**Drago Katović,**
**Sandra Flinčec Grgac,**
**Sandra Bischof-Vukušić,**
***Andrea Katović**

**University of Zagreb,**
**Faculty of Textile Technology,**
**Department of Textile Chemistry & Ecology**
Savska 16/9 10000 Zagreb, Croatia
E-mail: sbischof@ttf.hr

***University of Calabria,**
**Faculty of Engineering**
**Department of Chemical Engineering and Materials**
Via P. Bucci, Cubo 44 A, Rende (CS), Italy
E-mail: katovic@unical.it

# Formaldehyde Free Binding System for Flame Retardant Finishing of Cotton Fabrics

**Abstract**
*The promising application of citric acid (CA) and 1,2,3,4-butanetetracarboxylic acid (BTCA) for the purpose of flame retardant (FR) finishing was investigated. Both polycarboxylic acids (PCAs) were applied as an environmentally friendly binder in a reaction with N-hydroxymethyl-3-dimethylphosphonpropionamide. The results were compared with a conventional agent based on melamine formaldehyde. The purpose of melamine resin is to provide nitrogen in order to enhance the flame retarding performance of the treated fabric through synergism with phosphorus. In our previous investigations it was determined that the best catalyst to be used with PCAs is sodium hypophosphite monohydrate (SHP). The FR effectiveness was tested according to the ISO 6940 method, as well as with the limiting oxygen index (LOI) technique according to ASTM D 2863-97. Moreover, the thermal degradation of raw cotton and FR treated cotton fabrics was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).*

**Key words:** *flame retardant finishing, cotton, citric acid, BTCA, organophosphorus agent, TGA, DSC, LOI.*

## Introduction

Incorporating a flame retardant in combustible materials is a common procedure in preventive fire safety measures and is applied to reduce the risk of fires. One of the most commercially successful agents is N-methylol dimethylphosphonpropionamide (FR), known under the trade name of Pyrovatex CP New. Its reaction with cellulose hydroxyl is shown in the following scheme:

$$R\text{-}NHCH_2OH + HO\text{-}Cell \rightarrow R\text{-}NHCH_2O\text{-}Cel + H_2O$$

Besides this, it can self polymerise and form oligomers by condensation reactions, such as the following:

$$R\text{-}NHCH_2OH + HOCH_2HN\text{-}R \rightarrow R\text{-}NHCH_2OCH_2HN\text{-}R + H_2O$$

The laundering durability of cotton fabrics treated with FR agents can be improved with resin applications. Organophosphorus agents are combined with melamine resins and an acid as catalyst i.e. phosphorus acid. The purpose of melamine resin is to provide nitrogen in order to enhance the flame retarding performance of the treated fabric through synergism with phosphorus [1]. Phosphoric acid might decrease the tensile or tear strength of cellulose fabrics, and hence after FR treatment, the treated material is typically neutralised in an alkaline bath. A further negative consequence of the usual organophosphorus compound is formaldehyde release [2], in particular when trimethylolmelamine resin (MF) is used [3].

In this way, more durable linkages are obtained with the organophosphorus agent and a binder which actually reacts efficiently with cellulose than in the system without the binder, presented in the first scheme. The organophosphorus agent can react via its methylol group with cellulose. As binders for organophosphorus FR agents, either resins or reactants with at least 2 carboxylic groups can be applied. C. Q. Yang and co-authors investigated the applicability of 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU) as a binder in FR finishing [4, 5], while experiments with 1,2,3,4-butanetetracarboxylic acid (BTCA) applied to cotton or cotton/PA blends are thoroughly described in [6]. Blanchard et al. investigated the applicability of some phosphorus based polycarboxylic acids (PCA) as FR agents for cotton and cotton/PES blends [7], while Wu et al. investigated the FR effectiveness of fleece treated with different PCAs [8].

The polycarboxylic acid is linked to the cellulose hydroxyls with ester linkages. Under the influence of heat, during the curing process, at the first step of the reaction cyclic anhydrides are formed, while in the second step they react in the presence of a phosphorus-based catalyst, hence ester bonds are formed with cellulose hydroxyls. The role of the catalyst is to cause the formation of linkages among polycarboxylic acid and cellulose, while one of the parallel reactions is cellulose phosphorylation.

