Fundamental aspects of fibre and fabric flammability and flame retardancy

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University of Bolton

Contents

- Flammability of Textiles : The Problem
- Measurement of Fabric Flammability
- Methods of Flame Retarding Textiles
- Current and future trends

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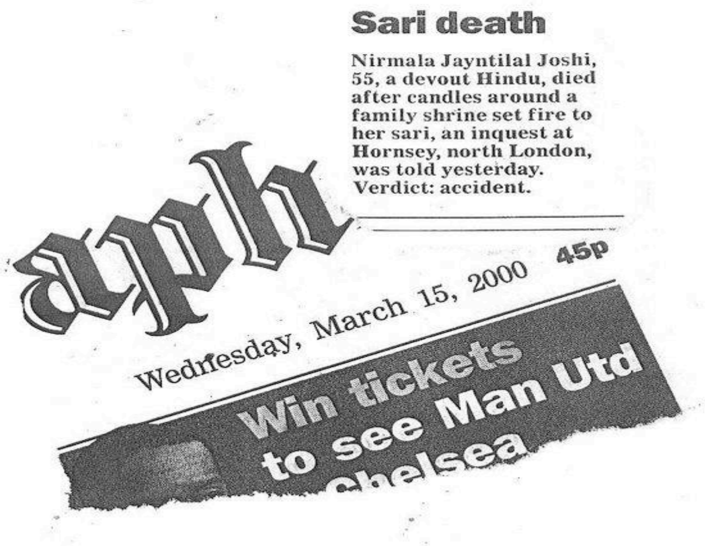

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Sari death

Nirmala Jayntilal Joshi, 55, a devout Hindu, died after candles around a family shrine set fire to her sari, an inquest at Hornsey, north London, was told yesterday. Verdict: accident.

Wednesday, March 15, 2000 45p

Win tickets to see Man Utd Chelsea

...ections are still a rubber-stamping process to legitimise the political status quo — Anatole Kaletsky,

THE TIMES

THURSDAY MARCH 30 2000 4M

Three children die in fire started by cigarette

By Conal Urquhart

THREE children died after a dropped cigarette started a house fire yesterday. Two others were pulled unconscious from the burning maisonette at Hutton, Essex and doctors were trying to save their lives last night.

The children's mother, Kerri Emptage, 32, managed to escape the blaze and called for help, but by the time firefighters arived about 1am, the children had been overcome by fumes. Ricky, 12, Lewis, 9, and Jack, 6, died before paramedics could resuscitate them. Danielle, 11, and her brother, Jo-Jo, 9, survive.

Divisional Officer Barry Cable, of the Essex fire service, believed that the fire was caused by a cigarette left on a sofa in the downstairs sitting room. A smoke alarm was not activated because its batteries were not working. "A smoke detector without a battery is not a smoke detector," he said.

His colleague, Station Commander Martin Powell, said that the house was blazing when the fire engines arrived. "Flames were shooting and punching out of the ground floor. Toxic gases would have put the children to sleep. They would have gone to sleep and not woken up."

Mr Powell praised a neighbour who tried to rescue the children using a ladder. "He did a brilliant job but there was just too much heat and too much smoke."

Mrs Emptage was being treated at Basildon Hospital. Her estranged husband, Steven, was with their two surviving children in London, where one is at Guy's Hospital and the other is at Great Ormond Street Hospital.

Neighbours and friends laid flowers and teddy bears by the burnt-out maisonette yesterday. Amanda Johnson, 17, used to babysit the children regularly. "They were brilliant to me," she said. "They were always well behaved. They were very loving children to their mother."

Lewis, Jack and Jo-Jo were pupils at Long Ridings Primary School while Ricky and Danielle attended Shenfield High School.

★★★

2 — Bolton Evening News,

Woman burned in horror accident

A WOMAN was fighting for her life in hospital today after her nightdress caught fire in a freak accident at her Bury home.

Miss Sarah Cunningham, aged 27, was turned into a human fireball as her clothing caught fire.

Firefighters believe the badly burned woman, who has learning difficulties, was playing with matches.

She suffered 25 per cent...

July 1999

Major UK Fires

Fires	Cause	Casualties	
		Deaths	Injuries
Taunton, 1978	Laundry	12	15
Woolworths, 1979	Furniture	10	53
Stardust, 1981	Seating	48	128
Manchester airport, 1985	Fuel/Furnishing	55	15
Windsor Castle	Curtain	-	-

The Problem:

- Clothing on the person
  - Nightdresses (UK Regulations: *Consumer Protection Act…The Nightwear (Fire) Safety Regulations 1985)*
  - Typical fabrics: Cotton, polyester/cotton, acrylic, acetate, nylon, polyester,wool, silk
- Furniture and furnishings, bedding
  - The Furniture and Furnishings Fire Safety Regulations 1988
- Curtains and drapes
- Floor covering

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- Flammability of Textiles : The Problem
- Measurement of Fabric Flammability
- Methods of Flame Retarding Textiles
- Application Based Performance Requirements and FR Technologies

