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## DEVELOPMENTS IN FLAME RETARDANT TEXTILES – A REVIEW

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### Abstract

The many, and varied flame retardant chemistries researched, and developed during the 1950-80 period for improving the fire performance of both natural, and chemical fibres have not been significantly added to during the last 25 years or so. This is a consequence of increasing commercial demands in terms of cost-effectiveness coupled with increasing concerns for the environmental, and general toxicological character of these materials, and treatments. The only real exception to this is the recent inclusion of functionalised nanoclays into polymers which has been found to improve fire performance in terms of reduced peak heat release rates. This review considers recent developments which have tried to increase the efficiency of known chemistry to enhance char-formation by intumescent action on the one hand with the effect of inclusion of nanoclays on the other. Consideration is also given to recent attempts to replace antimony-bromine formulations in textile back-coatings by phosphorus-based species.

**Keywords:** Flame retardant, char, nanoclay, nanocomposites, intumescent, textile, fibre

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## **1. Introduction**

Most flame retardant treatments, formulations, and additives were derived from chemistry developed in the 1950-80 period <sup>1</sup>, and those having current commercial interest, have been very recently reviewed <sup>2,3</sup>. Since this time, increasing concerns over the toxicological, and environmental consequences of using such chemical species on textile substrates which have high specific surface areas, and close contact with the skin, have created a barrier to the development, and applications of new chemistry. Therefore, during the last 20 years or so, reaction to these concerns coupled with the perceived need for enhanced flame retardant performance at an acceptable cost, has caused both research scientists, and industry to consider enhancing the efficiency of presently used retardants, replacement of those where concerns lie with other existing formulations or by using known chemistry in novel ways.

This paper provides an overview of a number of areas of present interest, and recent research, particularly that undertaken in our own laboratories, that attempts to address these. Notable issues include the continuing interest in enhancing char-forming efficiency <sup>4</sup>, both by the search for durable intumescent systems which through expanded char formation, increase thermal barrier properties, and invoking nano-particle presence to assist this same process. In addition, the increasing pressures to replace both antimony-halogen systems in textile back-coatings, and formaldehyde-free treatments in durable finishes are discussed.

## 2. Enhanced Char Formation

### Substantive intumescent

Considerable work has been undertaken since the early 1990s to investigate the behaviour of intumescent in textile structures<sup>4</sup>, and our own work, in particular, has demonstrated that certain intumescent-flame retardant fibre combinations produce enhanced chars of improved fire performance<sup>5-12</sup>. However, a major drawback of these systems is that even the most water insoluble intumescent can not survive textile laundering processes. If, therefore, intumescent are to be successful in fibre, and textile applications, they must be either bonded into a hydrophobic resin which assures their wash durability or they are substantive to the textile fibre molecular structure. As a consequence, we have made attempts to develop substantive intumescent treatments for cellulose, flame retarded cellulose, polyamides 6, and 6.6, and wool have been intensively researched since 1999 with varying degrees of success. This work is reviewed below.

Fibre-substantive intumescence requires that:

- i) the intumescent moiety within the fibre structure is a single molecular species; or
- ii) the fibre functions as one of the intumescent components.

With regard to (ii), fibrous substrates like cellulose, and to a lesser extent nylon 6.6 are char-formers or cross-linkers, and when heated may form a part of the overall intumescent activity (method (ii)).

Halpern et al<sup>13</sup> have demonstrated that by reacting spirocyclic pentaerythritol diphosphoryl chloride (SPDPC, structure I in Figure 1) with melamine, a single intumescent molecule may be synthesised. More recently Ma et al<sup>14</sup>, have incorporated SPDPC as a comonomer in selected polyesters, and demonstrated its char-forming activity in these thermoplastic polymer matrices.

We have extended these ideas to demonstrate that polyol phosphoryl chlorides will substitute active hydrogens in fibre-forming polymers to confer inherent intumescence, and review this work below<sup>15-19</sup>. Active hydrogen sites substituted to date are those in cellulose at primary (C6

position), and secondary hydroxyl (C3,C4 positions) groups<sup>16,17</sup>, some durably flame retarded cellulosic fibres contain functional groups such as secondary amines<sup>17,18</sup>, and amine groups in wool, and polyamide fibres<sup>19</sup>. For the linear polyamides, nylon 6, and 6.6, for which no effectively durable flame retardant exists when in fibre form, and which are thermoplastic, this is especially relevant.

Based on our initial studies<sup>15</sup>, and subsequent work in this project, SPDPC has been shown to transfer its intumescent properties onto cellulosic fibres following their phosphorylation<sup>16</sup>. A feature of SPDPC is the 6-membered cyclic phosphate structure which contributes to its high yield during synthesis, and its general stability apart from its tendency to form char when heated. However, its relatively large molecular size may prevent its effective diffusion into fibrous substrate microstructures, and so we have also reported 1,3 propanediol, and its derivative, 2,2-diethyl-1,3-propanediol, as possible alternatives to pentaerythritol as the polyol<sup>17</sup>. Phosphorylation of 1,3-propanediol derivatives should give rise to six-membered ring cyclic propanediol phosphoryl chloride or CPPC (Figure 1), and its derivatives<sup>16</sup>. Hence, cyclic 1,3-propanediol phosphoryl chloride (CPPC) (or 2-chloro-2-oxo-1,3,2-dioxaphosphorinane), and cyclic 2,2-diethyl-1,3-propanediol phosphoryl chloride (CDPPC) (or 2-chloro-5,5 diethyl-2-oxo-1,3,2-dioxaphosphorinane) have been synthesised (see Figure 1)<sup>17</sup>.

Reactions of SPDPC, CDPPC, and CPPC, and cellulosic substrates were carried out in dimethylformamide, DMF in a flask under reflux at various mass ratios, and the preferred reaction temperature of 160°C<sup>15-17,20</sup>. Table 1 shows that the Proban-treated cotton sample can be more easily phosphorylated than a pure cotton sample at 160°C at all SPDPC:fibre ratios<sup>17,18</sup>, and that yields approaching 80% are possible. The greatest phosphorus value occurs for a Proban-treated cotton:SPDPC ratio of 3:1 at 160°C for 2h. Similar results were obtained for CPPC, and CDPPC-phosphorylated samples. The lower levels for CDPPC analogues arise possibly because of steric hindrance caused by the two ethyl substituents present. All

phosphorylated cellulose, and Proban-cotton samples lose minimal phosphorus levels after boiling in water for 30 min, and so have considerable durability<sup>15-19</sup>.

