

“Textile flammability research since 1980 – Personal challenges and partial solutions”, A R Horrocks, *Polymer Degradation and Stability*, 98, 2813-2824 (2013)

Textile flammability research since 1980 – Personal challenges and partial solutions

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Abstract

This paper reviews the changing textile flammability research themes within the author’s research group over the last 35 years and which reflect those of the academic and research communities often influenced by industrial and societal pressures. For instance, ignition studies undertaken in the early 1980s together with the effect of textile fabric structural variables reflected academic contemporaneous interests as well as those related to real hazards posed, for example, by nightwear fabrics. Also, work undertaken to study flame retardant mechanisms, especially on cotton substrates, reflected the need for commercial interests to more fully understand their chemical treatments largely developed during the 1960-1970 period.

During the subsequent 1980 period, the ecotoxicological concerns regarding flame retardants in general started to develop which continue with even greater vigour at the present time. Thus research effort focussed on developing low or zero formaldehyde treatments for cotton and alternatives to bromine-based flame retardants present in back-coatings applied to furnishing fabrics which also promoted interest in the study of novel intumescent. By the 1990s, the demonstration of the potential of nanocomposite polymers with improved fire performance raised the possibility of novel textile flame retardant developments with

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improved environmental sustainability. More recently, nanotechnological engineering of fibre surfaces to promote improved substrate flame retardancy has created a significant literature.

In conclusion, it is evident that while most of this research has improved scientific knowledge, its translation into novel commercial opportunity has been more elusive and this will probably remain the case as we move into the next ten years or so where the environmental challenges of reducing real or apparent ecotoxicological properties of flame retardant textiles remain.

Keywords: Textile, flammability, flame retardant, mechanism, intumescent, environment, nanotechnology

1. Introduction

Comprehensive reviews [1, 2] have critically reviewed the research period up to about 1980 during which period most of the presently used commercial flame retardants for fibres and textiles were developed and references within these direct the reader to more contemporary specific reviews of particular flame retardant types. Specifically, these include the established durable and flame retardant treatments for cotton and wool fibres as well as those additives and comonomers introduced into both regenerated (e.g. viscose) and synthetic (notably polyester, polypropylene and the modacrylics) fibres. During the years 1975-1980 the back-coatings used in a number of applications, including furnishing fabrics were developed and their popularity has derived from their having little effect on fabric face aesthetics as well as their extreme cost-effectiveness [3, 4].

The history of the development of these commercially-acceptable flame retardants for fibres and textiles during this period has been reviewed by me quite recently [5] and I used the descriptor “golden era” to signify the importance of these years. While other reviews have considered developments since that time [4, 6, 7], they all show that few new commercial developments since 1980 have been achieved. The period 1979-2013 coincides with research undertaken by my own research group, often in collaboration with that of Denis Price, previously at the University of Salford and now at Bolton.

This review covers research undertaken during this period within my own research group and is not meant to be a comprehensive overview of all textile flammability research undertaken. However, it does reflect the changing interest world-wide within flame retardant textiles and the industrial flame retardant industries that supported this research. Working with colleagues, the following major areas have been studied in the almost chronological order:

- Ignition studies and burn hazards
- Effects of textile structural variables on burning behaviour

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- Flame retardant textile mechanisms: pyrolysis, gas emissions and smoke
- Novel intumescent textiles
- Environmentally sustainable flame retardant textiles and novel back-coating systems
- Effect of dispersed clays in fibre-forming polymers.
- Burning behaviour of flame retarded textiles subjected to high heat fluxes.
- Surface treatments based on nanotechnology

These studies in the majority of cases were undertaken within externally-funded projects, most with some level of industrial input and so they reflect contemporary interest within the international flame retardant textile community. *It is instructive to note that most industrial sponsors were manufacturers of flame retardants and treatments and rarely synthetic fibre producers and so the review.* Furthermore, the paper will discuss the challenges and achievements, as well as failures, during this time *although* the lack of definitive success is all too often accompanied by increased understanding of the problems being addressed and sometimes incremental improvements in commercial products and processes can *and have* followed.

2. Ignition and textile burn hazards

Ease of ignition is a feature of many standard textile flammability tests for obvious reasons and yet the underlying science is still poorly understood. While often simply determined as the time to ignite of a fabric subjected to a standard flame, often a simulant of a simple match flame (eg BS ISO 6940), other measures of ease of ignition include either the time to ignite when exposed only to a defined radiant heat flux or the temperature at which a sample ignites when exposed to such a source [8, 9]. For polymeric materials generally, the Setchkin furnace (ASTM D1929) is a well-established and simple means of determining the ignition temperature with results quoted by many authors [10]. Since the advent of the cone

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calorimeter, it is well-established that the common textile fibres like cotton, viscose and polyester, for example, will ignite when exposed to heat fluxes in the range 20-25 kW/m² [11]. Flame retarded textiles usually require higher heat fluxes in the range 30-50 kW/m² and so for decorative flame retardant textiles attached to wall and other internal panels in commercial aircraft, for example, they are tested under a heat flux of 35 kW/m² as defined in the aviation standard FAR 25.853 Part IV Appendix F for their ability not to spread fire using the Ohio State University (OSU) calorimeter [12] (see also section 8).

The question of ignition arose in my own research over 35 years ago while starting to investigate the comparative flame retardant mechanisms of a range of commercially flame retarded cotton fabrics (see Section 4 below). Initial studies used thermal analysis and in particular, differential thermal analysis (DTA) of these fabrics under flowing air conditions showed that for pure bleached cotton, above a critical air flow rate, the sample did not simply pyrolyse oxidatively but spontaneously ignited [13]. Subsequent work, which studied the effect of oxygen concentration and the effect of flame retardants present, enabled activation energy of cellulose oxidation, E_{ox} values to be calculated [14] as well as activation energies of pyrolysis, E_p [15]. Table 1 summarises results from these experiments.

Table 1 here

Here it is clear that while the presence of a flame retardant may have little or considerable effect on the pyrolysis activation energy, ease of oxidation is considerably reduced relative to when none is present.

Later, renewed interest during the late 1990 period occurred within the EU especially [16], because of concern regarding the burn hazard provided by lightweight nightdress fabrics [17] (and which led to the standard EN 14878:2007) caused us to undertake work, part funded by the British Burns Association, to investigate the ease of ignition of a range of fabrics by both a

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modified Setchkin furnace method [18] and cone calorimetry [11]. Using the former method, it was proposed that the sensitivity of ignition time, t , to oven temperature, T , will relate to ease of ignition and hence the potential hazard of causing severe burns. Thus extrapolation of time-to-ignition versus $1/T$ each plot for each fabric enabled the ignition temperature at $t=0$, $T_{ig(t=0)}$ (see Table 2) [18]. The highest $T_{ig(t=0)}$ values should represent reduced sensitivities to ignition which suggests that the more flammable fabrics cotton and polyester-cotton present higher ignition hazards than light weight silk and wool. The apparently lower heavy weight silk $T_{ig(t=0)}$ value is difficult to explain and could be anomalous (see below).

Table 2 here

Later work [11], described a method of reproducibly measuring the ignition and heat release properties using cone calorimetry in which the thermally thin, unstable fabrics were superimposed with a thin wire grid assembly. This work showed the effect of heat flux on the ignition characteristics of these same fabrics from which FIGRA (fire growth index) measurements under 50 kW/m^2 were determined and listed in Table 2. The lower the FIGRA rating, the lower is the burn hazard from a given fabric once it is ignited. The hazard ratings listed suggest that again wool is the least hazardous fabrics in terms of ease of ignitability and burn propensity. FIGRA results for heavy weight silk are intuitively sensible unlike the value its respective $T_{ig(t=0)}$ value.

