

Flammability studies of sodium thiosulphate or metabisulphite impregnated wood using cone calorimeter

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SUMMARY

Spruce wood boards impregnated with $\text{Na}_2\text{S}_2\text{O}_3$ or $\text{Na}_2\text{S}_2\text{O}_5$ were studied with the cone calorimeter. The presence of $\text{Na}_2\text{S}_2\text{O}_3$ lowered the average heat release rate in comparison to untreated material. The total amounts of CO and CO_2 production were reduced by the treatment and also the specific extinction area and mass loss rate decreased. Washing of the salt from the material with water caused partial loss of the properties. Addition of the second impregnation step using acids (HCOOH , H_3BO_3 or H_3PO_4) resulted in the fixation of the sulphur in wood, but gave not the results of single-step modification for thiosulphate. With $\text{Na}_2\text{S}_2\text{O}_5$ and without acid, the CO and time-to-ignition values were higher and average heat release rate smaller in comparison to unmodified material. Combined one step $\text{Na}_2\text{S}_2\text{O}_5/\text{H}_3\text{BO}_3$ treatment lowered the CO, CO_2 and specific extinction area values in comparison to the modification with $\text{Na}_2\text{S}_2\text{O}_5$, similarly like it was observed for $\text{Na}_2\text{S}_2\text{O}_3/\text{H}_3\text{BO}_3$ two-step-treatment. According to time-to-ignition values, $\text{Na}_2\text{S}_2\text{O}_5$ alone at 5% addition is a better flame retardant than $\text{Na}_2\text{S}_2\text{O}_3$ at 7%, but the effect is diminished at 10% amount or presence of acids. The total smoke release curves showed decrease due to modification in both phases of the process. Introduction of water washing as well as the acid treatment further lowered the values. The best results were achieved with 15% $\text{Na}_2\text{S}_2\text{O}_3$ –2% H_3PO_4 – H_2O system. According to the total smoke release curve the specimen produced more than five times smaller amount of smoke than untreated material in the first phase of the process. It seems that the concentration of $\text{Na}_2\text{S}_2\text{O}_5$ is less affecting the properties than the synergistic effect of the $\text{Na}_2\text{S}_2\text{O}_3$ or $\text{Na}_2\text{S}_2\text{O}_5/\text{H}_3\text{BO}_3$ system. Although the level of smoke is low, the presence of elemental sulphur causes smaller times-to-ignition than on starting material. Copyright © 2006 John Wiley & Sons, Ltd.

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1. INTRODUCTION

Wood materials could be impregnated with inorganic salts to improve their flame retarding properties [1–3]. After diffusion into the material they must be transformed into water-insoluble compounds to prevent the salt-washing. This could be achieved with sodium thiosulphate or metabisulphite as these compounds release the elemental sulphur by the action of acids in water solution [4–6]. Use of acids results also in negative hydrolysis of wood polysaccharides. The goal of the present paper was to find out how these processes affect the flammability and combustion process. We have used formic, phosphoric and boric acid. Boric acid is environmentally-friendly and known as wood protective agent against wood destroying organisms [7]. The samples were studied with the cone calorimeter, which simulates conditions different than limited oxygen index (LOI), thermogravimetry (TGA) and differential scanning calorimetry (DSC) methods used previously [1, 8]. The advantage of cone calorimeter is the quantity of data obtained in one experiment. We examined $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{Na}_2\text{S}_2\text{O}_5$ as the potential flame retardants, how washing with water affects the process and how effective is boric acid in comparison to formic and phosphoric acid. It is known that $\text{Na}_2\text{S}_2\text{O}_3$ slightly inhibits smouldering and also inhibit flaming. $\text{Na}_2\text{S}_2\text{O}_5$ inhibits only flaming and boric acid inhibits both flaming and smouldering when tested on cellulose [9].

2. EXPERIMENTAL

Spruce boards ($100 \times 100 \times 15$ mm) were impregnated with 5 or 15% water solutions of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ or $\text{Na}_2\text{S}_2\text{O}_5$ for 100 hours at room temperature (23°C), air-dried to constant weight and subsequently impregnated by dipping into 2% solution of formic, phosphoric or boric acid (Table I). The water-elution experiments were performed in distilled water for 100 hours. In one case (sample **12**) the impregnation was performed in one step with freshly prepared solution containing 5% $\text{Na}_2\text{S}_2\text{O}_5$ and 2% H_3BO_3 .

Table I. Uptake of chemicals in samples treated with fire retardants (FR).