Reactions of CPPC, CDPPC, and SPDPC-nylon, and wool fabrics undertaken in DMF solution with various recipes shown in Table 2<sup>19</sup> show for polyamides that the presence of NaOH, and pyridine promotes the phosphorylation level of, and that pyridine alone has little effect when the reaction time is 1 h or more. The swelling agent phenol does not show any significant effect on the phosphorylation level. CDPPC appears to be more difficult to react with nylon 6.6 than CPPC, which may be due to the steric hindering effect of the former. Assuming that the amine end group concentration is typically 40  $\mu\text{moles/g}$  in each polyamide, and that phosphorylation only occurs at this group, then calculation shows that expected maximum phosphorus levels are of the order of 0.6-0.7%. Clearly the results indicate that indeed reaction is occurring only at the amine end group.

Successful results have also been achieved with both SPDPC, and CPPC on wool with temperatures of curing being reduced to 120°C, and 1 h reaction times yielding 2.06% phosphorus levels; after water boiling, 1.96% P is still present, and char enhancement at 700°C is close to 60%<sup>19</sup>.

### ***Char characterization***

The TGA results show that char formation from all phosphorylated fibrous substrates have been reported to be significantly higher above 500°C than expected from the calculated values<sup>15-19</sup>. Furthermore, the significant rise in char levels above 400°C for the substituted samples with increasing SPDPC, (and also for CPPC or CDPPC) : cellulose mass ratio suggests a more quantitative relationship with the degree of substitution as indicated by phosphorus content.

In the case of SPDPC-phosphorylated cotton previously treated with the commercial polyphosphine oxide flame retardant, Proban (Rhodia), plotting the function  $(C_s - C_p)/C_p$  versus phosphorus level gives the trends in Figure 2 where  $C_s$  is the char residue from substituted cotton, and  $C_p$  is the value of control Proban-treated cotton at any temperature from respective

TGA responses. These indicate that enhanced char levels are solely determined by respective phosphorus levels, and hence degree of phosphorylation. The increasing  $(C_s - C_p)/C_p$  values above 500°C suggest that the char formed by SPDPC-treated samples are more oxidation resistant than the char formed by the control samples itself.

SEM studies (Figure 3) have shown apparent increases in fibre char diameters following phosphorylation to be unaffected by preboiling the sample before char formation, and analysis of char diameters suggests that char volume has increased by as much as 70%, and hence is intumescent<sup>18</sup>. Similar behaviour has been reported for wool keratin (Figure 4), and following determination of average fibre char diameters for the control, and reacted samples, and assuming that char retains the circular cross-section of their parent fibre forms volume ratios were calculated. For fibre chars in Figures 4(b) (absence of NaOH), and 4(c) (NaOH present during phosphorylation) are 1.47, and 3.49 respectively<sup>19</sup>. Thus it is seen that the SPDPC-reacted samples not only have higher fibre char diameters, especially when the phosphorylation occurs in the presence of NaOH (P=2.06%, see Table 2), but also considerably higher volumes suggesting that intumescent character is present. Similar calculations have shown the same evidence in reacted Proban-treated cotton<sup>18</sup>. In addition,, and in the presence of NaOH during wool phosphorylation, fibre char surfaces display numerous roughly hemispherical protrusions, which have the appearance of localized, surface blistering following volatile emissions. The cause of these are either that the presence of NaOH has promoted greater phosphorylation, or that saponification of the unreacted SPDPC on the fibre surface has occurred to give the sodium salt of the spiro-pentaerythritol dihydrogen diphosphate or SPDPONa<sup>19</sup>.

The additional flame retardancy conferred upon the Proban-treated cotton has been demonstrated as increases in both limiting oxygen index, LOI, and char length according to BS5438:1989 Test 2, and reported elsewhere<sup>18</sup>.

### *Alternative solvents*

The above phosphorylations were undertaken in a DMF solvent which is not suitable for possible scaling-up to assess commercial potential. DMSO (dimethyl sulphoxide) is a less toxic, and more environmentally compatible solvent having similar characteristics to DMF, unfortunately, experiments suggest that reaction occurs between DMSO, and SPDPC above 120°C. Propylene carbonate, and NMP (1-methyl-2-pyrrolidinone) were also studied but experiments have shown that the former is not an ideal alternative solvent, because of side reactions causing discoloration of the substrate, and NMP can even react with SPDPC at room temperature.

Ideally, for a scaled-up textile-acceptable process, an aqueous solvent would be ideal. However, while SPDPC, and similar phosphonyl chlorides can be slightly dissolved in water, they also hydrolysed, and so reactivity with active hydrogens is significantly reduced. Research is continuing in this area, however.

### **Inclusion of nanoparticles**

Very little reported research has been undertaken regarding development of nano-composite structures in textiles apart from that of Bourbigot *et al* regarding the behaviour of nanoclays in nylon 6<sup>21</sup> where their behaviour has been marginal. Work with other nanocomposites has indicated that the presence of nanoclays alone will not fully flame retard polymeric matrices<sup>22</sup>. Recent work in our laboratories<sup>22</sup> has investigated the effect of adding selected flame retardants based on ammonium polyphosphate, melamine phosphate, pentaerythritol phosphate, cyclic phosphonate, and similar formulations listed in Figure 5 into nylon 6, and 6.6 polymer films in the presence, and absence of nanoclay (polyamides supplied by RTP Plastics).

### ***Polyamide 6.6***

In order to determine whether particular flame retardants acted positively or negatively in the presence of the nanoclay present, LOI results obtained for all the generated films, were initially represented as the difference between respective film values with, and without the presence of a



nanoclay, ie  $\Delta\text{LOI} = \text{LOI}_{(\text{nanoclay} + \text{FR})} - \text{LOI}_{(\text{FR})}$ . These difference curves are illustrated in Figure 5, and suggest that the incorporation of a nanoclay, in conjunction with the FR additive, does not necessarily increase the LOI value of the film sample containing FR only. Certain FR additives, in particular Antiblaze CU, and melamine phosphate NH, behave in a negative manner. The remainder of the films examined indicate a positive effect at FR levels < 20%. Above this concentration level, however,  $\Delta\text{LOI}$  exhibits an overall decline.

