Drago Katović,
Sandra Bischof Vukušić,
Sandra Flinčec Grgac,
***Branka Lozo,**
***Dubravko Banić**

Faculty of Textile Technology, University of Zagreb
Department of Textile Chemistry & Ecology,
Savska 16/5, 10 000 Zagreb, Croatia
E-mail: dkatovic@ttf.hr

***Faculty of Graphic Art, University of Zagreb**
Department of Materials in Printing Technology,
Savska 16/5, 10 000 Zagreb, Croatia
E-mail: lozob@grf.hr

Flame Retardancy of Paper Obtained with Environmentally Friendly Agents

Abstract
Flame retardancy was imparted through the addition of an organophosphorus agent which enhances paper utilisation and increases the value of paper products. For that purpose paper was impregnated with a solution containing a flame retardant agent, a binder and its catalyst, which was then linked during the curing step. N-hydroxymethyl-3-dimethylphosphonpropionamide was used as the organophosphorus flame retardant (FR) agent with two types of binders: either melamine formaldehyde or citric acid. The use of a bonding agent is necessary in order to form covalent linkages between the FR agent and cellulose macromolecules. The first binder type implements an etherification mechanism which requires phosphoric acid for the catalysation. Second binder type implements esterification mechanism which requires phosphono based catalysts. Citric acid represents a new class of environmentally friendly agents, and as such is recommended for usage. A non-durable flame retardant based on boron compounds was used in the study for comparison. Flame retardancy was tested according to the ISO 6940 and 6941 methods, as well as with the limiting oxygen index (LOI) technique according to ASTM D 2863-97, while the tensile indices were measured according to ISO 1924–2.

Key words: *paper, flame retardant finishing, organophosphorus agent, citric acid, LOI.*

Introduction

Man has been using fire for thousands of years, been studying it scientifically for a century or two, and yet he still barely knows what happens in a match flame and even less regarding the chemical process taking place in flaming conditions.

Cellulose, the basis of wood, cotton and most other plant-derived raw materials, is in widespread use. It is inherently flammable in many of its forms - paper being a typical example. Paper from low-grade wood pulp, such as newsprint manufactured mainly from mechanical wood pulp, has been used extensively in more recent years. Paper, which has an ignition temperature of approximately 232 °C, can easily ignite from open flames. Different types of paper products have been subjected to flame retardant treatments. Examples of paper and board types are:

- paper: art rolls, construction paper, copy paper,
- corrugated fibreboard and corrugated boxes
- solid fibreboard: acoustical board and roofing felt.

In reality fireproof papers cannot be absolutely fireproof but can be made sufficiently fire-resistant (flame retardant) to meet many fire code requirements. The principle is to prevent the paper product from bursting into flames upon exposure to a high temperature.

Preventive flame protection, including the use of flame retardants, has been practised since ancient times. Already in 450 BC the Egyptians used alum to reduce the flammability of wood. The use of flame retardant chemicals is one way of imparting flame retardancy, enabling treated products to meet stringent safety standards and regulations [1].

Types of flame retardants

Inorganic flame retardant (IFR) agents are represented by aluminium trihydroxyde, antimony compounds, boron compounds, phosphorus compounds. Within the class of boron compounds, the most widely used is boric acid. Boric acid (H_3BO_4) and sodium borate (borax) ($Na_2B_4O_7{\cdot}H_2O$) are the two flame retardants with the longest history, primarily used with cellulosic material, e.g., cotton fabric and paper. Boron compounds have a rather low melting point and form glassy films when exposed to high temperatures in fires. The formation of a film barrier inhibits the flow of combustible volatiles to the fire exposed surface. Borax tends to reduce flame spread but can promote smouldering or glowing, while boric acid suppresses smouldering but has a low effect on flame spread. Therefore, these compounds are normally used together [2]. Both products are effective, but their use is limited to products for which non-durable FR is acceptable, since both are very water-soluble.

Halogenated flame retardants can be divided into three classes: aromatic, aliphatic and cycloaliphatic. Among this category bromine and chlorine compounds are the only halogen compounds having commercial significance as FR chemicals. Nitrogen-based FR is used mainly in nitrogen containing polymers and represented mostly by melamine, and melamine salts.