The efficiency of citric acid as a crosslinking agent has already been proven for durable press (DP) finishing [9], as well as for the FR treatments of paper [10]. At the same time, it is economically and environmentally friendly. Its greatest disadvantage is the yellowing of white material under a high curing temperature [11, 12]. This eco-friendly agent was used in our study as a substitute for the melamine resin, whose nitrogen enhances the flame retardant performance through synergism with phosphorus. The possibility of replacing MF resin with CA and BTCA has been investigated in this paper. The effectiveness of this novel low formaldehyde release treatment is presented.

## Experimental

The fabric used was 100% cotton, desized, scoured, bleached and mercerised, weighing 155.5 g/m². Impregnation was performed by means of a laboratory padder at Benz, Zurich, Switzerland with a wet pick-up of approximately 100%. The bath formulations are shown in ***Table 1***.

After the impregnation step, the samples were dried at 110 °C for 2 minutes and cured according to the conditions shown in ***Table 1***. Home domestic laundering washing (HDLW) was performed at 70 °C for a duration of 30 minutes in the presence of 5 g/l of standard detergent (ECE detergent 77, produced by Henkel). Thermal analyses of the cotton materials were performed in a flowing synthetic air atmosphere (30% oxygen, flow rate of 150 ml/min) using a Netzsch STA 409 analyser controlled by a PC system. TG (thermal gravimetric) and DSC (differential scanning calorimetry) thermograms of the samples were obtained from ambient temperature to 1000 °C at a heating


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rate of 10 °C/min. Prior to the thermal analyses, the cotton fabrics were cut into small pieces with an average weight of ca. 1 mg, while the samples analysed were approximately 11 mg. Moisture transfer was avoided by using latex gloves for the sample preparation.

The wrinkle recovery angles (WRA) were determined according to ISO 2313, vertical flammability according to ISO 6940 and LOI (limiting oxygen index) according to ASTM D 2863-97 on a Dynisco model 230. Formaldehyde content was determined according to ISO 14184-1:1998. The whiteness degree was measured on a spectrophotometer: Datacolor – Spectraflash SF 300 with a Data Match 300 programme according to AATCC 110-2000, and the phosphorus content was determined by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) at Varian, Vista MPH.

## Results and discussion

The organophosphorus compound (Pyrovatex new) was combined with BTCA or CA as binders and sodium hypophosphite (SHP) as catalyst. Moreover two reference samples were prepared with and without theMF agent, respectively. The vertical flammability of the cotton materials treated following the four baths' conditions is presented in ***Table 2***. It can be noticed from the results that all baths significantly improved the flame retardant properties of the cotton materials treated.

The untreated material completely burned, as expected. The FR finishing with the organophosphorus agent combined with MF was found to be the most effective for unwashed samples as well as those tested after the 1-30 HDLW cycles. The materials treated with the FR agent without MF gave satisfactory flame retardant (FR) effects, durable up to 15 washing cycles. Treatment with CA and BTCA gave improved FR results in comparison to the samples treated solely with the FR agent. The bath containing CA could withstand 20 washing cycles, while BTCA gave a durability of up to 15 washing cycles. The bath containing MF agents gave superior FR effectiveness, durable for more than 30 HDLW cycles; however, its greatest disadvantage is the negative environmental impact due to the free formaldehyde release.

***Table 1.*** *Treatment conditions.*

| Number of bath | FR agent / conc, g/l | Other agent / conc, g/l | Catalyst / conc, g/l | Tenside / conc, g/l | Curing time, s | Curing T °C |
|---|---|---|---|---|---|---|
| 1 | Organophosphours / 400 | / | / | NI / 1 | 300 | 150 |
| 2 | | MF / 65 | $H_3PO_4$ / 20 | | | |
| 3 | | BTCA / 70 | SHP / 65 | | 90 | 180 |
| 4 | | CA / 70 | | | | |