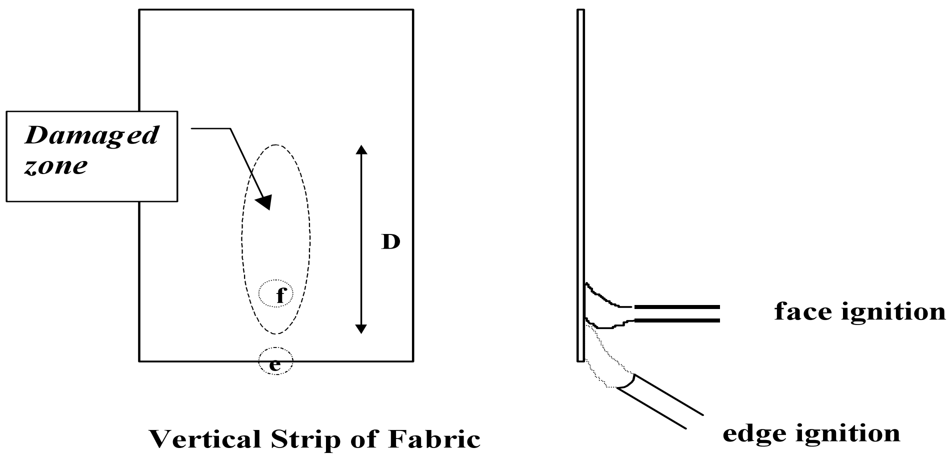
Flammability testing

- Ignitability
- Ease of extinction
- Burning rate

- Heat release tests
- Mannequin tests
- Full products tests

Ignitability

Simple Vertical Fabric Strip Burning Test

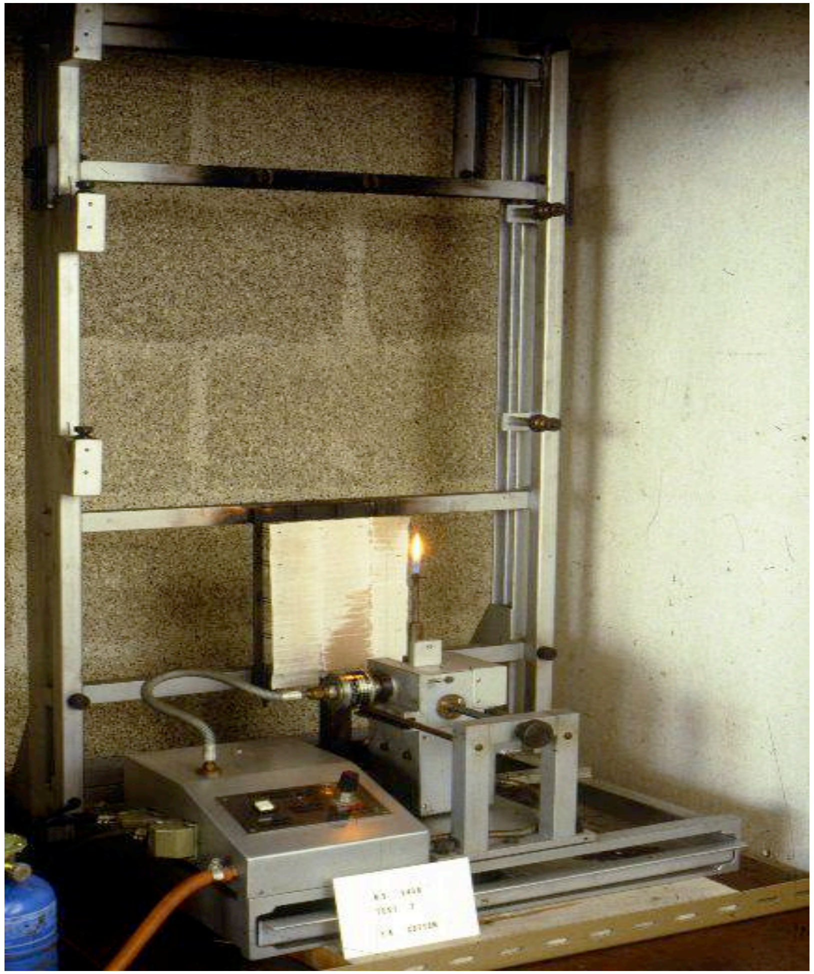


Can We Measure Burning Hazard?

Fabric	Ignition time (Edge), s	Ignition time (Face), s
Poly/cotton (55/45)	2	3
Poly/cotton (65/35)	1	2
Cotton (lightw’t)	1	2
Cotton (heavyw’t)	1	4
Acrylic	1	2
Silk	2	2
Wool	3	3
Polyester	melts	melts

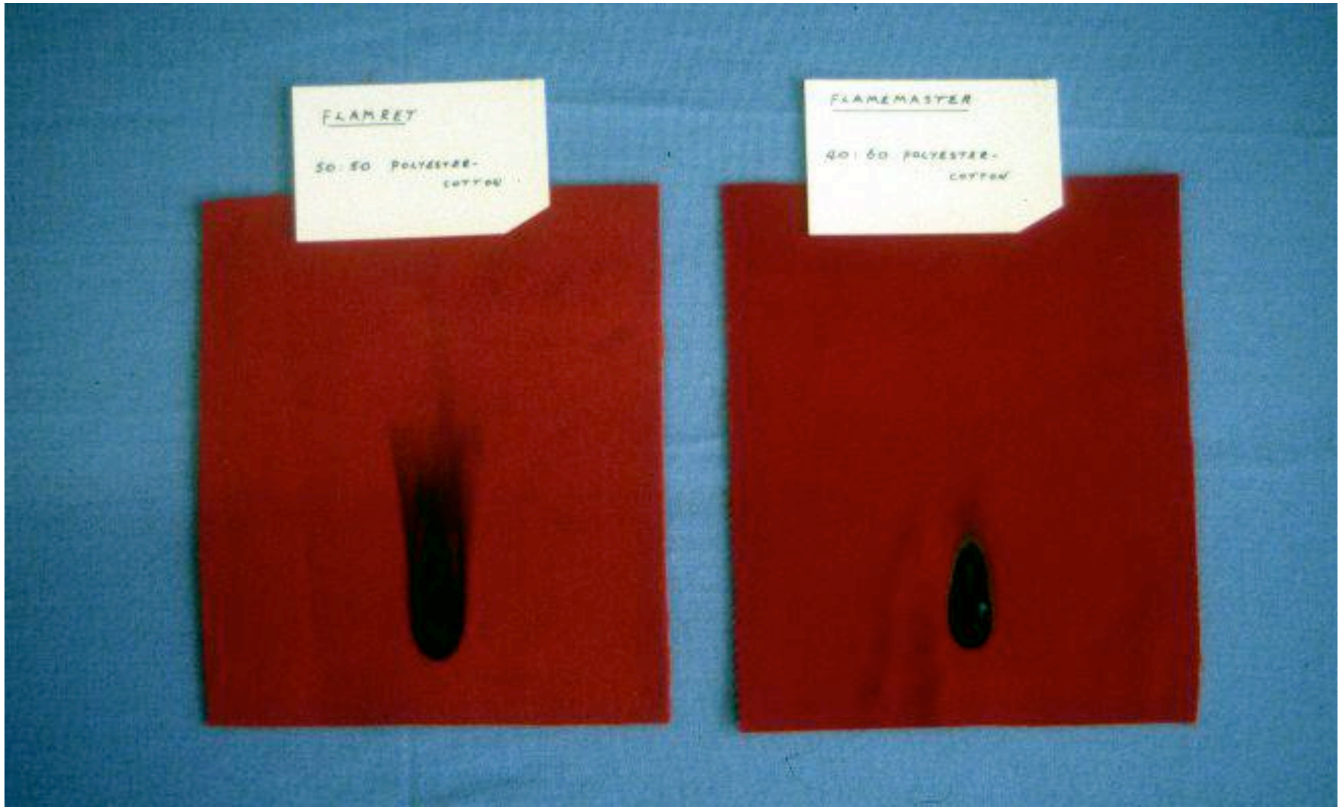
Ease of extinction

BS 5438 : Test 2 (EN ISO 6941)