Organophosphorus flame retardants (OFR) represent one of the principal classes of FR used in textiles and plastics containing phosphorus, phosphorus-nitrogen and phosphorus-halogen compounds. The predominant phosphorus-based FR in use is phosphate esters, with or without a halogen and/or nitrogen compound. For textiles, phosphorus-containing materials are the most important class of compounds used to impart FR to cellulose. In our previous papers they were used for the treatment of either textile [3] or wood products [4].

Reaction mechanism

Organophosphorus agents (OF) are usually combined with melamine resins with phosphorus acid as a catalyst. As a result, firm covalent bonds are formed between

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the FR and cellulose molecules, as presented at ***Figure 1***.

The additional purpose of melamine resin is to provide a nitrogen content in order to enhance the flame retarding performance of the treated fabric through synergism with phosphorus. Phosphoric acid might decrease the tensile strength and elasticity of cellulose material, so after FR treatment the material should be neutralised in alkali bath. A further negative effect of FR treatment is formaldehyde release when trimethylol based resin – melamine formaldehyde (MF) is used as a binder.

As binders for organophosphorus FR agents, either resins or reactants with at least 2 carboxylic groups can be applied. Such polycarboxylic acids are linked to cellulose hydroxyls with ester linkages. During the curing process, under the influence of heat,, at the first step of the reaction cyclic, anhydrides are formed, while at the second step they react with the phosphono based catalyst. During the second step, ester bonds are formed with cellulose hydroxyls (***Figure 2***).

Up to now, citric acid has not been used as the binder in FR finishing. It has already proved to be an efficient crosslinking agent in DP finishing [5]. At the same time it is economically and environmentally friendly. Its greatest disadvantage is the yellowness of white material at high curing temperatures.

This eco-friendly agent will be used as a substitute for melamine resins where additional nitrogen enhances the flame retardant performance through synergism with phosphorus. The effectiveness of this novel environmentally friendly treatment will be presented.

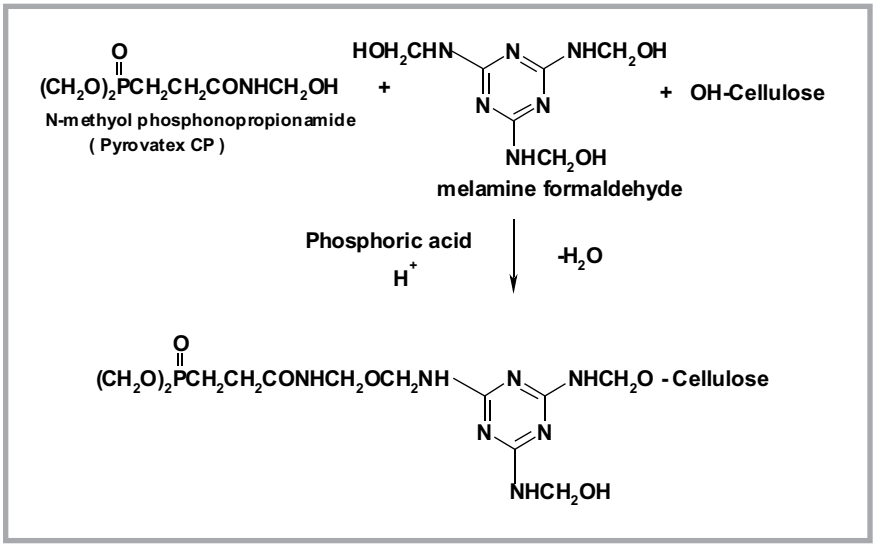

Figure 1. *Etherification mechanism of organophosphorus agent crosslinking with MF and hydroxyl groups of cellulose.*