***Table 2.*** *Vertical flammability of the cotton fabric treated with baths 1-4; * Material is completely burned.*

| Number of washing cycles | Number of bath | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 (FR) | | 2 (FR+ MF) | | 3 (FR + BTCA) | | 4 (FR + CA) | |
| | Time of burning, *s* | Char length, *mm* | Time of burning, *s* | Char length, *mm* | Time of burning, *s* | Char length, *mm* | Time of burning, *s* | Char length, *mm* |
| 0 HLWD | 0 | 40 | 0 | 41 | 0 | 42 | 0 | 42 |
| 1 HLWD | 23 | 55 | 1 | 45 | 10 | 55 | 9 | 45 |
| 5 HLWD | 45 | 60 | 2 | 50 | 10 | 68 | 11 | 50 |
| 10 HLWD | 45 | 65 | 7 | 58 | 15 | 80 | 35 | 60 |
| 15 HLWD | 55 | 70 | 7 | 65 | 23 | 82 | 43 | 70 |
| 20 HLWD | 55 | * | 8 | 70 | 26 | 95 | 46 | 76 |
| 25 HLWD | 50 | * | 19 | 73 | 30 | * | 52 | 88 |
| 30 HLWD | 45 | * | 21 | 78 | 39 | * | 59 | * |

***Table 3.*** *The LOI of the cotton treated with baths 1-4.*

| Number of washing cycles | Number of bath | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 (FR) | | 2 (FR+ MF) | | 3 (FR + BTCA) | | 4 (FR + CA) | |
| | Time of burning, s | LOI, % | Time of burning, s | LOI, % | Time of burning, s | LOI, % | Time of burning, s | LOI, % |
| 0 HLWD | 60 | 38 | 59 | 39 | 51 | 34 | 54 | 33 |
| 1 HLWD | 70 | 36 | 63 | 37 | 65 | 32 | 72 | 32 |
| 5 HLWD | 92 | 33 | 65 | 35 | 61 | 30 | 77 | 29 |
| 10 HLWD | 88 | 30 | 64 | 33 | 72 | 29 | 86 | 29 |
| 15 HLWD | 108 | 28 | 60 | 29 | 68 | 27 | 92 | 27 |
| 20 HLWD | 98 | 25 | 69 | 29 | 58 | 27 | 92 | 27 |
| 25 HLWD | 96 | 25 | 80 | 28 | 60 | 26 | 90 | 26 |
| 30 HLWD | 94 | 24 | 88 | 28 | 68 | 24 | 84 | 25 |

The limiting oxygen index technique provides a quantitative measure of reduced flammability for fabrics over a range of chemical treatments. The results of the LOI measurement are presented in ***Table 3***. The LOI of the untreated sample was determined to be 18% (with a time of burning of 180 s), which is rated as easily flammable. The LOI of all the durably treated fabrics is similar when measured for unwashed samples. After the samples were subjected to 5 laundering cycles there were already some differentiation, ranging from 33 (for the fabric treated without MF) to 35 (the fabric treated with an MF binder). After the samples were subjected to 10 home laundering cycles, only the fabric treated with an MF binder still gave a high value of 33. The explanation for this lies in the synergistic effect of phosphorus and nitrogen, which improves the effectiveness of FR treatment.

The samples treated with the organophosphorus agent and both PCAs are 29. According to the requirements of the ASTM D 2863-97 standard, the LOI value for flame-retardant cotton should be ≥ 27. Baths containing both PCAs met the requirement when tested after 10 HLWD cycles. Treatment with BTCA gave similar LOI results compared to that with CA. Therefore, the use of the FR/CA system proposed can be recommended for treatments which require lower durability *i.e.* up to 10 washing cycles. Except by the vertical flammability and LOI method, the flammability of samples tested was indirectly determined by measuring the amount of phosphorus in them. The phosphorus content (%) is presented in ***Figure 1*** (see page 96).

The amount of phosphorus in cotton fabrics treated using baths 1 - 3 is plotted against the number of washing cycles, confirming the ability of FR to crosslink cotton cellulose, with a % P value of

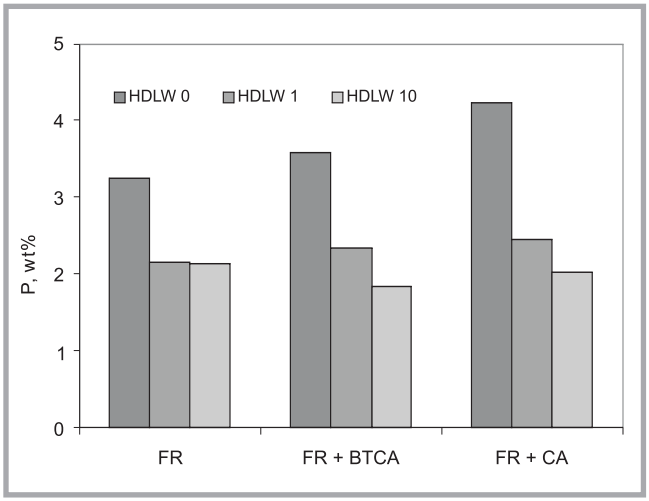


***Figure 1.*** *Percentage of the phosphorus content of cotton twill treated with 1) FR, 2) FR + BTCA & 3) FR + CA, after different numbers of washing cycles.*