Sample	Uptake of FR	Residue of FR after acid modification [% of original mass]	Residue of FR after leaching
1 (Unmodified)	—	—	—
2 (15% $\text{Na}_2\text{S}_2\text{O}_3$ modified)	7	—	—
3 (15% $\text{Na}_2\text{S}_2\text{O}_3$ - H_2O elution)	6	—	2
4 (15% $\text{Na}_2\text{S}_2\text{O}_3$ -2% HCCOH)	7	3	—
5 (15% $\text{Na}_2\text{S}_2\text{O}_3$ -2% HCOOH - H_2O)	7	3	3
6 (15% $\text{Na}_2\text{S}_2\text{O}_3$ -2% H_3BO_3)	7	4	—
7 (15% $\text{Na}_2\text{S}_2\text{O}_3$ -2% H_3BO_3 - H_2O)	6	—	3
8 (15% $\text{Na}_2\text{S}_2\text{O}_3$ -2% H_3PO_4)	4	2	—
9 (15% $\text{Na}_2\text{S}_2\text{O}_3$ -2% H_3PO_4 - H_2O)	6	4	3
10 (5% $\text{Na}_2\text{S}_2\text{O}_5$ impregnation)	5	—	—
11 (15% $\text{Na}_2\text{S}_2\text{O}_5$)	10	—	—
12 (5% $\text{Na}_2\text{S}_2\text{O}_5$ -2% H_3BO_3)	6	—	—

Materials were tested using a cone calorimeter, by the procedure defined in the ISO 5660 (1993) standard method. The tests were done at the horizontal orientation. The data obtained were: heat release rate (HRR; the heat evolved from the specimen, expressed per unit of exposed specimen area, per unit of time; kW/m^2); effective heat of combustion (the measured heat released, divided by the mass loss for a specified time period; MJ/kg); total heat release (total heat evolved by the sample over the entire test period, calculated by integrating the curve of heat release rate vs time; MJ/m^2); mass-loss rate (mass lost per time; g/s); specific extinction area (a measure of smoke obscuration averaged over the entire test period; m^2/kg); total smoke release (total smoke evolved by the sample over the entire test period, calculated by integrating the curve of rate of smoke release vs time; m^2); carbon monoxide production rate (g of CO /s); carbon dioxide yield (yield of CO_2 averaged over the entire test period, based on mass of sample consumed; kg of CO_2/kg of material) and time to ignition (determined visually and taken to be the period required for the entire surface of the sample to burn with a sustained luminous flame; s). Prior to the testing, the samples were conditioned at RH 55% and temperature 23°C for two weeks. All the samples were tested at the 50 kW/m^2 flux and the edge frame was used for all tests. In some experiments three identically modified samples were analysed, for reproducibility proof. According to the obtained values the fluctuation of results was less than 7%. We assume this was mainly due to fluctuation of the specimen's initial mass as this was the most fluctuating parameter.

3. RESULTS AND DISCUSSION

3.1. Effect of $\text{Na}_2\text{S}_2\text{O}_3$ impregnation on HRR/CO

Impregnation with $\text{Na}_2\text{S}_2\text{O}_3$ solution and drying the material gained 7% of weight (sample **2**). This resulted in smaller average HRR value as well as the effective heat of combustion (EHC; Table II) in comparison to untreated material (sample **1**). Also mass loss rate (MLR), specific extinction area (SEA), CO_2 and CO values decreased. The value of the lost mass was the smallest in comparison to all studied samples. As $\text{Na}_2\text{S}_2\text{O}_3$ decomposes, it might be possible that some released elemental sulphur is incorporated into the wood cell walls. On the other hand, the decrease of time-to-ignition indicates that a lot of the additive contributed to earlier ignition. By washing the sample in water 4% of the material weight could be eluted (sample **3**). The average value of HRR is smaller than on unmodified material, but increased in comparison with unwashed sample **2** (Table II). MLR value was higher than for the specimen **2**, while the SEA and CO_2 values were between those measured on sample **1** and **2**. This is probably due to partial washing of the salt. The total CO production was the smallest from all samples studied. It seems that even at 2% of additive incorporated the method is effective. That is why the HRR average value and CO production are the process main parameters. The decrease of times-to-ignition is caused by flaming of elemental sulphur.