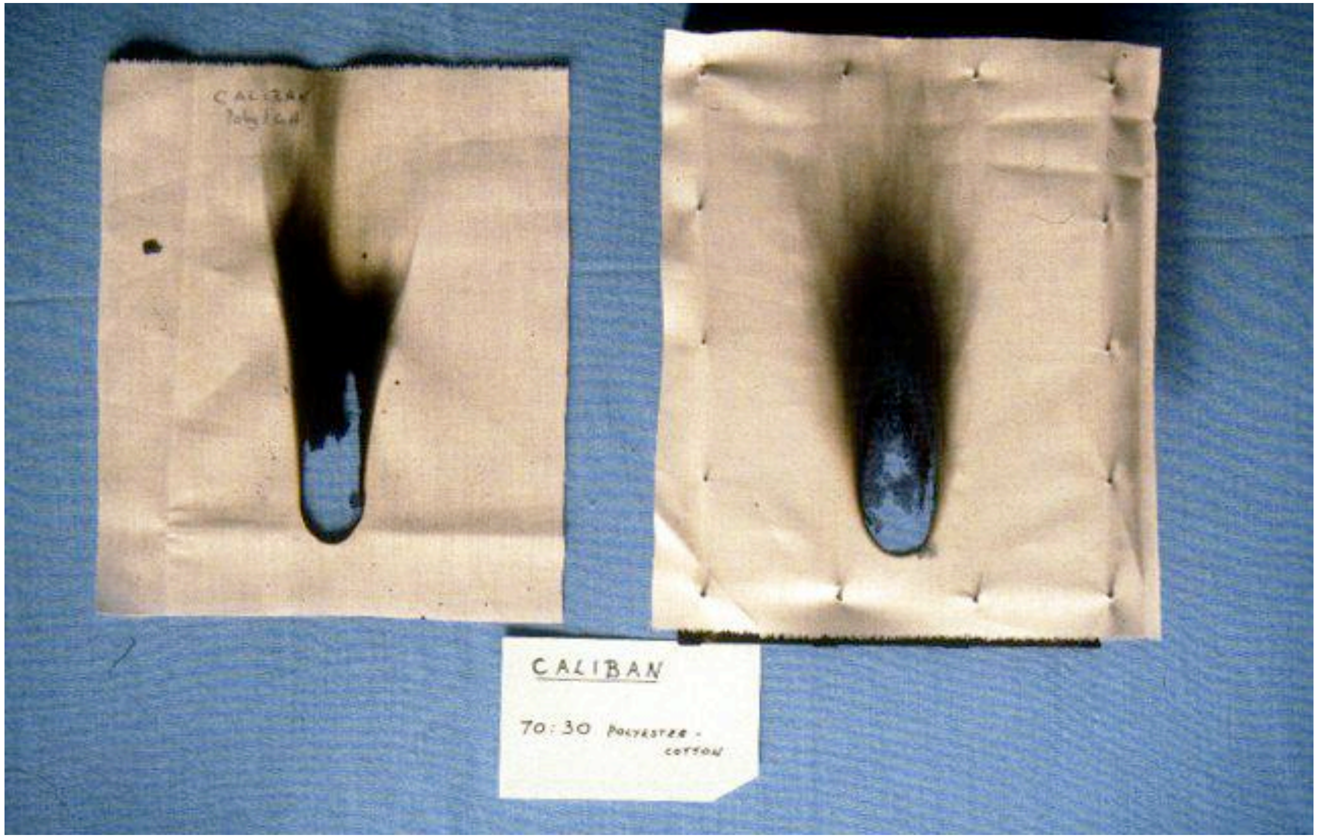


50 : 50 Polyester - Cotton

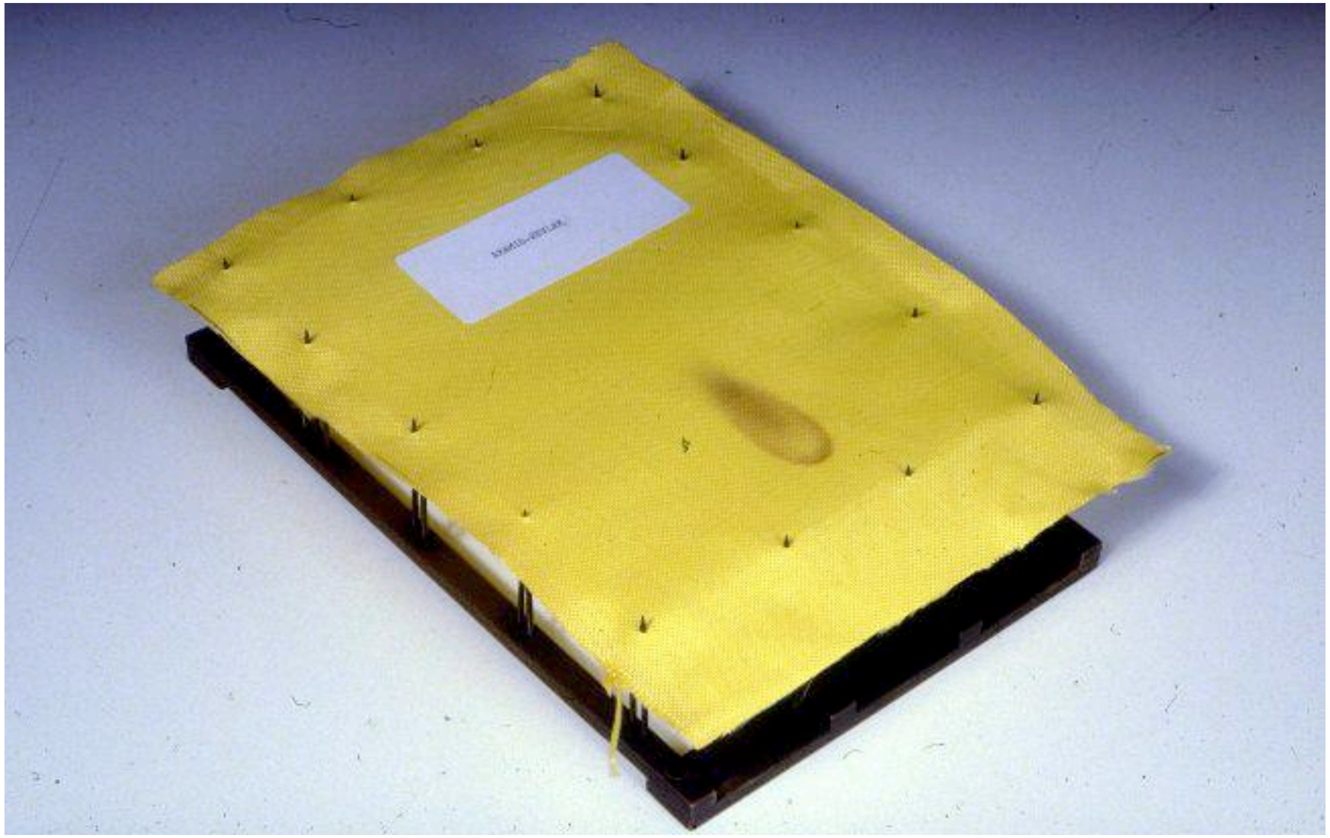
40 : 60 Polyester - Cotton



70 : 30 Polyester - Cotton



Aramid - Kevlar



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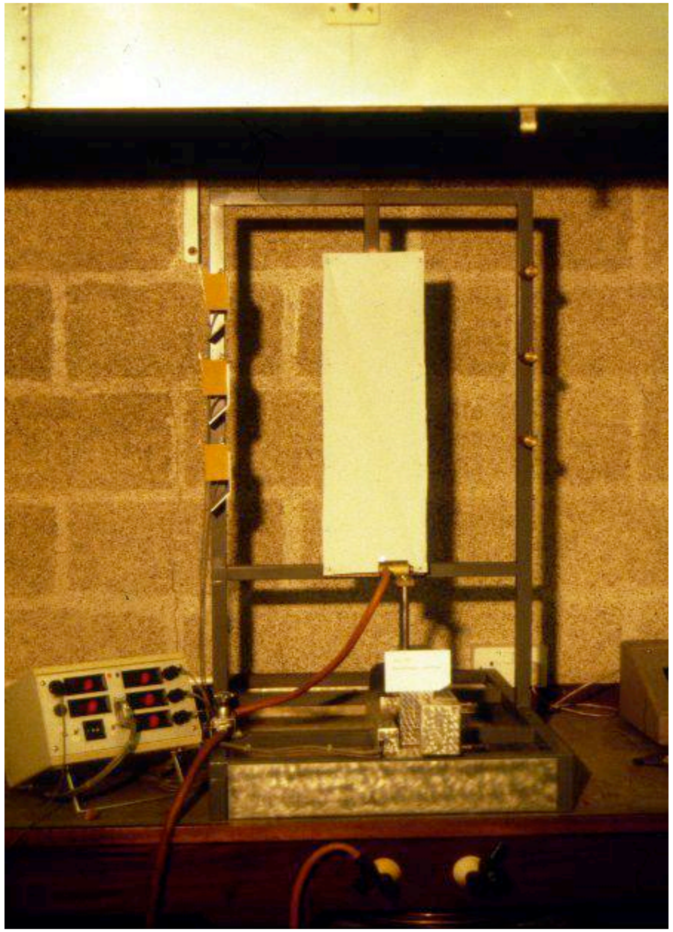