However, it must not be forgotten that ignition temperatures of bulk flammable materials can be significantly less than values obtained for low mass samples [10, 19] which presents storage hazards for large masses of fibres and textiles eg fibre bales, fabric piles in laundries. For such “piles” maximum volumes should be defined dependent up on the ambient temperature – the larger the pile, the lower is the temperature at which spontaneous ignition can occur, because any cause of self-heating inside the pile (usually of an oxidative,

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exothermic character) will generate heat in proportion to the radius or length to the power of three whereas cooling is proportional to the square of either parameter. This leads to a “runaway” exothermic heating of the inside of the pile with ignition being the inevitable outcome [20]. Causes of exothermic reaction may be microbiological (in the case of hay), although in cotton unsaturated species such as natural oils and even traces of oxidisable impurities are the major cause and using small, steel wire cubes (102x102x102 mm), we were able to show that piles or stacks of oil-contaminated cotton fabrics could spontaneously ignite at temperatures close to 100°C or so [21] and identify those oils that are most hazardous as impurities.

3. Effects of textile structural variables on retardant textile cotton based on oxygen methods

In parallel with our early work on ignition, we were interested in the effects of textile physical variables of burning behaviour because not only were semi-quantitative tests like oxygen index (OI) methods useful for assessing varying degrees of flame retardancy achieved during application of flame retardants to textiles but also the OI results (usually as Limiting Oxygen Index values [22]), depended on fabric structural variables such as yarn linear density, woven versus knitted versus nonwoven structures and area density [23].

Building on the work of Miller et al [24], who considered an alternative measure of the oxygen index at which the burning rate was zero, we defined the extinction oxygen index, EOI, [25-27] as the oxygen concentration at which the fabric just will not sustain any flame for a finite observable time when subjected to an LOI ignition source at the sample top for a defined ignition time. For simple flammable fabrics like cotton, nylon and polyester, respective EOI values decreased with decreasing igniter application time and extrapolation enabled EOI values at zero time, $[EOI]_0$, to be defined. For a single layer of a typical cotton fabric, a value of 13.5 vol% was derived which was considered to be independent of igniter

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variables. This compares well with Miller’s intrinsic oxygen index $(OI)_0$ value of 13 vol% for cotton and contrasts with the quoted LOI value of 18-19 vol%. Similar $[EOI]_0$ values for the thermoplastic fibres were determined in the absence of the problem of ignition problems caused by shrinkage and melt-dripping and for flame retarded cottons with removal of the influence of char. $[EOI]_0$, like LOI values, increased with area density of single and layered fabrics defined by linear trends, $[EOI]_0 = E_0 + E_1.M$, where so-called intrinsic fibre extinction oxygen index values and fabric area density sensitivity, E_1 , values were determined (see Table 3).

Table 3 here

These results show that the E_0 value for cotton of 13.5 vol% is an intrinsic fibre property. Both flame retardant cottons with LOI values of about 30% have E_0 values still less than but close to 21 vol% and so may be considered to be intrinsically flame retardant. Both polyester and nylon 6.6 have E_0 values close to respective LOI values, which is probably a consequence of the affect of melting and dripping. While fabric sensitivity values, E_1 are similar for the non-flame retarded fabrics indicating that the effect of area density is independent of fibre type, for the flame retardant cottons, the area density dependences are significantly higher, which may be a consequence of char formation. This means the behaviour of the final cotton fabric may be determined by a balance of flame retardant concentration present and area density as is commonly known in industry where lightweight fabrics require higher levels of retardant than heavier fabrics.

4. Flame retardant textile mechanisms: pyrolysis, gas emissions and smoke

During the 1980s it was clear that the actual mechanisms of cellulose charring were not well understood [28] and were based mostly on earlier studies of cellulose pyrolysis by Bradbury et al [29] in which the first stage is an activation of cellulose:

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Heat/air

Cellulose → Cellulose*

With sponsorship from both the former Albright and Wilson (now Solvay and previously Rhodia) and Ciba (now Huntsman) the mechanisms of Proban® and Pyrovatex®-treated cottons respectively were studied [30] including a study on the effects of detergent type and water hardness on respective durabilities [31]. The competition between volatile and char formation for pure cellulose was confirmed and while it was suggested that the low temperature DTA transition at about 300°C in pure cellulose could be associated with the formation of the activated form [30], subsequently we showed that it was both irreversible and was oxygen dependent suggesting it to be an oxidative exotherm [32]. Kinetic analysis of TGA data by using fitting degradation models for the major mass loss stage under nitrogen was best described by one of an advancing boundary representing char formation [33]. Subsequently, we considered the main pyrolysis to be a three stage process which depends on both temperature and the exact nature of the flame retardant present [34]. Figure 1 shows the overall scheme, which builds on previously published mechanisms [30, 35] and our own research based on evolved gas analytical, DTA, GC, pyrolysis-FTIR and temperature oxygen index studies of a range of flame retarded cotton fabrics. Thus Stage I shows the well-established competing mechanisms of char formation and volatilisation within the temperature range 300-400 °C, Stage II (400-600 °C) shows the competition between char oxidation and conversion of aliphatic char to an aromatic form and volatile oxidation and Stage III describes complete combustion of all carbonaceous species remaining to CO and CO₂. Vapour-phase active bromine-containing species (as ammonium bromide) influence the pyrolysis to the extent that they favour volatile reactions by enhancing the decomposition of

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laevoglucosan to flammable furans, aldehydes and similar species. Phosphorus-containing flame retardants increase char formation as expected, but evidence suggests that those with a greater dehydrating power, such as ammonium polyphosphate, have a greater tendency to form aromatic chars than those based on organophosphorus. Furthermore, most of the original phosphorus remains in the char, some of which is believed to combine with the carbon present via P-O-C bonds, for example, which both increases the oxidation resistance and char mechanical strength. Surprisingly, the bromine-containing retardants studied also appeared to have slight char-promoting effects.

Close relationships with the former Courtaulds Ltd., then manufacturers of Courtelle acrylic fibres, enabled us to investigate char-forming mechanisms in these fibre-forming copolymers, which unlike the other common synthetic fibres, polyester, polyamides 6 and 6.6 and polypropylene, have intrinsic char-forming properties. We showed [36] that the high flammability of acrylic fibres is associated with the rapid heating rate associated with the burning process which favours the volatilisation (probably by unzipping) of the polyacrylonitrile chains. Any effective char-promoting flame retardant should therefore reduce the former volatilisation tendency at high heating rates and enhance oligomerisation in the first instance.

Incorporation of a range of selected flame retardants as mixtures in a range of fibre-forming acrylic polymers provided the respective LOI versus residual char relationship [37]:

$$\text{LOI} = 14.6 + 0.36 [\text{char w/w\%}] \text{ LOI}$$

The most effective flame retardants were phosphorus-containing species and in particular, the ammonium phosphates and polyphosphate (APP). The proposed mechanism is that APP

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functions [38] as a physical barrier to oxygen following release of polyphosphoric acid and as a nucleophilic agent which promotes oligomerisation of the adjacent, pendant nitrile groups to form a ladder polymer followed by the dehydrogenation of the latter to a carbonaceous char with an empirical formula $C_{30}H_{13}N_7P_2$. The solubility of APP and its reaction with certain solvents used in acrylic wet spinning has prevented its exploitation as an effective flame retardant for acrylics.