The LOI versus FR concentration for the positive  $\Delta\text{LOI}$ -generating nylon 6.6/FR, and nylon 6.6/FR/nanoclay systems are illustrated in Figure 6. Trends for each formulation show general increase in LOI with FR concentration with APP, Proban CC, and MPC1000 retardants in the absence of nanoclays show “S”-shaped trends with significant LOI increases occurring only above 15%(w/w) presence. The presence of the nanoclay, smoothes each of these trend into a more uniform trend, and effectively shift each to the left hand side demonstrating the origin of the positive  $\Delta\text{LOI}$  trends in Figure 5.

Of specific interest, is the behaviour of APP which exhibits the lowest LOI values at low concentration in the absence of nanoclay, and yet yields the highest LOI values at 20% FR, and above in the presence of nanoclay. The intumescent APP-containing MPC1000 generally shows superior values in the absence of the nanoclay but, in contrast, exhibit the minimal increase when the nanoclay is present. However, all of the effective systems comprising the nanoclay demonstrate possible synergistic behaviour, showing that lower FR addition levels produce higher LOI values in comparison to the films without the inclusion of the clay.

The negative effect of the melamine phosphate NH is possibly a consequence of nanoclay aggregation because this sample produced a slightly opaque film because of the relative acidity (pH~3.2) of this FR. However, NH1197, and NH1511 additives, while each possesses a pH value of 4.5, and produced clear films, still only achieve minimal activity when incorporated with the nanoclay.

Further reasons the differences in FR/nanoclay activity could be a consequence of their becoming activated or not at the melting temperature of nylon 6.6 (~265°C). For example, APP starts to decompose at 251°C<sup>24</sup> with release of ammonia, water, and free P-OH acidic groups<sup>25</sup>. Melamine phosphate (Antiblaze NH) also starts to decompose at 256°C, but yields predominantly melamine pyrophosphate initially<sup>26</sup>. Both NH1511, and NH1197 pentaerythritol phosphate derivatives are far more stable with respective onsets of degradation occurring at 280°C, and 288°C<sup>24</sup>. Interestingly, Antiblaze CU is a liquid, and starts to lose mass at only 198°C<sup>24</sup> although whether this involves major chemical decomposition is not known.

Synergistic effectivities of each FR additive using the method of Lewin<sup>27</sup>, where  $\Delta\text{LOI}_{(\text{FR} + \text{synergist})} / \Delta\text{LOI}_{(\text{FR})}$  values were calculated for each FR in the presence of the nanoclay (ie the synergist), and expressed per unit % of FR. Figure 7 shows plots of effectivity represented as the increase in LOI for 1% of the FR element, and only those systems having effectivity values greater than unity are synergistic.

In conclusion, therefore, it is apparent from the results shown here that only the APP, and the Proban CC demonstrate synergistic behaviour. It can therefore be deduced that MPC1000, and APP/PER, previously categorised as effective systems in Figure 6 impart increased FR activity via the additive effect of nanoclay, and respective FR.

### ***Polyamide 6***

Based on the above results, films were cast comprising only APP, Proban CC, MPC1000, and APP/PER flame retardants. The combined effect of FR, and nanoclay on film LOI values is shown by considering respective  $\Delta\text{LOI} (= \text{LOI}_{(\text{nanoclay} + \text{FR})} - \text{LOI}_{(\text{FR})})$  values plotted in Figure 8. It would appear, therefore, that the presence of nanoclay acts in an antagonistic manner. However, the presence of nanoclay has depressed the LOI of nylon 6 film alone from 22.6 to 18.8, and so the effect of added flame retardant should be referred to this reduced value. This

may be undertaken by comparing the increase in LOI per unit phosphorus,  $\Delta\text{LOI/P}$  in the absence, and presence of nanoclay.

These results show that  $\Delta\text{LOI/P}$  values are significantly greater for nanoclay-containing, flame retarded nylon 6 films as noted for nylon 6.6 films. The lowering of the LOI of nylon 6 to 18.8 prevents synergistic effectivity values being calculated as for nylon 6. However, the potentially positive interaction between nanoclay, and the selected FRs in nylon 6 by defining the ratio  $R = [(\Delta\text{LOI/P})_{\text{nanoclay}} / \Delta\text{LOI/P}]$  for each flame retardant, and by plotting  $R$  versus FR% as shown in Figure 8.

These trends show clearly that the presence of nanoclay increases the FR efficiency by at least an average factor of 2, thereby indicating a positive nanoclay-FR interaction for each of these retardants. To explain why the nanoclay lowered the LOI value of the FR-free nylon 6 film but not that of the nylon 6.6 film we have proposed that the nanoclay reinforces the fibre structure both solid, and molten thereby reducing its dripping capacity<sup>23</sup>. Such an effect would be likely to reduce the LOI value as the melting polymer has greater difficulty receding from the igniting flame. Why there may be a difference in melt reinforcing effect between these two similar polyamides is not clear, but it could be related to the poor thermal stability of the nanoclay functionalising species as identified by Gilman et al<sup>28</sup>. The higher melting temperature of the nylon 6.6 would destroy the nanocomposite structure, and hence render any melt reinforcing effect negligible.