3.2. Effect of subsequent acid treatment and water leaching on HRR/CO

The addition of formic acid to the procedure resulted in sample with 3% of additive content (sample **4**). HRR, EHC and MLR average values were smaller than for unmodified material as well as SEA, CO_2 and CO values. In comparison to sample **2** the mass loss rate increased as well as CO and CO_2 values. By elution of the sample with water no further decrease of weight was observed (sample **5**) and also the average HRR values were close to sample **4**. The CO production decreased by water-washing similarly for sample **5**, in comparison to **4** or like on

Table II. Cone calorimeter data on Na₂S₂O₃ and Na₂S₂O₅ impregnation.

Sample*	1	2	3	4	5	6	7	8	9	10	11	12
Heat average release rate (kW/m ²)	108	83	88	95	91	81	80	71	79	97	90	89
Effective heat of combustion (MJ/kg)	12.4	10.0	11.4	11.5	11.8	11.5	11.9	10.2	11.5	10.6	10.0	10.0
Total heat release (MJ/m ²)	80.0	43.3	54.6	53.0	55.2	49.8	57.2	46.7	54.1	62.1	57.2	59.3
Mass loss rate × 1000 (g/s)	79	57	69	73	70	66	62	64	64	85	83	81
Mass lost (%)	68.34	57.63	64.77	63.19	64.71	63.75	67.09	60.36	65.94	61.72	59.59	61.40
Specific extinction area (m ² /kg)	44	40	30	43	31	15	10	11	7	44	38	18
CO production rate × 10 ⁷ (g/s)	995	188	2.27	291	6.15	338	140	4570	35.4	2200	2510	383
Total CO × 10 ⁵ (g)	728	95	1	161	4	210	99	2994	24	1353	1529	247
Total CO ₂ (g)	69.3	35.1	44.8	43.1	45.7	40.3	48.0	40.0	42.3	52.7	49.4	47.9
CO ₂ production rate × 10 ³ (g/s)	94	69	72	78	77	65	68	62	62	86	81	74
CO ₂ yield × 100 (kg/kg)	121	92	107	106	111	103	113	100	101	102	98	91
Time to ignition (s)	18	4	8	12	16	11	3	4	9	24	15	14

*Refer to Table I.

sample **3** when compared with **2**. It indicates that part of the additive, which could be washed from the surface, is not effective and only that part, which remained inside and could not be gasified, is effective.

The use of boric acid in the second step of modification gave 4% increase of material weight (sample **6**). HRR average value was smaller than for unmodified material, while the shape of both peaks of samples **2–6** on the HRR curve was similar (Figure 1). This demonstrates that from the shape of the curves it could not be distinguished how the mechanisms of individual processes are differing. It only shows that the areas under individual curves for treated samples are smaller than for unmodified material. This is also sufficiently demonstrated by average HRR value which we consider more illustrative. Total CO production was bigger than on samples **2–5**. By the elution with water 1% of sample weight was eluted and 3% of the additive on the weight of unmodified material remained (sample **7**). The average HRR value dropped slightly with water elution process, while EHC value increased. MLR decreased and SEA was the smallest in comparison to all previous samples. The total CO amount and CO₂ yield were bigger than on eluted samples after modification with Na₂S₂O₃ or Na₂S₂O₃/HCOOH. As we know that the process consists of two phases as well as the complexity defined with all the listed parameters the main factor seems to be the time-to-ignition. This value was smaller for samples **2–7** in comparison to unmodified material. It seems not to be the question of Na₂S₂O₃ concentration but the amount of elemental sulphur released and incorporated inside the material.

The introduction of H₃PO₄ in the second step (sample **8**) resulted in 2% additive content and decreased average HRR in comparison to samples **1–7**. While again the first HRR peak could not be distinguished from samples **2** to **7**, the second peak was flatter and smaller than for boric acid treatment and also smaller than on sample treated only with Na₂S₂O₃. The total CO