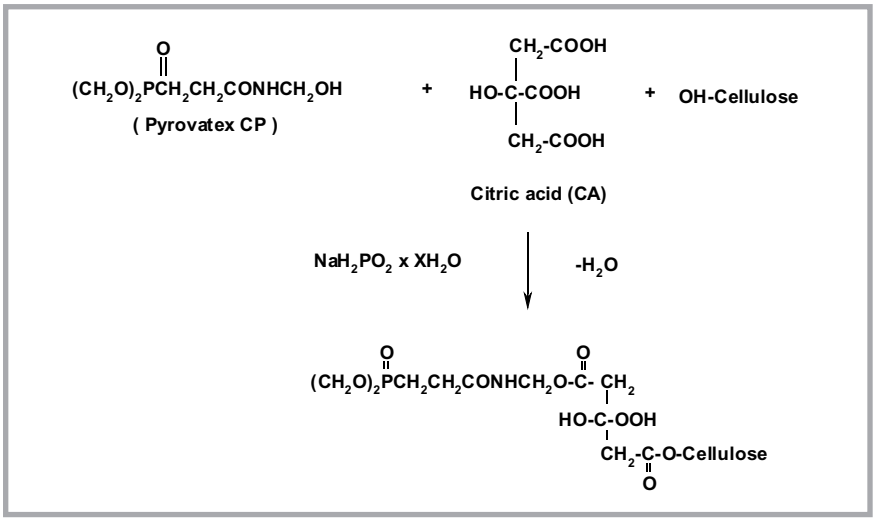

Figure 2. *Esterification mechanism of organophosphorus agent crosslinking with CA and hydroxyl groups of cellulose.*

Table 1. *Treatment conditions of FR treatment.*

Bath	I	II	III
Treatment type	**Non-durable**	**Durable**	
Agent	Borax/ Boric Acid	N-hydroxymethyl-3-dimethylphosphonpropionamide	
concentration, g/l	150/90	450	
Binder	/	Melamine Formaldehyde (MF)	Citric Acid (CA)
concentration, g/l		80	80
Catalyst	/	Phosphoric acid	Sodium Hypophosphite (SHP)
concentration, g/l		26	72
Curing time, s	/	300	60
Curing temperature, °C	/	150	180

Experimental

Materials

Two types of printing paper were used in the study: photocopy office paper, "Navigator", made by Soporcel S.A., Portugal; and permanent paper, ISO 9706, made by ICP, Slovenia. Both papers weight 80 g/m^2. The paper samples were surface-treated with distilled water and a water based solution of flame retardant agents, as presented in ***Table 1***. Water-treated paper samples were used as reference values because of the impact of the drying process on paper characteristics.

The drying process is considered to have the greatest impact on the change in properties of fibres. The changes that fibres undergo during every drying process cause a decrease in the bonding potential of fibres in a paper-sheet [6]. During the first drying process in the production of primary paper, the cell walls of fibres lose water and the lamellas shrink. In some places they adhere one to another so strongly that water molecules are unable to penetrate the lamellas when the fibres are dipped into water again. The macroscopic consequence of this shrinkage is that the fibre can never reacquire its primary swelling diameter [7]. The

impossibility of total swelling decreases the flexibility of the fibre, and the adhesion to neighbouring fibres is weaker, i.e. the fibre bonding potential is reduced. Reduced bonding has been described as irreversible hornification, which implies a stiffening or hardening of the fibre [6].

The first series of non-durable samples was dried at 110 °C after the impregnation step. The second and third series of samples required additional curing treatment, which was performed after the drying in order to impart the crosslinking of the reactive component with cellulose molecules.

Testing Methods

The ease of ignition of vertically oriented specimens was determined according to the ISO 6940:2004 [8] method, and ***Measurement of the flame spread properties of the vertically oriented specimens*** was performed according to ISO 6941:2003 [9].

Fire resistance testing (T 461 cm-00, M 7074, ISO 6940:2004)
The TAPPI test method [10] measures the resistance to flaming under specified test conditions in terms of flaming time, glowing time and char length. The same parameters are measured in test method ISO 6940:2004. The difference between the methods is in the ignition time. In the TAPPI method it is 12 s, while in ISO 6940:2004 the minimum ignition time has to be determined. It is defined as the minimum time of exposure of a material to an ignition source in order to obtain sustained combustion.

Flame spread rating (ASTM E-84, ISO 6941:2003)
Flame-spread is used to describe the surface burning characteristics, primarily of building materials. In the ASTM E-84 method [11] it is the number which indicates the relative rate at which the flame will spread over the surface of the material. If the fire retardant paper is certified as *class A* of the flame-spread ratings (0-25 s), fire authorities will allow treated paper to be displayed on public walls beyond the 20% maximum wall coverage. The 20% rule is enforced when non-certified fire retardant paper is used. These regulations are valid for Canada, while in USA regulations are even stricter and require that not more than 10% of the total wall is covered with combustible materials. In the ISO 6941:2003 test method, the flame spread time is defined as the time taken by a flame on a burning material to travel a specified distance (220 mm till the first, 370 mm till the second and 520 mm till the third marker thread).