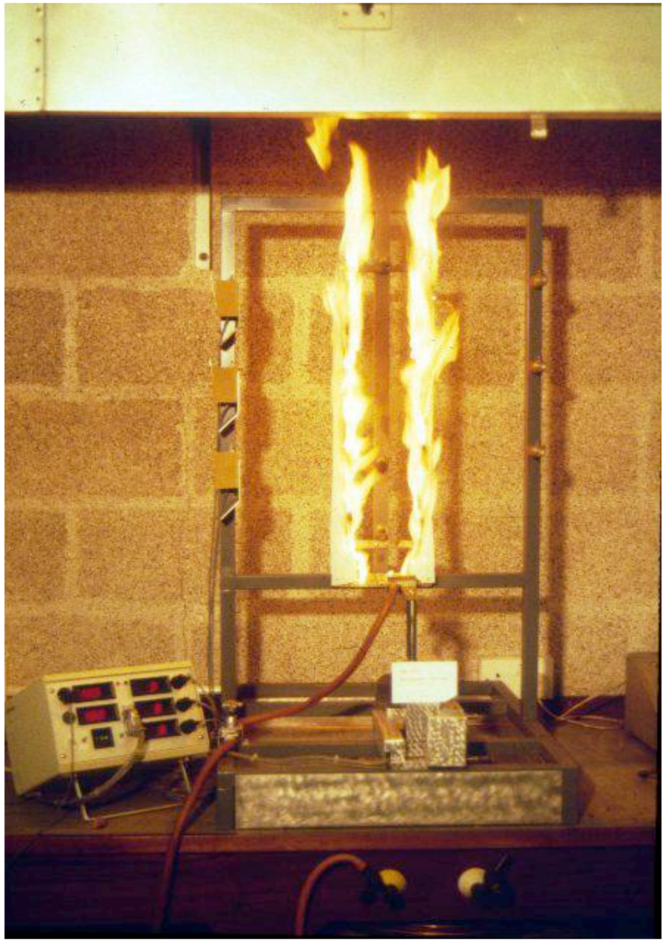
Flame spread

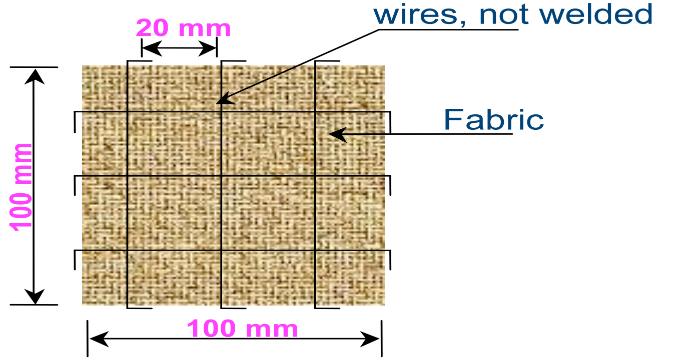
BS 5438 : Test 3 (EN ISO 6941)





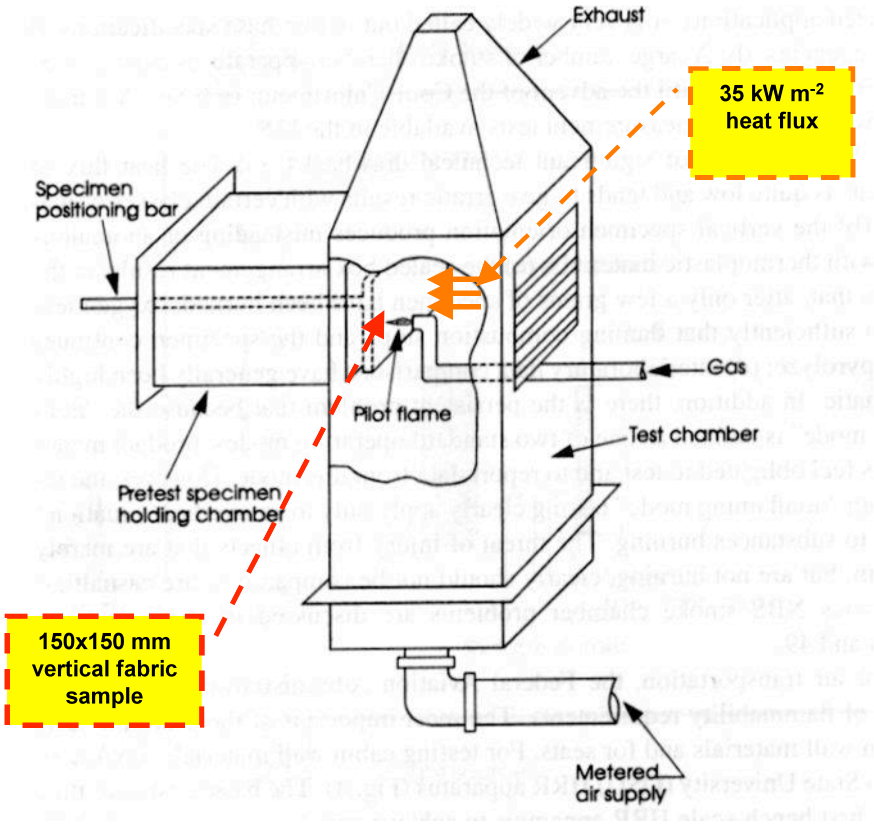
Heat release tests Cone Calorimeter (ISO 5660)