5. Novel intumescent textiles

While intumescent have a history in the coatings and paints industries going back to the Second World War period [39, 40], their mechanisms were not understood until the work of Camino *et al* during the late 1980s [41, 42]. This period coincided with the first concerns being raised with regard to the potential ecotoxicological effects of bromine-containing flame retardants [4] and so interest in intumescent flame retardants revived in both the polymer and textile sectors at this time. A review in 1996 showed that literature on intumescent materials applied to textile materials was exemplified largely in the patent literature where one early patent example describes the application of an intumescent coating to glass-fibre-cored yarns used in the woven or knitted structures [44]. During the late 1990s more interest developed [45, 46] including patented research by ourselves of a novel range of intumescent-treated textiles that derive their unusually high heat barrier properties from the formation of a complex char that has a higher-than-expected resistance to oxidation [47-54]. These required the intumescent to be in intimate contact with the surfaces of flame retarded, char-forming fibres and for respective char-forming mechanisms to be physically and chemically similar thus enabling simultaneous reaction to give a so-called "char-bonded" structure [49-52]. This integrated fibrous-intumescent char structure had a physical integrity superior to that of either charred fabric or intumescent alone and, because of reduced oxygen accessibility, demonstrated an unusually high resistance to oxidation when exposed to

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temperatures above 500°C and even as high as 1200°C [48, 49]. Subsequently, it was shown that intumescent, based on ammonium and melamine phosphate-containing intumescent applied in a resin binder, could raise the fire barrier properties of flame retarded viscose and cotton fabrics to levels associated with high performance fibres such as aramids and carbonised acrylics as shown in Figure 2 which plots the coherent fabric char residues after exposure for 10 minutes in air to 50 kW m⁻² heat flux [54]. Char structures were examined structurally by scanning electron microscopy and EDAX [53] and for thermal conductivity using embedded thermocouples at heat fluxes in the range 25–75 kW m⁻²[55].

Other intumescent systems, including melamine cyanurate, melamine borate, melamine oxalate, melamine pyrophosphate and an inorganic silicate-based intumescent were studied in combination with both flame retardant cellulosic and two non-cellulosic fibres, a novoloid (Kynol®) and a melamine-formaldehyde (Basofil®). Of these intumescent, only melamine borate and melamine pyrophosphate showed interactions with flame retardant cellulosic fibres and both Kynol® and Basofil® indicated char interactive tendencies with some of the phosphorus-containing intumescent [55].

Parallel studies with wool and wool-containing blended fabrics [56, 57] also showed that the presence of intumescent applied as fibre surface coatings promoted char-forming interactions.

However, two major disadvantages in using intumescent on textile substrates generally exist, namely their presence as a surface coating and their general water solubility, although the use of surface coatings can significantly reduce intumescent particle solubility.

Substantive intumescent: It is evident, therefore, that if intumescent are to be successful in durable fibre, and textile applications, they must be either bonded into a hydrophobic resin or they are substantive to the textile fibre molecular structure. Based on the earlier work of

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Halpern et al [59] who demonstrated that reaction of spirocyclic pentaerythritol diphosphoryl chloride (SPDPC, structure I in Figure 3) with melamine yields a single intumescent molecule and Ma et al [60], who managed to incorporate SPDPC in selected polyesters to enhance their char-forming activity, we demonstrated that such polyol phosphoryl chlorides will substitute active hydrogens in fibre-forming polymers to confer inherent intumescence [61-65]. These active hydrogen sites include –OH in cellulose primarily at the C6 position [62] and >NH groups in some durably flame retarded cellulosic fibres such as Proban®-treated cotton [63], wool and polyamide fibres [64]. 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 even if their respective reactive –NH₂ end groups are quite low (typically $\leq 40 \mu\text{mole/g}$).

Alternative carbon sources to pentaerythritol studied were 1,3-propanediol, and its derivative, 2,2-diethyl-1,3-propanediol [65] and their phosphorylation gave rise to six-membered ring cyclic 1, 3-propanediol phosphoryl chloride (CPPC) (or 2-chloro-2-oxo-1,3,2-dioxaphosphorinane, structure II, Figure 3) and cyclic 2,2-diethyl-1,3-propanediol phosphoryl chloride (CDPPC) (or 2-chloro-5,5-diethyl-2-oxo-1,3,2-dioxaphosphorinane, structure III, see Figure 3). The various phosphorylations required the use of alkaline (NaOH) non-aqueous solvents such as dimethylformamide (DMF)/pyridine mixtures (for cotton and Proban® cotton) and pyridine or phenol for nylon 6.6 which would prove to be a disadvantage for any subsequent commercial exploitation, however.

Table 4 collates some of the reported results of these phosphorylation reactions which list the particular conditions and respective phosphorus levels achieved and TGA (air) char residues at 600°C. All phosphorylated cellulose, and Proban-cotton samples lost minimal phosphorus levels after boiling in water for 30 min, and so have considerable durability [62, 63].

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Table 4 here

Reactions of CPPC-, CDPPC-, and SPDPC-nylon and SPDPC-wool fabrics undertaken in DMF required the presence of NaOH solution to promote phosphorylation. CDPPC appeared 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 about 40 $\mu\text{moles/g}$ in each polyamide and that phosphorylation only occurs at this group, then calculation shows that expected maximum phosphorus levels should be of the order of 0.6-0.7wt% as in fact were achieved. Water-boiled samples showed some loss of phosphorus this indicating a level of durability.

The TGA-derived char levels from all phosphorylated fibrous substrates significantly increased above 500°C and SEM studies showed apparent increases in fibre char diameters following phosphorylation which were little affected by pre-boiling the sample.

Ideally, for a scaled-up textile-acceptable process, an aqueous solvent would be ideal in spite of the hydrolysis sensitivity of SPDPC and similar phosphoryl chlorides. This and other scale-up difficulties has prevented commercial exploitation to date.

6. Environmentally sustainable flame retardant textiles and novel back-coating systems

The environmental concerns regarding halogen-based flame retardants that arose in the late 1980s [4] and exacerbated by the outcomes of recent risk assessments [66, 67] and general environmental pressures [68] has driven research since this period towards finding more environmentally sustainable alternatives. This is especially the case in the UK, which because of its furnishing regulations [69] that became operative from 1988 onwards and the current position that over 90% of domestic furnishing fabrics on sale comprise a brominated flame retardant/antimony III oxide formulation present as a back-coating. Within the UK's furnishing textile back-coatings market, the standard formulations based on antimony III

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oxide and brominated hydrocarbons, notably decabromodiphenyl ether (decaDBE), and hexabromocyclododecane (HBCD), still dominate the market in spite of environmental concerns and the latter will be withdrawn from use in the EU by October 2015 a consequence of the adverse risk assessment for the latter [67]. Pressures continue with regard DecaBDE especially because of its inclusion on the European Chemicals Agency list of Substances of Very High Concern under Article 57 of the EU Reach regulation [70] as being persistent, bioaccumulative and toxic (Article 57d:PBT) and very persistent and very bioaccumulative (Article 57 e:vPvB).