### 3. Environmentally Sustainable Flame Retardants

#### Formaldehyde-free treatments

These are of interest particularly for cotton where both the major durable finishes (THPC-based, eg Proban®, Rhodia, and phosphonamide derivatives, eg Pyrovatex ®, Ciba) involve use of HCHO during manufacture or application with associated health risks during processing, and end-use. While there have been a number of recent attempts to find alternative reactive alternatives to these commercially well-established treatments for cotton, formaldehyde-based chemistry is still required to ensure bonding to cellulose –OH moieties<sup>29-31</sup>. For example, Abdel-Mohdy et al have published the use of aminomethyl phosphonic acid diamide, and derivatives<sup>29</sup>, and triethylamino phosphine oxides<sup>30</sup> as phosphorus, and nitrogen-containing synergistic flame retardants for cotton but unfortunately their respective methylation using formaldehyde is an essential feature for their subsequent reactivity with anhydroglucopyranose –OH groups. Furthermore, their application with methylolated melamine, and similar resins is required in order to achieve desired levels of durability. In a not dissimilar vein, Akzo Nobel have re-introduced their former Fyrol 51 product<sup>31</sup> as Fyroltex HP based on the phosphate-phosphonate oligomeric structure:



as a potentially durable flame retardant for cellulosic textiles<sup>32</sup>. Unfortunately, recent work by Wu, and Wang<sup>33</sup> shows that if it is to achieve acceptable levels of multiple laundering durability, its application requires the presence of methylolated resin species like dimethylol dihydroxyethylene urea (DMDHEU) or methylated formaldehyde-urea. It is feasible, however, that the use of low formaldehyde resins in combination with these organophosphorus compound developments may provide successful retardants in the not-too-distant future.

A similar position is perhaps evident with the recently introduced Firestop product Noflan, a phosphorous, and nitrogen-containing molecule reported to have the structure in which an alkyl phosphoramidate is stabilized as a salt adduct with ammonium chloride <sup>34</sup>.

While this is obviously a formaldehyde-free molecule, it may react only with cellulosic substrates via the phosphoramidate - NH<sub>2</sub> group, which is not very reactive. It is most likely that for this to be effective in cellulosic-based textiles, it may be applied either in a resin binder or cross-linked using a methylolated resin as required for the previous recent examples.

However, the quest for a truly formaldehyde-free, durable, and effective flame retardant for cellulose in particular remains a challenge sufficient to attract interest. Principal work in this area of late has come from the USA where interest in char-forming polycarboxylated species like butyl tetracarboxylic acid (BTCA) along with other functional species may interact with cellulose in particular to generate levels of flame retardancy acceptable for certain textile applications such as carpets with moderate levels of durability to washing <sup>35</sup>. Unfortunately, because of the ease of hydrolysis of the BTCA-cellulose ester links formed, durability to domestic laundering is limited, and so flame treatments based on this chemistry may only lead to semi-durability. More recent work has combined BTCA with phosphorylated species such as the hydroxyalkyl organophosphorus oligomer, Fyroltex, discussed above to enhance both flame retardancy, and durability <sup>36,37</sup>. While the oligomer forms a bridge between the BTCA, and cellulose molecules, and durability is somewhat improved, the ease of ion exchange between free carboxylic acid group hydrogen ions with calcium ions during washing in hard water is accompanied by a loss in flame retardancy as a consequence of calcium salt formation <sup>37</sup>.

### **Antimony-halogen-free formulations**

These are especially used in textile back-coatings used in UK furnishing fabrics, have been, and continue to be cause for concern as the media, and public are made aware of the health implications of antimony III oxide, and the environmental claims associated with brominated

hydrocarbons notably decabromodiphenyl oxide (DBDPO), and hexabromocyclododecane (HBCD)<sup>38</sup>. The challenge of replacing these systems by phosphorus-containing species only has been investigated by ourselves<sup>24,39</sup> with varying degrees of success, and some commercial products are also available including the recently developed Devan Chemicals *Eco-flam* halogen-free back-coating treatment<sup>40</sup>. The main scientific, and technological hurdles to be overcome in the development of antimony-halogen replacements are primarily the replacement of a diffusive, vapour phase system by an equivalent based on phosphorus/nitrogen in which poor durability, and low volatility/vapour phase activities are key features<sup>2,24,39</sup>. We have shown that while replacement by a number of phosphorus-nitrogen formulations including intumescent formulations (eg Flammentin NAH, Thor Chemicals; Antiblaze NH, Albemarle<sup>2</sup>), and cyclic organophosphonate species (Afflammit PE, Thor; Antiblaze CU/CT, Rhodia) is possible, their effectiveness is limited by durability following the 40°C water soak required in the 1988 UK Furniture, and Furnishing (Fire) (Safety) Regulations<sup>41</sup> prior to testing to BS5852:Part 1:1979 for match, and cigarette ignition resistance. Furthermore, for char-forming, phosphorus-based formulations to be effective, we have shown that if the face of the fabric is not to ignite, then the flame retardant in the back-coating must be released at temperatures well below the ignition temperature, which in the case of cotton, is of the order of 350°C<sup>24</sup>. Ideally, this requires decomposition, and release of active flame retardant species at temperatures below 300°C; these conditions were met only by ammonium polyphosphate-containing formulations, and cyclic organo-phosphonate oligomeric species exemplified by Antiblaze CU (Rhodia). The former, unfortunately, has a water solubility too high, typically 1-4 g/100ml at 25°C, for the durability requirements, although higher degree of polymerization, and/or encapsulated variants may prove otherwise claiming solubilities <1 g/100ml at 25°C<sup>2</sup>. The latter, because it is a high boiling liquid volatilizing at 198°C<sup>24</sup>, and above, may generate an unacceptable level of tackiness to the final formulation<sup>39</sup>. However, this volatility, relative to other candidate phosphorus-containing species, will ensure that it is released into the flame under an applied ignition source.

Recent unpublished work in our own laboratories has attempted to use cone calorimetry<sup>42</sup> as an indicator of BS5852: Part 1:1979 performance for a series of back-coated cotton fabric/foam combinations with coatings comprising 71% flame retardant, and 29% ethylene-vinyl acetate copolymeric resin (as solids)<sup>43</sup>. Indicative results in Table 3 show that for fabrics which do pass this test before being subjected to the mandatory water soak test, the presence of the back-coating does reduce peak (PHRR), and average (AvHRR) heat release rate rates when exposed to a  $35\text{kW}^{-2}$  heat flux. However, the advantage of the standard antimony-bromine formulation is clearly seen in that it produces both PHRR, and AvHRR values close to those for a 100% commercial aramid barrier fabric; its disadvantage lies in excessive smoke production measured as specific surface area (SEA). The two phosphorus-containing formulations containing APP, and melamine, and APP, and zinc sulphide show some degree of smoke suppression, carbon monoxide, and carbon dioxide reductions compared with the untreated cotton fabric/foam composite.