Sample holder with fabric sample: 100x100 mm

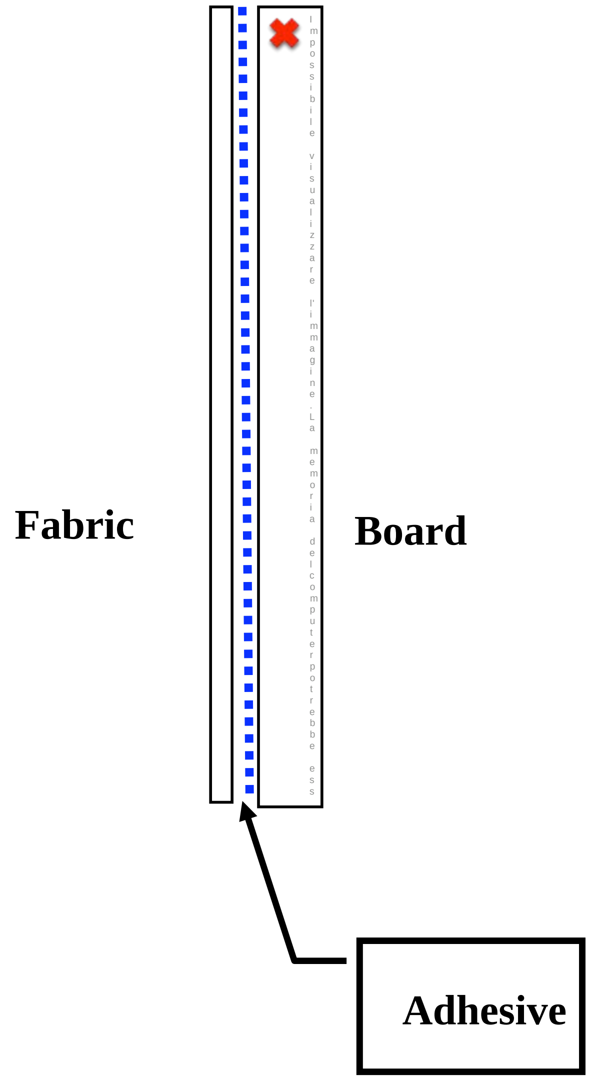


OSU Calorimeter

(FAR 25.853 Part IV Appendix F)



Fabric Composites for OSU testing:



Full product tests

BS 5852 - Flammability test for upholstered furniture

Ignition Sources

0 : Cigarette
1-3 : Gas flames, progressively increasing size
4-7 : Wooden cribs, progressively increasing size

Contents

Flame Retardant

Ability to withstand ignition by a small heat source and/or to sustain flame.

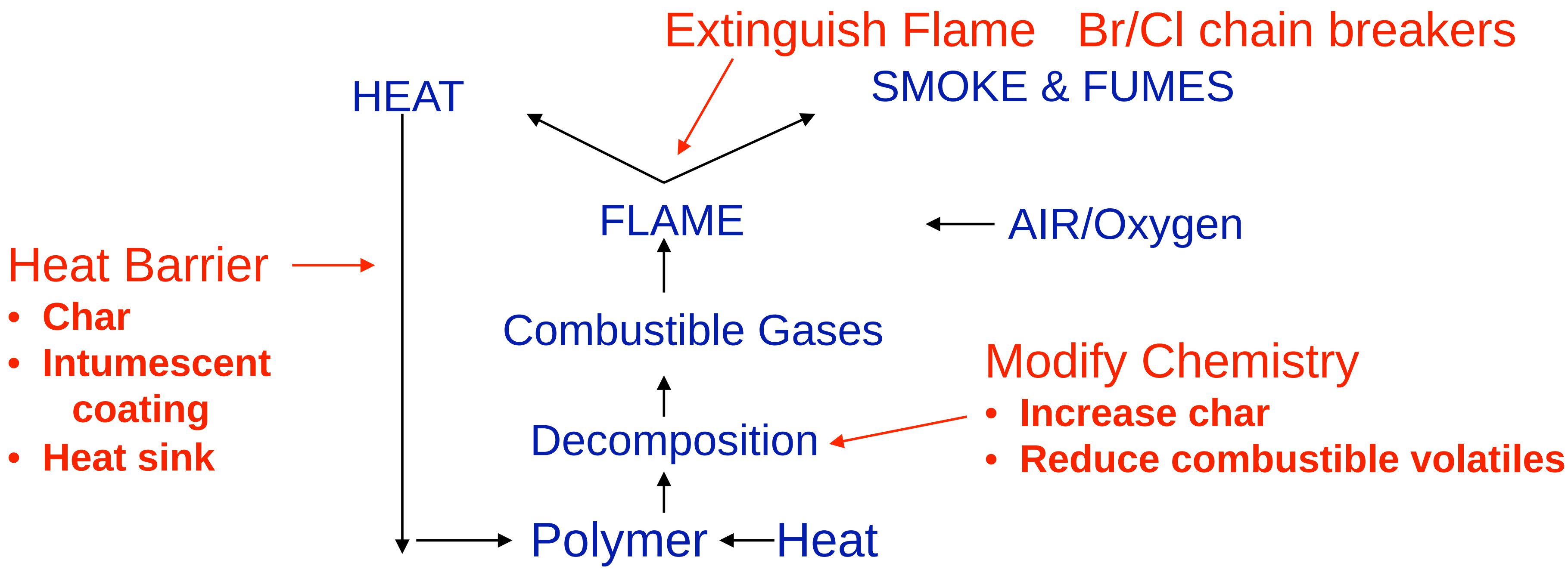
Heat Resistant

As above + continued capability of retaining geometrical coherence under defined heat hlux.

Thermoplastic fibres are not heat resistant

eg polyester, polyamide, polypropylene

How do polymers burn?



Flame retardant strategies

Flame retardant strategies for textiles

- Surface treatments
- FR additives / copolymers in synthetic fibres
- Heat resistant and inherently FR fibres

Nanocomposite based FRs

- FR finishes
- Coatings
- Back-coatings
- Intumescent coatings
- Plasma coating

- Aramid : Nomex & Kevlar (DuPont)
- Aramid- arimid : Kermel (Rhone Poulenc)
- PBI
- Novoloid : Kynol
- Oxidised acrylic : Panox (RK Textiles)