The challenge of replacing these systems by phosphorus-containing species was addressed by ourselves initially over ten years ago [71, 72]. 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 in which bromine radicals released into the flame effectively terminate the flame reactions independently of the substrate pyrolysis mechanisms, by an equivalent based on phosphorus/nitrogen in which poor durability and low volatility/vapour phase activities are often key features. We have shown that while replacement by a number of phosphorus-nitrogen formulations including intumescent formulations and cyclic organophosphate species is possible, they are substrate-specific with cotton, wool and respective fibre-rich blends being most easily flame retarded [57, 71, 72]. However, their effectiveness is limited also by durability following the 40°C water soak required in the 1988 UK regulations [69] 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. Ideally, this requires decomposition and release of active flame retardant species at temperatures below

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300°C; these conditions were met only by ammonium polyphosphate-containing formulations, and cyclic organo-phosphate oligomeric species exemplified by Antiblaze CU (Solvay, formerly Rhodia). The former, unfortunately, has a water solubility too high (typically 1-4 g/100ml at 25°C) for the durability requirements, although higher degrees of polymerization and/or encapsulated APP variants reduce solubilities <1 g/100ml at 25°C [73]. The cyclic organophosphate, because it is a high boiling liquid volatilizing at 198°C [72] and above, generated an unacceptable level of tackiness to the final formulation [71].

Following this research, we pursued a number of strategies in attempts to overcome these perceived challenges, namely:

- i. the sensitisation of decomposition or flame retarding efficiency of phosphorus-based systems [74]; and
- ii. the introduction of a volatile and possible vapour phase-active, phosphorus-based flame retardant component [75, 76].

With regard to the first, we have demonstrated that the inclusion of small amounts of certain transition metal salts, notably those of zinc II and manganese II can reduce the onset of decomposition of ammonium polyphosphate (APP) from 304°C to as low as 283°C in the case of 2 wt% manganese II sulphate addition [74]. When applied in a back-coating formulation with APP, the presence of these metal ions increased LOI values slightly from 25.1 for APP-only coated cotton to 26.6 vol% in the presence of 2% manganese acetate, for example. However, all coated fabrics still failed the simulated small flame ignition version of BS 5852, which is not perhaps surprising since our earlier research indicated that an LOI value for a coated cotton fabric above 26 and closer to 29 vol% was required for a pass [71]. It should be pointed out, however, that even if passes had been obtained, the problem of durability to water soaking would still remain.

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An obvious replacement for halogen vapour-phase activity is the similarly efficient phosphorus vapour-phase activity[75] which Rohringer et al [76] also advocated to explain the relatively superior flame retarding efficiency of tetrakis (hydroxymethyl) phosphonium chloride (THPC)-based flame retardants applied to polyester-cotton blends (via the evolution of volatile phosphine oxides) and Day et al [77] proposed to explain the flame retarding efficiency of the now-banned tris (2,3-dibromopropyl) phosphate or “tris” when applied to polyester. Flame active radicals include HPO^{\cdot} And HPO_2^{\cdot} radical which interact with H^{\cdot} and OH^{\cdot} radicals in a manner similar to halogen radicals, which subsequent research confirmed are possibly more effective than the latter [78].

Our most recent work in this area [79, 80] initially considered four potentially volatile phosphorus flame retardants selected from their reported boiling or decomposition data. TGA studies of monomeric cyclic organophosphate (Antiblaze CU, Solvay, formerly Rhodia), tributyl phosphate (TBP), triphenyl phosphate (TPP) and triphenylphosphine oxide (TPPO) suggested that TBP (b.pt. = 289°C with decomposition) would be most suitable because it begins to volatilise at about 150°C, well below the melting temperature of polypropylene (~165°C) and the ignition temperature of cotton (~350°C) fibres. TBP was combined with the intumescent char-forming agent, Great Lakes NH 1197(Chemtura) comprising phosphorylated pentaerythritol [72]. When back-coated on to 220 gm⁻² cotton and 260 gm⁻² polypropylene fabrics to achieve nominal dry add-ons in the 40-70 wt% range, the best results were obtained for cotton fabrics where increased LOI and passes to the simulated BS5852 test were recorded for a mass ratio Intumescent : TBP = 4:1 was present. Further evidence of the volatile phosphorus activity was gained by determining the retention of phosphorus in charred residues from back-coated cotton samples which for Amgard CU and oligomeric phosphate-phosphonate Fyrol 51 (formerly Akzo Nobel, now ALC HP/51, Allison Group, Burlington, NC) formulations were very low confirming vapour-phase activity and

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which yielded the highest LOI values. These results suggested that an ideal back-coating might, therefore, comprise a non-volatile, char-former like APP or MP in combination with volatile phosphorus- or even nitrogen-containing species. Addition of melamine (Mel) as an insoluble and yet volatile solid (subliming above 400°C) raised LOI values of all samples above 27 vol% enabled cotton fabrics to pass the simulated BS 5852: Part 1 test before water-soaking. Unfortunately, similar high performance was not observed after coated fabrics had been subjected to a water-soak at 40°C as shown in Table 5. Although retention of the applied formulations often exceeded 70%, it is probable that the major part of the losses will be the APP component although the APP/Mel/Fyrol 51 formulation after water soaking yielded a pass after a 10s ignition time. We still consider that this result points the way towards achieving passes after water soaking and after 20s ignition times if the water insolubility of the char-former present can be increased.

Table 5 here

Obviously, reducing solubility of the more soluble components is the major challenge and while we have not addressed this, work by Bourbigot and coworkers [81] has shown that microencapsulation of otherwise soluble flame retardants like ammonium phosphate with polyurethane shells can improve the durability of coatings containing them. However, the preparation of these microencapsulated agents is not an easy process and different methods were reported in attempts to improve yields [82, 83].

7. Effect of dispersed clays in fibre-forming polymers.

Since the late 1990s, interest has grown in exploring the potential of the inclusion of nanoparticles within fibre-forming polymers in order to improve initially their tensile properties [84] and subsequently their fire performance [85]. With respect to fibres and textiles, Bourbigot [86, 87] and Horrocks [88] have reviewed this whole area and with the

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special focus on developing nanocomposite or nanostructured fibres. In 1990, Bourbigot et al [89, 90] demonstrated the potential advantages of including functionalised nanoclays in polyamide 6 filaments, thus paving the way for future studies including our own outlined below. Notwithstanding the associated problems of functionalising group stability at processing temperatures, changes in rheology and the need to optimise dispersion at the nanolevel, most initial flammability studies of nanocomposite polymers [85] and fibres [89, 90] showed a clay-dependent reduction in peak heat release rate using cone calorimetry and increases in char formation which we were able to confirm in both PA6 and PA6.6 films [91, 92]. However, we noted that acceptable flame retardancy was observed only when more conventional flame retardants were also present often at lower-than-normal concentrations because of additive and sometimes synergistic clay-FR interactions. Of the various phosphorus-containing flame retardants studied, ammonium polyphosphate was found to act synergistically with the nanoclays but its decomposition temperature in the range 250-300°C overlaps the melting point of nylon 6.6 (~265°C) and processing temperature of PA6 (~250°C) which create processability problems for both polyamides. The effectiveness of adding nanoclay at the 1-5wt% levels was shown by its ability to reduce by 25-33 wt% the normal concentration of APP required to create a defined level of flame retardancy [91]. Bearing in mind the need to maintain maximum flame retardant concentrations $\leq 10\text{wt}\%$ for fibre applications, in the case of polypropylene polymer (PP), we studied the effects of adding nanoclays to a flame retardant formulation based on a hindered amine stabilizer and a char-promoting ammonium polyphosphate at concentrations of the order of only about 5wt% [94]. However, while enhancing char formation an increase of LOI above 22 vol% was not achieved. Extending the work to PP filaments, we studied the effects of nanoclays alone [95] and in the presence of more conventional flame retardants [96].