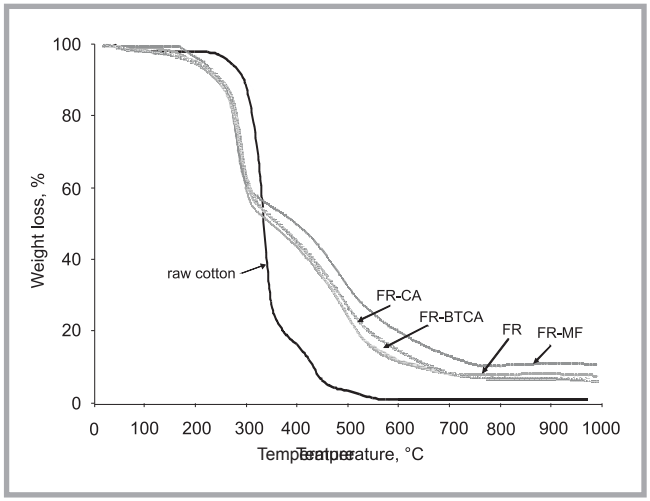


***Figure 2.*** *TGA data for raw cotton and four differently treated cotton samples.*

3.31. The percentage of phosphorus increases to 3.64 with the addition of a BTCA binder and up to 4.29 with the addition of a CA binder. Higher values of the phosphorus amount obtained with the FR/CA system indicate that α- hydroxyl groups of citric acid additionally esterifies cellulose hydroxyls. The previous assumption was that the crosslinking of citric acid with the cellulose hydroxyls is performed primarily through the covalent linkages of carboxylic groups. An increase in the number of washing cycles influences differently the decrease in the amount of phosphorus in the samples treated. The lowest decrease after 1 HDLW is observed for cotton fabrics treated only with the FR agent, confirming the statement of Wu and Yang [4] that FR bonding to cotton is highly hydrolysis-resistant.

The wrinkle recovery angles (WRA), presented in ***Table 4***, were determined for all samples as a measure of either esterification (in the case of CA and BTCA) or etherification (in the case of MF) performance, which occurs at elevated curing temperatures. In this way the extent of crosslinking can be easily detected and quantitatively determined. The wrinkle recovery angle (WRA) of untreated cotton is 98. As assumed from our previous work [11], the PCAs applied improved the crosslinking with cellulose hydroxyls. Additionally they enable bonding with the FR hydroxyls and increase the number of crosslinkages. Therefore the highest WRA results were determined for samples treated with FR and BTCA or CA. The application of CA gave high WRA results (199) only when measured for an unwashed sample. Already after the first washing cycle, the value decreased to 169. Both crosslinking agents show similar WRA results and a linear decrease, depending on the number of washing cycles.

***Table 4.*** *Wrinkle recovery angles (WRA) of cotton fabric treated with baths 1 - 4.*

| Number of washing cycles | WRA Σ W+F, ° | | | |
|---|---|---|---|---|
| | 1 (FR) | 2 (FR+ MF) | 3 (FR + BTCA) | 4 (FR + CA) |
| O HLWD | 153 | 159 | 196 | 199 |
| 1 HLWD | 150 | 152 | 185 | 169 |
| 5 HLWD | 148 | 150 | 165 | 157 |
| 10 HLWD | 146 | 145 | 160 | 155 |
| 15 HLWD | 132 | 141 | 157 | 150 |
| 20 HLWD | 131 | 134 | 155 | 152 |
| 25 HLWD | 130 | 131 | 147 | 148 |
| 30 HLWD | 126 | 120 | 145 | 148 |