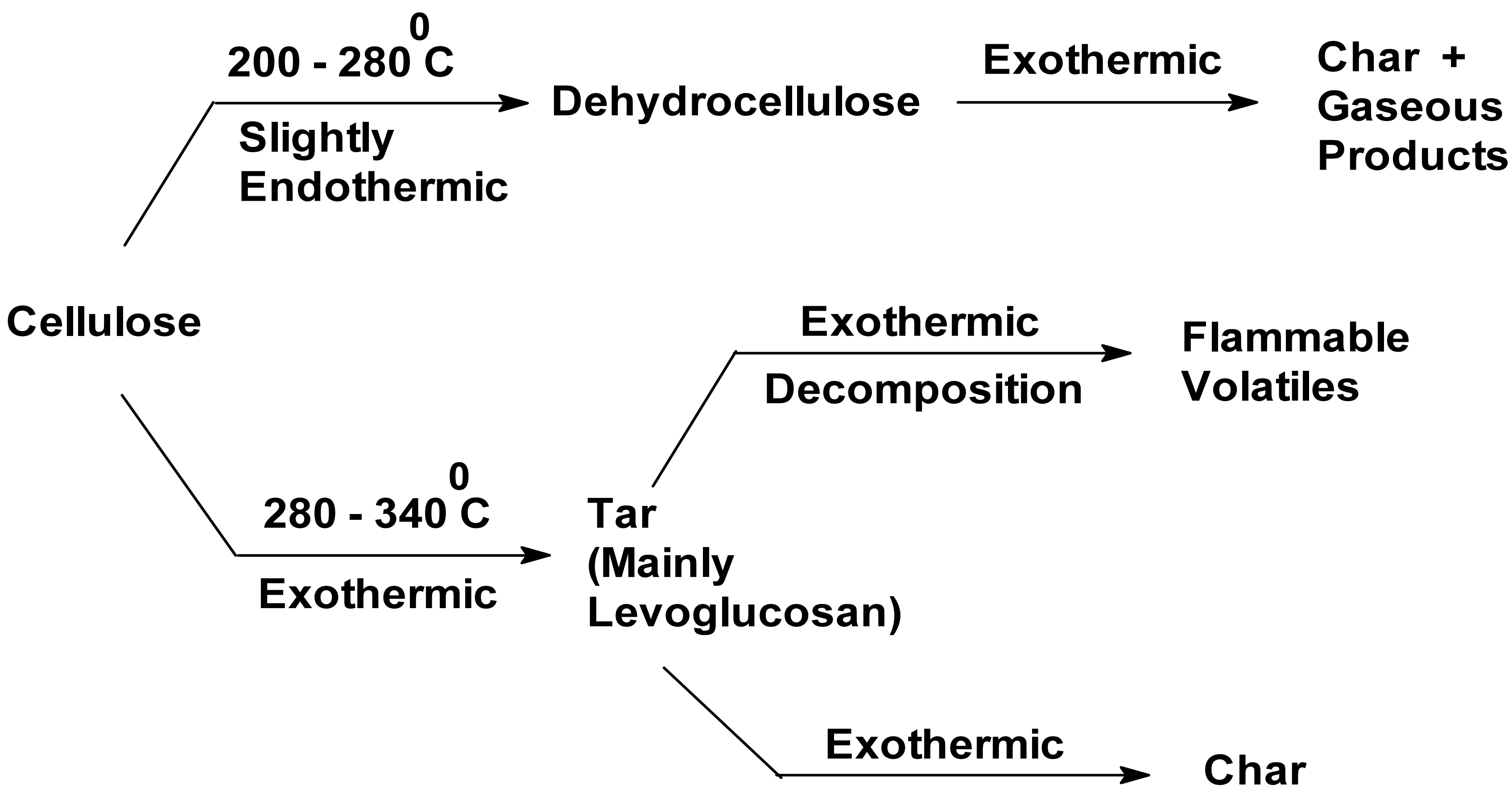
Flame Retardant Cellulosics

- Flame Retardant Cotton

  :*Chemical after-treatments*
- Flame Retardant Viscose (incl. all regenerated cellulosics)

  :*Spinning dope additives*
- Blends of cellulosics with other (usually synthetic) fibres

Decomposition of cellulose



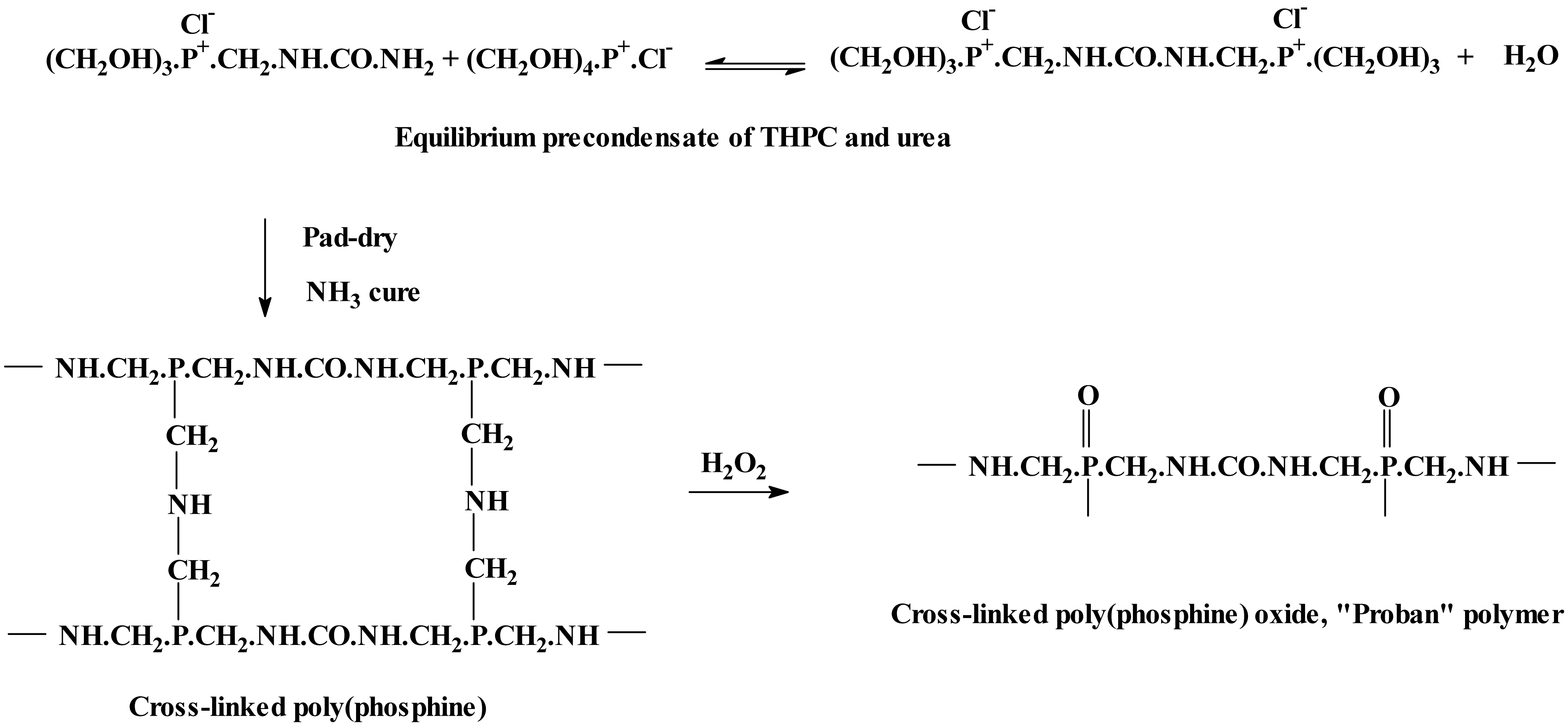
Currently available flame retardants for cotton

Type	Durability	Example
Salts		
Ammonium polyphosphate	Non or semi durable	
Diammonium phosphate	Non durable	
Borax/Boric acid (7:3 % w/w)	Non durable	
Organophosphorus		
Methylolated phosphonamide	Durable (50 w)	Pyrovatex CP (Ciba)
THPC - urea - NH_3	Durable (50 w)	Proban CC (A & W)
(Back) Coatings		
Chlorinated paraffin waxes	Semi durable	$C_nH_{(2n-m+2)}.cl_m$
Sb/halogen	Semi to fully durable	Sb_2O_3 + DBDPO + acrylic resin eg Myflam (Mydrin)

Durable FR Finishes for cellulosic are polyfunctional P-, N- containing formulations

- Self crosslinking
  - eg THPC - condensates
- Cellulose crosslinking
  - eg methylolated phosphonate - melamine systems