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While nanoclays alone promoted expected improvements in fibre tenacity and modulus and decreases in peak heat release rate determined by cone calorimetry at a heat flux of 35 kW/m², the addition of a compatibilising maleate-grafted PP reduced the tensile properties as expected, but reduced PHRR values further. These effects were associated with the improved dispersion as corroborated by TEM. However, no improvements in LOI were achieved, confirming the absence of any significant flame retarding property [95].

Compounding selected phosphorus-containing flame retardants including ammonium (APP) and, melamine polyphosphates, pentaerythritol phosphate, the hindered amine stabiliser NOR 116 (Ciba), tris(tribromoneopentyl) phosphate (TBP) and tris(tribromophenyl)cyanurate with a number of clays (Cloisite 20A and 30B, Bentone 107, Elementis: a bentonite clay modified with dimethyl, dehydrogenated tallow quaternary ammonium ion and a montmorillonite modified with vinyltriphenyl phosphonium bromide) and compatibilisers (Polybond) Pb and polypropylene grafted with diethyl-p-vinylbenzyl phosphonate (DEP)) presented few problems. However, subsequent extrusion into filaments proved to be challenging because of poor clay and flame retardant dispersion [96]. This was especially the case when APP was present because of its polar character and relatively large particle size (25-30 µm). In spite of excessive numbers of broken filaments and their reduced tenacities and moduli, the limited fibre and hence, derived fabric quantities available, were sufficient only for small-scale burning tests. While the presence of clays had little if any additional effect on char formation with respect to levels expected from analogous samples without clays, the burning behaviours of derived knitted fabrics, recorded as times to burn for successive 60 mm distances when subjected to the standard vertical strip test BS 5438:1989:Part 3, indicated varying levels of retardant activity. While the presence of clay alone slightly reduced the burn rate, subsequent addition of the various flame retardants had a similar effect with clay/hindered amine/TBP combinations showing the greatest reduction.

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More recently, we studied the effect of applying ultrasound during compounding to improve dispersion of nanoclays and flame retardants [97] in both PP and PA6. While image analysis showed that application of ultrasound improved particle dispersion during compounding and qualitatively improved the resulting ease of extrusion into filaments, resulting burning properties of derived fabrics showed slight improvements in flame retardancy for PP but no clear cut advantages of ultrasound for PA6 fabrics.

Work with fibre-grade poly(acrylonitrile) copolymer containing a functionalised nanoclay, followed by wet-extrusion into an aqueous bath containing ammonium polyphosphate, yielded filaments having $LOI > 40$ vol% [98]. Synergy between nanoclay and flame retardant was observed and filament properties were acceptable for normal textile applications. Table 6 summarises some of the results of this work which show that the introduction of clays at the 1% level yields tenacity values comparable to commercial values, typically in the range 2.3-3.5 cN/dtex. More importantly, the clays acted synergistically with the APP present to yield improved flame retardancy quantified as values of ΔLOI_{nano} . Unfortunately, APP is not durable to water soaking or washing and so introduction of a cross-linkable or insoluble flame retardant would be required to achieve required levels of launderability.

Table 6 here

Other workers, notably Bourbigot et al [99] and Alongi et al [100-102] have demonstrated similar improvements in fire performance of poly (lactic) acid and poly(ethyleneterephthalate)(PET) fibres respectively in the presence of nanoparticles. However, only when both clay and flame retardant were present in PET fibres did derived fabrics show both reduced PHRR values and increased LOI values ($LOI = 33$ vol% for a PET/sepiolite/zinc phosphinate formulation) [102].

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Finally, not unrelated are the attempts to improve the fire performance of textile coatings containing nanoparticles by Bourbigot et al. [89, 90, 103, 104] which have been shown to reduce the peak heat release rates when present on cotton and knitted polyester fabrics although reduced times-to-ignition and prolonged the times of burning were also observed which are not commensurate with normal flame retardant properties. When tested to BS 5852: Part 1 1979 we showed that the addition of a nanoparticle to a back-coating polymeric film added no beneficial effect when present alone [79].

8. Burning behaviour of flame retarded textiles subjected to high heat fluxes.

While most of the work has followed a chronological path from the late 1970s to the present time and was largely influenced by external factors, such as increased realisation of specific and textile-related fire hazards, there have also been both underlying academic and commercial interests in understanding textile burning behaviour under external heat fluxes. Under such conditions, the burning behaviour may be influenced by infrared-absorbing characteristics of a fabric in addition to fibre type and yarn and fabric structures.

So-called reaction-to-fire tests which study and test the behaviour of materials under simulated fire conditions include the calorimetric techniques such as the heat release calorimeter, exemplified by the so-called Ohio State University (OSU) calorimeter [12, 105] and the later cone calorimeter [106]. Application of the former technique to textiles has usually involved assessing the fire spreading potential of a textile fabric décor adhered to an interior structural panel surface in commercial aircraft using the test protocol within both ASTM E906-1985 and the US Federal Aviation Standard FAR 25.853 Part IV Appendix F. Here a textile fabric composite used as a decorative panel is exposed to an incident heat flux of 35 kW/m^2 and, to pass, must emit a maximum or peak heat flux after ignition $\leq 65 \text{ kW/m}^2$ and over a 2 minute period, an average heat release rate $\leq 65 \text{ kWm}^2$.

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We undertook a commercially-supported project during the 2001-2004 period to develop and optimise a flame retardant formulation for treating high value fabrics comprising exotic animal hairs and silk for use in the growing private executive jet market, which required materials to pass both US and international material fire specifications for commercial aircraft [107]. In this work we used the cone calorimeter as defined in ISO 5660 to assess a large number of trial fabrics and then correlate the results with optimised samples tested using the OSU calorimeter to the FAR 25.853 Part IV Appendix F protocol. We were able to correlate the two techniques and show that OSU results using a 35 kW/m² heat flux with a small gas flame igniting source were equivalent to those following exposure of the same fabric/panel (3.5mm thick phenolic resin/glass honeycomb boards from Schneller Inc, type S-SSCP) composites to cone calorimetry using a 50 kW/m² heat flux and an electrical igniter. Table 7 shows the results for a series of fabric types, which were flame retarded, back-coated with a resin to enable their adhesion with a proprietary adhesive to Schneller honeycomb boards and then subjected to each method. All but one (polyester warp/mohair weft) composite showed peak heat release rate and average heat release rate values ≤ 65 kW/m² and so were deemed suitable for use in the target luxury jet market.

Table 7 here

Also of concern in this research was the possible influence of the fabric structure upon the calorimetric results since the designs involved were often complex and involved jacquard woven motifs of the type shown in Figure 4 for the 39% polyester warp/61% mohair weft fabric in Table 7. The relative effects of warp and weft yarns, each of which has different burning behaviours, on the overall calorimetric behaviour are determined by the respective percentages of each on the face of each fabric exposed to the incident heat flux. Using image analysis software, the designs of a number of fabrics were studied in both the pattern and between pattern areas and data translated into percentages weft face yarn. For instance the

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fabric in Figure 4 comprises 46.1% weft within a motif area and 49.5% in the inter-motif areas which correspond to respective PHRR values by cone calorimetry 58 and 55 kW/m² after treatment and mounting on a honeycomb panel board as above. Generally the results showed that for a number of fabrics 40-57% surface weft levels (which covered all the fabric designs studied) on the fabric face can pass OSU requirements with those containing silk warps having the lowest PHRR and average HRR values.