***Table 5.*** *Free formaldehyde amount determined according to the AATCC 112 method.*

| Number of washing cycles | Free formaldehyde, ppm | | | |
|---|---|---|---|---|
| | 1 (FR) | 2 (FR+ MF) | 3 (FR + BTCA) | 4 (FR + CA) |
| 0 HLWD | 330 | 550 | 335 | 325 |
| 1 HLWD | 55 | 150 | 50 | 50 |
| 5 HLWD | <25 | 75 | <25 | <25 |

***Table 6.*** *Whiteness Index of cotton fabric treated with baths 1 - 4; Untreated sample has WI 76.8*

| Samples | 1 (FR) | 2 (FR+ MF) | 3 (FR + BTCA) | 4 (FR + CA) |
|---|---|---|---|---|
| 0 HLWD | 70.5 | 74.9 | 76.4 | 53.7 |
| 1 HLWD | 72.9 | 73.5 | 76.6 | 56.9 |
| 10 HLWD | 74.5 | 75.3 | 76.8 | 69.8 |

Results of the free and hydrolysed formaldehyde amounts determined by the ISO 14184-1:1998 method are shown in ***Table 5***. Measurements were performed on unwashed samples where the highest formaldehyde amount was determined for samples treated with the organophosphorus agent and MF binder. Because of the high number of N-methylole groups present both in the organophosphorus agent and TMM binder, the formaldehyde content reaches the highest values measured for sample 2 (FR+MF). There is a correlation of these results with those of LOI since in the case of sample 2 the best FR effectiveness, measured both by the LOI and vertical flammability tests, was obtained.

The value of 550 ppm measured for the unwashed FT+MF treated sample is too high, according to the requirements of the Öko-Tex 100 standard, to be used

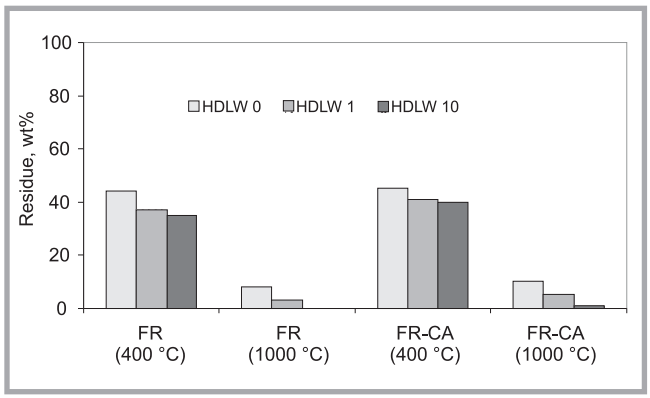


***Figure 3.*** *Residues after thermal treatment for FR and FR-CA treated cotton samples at 400 °C and 1000 °C, respectively, after 0, 5 and 10 baths.*

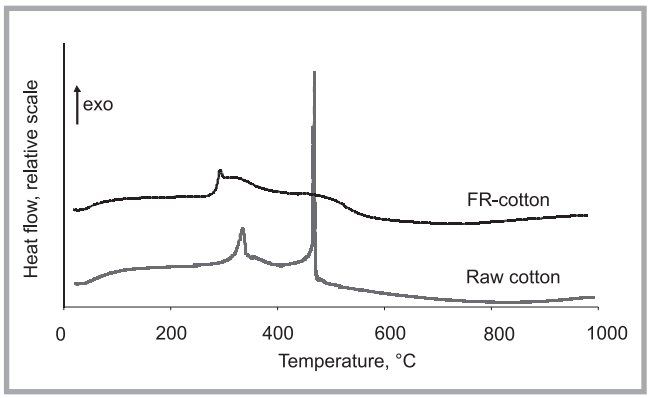


***Figure 4.*** *DSC curves for raw cotton and the FR-treated cotton sample.*

even for clothes which are not in direct contact with the skin. For such clothes, the maximum value allowed is 300 ppm, while the requirements are even stricter for clothes in direct contact with the skin (75 ppm).

The results measured for the fabric treated solely with FR or with a combination of FR and CA binder are in the same range - around 300 ppm, which was to be expected since BTCA and CA, as hydroxytricarboxylic acids, have no influence on formaldehyde content. Further reduction in free formaldehyde content could be obtained with the application of CA and some other type of organophosphorus agent which does not contain N-methylol groups. The whiteness Index was determined and is presented in ***Table 6***.