THPC - urea - NH_3 condensate



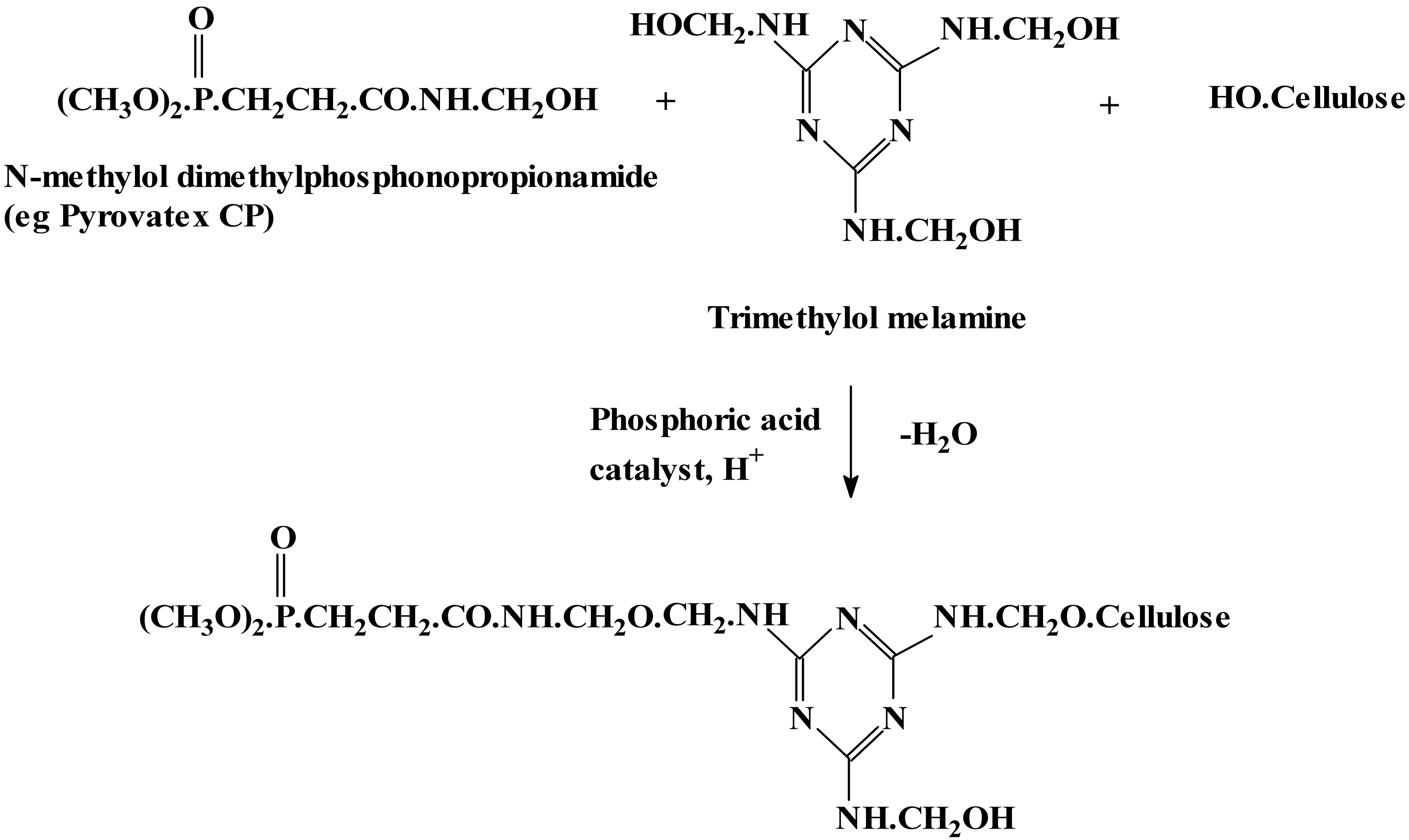
THPC - urea - NH_3 condensate

Proban (Rhodia)

Application scheme :

- Pad on Proban
- Dry to 12 - 15% relative humidity
- React fabric with dry ammonia gas
- Oxidise with hydrogen peroxide
- Wash in sodium carbonate
- Wash in water
- Stenter dry
- Soften by compressive shrinkage

Methylolated phosphanamide condensate



Methylolated phosphanamide condensate

Pyrovatex CP (Ciba)

A typical formulation :

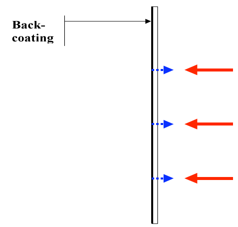
• Pyrovatex CP	350g
• Melamine Resin	35g
• Silicone Softner	20g
• Wetting Agent	1g
• Catalyst	15g
• Water	579g

Application Scheme :

- Pad on solution of Pyrovatex
- Dry at 120°C
- Cure at 160°C for 3 minutes
- Neutralise with dilute sodium carbonate
- Wash in water
- Stenter dry

Typical Back-coating formulation

Antimony III Oxide	17 pph
Decabromodiphenyl oxide	33 pph
Resin	50 pph

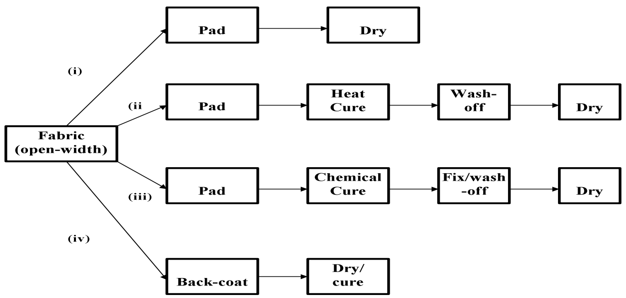


Applied at 20-30% w/w on fabric

Very successful <u>but</u>

- **Environmental concerns wrt certain Br compounds**
- **Toxicological concerns wrt Sb_2O_3**

FR Finishing & Coating Techniques



Flame Retardant Viscose

- Viscose FR (Lenzing, Austria)
  - Sandoflam 5060 (2,2 oxybis(5,5-dimethyl-1,2,3-dioxaphosphorinane-2,2-disulpfide))
- Visil (Sateri, formerly Kemira, Finland)
  - Polysilicic acid, as 30 % by silica

FR finishes for wool

Non- and semi- durable

- Ammonium polyphosphate (+ ammonium bromide)
- Organic P- & N- containing compounds
- Borax : Boric acid (2:1 w/w)

Durable

ZIRPRO : K_2ZrF_6 or K_2TiF_6

$$\text{Wool - NH}_2 + H^+ \longrightarrow \text{Wool - NH}_3^+$$

$$[Zr\ F_6]^{2-} + 2[\text{Wool - NH}_3^+] \longrightarrow [\text{Wool - NH}_3^+]\ [Zr\ F_6]^{2-}$$

The challenges of Blends

Flame retardant effective on one fibre in contact with other differently flame retarded fibre can prove antagonistic

- Apply the flame retardant to majority fibre present
- Apply halogen based backcoating

Synthetic Fibres

- Thermoplastic: PET, N66, N6, PP
- Melt (flaming) drips
- Sb-Br & P-based systems often work only in vapour phase
- Non-flaming melt drips (>300^{o}C!)
- Rarely char-forming
- No currently available FR conventional synthetics are char-forming

Synthetic Fibres

Polyester

- Trevira CS (GmbH), incorporating a comonomeric phosphinic acid unit into the PET chain
- Bisphenol-S-oligomer derivatives (Toyobo GH)
- Cyclic phosphonates (Antiblaze CU and 1010, Rhodia)
- Phosphinate salts (Clariant).