In tests in which an external heat flux is applied, it might be expected that the colour and its depth may also influence results because of the different infrared absorbing behaviours of differently coloured fabrics. However, we have studied the effects of different weaves and very different colours on a number of flame retarded polypropylene furnishing fabrics having the same nominal area density (260 g/m²) and which gave an unacceptable failure level when tested to the French ‘Epiradiateur’ or ‘M’ test NF P 92-503 [108]. This test assesses the ease of extinction of a fabric subjected to a small flame igniting source under an external heat flux. However, no sensitivity of the test results to the colour, especially the degree of light absorption in the red region adjacent to the infrared, was observed.

9. Surface treatments

During the last 3 or 4 years, significant interest has been increasing in studying novel chemistries and technologies to apply surface coatings to fibres that can confer acceptable levels of flame retardancy without affecting the desirable textile properties of aesthetics, mechanical properties, abrasion resistance and durability, for example. These recent developments are not to be confused with the established coating processes and previously researched grafting chemistries reviewed elsewhere [109]. They do, however, include the processes of layer-by-layer assembly, sol-gel and dual cure processes and plasma deposition which have been recently reviewed by Alongi et al [110].

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Within this context, we have demonstrated the effectiveness of atmospheric plasma treatments, in which either a functionalised clay, a polysiloxane (poly(hexamethyldisiloxane)) or both are deposited on to plasma-activated fibre surfaces. It was found that the generated surface layer has a measurable effect on fabric ignition and burning characteristics of the underlying fibres when exposed in a cone calorimeter to heat flux levels up to 70 kW/m² which are approaching those in flash fires. PHRR values decreased for all substrates especially for argon/clay and argon/clay/polysiloxane plasma-treated samples, with reductions of over 50% being observed for Proban[®] cotton and smaller reductions (<20%) for Nomex[®] fabrics. The results also have demonstrated that while surface treatments alone may be insufficient to fully flame retard an underlying textile substrate, they are able to add additional fire performance to whatever flame retardant properties are already present.

10. Conclusions and future priorities

It is evident that from the above various studies and topic areas, that answers to all problems are rarely forthcoming, especially when industrial challenges are being addressed. Our experience shows that it is easier to increase our scientific understanding underlying a particular problem than generate a solution that may give rise to both fundamental scientific satisfaction and possible commercial application. While much of our research outlined above has increased understanding, whether for the academic community or for the commercial sponsors where appropriate, some has enabled the latter to derive successful commercial application. However, some major areas still remain unsolved such as the development of satisfactory replacements of brominated flame retardants, especially in back-coated textiles. More optimistically, the still new areas of nanotechnology and surface

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modification/engineering are expanding rapidly and are providing interesting scientific advances if not commercial achievements, as yet.

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Table 1: Activation energies of cellulose pyrolysis , E_p , and oxidation, E_{ox} , during spontaneous ignition

Sample	E_p, kJ mole⁻¹*	E_{ox}	Ref
Cotton	146	215	13, 14
Ammonium polyphosphate- treated cotton (2.2 %P)	145	270	15
Proban®-treated cotton (2.9%P)	230	536	15

Note: * under 21 vol% oxygen (air) conditions

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Table 2: $T_{ig(t=0)}$ and FIGRA values for typical nightdress fabrics with respective hazard rankings in parentheses (1 = lowest hazard) [11, 18]

Fabric	$T_{ig(t=0)}$, °C	FIGRA (at 50 kW/m² heat flux)
(i) Light-weight cotton (87 g/m ² , 0.17mm thick)	480 (6=)	27.0 (3)
(ii) Heavy-weight cotton (180 g/m ² , 0.30mm thick)	480 (6=)	27.0 (3)
(iii) Polyester/ cotton (65:35,105 g/m ² 0.16 mm thick)	574 (3=)	29.4 (4)
(iv) Polyester/Cotton (55:45, 118 g/m ² 0.26mm thick)	574 (3=)	-
(v) Acrylic (118 g/m ² , 0.26mm thick)	-	35.0 (5)
(vi) Light-weight silk (71 g/m ² 0.14 mm thick)	909 (1)	-
(vii) Heavy-weight silk (174 g/m ² 0.30 mm thick)	505 (5)	9.5 (1)
(viii) Wool (173 g/m ² 0.33 mm thick)	746 (2)	18.0 (2)

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Table 3: Collated results of extinction oxygen E_0 and E_1 values together with and respective LOI values [26]

Fabric	E_0, vol%	$E_1/10^{-3}$	LOI, vol%
Cotton	13.5	3.28	19.0
Proban Cotton	19.9	9.60	31-33
Pyrovatex Cotton	18.7	10.70	29-30
Polyester	22.6	3.18	20-21.5
Nylon 6.6	22.1	2.89	20-21.5

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Table 4: Phosphorus concentrations in SPDPC/CPPC/CDPPC-phosphorylated cotton, and Proban-treated cotton [62-65]

Sample	Ratio (phosphoryl chloride/sample, w/w)	Time, h/ temperature, °C	Phosphorus, %				Char (TGA in air), %600°C			
			Control	SPDPC	CPPC	CDPPC	Control	SPDPC	CPPC	CDPPC
Cotton	-	-	0				0			
	4:1*	2/160*		2.39	-	-		37.8	-	-
Proban-cotton	-	-	3.96*							
	1:1**	2/160		4.96			32.2	35.7		
	2:1***				6.92	6.05			42.1	40.0
Wool	-	-	0				16.3			(700°C)
	10:1	2/160		4.98	-	-		35.0		(700°C)
<i>After washing</i>				1.98				26.5		(700°C)
Nylon 6.6	-	-	0				7.5			
	2:1†	1/160		0.70	0.65	0.30		10.2	9.8	9.1
Nylon 6	-	-	0				4.1			
	2:1†	1/140		0.31	-	-		6.3	-	-

*100mg cotton, 5mL DMF, 1mL pyridine and 50mg NaOH; **SPDCPC only- 200mg Proban-treated cotton, 5mL DMF, 1mL pyridine and 50mg NaOH at SPDPC/fabric mass ratio = 1, *** as for SPDPC/Proban-cotton but polyol/fabrics mass ratio=2; † 100mg polyol, 50mg nylon 6.6 or 6, 5mL DMF and 25mg NaOH

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Table 5. Durability Results and Flammability Testing (before and after water soak) [80]

	Add-on (%)	LOI (vol%)	Add-on retention after soak (%)	Indicative BS5852 “match” Source 1 test after water soak;	
				Ignition time	
				10s	20s
APP / Mel	52	27.1	75	x	-
APP / Mel / CU	37	27.9	52	x	-
APP / Mel / F51	52	29.6	65	√	x
APP / Mel / TBP	43	28.6	78	x	-

Note: “√” denotes a pass, “x” denotes a fail and “-“ denotes no test undertaken

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Table 6. Tensile and limiting oxygen index properties for experimental polyacrylic filaments containing 1% w/w of either Cloisite Na⁺ or 30B clays and P_F% phosphorus after subjecting to ammonium polyphosphate absorption from the spin bath [98]