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## Tables

**Table 1** Phosphorus concentrations in SPDPC/CPPC/CDPPC-phosphorylated cotton, and Proban-treated cotton

Sample	Ratio (phosphoryl chloride/sample, w/w)	Time at 160°C, h	Phosphorus, %			
			Control	SPDPC	CPPC	CDPPC
Cotton*			0			
	2:1	1		0.75		
	2:1	2		1.01		
	4:1	2		2.39	2.26	
Proban-cotton**			3.96**			
	1:1	2		4.96		
The effect of time, and ratio	1:1	3		5.91		
	1.5:1	2		6.47		
	1.5:1	6		7.08		
	2:1	0.5		4.76		4.87
	2:1	1		5.47	5.86	5.03
	2:1	2		7.53	6.92	6.05
	2:1	3		7.99		
	3:1	2		11.15		
	4:1	1			5.95	
	4:1	2			6.84	

\*100mg cotton, 5mL DMF, 1mL pyridine, and 50mg NaOH

\*\*200mg Proban-treated cotton, 5mL DMF, 1mL pyridine, and 50mg NaOH

**Table 2** Char, and phosphorus levels of CPPC, and CDPPC phosphorylated nylon 6, and 66<sup>20</sup>

Formulation: Polyol chloride: polymer : NaOH mass ratio	Temperature °C	Time, h	P, %	Char at 600°C	
<b>Nylon 6.6 Control</b>				7.9	
CPPC (2:1:0.5), pyridine	160	1	0.62	12.9	
CPPC (2:1:0), pyridine	160	1	0.30	10.5	
CPPC (2:1:0.5), phenol	160	1	0.2	10.1	
CDPPC (2:1:0.5)	160	1	0.3	11.0	
SPDPC (2:1:0.5)	160	0.5	0.5	15.0	
	160	1	0.7	17.1	
<b>Nylon 6 control</b>				4.1	
CPPC (2:1:0.5)	140	1	0.31	6.3	
<b>Wool</b>				<b>Char at 700°C</b>	
<b>SPDPC: fabric, w/w</b>					
SPDPC/NaOH mass ratio =4:1	Control	20	0	0.00	16.3
	10:1	120	50	2.35	22.0
	10:1	140	120	3.24	31.0
	10:1	160	120	4.98	35.0
	1:1	100	60	1.50	24.4
	1:1	120	60	2.06	24.7
Water-boiled wool sample	1:1	120	60	1.97	26.5

**Table 3** Cone Calorimetry data under 35kWm<sup>-2</sup> heat flux for PU foam/fabric composites

<b>Fabric</b>	<b>Add-on, % w/w</b>	<b>Peak heat release rate, kW/m<sup>2</sup></b>	<b>Ave. heat release, kW/m<sup>2</sup></b>	<b>Ave. SEA, m<sup>2</sup>/kg</b>	<b>Ave. CO yield, kg/kg</b>	<b>Ave. CO<sub>2</sub> yield' kg/kg</b>
Cotton control, 230 g/m <sup>-2</sup>	-	235	199	200	0.0084	1.41
Standard DBDPO-Sb <sub>2</sub> O <sub>3</sub>	39.9	136	55	3686	0.4092	3.56
APP-Melamine	34.4	160	124	85	0.0069	1.08
APP-ZnS	40.0	162	148	176	0.0065	1.13
FR (Proban) cotton, 323 g/m <sup>-2</sup>	-	180.8	119.8	197.2	<0.005	1.17
Recycled aramid (Dufelt 535) 150 gm <sup>-2</sup>	-	128.3	66.1	95	0.0090	1.52

## Captions to Figures

**Figure 1** Full names, and structures of SPDPC, CPPC, and CDPPC

**Figure 2** Plots of  $(C_s - C_p)/C_p$  versus P% for all SPDPC-treated samples at designated reaction conditions in Tables 1 for Proban-treated cotton

**Figure 3** Char structures of (a) Proban cotton control, and reacted with SPDPC (b) before, and (c) after boiling (SPDPC/Proban-treated cotton mass ratio=2:1, 160°C, 2h) heated at 420°C for 10min, 1170x mag

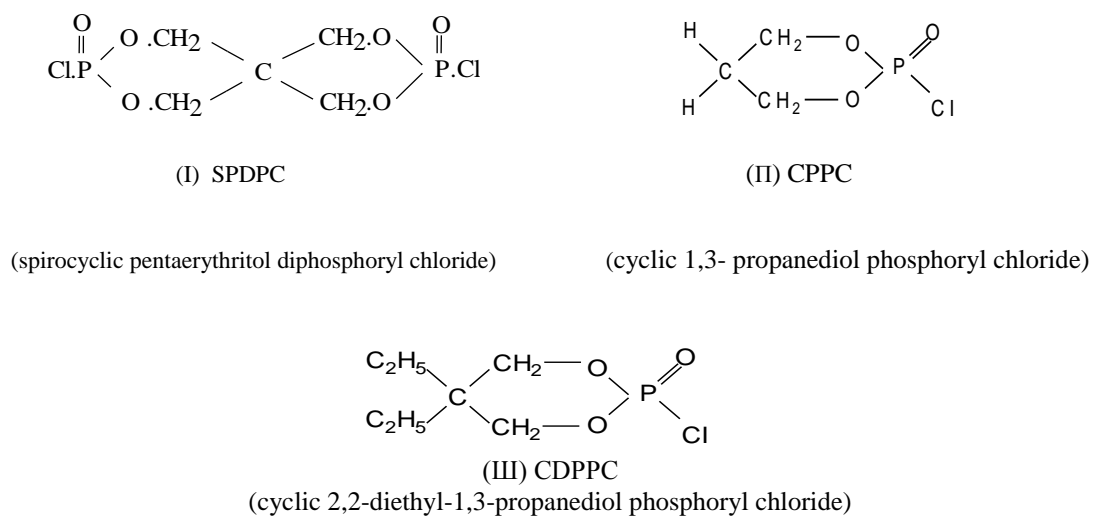
**Figure 4** Residual char structures of SPDPC-reacted pre-treatment wool samples after heating at 500 °C for 10 min.