Table 2. *Ease of ignition of paper treated with baths I - III, according to ISO 6940:2003 (sample 80 × 210 mm); * Completely burned sample.*

Parameters	Untreated	Paper for documents			Copy paper		
		Bath I	Bath II	Bath III	Bath I	Bath II	Bath III
Ignition time, s	1	1	1	1	1	1	1
Afterflame time, s	14	0	0	20	9	0	0
Afterglow time, s	10	0	0	12	1.1	0	344
Char length, mm	*	80	35	*	*	64	200

Table 3. *Flame spread properties of paper treated with baths I - III, according to ISO 6941:2003 (sample 560 × 1550 mm); ● Sample does not burn.*

Parameters	Untreated	Paper for documents			Copy paper		
		Bath I	Bath II	Bath III	Bath I	Bath II	Bath III
Ignition time, s	5	15	15	5	15	15	15
Time to the severance of the first marker thread [s]	3	●	●	5,5	●	●	●
Time to the severance of the second marker thread [s]	5	●	●	8	●	●	●

Table 4. *Limiting Oxygen Index (LOI) of paper treated with baths I - III, according to ASTM D 2863 - 77.*

Parameters	Untreated	Paper for documents			Copy paper		
		Bath I	Bath II	Bath III	Bath I	Bath II	Bath III
LOI, %	19	26	25	25	25	27	25
Time of after flame, s	49	38	48	40	25	34	151

Table 5. *Thickness and grammage of the treated paper samples.*

Properties	Copy Paper				Paper for documents			
	Ref.	I	II	III	Ref.	I	II	III
Thickness, mm	0.115	0.129	0.146	0.132	0.146	0.136	0.156	0.156
Grammage, g/m^{-2}	84.55	92.83	112.42	99.31	87.22	92.33	102.41	99.82

Testing of physical and mechanical Properties

Evaluation of the influences of FR agents on the physical and mechanical properties of paper samples was done using the following measurements : Tensile indices ISO 1924 – 2 [12]; Bendtsen roughness ISO 8791 – 2 [13]; Grammage ISO 536 [14]; Thickness ISO 534 [15].

Results and discussion

Results of the burning behaviour of the test paper are shown in ***Tables 2*** and ***3***.

Table 2 presents results of the determination of the ease of ignition, while ***Table 3*** presents results of the measurement of flame spread properties, in both vertically oriented specimens were used.

Both methods are used for the burning behaviour determination of textile fabrics and have been utilised in the current study with the aim of providing more information. The T 461 method was also used, which is usually applied for paper and paperboard.

When paper is impregnated with easily penetrating monomers after their polymerisation, carried out during curing, even the distribution of the reagents as well as fire retardancy can be expected. As predicted, the best FR results were obtained with bath II, containing an MF binding agent, for both paper types. Bath III, containing CA, showed satisfying results only when regular copy paper was used and it can not be recommended for the FR treatment of papers for documents. Other than the char length, the after flame and after glow times were also measured as burning behaviour parameters for the

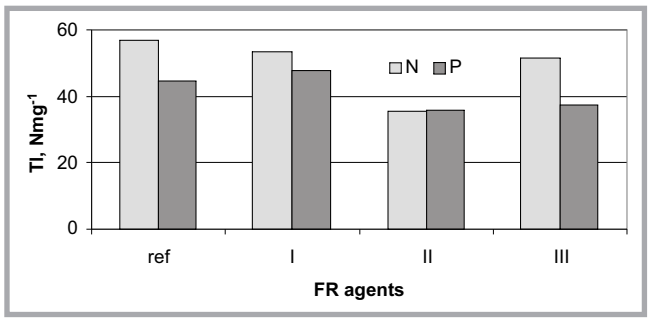

Figure 3. Tensile index of N - copy paper, and P - paper for documents.