Dope-blended samples	Tenacity, cN/dtex	P _F , % w/w	LOI, vol%	ΔLOI _{nano} , vol%
Control (Courtelle)	2.6	0.0	19.0	-
		1.2	21.0	-
		3.5	26.0	-
		6.5	36.0	-
Cloisite Na ⁺ , 1%	2.5	0.0	20.4	1.4
		1.5	21.8	0.8
		4.4	31.0	5.0
		6.8	41.0	5.0
Cloisite 30B, 1%	2.7	0.0	19.0	0.0
		1.8	21.8	0.8
		4.3	30.0	4.0
		6.5	36.6	0.6

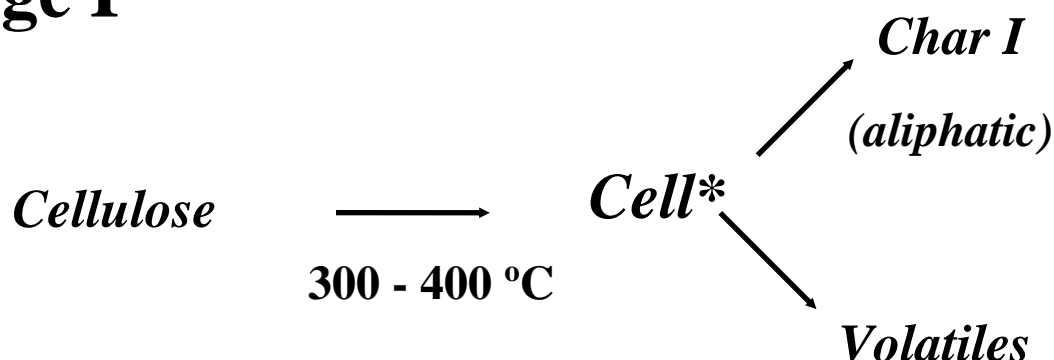
Notes: P_F = % w/w P on fibre; ΔLOI_{nano} = (LOI_{nano} – LOI_{FR control})

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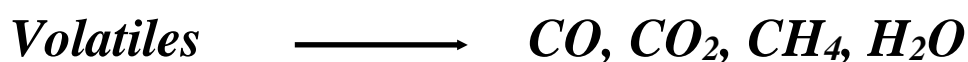
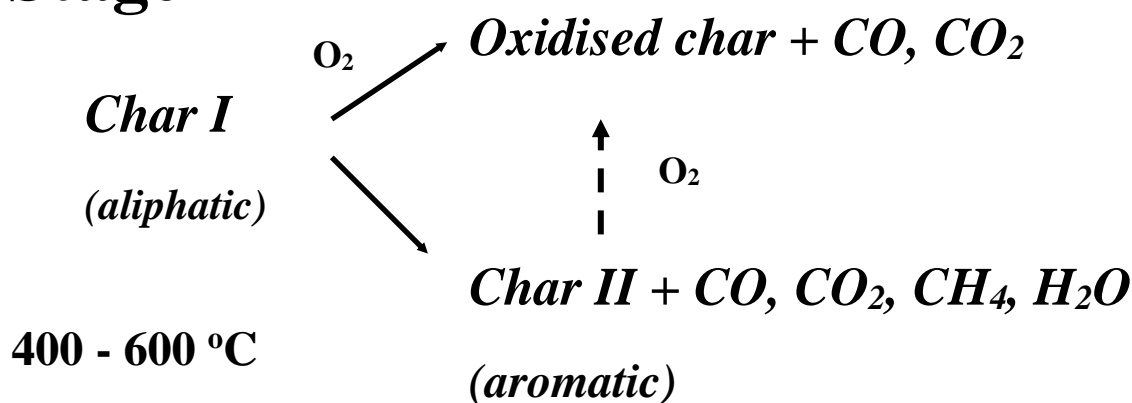
Table 7: Peak heat release rate results for fabrics (nominal area densities, 150 g/m²), flame retarded, back-coated and glued to Schneller (S-SSCP) boards using the OSU calorimeter at 35kW/m² heat flux and cone calorimetry at 50 kW/m² heat flux [107]

Sample	Heat release rate, HRR, kW/m ²			
	OSU at 35 kW/m ² incident flux		Cone calorimeter at 50 kW/m ² incident flux	
	Peak HRR	Average HRR over 2	Peak HRR	Average HRR over 2
		min		min
Silk warp/mohair weft	58	26	56	8
Silk warp/alpaca weft	58	25	48	14
Silk warp/cashmere weft	61	26	57	20
Silk warp/Sea Island cotton weft	39	25	46	19
Polyester warp/alpaca weft	59	32	64	20
Polyester warp/mohair weft	62	30	66	16

Stage I



Stage II



Stage III

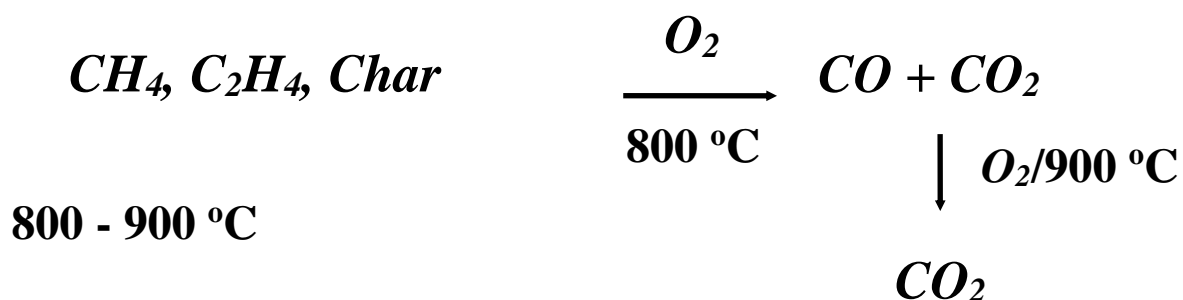


Figure 1: Mechanism of cellulose pyrolysis [34]