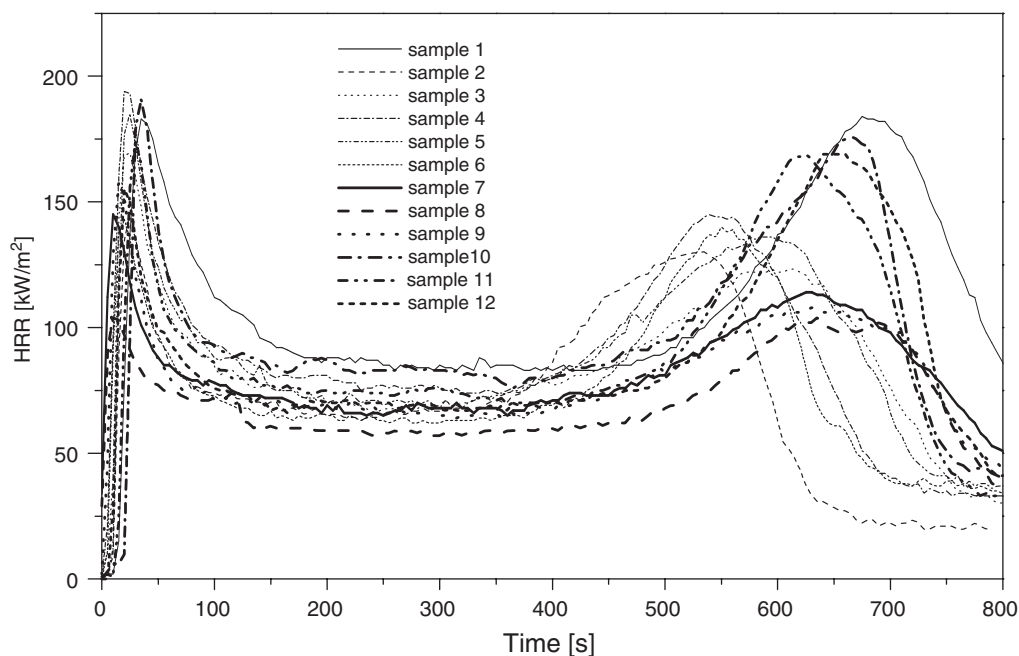


Figure 1. Heat release rates of samples (legend as in Table I).

amount was the biggest from all studied samples and CO_2 yield was smaller than on analogical samples when formic or boric acids were used. It might be due to the effect of acid strength. By washing with water (sample **9**) there was only 1% decrease in sample weight and the measured HRR increased in comparison to sample **8**. The specific extinction area decreased with the water elution and was smaller than for samples **1–8**. This is related to the amount of smoke produced.

3.3. Effect of $\text{Na}_2\text{S}_2\text{O}_5$ impregnation on HRR or CO production

The treatment of spruce boards with 5% solution of $\text{Na}_2\text{S}_2\text{O}_5$ results in 5% increase of weight of the material (sample **10**). The average HRR and CO_2 yield is smaller than on starting material while total CO production increased. Although only 5% concentration was used in this case, the results are comparable to data obtained on samples treated with 15% $\text{Na}_2\text{S}_2\text{O}_3$. With 15% $\text{Na}_2\text{S}_2\text{O}_5$ solution the impregnation resulted in 10% content of additive (sample **11**). All the measured values except CO value, were smaller than for sample **10**. By impregnation of spruce boards with freshly prepared solution containing 5% $\text{Na}_2\text{S}_2\text{O}_5$ and 2% H_3BO_3 (sample **12**; 6% additive content), HRR, MLR and SEA values further decreased and also CO amount and CO_2 yield values decreased. The average HRR value for $\text{Na}_2\text{S}_2\text{O}_5$ treatment (sample **11**) was bigger than obtained with $\text{Na}_2\text{S}_2\text{O}_3$ (sample **2**). This might be due to greater content of thiosulphate than metabisulphite in the specimens.

3.4. Time to ignition

Unmodified spruce board was ignited after 18 s from the beginning of the process (Table II). Most of the samples modified with $\text{Na}_2\text{S}_2\text{O}_3$ or $\text{Na}_2\text{S}_2\text{O}_5$ had smaller times to ignition. The only

sample with longer time to ignition was sample **10** impregnated with 5% of $\text{Na}_2\text{S}_2\text{O}_5$. The smallest time was obtained on sample treated with 15% $\text{Na}_2\text{S}_2\text{O}_3$ –2% H_3BO_3 – H_2O (sample **7**). It indicates that the elemental sulphur is more intensively produced by boric acid, which accelerates the formation of burning gases more than other samples. The greatest value for sample **10** indicates the better flame-retardant properties of $\text{Na}_2\text{S}_2\text{O}_5$ than with $\text{Na}_2\text{S}_2\text{O}_3$ and sufficient effectiveness of 5% concentration in comparison to higher amounts of additive.

