.70	11.05
1AH3D	43.73	43.99	9.95
2.5AH1D	43.69	43.61	10.18
2.5AH2D	42.99	44.16	10.66
2.5AH3D	44.61	43.02	10.98
5AH1D	42.91	43.84	11.53
5AH2D	43.13	43.77	11.61
5AH3D	43.97	43.12	12.19

Table 8 presents the CIE L*, a*, and b* values of fluting papers treated with AH. The findings show a reduction in brightness (L*), an increase in the red component of the magenta hue (a*), and only a slight increase in yellowing (b*). Neither the increase in chemical concentration nor the number

of immersion cycles produced a significant influence on these results.

CONCLUSION

This study demonstrated that the application of different fire-retardant chemicals through immersion significantly influenced the physical, thermal, and combustion-related properties of fluting papers. The most favorable hydrophobic and flame-retardant performance was obtained in the BA-treated samples, particularly at a 5% concentration with a single immersion, whereas higher concentrations led to a reduction in water repellency. In contrast, BX showed limited effectiveness, with improvements observed only at low concentrations and minimal immersion cycles, while most other treatments underperformed compared to the control. AH, on the other hand, exhibited poor solubility in water, which restricted its applicability and limited its effectiveness as a flame-retardant agent.

LOI tests confirmed that BA and BX could successfully upgrade paper samples from the flammable B2 class to the non-inflammable B0 class, while AH-treated groups did not achieve comparable improvements. TGA results further supported these findings, showing the highest char residues in BA-treated papers, followed by BX, AH, and the control. Together, the LOI and TGA analyses indicated that BA provided the most effective enhancement in fire resistance among the tested chemicals.

In addition to fire performance, immersion treatments influenced the printability of the papers. Across all chemical groups, a decrease in brightness and an increase in redness were observed, whereas yellowness remained largely unaffected. Although such color shifts may limit aesthetic applications, these papers hold promise for functional use in areas where enhanced fire resistance is prioritized over visual appearance, such as in honeycomb cores used within doors or similar protective applications.

Finally, repeated immersion and drying cycles rendered the papers brittle and fragile, preventing mechanical testing. Adjustments to the immersion–drying sequence, as well as further exploration of immersion duration, could help reduce this brittleness and provide valuable insights for future studies. Overall, the findings highlight BA as the most effective fire-retardant additive among those tested, while also pointing to areas where further process optimization is required.

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