**Figure 5**  $\Delta$ LOI values for all additives examined in polyamide 6.6 films

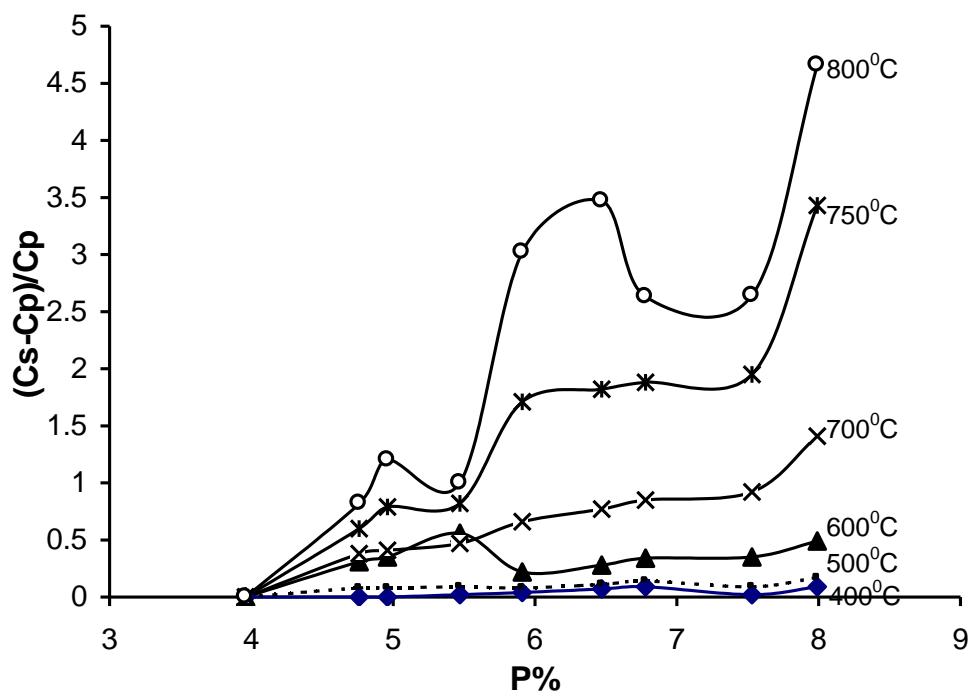
**Figure 6** LOI values for FR/polyamide 6.6, and FR nanocomposite polyamide 6.6 films for FRs showing positive behaviour in the presence of nanoclay

**Figure 7** Synergistic effectivity of nanoclay presence for all FR systems in polyamide 6.6 films

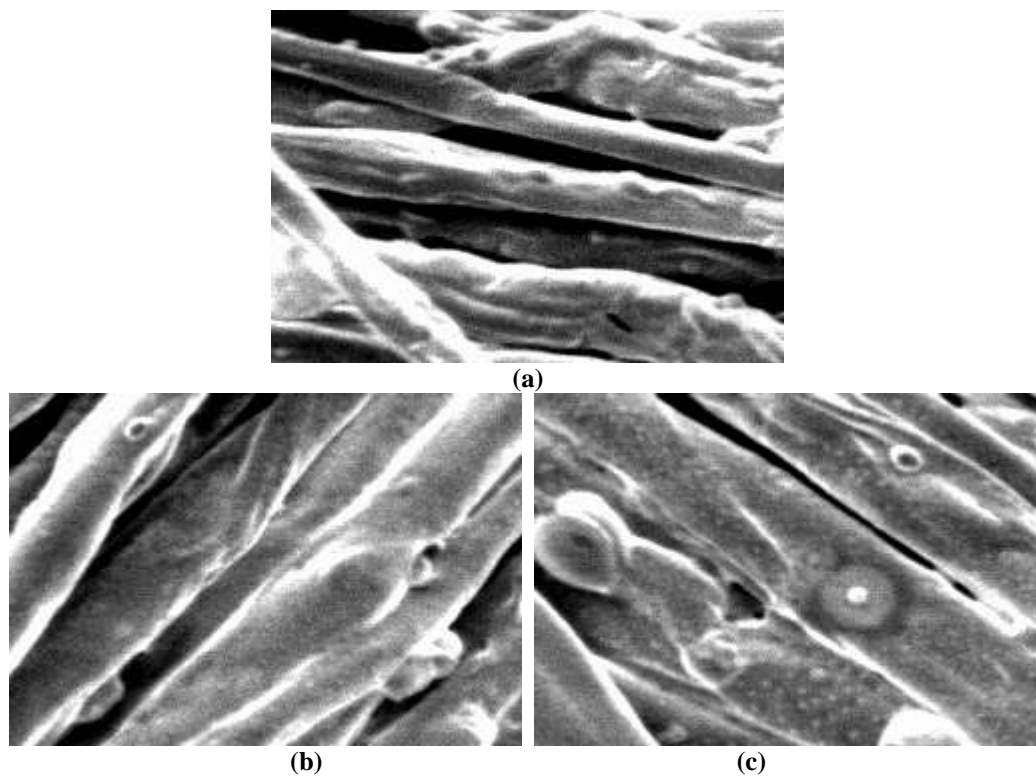
**Figure 8** The LOI behaviour of selected flame retardants in polyamide 6 films (a)  $\Delta$  LOI values; (b) the ratio,  $R = [(\Delta \text{LOI}/P)_{\text{nanoclay}} / \Delta \text{LOI}/P]$ , of increase in LOI per unit phosphorus in nanoclay-containing nylon 6 films compared to the standard film



**Figure 1** Full names, and structures of SPDPC, CPPC, and CDPPC



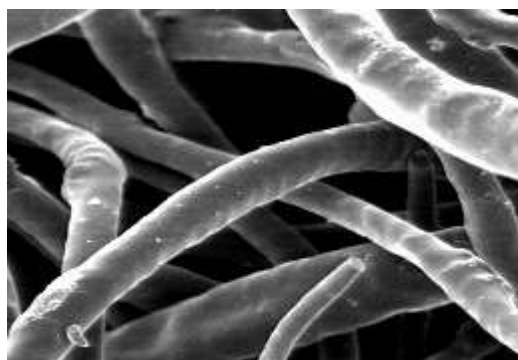
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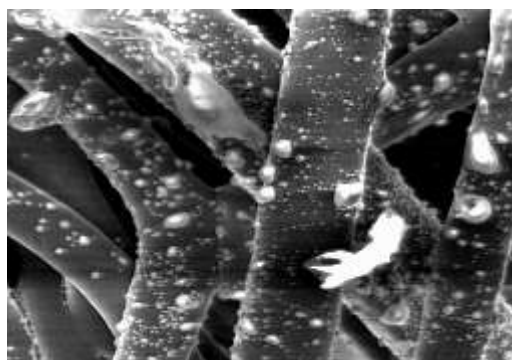
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(a) Control sample (977x)