3.5. Total smoke release effect

The total smoke release (TSR) process during the test for unmodified material had two phases (Figure 2). The first ended after about 300 s and is related to surface degradation, while the second started after about 500 s from the beginning of the test and might be related to residue degradation. On sample **2** the shape was similar, but less smoke was produced in both phases and phase two started earlier. Due to partial elution of additive on the surface with water (sample **3**), less smoke was produced on sample **3** than on samples **1** and **2** at both phases. Second step impregnation with HCOOH increases TSR values of specimen **4** in comparison to samples **2** and **3**, but they gave slightly smaller response in both phases than unmodified material. Water-eluted sample **5** gave smaller TSR value in first phase than specimen **4** and also less smoke was released than on samples **2** and **3**. The treatment with H_3BO_3 (sample **6**) further lowered TSR values in both phases in comparison to previous samples. Water-elution on sample **7** resulted in additional decrease of TSR values. The shape of curves **8** and **9** indicates that the best TSR results were obtained on samples modified with H_3PO_4 while also the water-elution improved the result. Treatment with 5% $\text{Na}_2\text{S}_2\text{O}_5$ (sample **10**) gave similar results like one-step 15% $\text{Na}_2\text{S}_2\text{O}_3$ treatment and logically with 15% $\text{Na}_2\text{S}_2\text{O}_5$ (sample **11**) more smoke was produced than on sample **10**. The subsequent boric acid treatment (sample **12**) resulted in

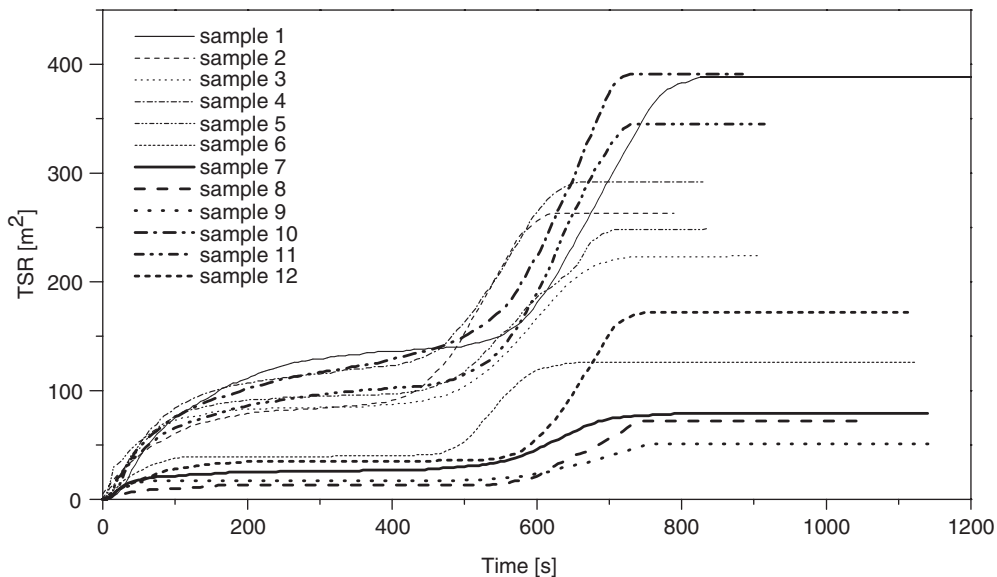


Figure 2. Total smoke release of samples (legend as for Figure 1).