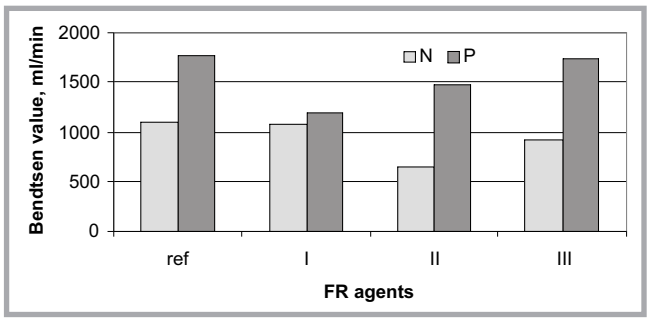

Figure 4. Roughness, Bendtsen type of N - copy paper, and P - paper for documents.

test samples. When testing the copy paper, the after burning values were significant only in the case of samples treated with the non-durable FR type, while both durable FR types successfully protected the paper from bursting into flames.

Equally good FR results were obtained with all three baths when measuring unwashed impregnated samples of Copy paper. Even after an ignition time of 15 s the flame did not spread over the ignited Copy paper.

As far as paper for documents is concerned, the samples treated with CA showed low results, almost in the range of untreated paper. With the lower ignition time of 5 s, the flame reached the second marker in 8 s.

LOI measurement results for the treated samples showed almost the same improvement of FR properties compared to the untreated ones. While the untreated samples (both paper types) are in a group of easily combustible materials (LOI < 20), all treated samples are in a group of materials with low combustibility (20 < LOI < 40), showing results in a range of 25 - 27% (***Table 4***).

The impact of the flame retardant agents on the tensile properties of the samples is shown in ***Figure 3***. FR agents only slightly influenced the tensile strength of the samples, mostly decreasing its value. The strongest decrease was observed in melamine formaldehyde treated samples, particularly the Copy Paper.

This can be due to the acidity of the catalyst (phosphoric acid) applied with the MF binder, which causes the degradation of fibre cell walls. It can be assumed that the strength of the inter-fibre bonds in the paper sheet diminishes as well. The acidity of the paper can have the greatest impact on its physical properties if the factor of time/aging is included [16].

When citric acid and its catalyst SHP were applied, the decrease in mechanical strength was lower, particularly for Copy paper (Navigator**).** Due to the possible acidic influence of phosphoric acid, which might cause severe loss of mechanical strength, the obligatory washing is done after the FR treatments for materials which can be exposed to the washing procedure, such as textiles. Since such requirements are quite inappropriate for the paper industry, it necessary to highlight that bath III, containing the CA and SHP catalyst, has an obvious advantage over bath II.

The impact of the FR agents on the surface properties of the paper samples was evaluated by the Bendtsen type roughness test, the results of which are presented in ***Figure 4***.

The surfaces of the treated samples became slightly smoother in comparison to the water treated samples, particularly the Copy paper treated with melamine formaldehyde. The thickness and grammage of the treated samples are shown in ***Table 5***.

Both the thickness and grammage increased with the use of the FR agents in most of the samples. Paper for documents showed a slight decrease in thickness when treated with borax / boric acid. The increase in both properties is the mostremarkable for Copy paper treated with melamine formaldehyde - Δ 0.031 mm in thickness and Δ 27.87 g/m^{-2} in grammage.

Summary and conclusions

Flame-resistant papers cannot be absolutely fireproof but can be made sufficiently fire resistant to meet many fire code requirements. The principle is to prevent paper products from bursting into flames upon exposure to high temperatures. They can be made flame-resistant so that they are difficult to ignite, and they neither will support combustion nor self-extinguish after the source of heat has been removed. The FR results measured for Copy paper were satisfying for both durable treatments applied and proved the capability of the FR treatments to self-extinguish flames.

The non-durable group of products, represented by bath I, can be used solely in areas where wetting does not occur. With severe wetting, obtained by soaking, the FR properties will be eliminated from such paper. When organophosphorus based products are used it is necessary to add a bonding agent to the bath in order to link the FR agent to the cellulose. Melamine formaldehyde, which is currently used in textile finishing, showed to be environmentally unfriendly and will soon be replaced with an eco-friendlier agent. Citric acid, as a representative of novel agents, is used to link the FR agent to the cellulose. Until now, CA has not been used for the treatment of paper, and as such its application in the paper industry is a novelty. An additional advantage of finish bath containing CA lies in the SHP catalyst, which has a milder influence on the decrease in tensile indices. All the advantages stated confirm the idea of CA usage as a binder for the attachment of an FR agent to cellulose molecules, offering satisfying FR properties.

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