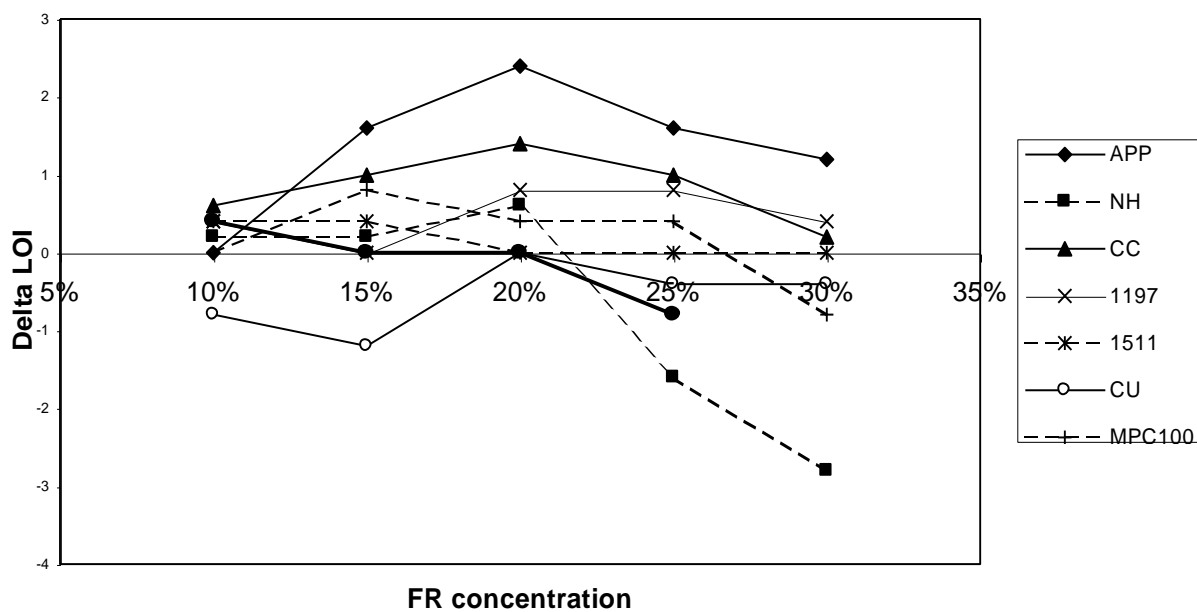
(b) SPDPC reacted without NaOH (962x)



(c) SPDPC reacted with NaOH (962x)