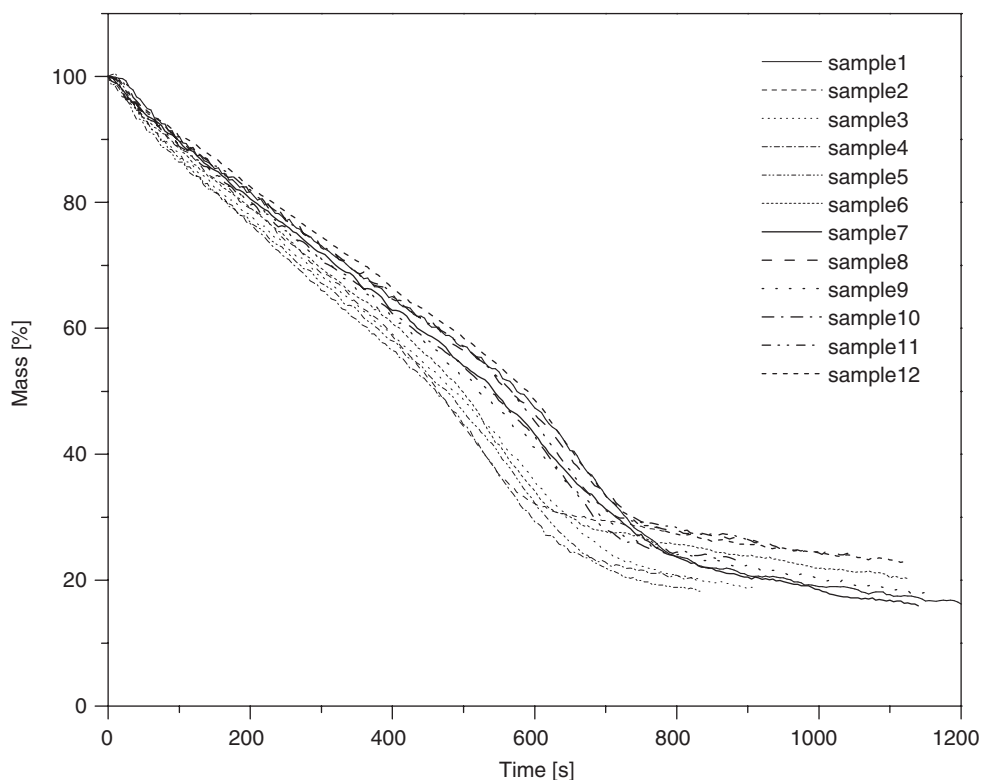


Figure 3. Mass release of samples (legend as for Figure 1).

similar TSR first step as on 15% $\text{Na}_2\text{S}_2\text{O}_3$ –2% H_3BO_3 – H_2O treated sample 7. It could be concluded that phosphoric and boric acid affected the TSR values more than the presence of sulphur-containing compounds. According to the TSR curve the specimen 7 produced more than five times smaller amount of smoke than untreated material in the first phase of the process. It seems that the concentration of $\text{Na}_2\text{S}_2\text{O}_5$ is less affecting the properties than the synergistic effect of the $\text{Na}_2\text{S}_2\text{O}_3$ or $\text{Na}_2\text{S}_2\text{O}_5/\text{H}_3\text{BO}_3$ system.

3.6. Mass loss of specimens

Mass loss of samples during initial 600 s of the treatment was greater or close for all the modified samples in comparison to unmodified wood (Figure 3). The exception was 5% $\text{Na}_2\text{S}_2\text{O}_5$ –2% H_3BO_3 sample modified in one step. This could be due to formation of bigger amount of insoluble compounds inside the specimens. Similarly like on samples analysed with dynamic TG the H_3PO_4 -treated samples 8 and 9 gave bigger residues at later stages of the process in comparison to the unmodified material although the temperature profile of these two processes is dramatically different [10]. In comparison to slow linear increase of temperature programmed for TGA experiments, the temperature increases much quicker when cone calorimeter is used [11, 12]. The bigger residues are due to phosphorus incorporation into the material during

burning. From the comparison of Figures 1–3 it is evident, that all three types of relations are affected by the effect of thickness of specimens [13]. This effect was not observed on synthetic polymers, when the third dimension was minimalized [14, 15]. The differences in HRR or mass vs time relations were not that evident like those of TSR on Figure 2.

4. CONCLUDING REMARKS

The treatment of spruce wood boards with $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{Na}_2\text{S}_2\text{O}_5$ resulted in a decrease of HRR, while the subsequent elution with water and further treatment with acids increased the values of this parameter. Total CO production was the smallest on $\text{Na}_2\text{S}_2\text{O}_3\text{-H}_2\text{O}$ treated sample **3**, while the smallest CO_2 yield was on sample **12** treated with $\text{Na}_2\text{S}_2\text{O}_5/\text{H}_3\text{BO}_3$. Time-to-ignition values decreased with modification due to flaming of formed elemental sulphur in all cases except for 5% $\text{Na}_2\text{S}_2\text{O}_5$ treatment. TSR values were positively affected more with boric and phosphoric acid, than with $\text{Na}_2\text{S}_2\text{O}_3$ or $\text{Na}_2\text{S}_2\text{O}_5$. The modification causes greater loss of mass with the exception of 5% $\text{Na}_2\text{S}_2\text{O}_5\text{-2% H}_3\text{BO}_3$ sample modified in one step. In this way the elemental sulphur was incorporated inside the material in the most effective way. According to HRR and mass vs time graphical relations, the results were similar, while according to TSR curves the most effective treatment was with 15% $\text{Na}_2\text{S}_2\text{O}_3\text{-2% H}_3\text{PO}_4$ (sample **8**) when the subsequent washing (sample **9**) did not affect the product.

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