The problem of yellowness, which might occur during treatment with CA at elevated curing temperatures, is known from our initial research [12]. A decrease in WI is, as expected, the most noticeable with the application of CA for binding purposes; however, the WI results will increase again already after the first washing cycles. BTCA as a binder has a much lower influence on the whiteness and, accordingly, the yellowness degree, and hence it can be recommended for the treatment of white goods.

The flammability of cotton fabrics can be evaluated from the thermal degradation behaviour of raw and treated samples using a conventional thermogravimetric technique [13, 14]. All flame retardant treated cotton samples have a more or less similar thermal decomposition behaviour, as seen from the thermograms presented in ***Figure 2***. Three weight loss regions can be observed. The first weight loss region, located between the ambient temperature and 150 °C, corresponds to the loss of water molecules bonded to the hydroxyl groups in the cellulose polymer. In this region the weight loss is approximately less than 3% for all samples analysed.

Major weight loss occurs in the second region, which can be located between ca. 220 and ca. 420 °C, accounting for about 77% of the raw cotton material and ca. 42% of all the FR treated cotton fabrics. A shift to a lower temperature can be observed in the case of the cotton fabrics treated. Taking into account that washing treatments alter the material, the TG curves for the washed samples progressively shift with the number of treatments towards higher values. After one washing treatment the weight loss in this region is approximately 51%. Finally the weight loss in the third region between 420 and 600 °C slightly increases in the case of chemically modified cotton materials i.e. ca. 10% compared to 4% for the raw cotton sample.

The total weight loss corresponds to the amount of char formed during the thermal decomposition of cotton materials (***Figure 3***). The char quantity is related to the degree of flame retardance [15]. Char yields of the samples analysed at 400 °C indicate a much higher value for all samples treated - ca. 40% than that of the raw cotton - ca. 16%. On the other hand, the final residues after thermal treatment at 1000 °C decrease to less than 10% for all cotton samples treated. The better flame retardant property of cotton fabrics is due to the reduced formation of volatile compounds that enhance the combustion process, therefore the thermal decomposition of the cotton samples treated appeared to be partly inhibited. On the other hand, after washing, a char yield decrease can be observed at both temperatures, as presented for the samples treated with MF and MF-CA. These values are related to the degree of flame retardance and correspond to the LOI results, as well as to the amount of phosphorus found in the samples.

The changes observed from the DSC curves indicate the suppression of the formation of flammable products. As seen in ***Figure 4,*** an endotherm is not visible below 80 °C due to the desorption of moisture. In the case of raw cotton, the DSC curve presents two exothermic peaks: the first one at about 340 (small and broad) usually associated with the formation of volatile production during the decomposition of cellulose, while the second one at about 470 °C (very sharp) presents the oxidation of previously formed char and volatiles. The DSC pattern in the case of all cotton samples treated changes, indicating the chemical modification of the original cellulose matrix. The first exotherm, smaller or larger compared to that of the raw cotton material, shifts to a lower temperature (ca. 290 °C), accompanied by a shoulder at ca. 325 °C, while at ca. 470 °C there is a very broad shoulder for the FR-cotton sample.

## Conclusions

The global move towards less toxic products and strict fire safety regulations has increased demand for a fire retardant that is effective and yet safe for humans. The results presented in this paper demonstrate the applicability of polycarboxylic acids for binding purposes in durable flame retardant finishing, which consequently offers the possibility of replacing

the environmentally unfavourable melamine formaldehyde binder.

The combination of organophosphorus agent, polycarboxylic acids and its phosphorus based catalyst (sodium hypophosphite) improved the flame retardant properties, which proved to be durable to several washing cycles. The main advantage of the reactive systems, such as baths 2 - 4, is their chemical bond by which the flame retardant agent is firmly linked to the textile substrate. In our previous research, CA was used for the purpose of durable press finishing, where it proves its crosslinking performance when combined with SHP catalyst. The best flammability effectiveness among the systems applied was obtained with the melamine formaldehyde binder, whose good performance was retained after 30 HLWD cycles.

Nevertheless, the primary advantage of PCA is its eco-friendliness since it has no unfavourable influence on formaldehyde release, which is a major issue in the usage of conventional agents based on N-methylol compounds. In order to fulfil the rather strict regulatory requirements and obtain very low levels of free formaldehyde, it may be necessary to find a non-methylol substitute for the organophosphorus agent, as well as an oligomeric phosphorus reagent, as studied by Yang and co-authors [16, 17].

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