**Figure 4** Residual char structures of SPDPC-reacted pre-treatment wool samples after heating at 500 °C for 10 min.

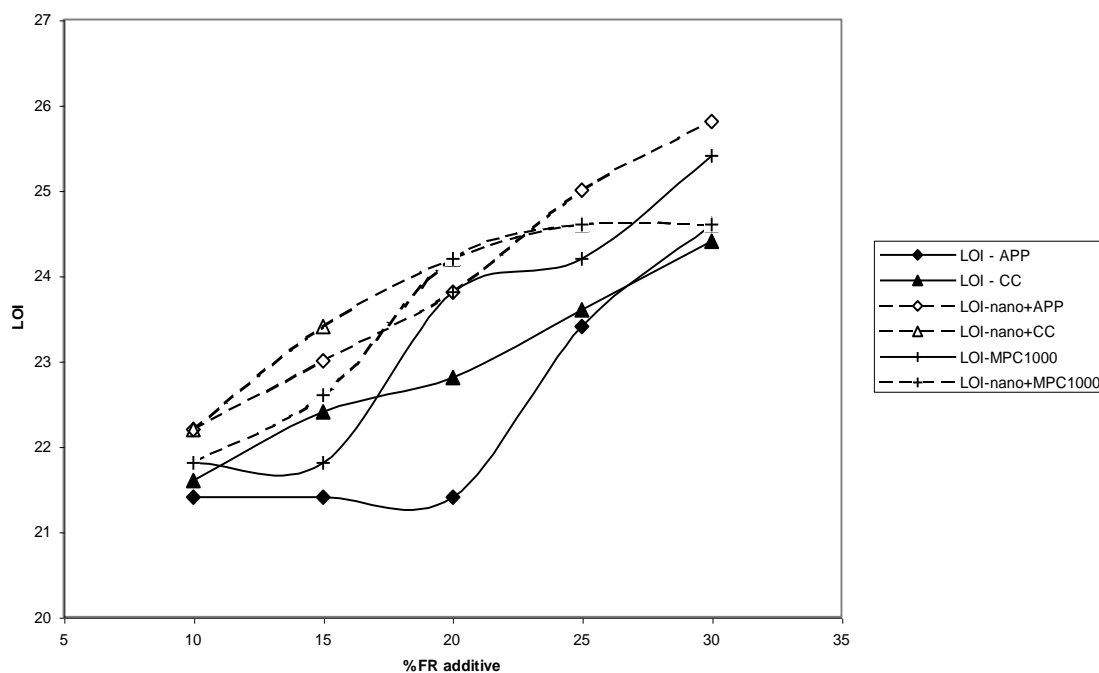




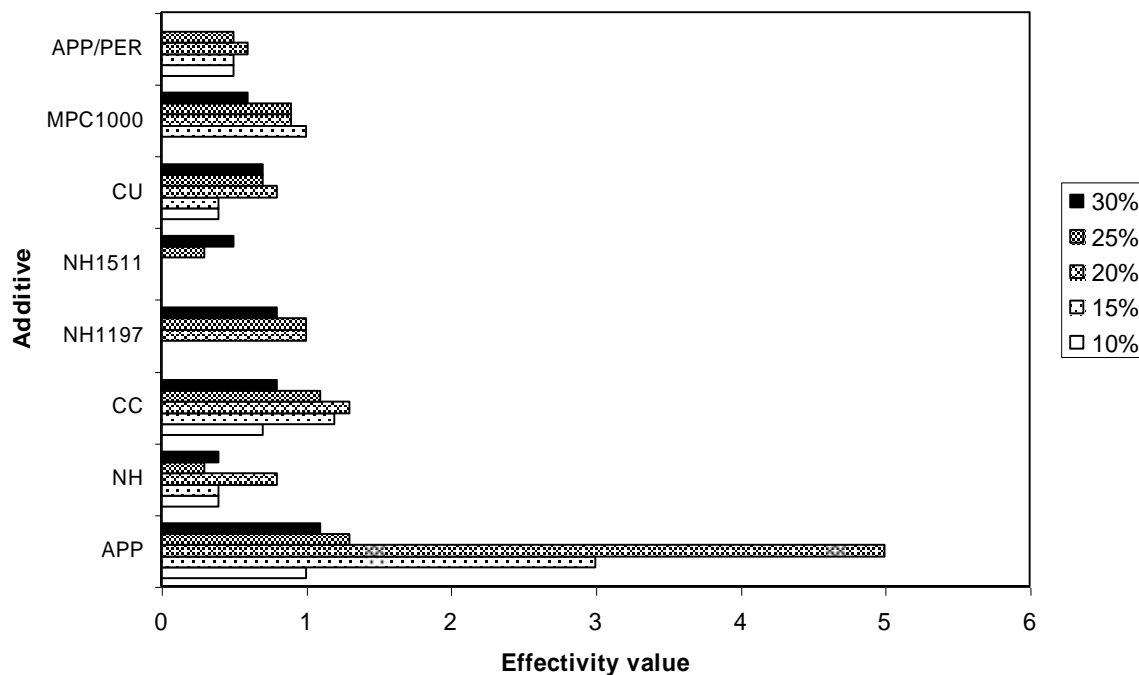
**Key:**

Code: Constitution	Commercial name	Manufacturer
APP: Ammonium polyphosphate	Antiblaze MCM	Rhodia
NH: Melamine phosphate	Antiblaze NH	Rhodia
CU: Cyclic organophosphonate	Antiblaze CU	Rhodia
CC: Poly (phosphine oxide)	Proban CC polymer	Rhodia
APP/PER	Antiblaze MCM/pentaerythritol	Rhodia
APP/PER/melamine	MPC 1000	Rhodia
1197: Pentaerythritol phosphate	NH 1197	Great Lakes
1511: PER phosphate/melamine	NH 1511	Great Lakes

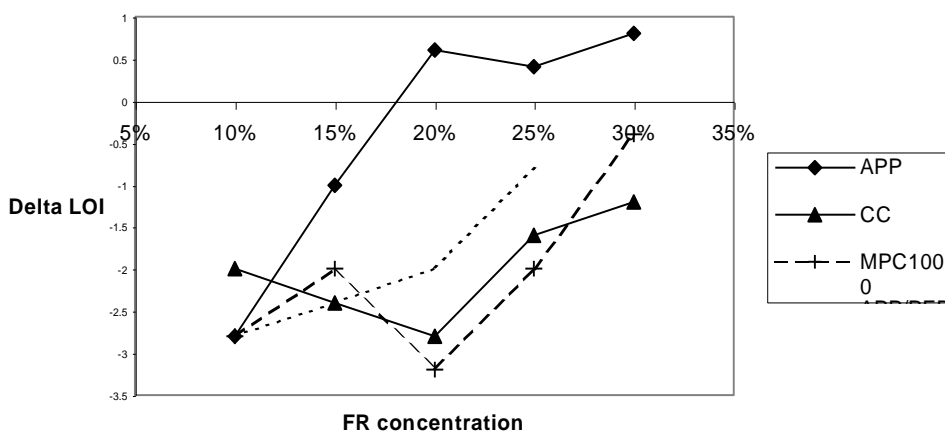
**Figure 5**  $\Delta$ LOI values for all additives examined in polyamide 6.6 films



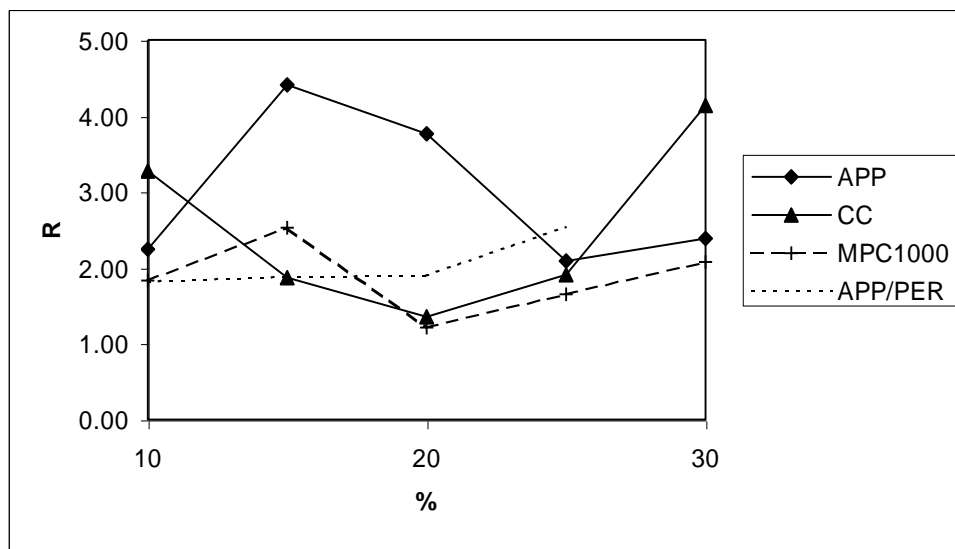
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**Figure 7** Synergistic effectivity of nanoclay presence for all FR systems in polyamide 6.6 films



(a)



(b)

**Figure 8** The LOI behaviour of selected flame retardants in polyamide 6 films (a)  $\Delta$  LOI values; (b) the ratio,  $R = [(\Delta \text{ LOI/P})_{\text{nanoclay}} / \Delta \text{ LOI/P}]$ , of increase in LOI per unit phosphorus in nanoclay-containing nylon 6 films compared to the standard film