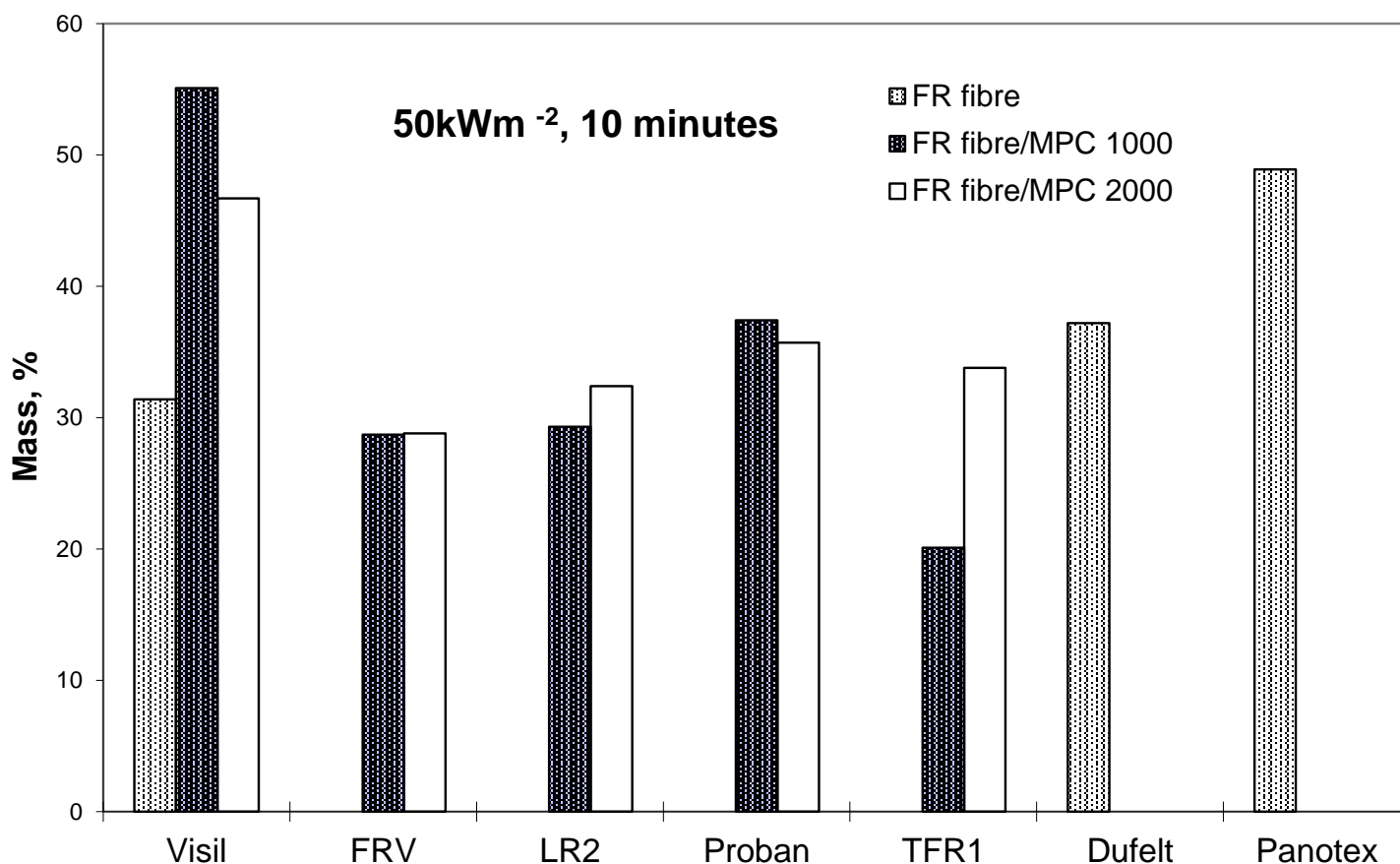
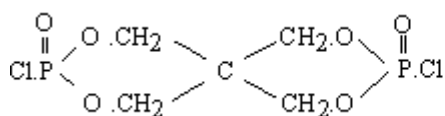


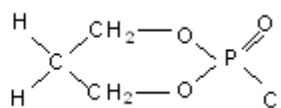
Figure 2: Residual coherent fabric chars following exposure to 50 kW m⁻² heat flux for 10 minutes in air (Key: FRV= Lenzing Viscose FR, LR2=APP-treated cotton, Proban=Proban-treated cotton, TFR1=phosphonamide-treated cotton, Dufelt=aramid fabric, Panotex=carbonised acrylic fabric. MPC 1000=APP/Melamine/Pentaerythritol intumescent, MPC 2000= Antiblaze NW intumescent).[54]

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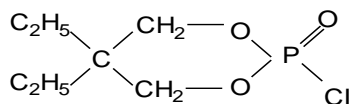
(I) SPDPC

(spirocyclic pentaerythritol diphosphoryl chloride)



(II) CPPC

(cyclic 1,3- propanediol
phosphoryl chloride)



(III) CDPPC

(cyclic 2,2-diethyl-1,3-propanediol phosphoryl chloride)

Figure 3: Full names, and structures of SPDPC, CPPC, and CDPPC

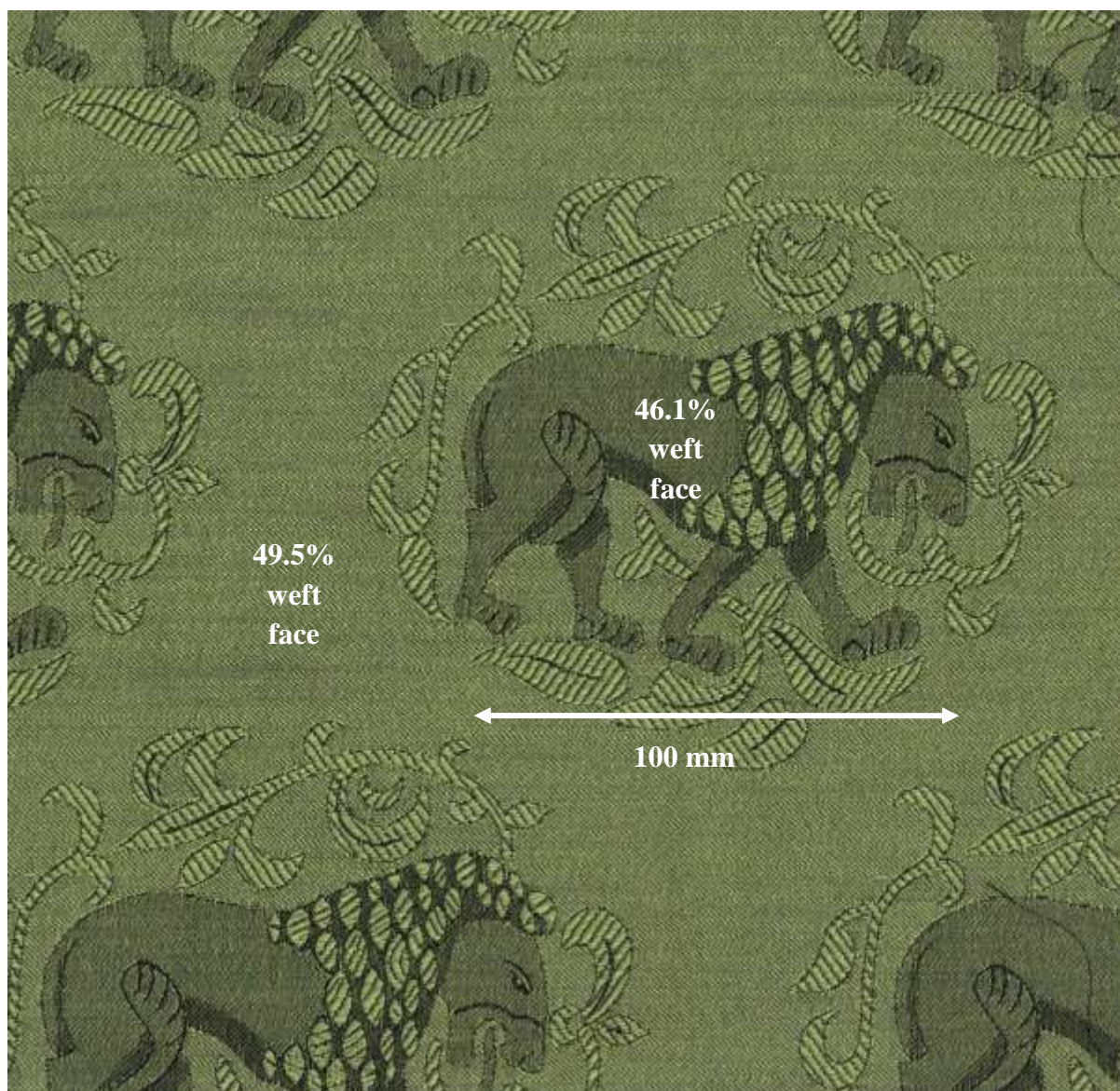


Figure 4: Design with lion motif of the 39% polyester warp/61% mohair weft fabric showing the inter- and intra-motif percentages of weft on the face of the fabric [107].