Polyamides

Very difficult to incorporate additives in polyamides because of their melt reactivities

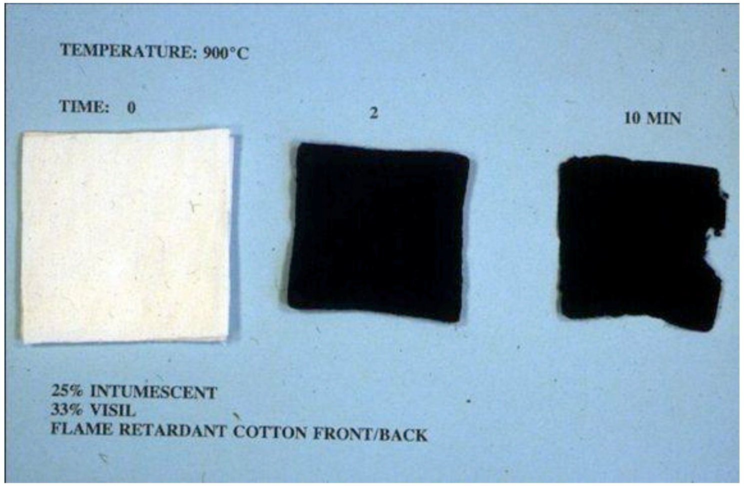
Polypropylene

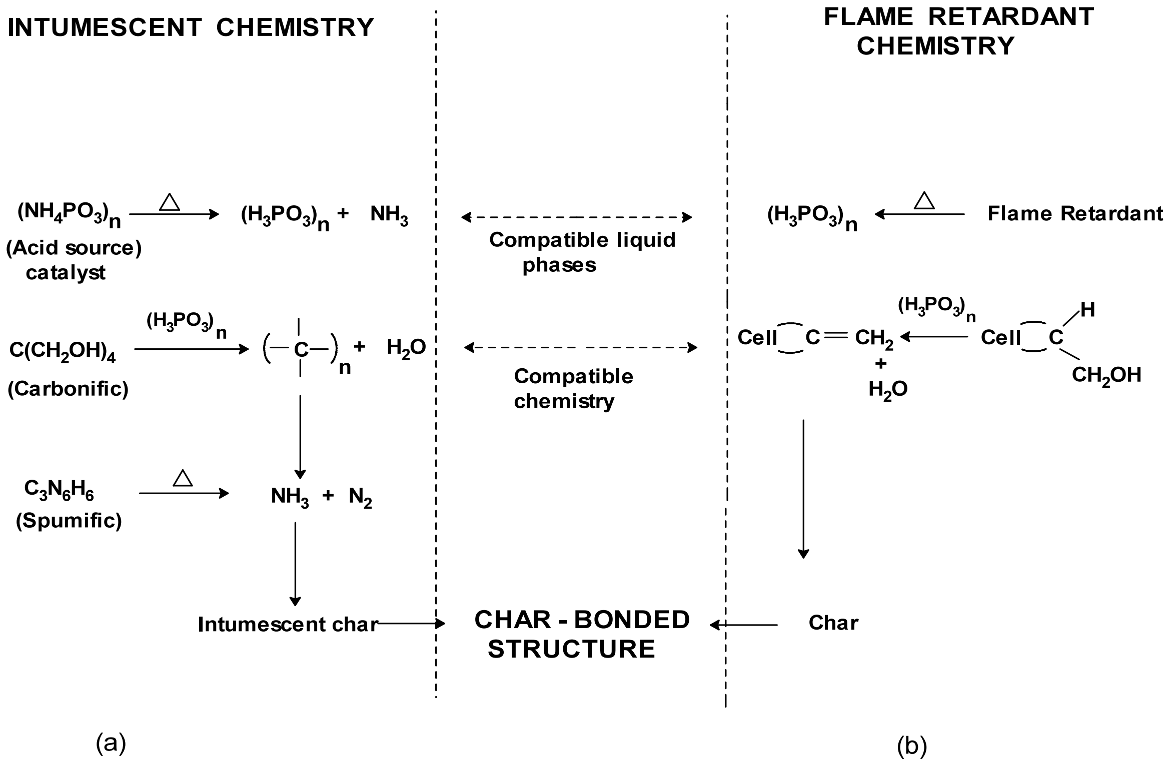
- Antimony–halogen formulations
- Tris(tribomoneopentyl) phosphate (FR 372, ICL)

All these flame retardants do not promote char formation

Use of intumescents as interactive flame retardants for char promotion

Heat treatment of fabric composite : 900^{0}C





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Use of Nanocomposites in Textiles

Nanocomposite : A polymer system containing an inorganic particle with one dimension in the nanometer range

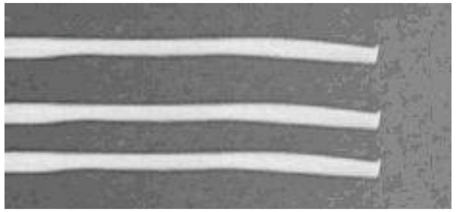
Mechanism of flame retardancy :

- On heating, polymer starts to degrade and nanoclays offer a barrier to diffusing products especially volatiles
- Polymer liquifies/melts – nanodispersed clays aggregate and diffuse to surface forming a ceramic layer

In presence of conventional FR, clay may enhance activity (char-bridging)

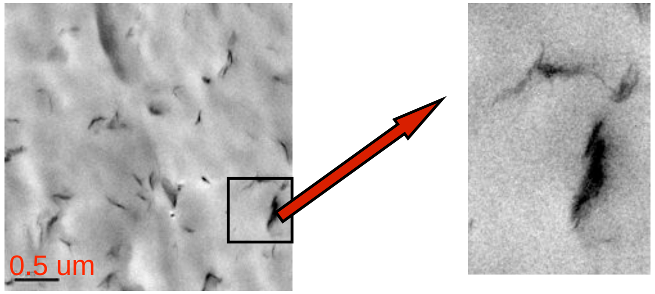
Nanocomposites in Synthetic Fibres – Bolton work

PP + additives (NOR 116, compatibiliser, clay, FR)



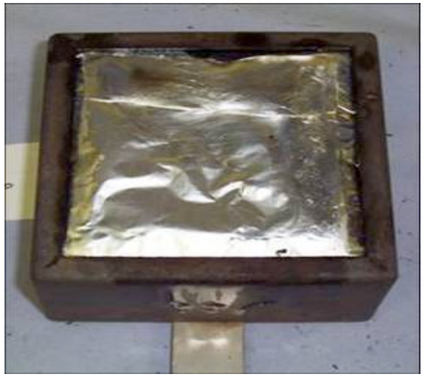
Nanocomposites in Synthetic Fibres – Bolton work

Dispersion - TEM



PP-combatibilzer – clay 20A

Nanoclays promote char formation



PP

PP-Compatibilser-clay

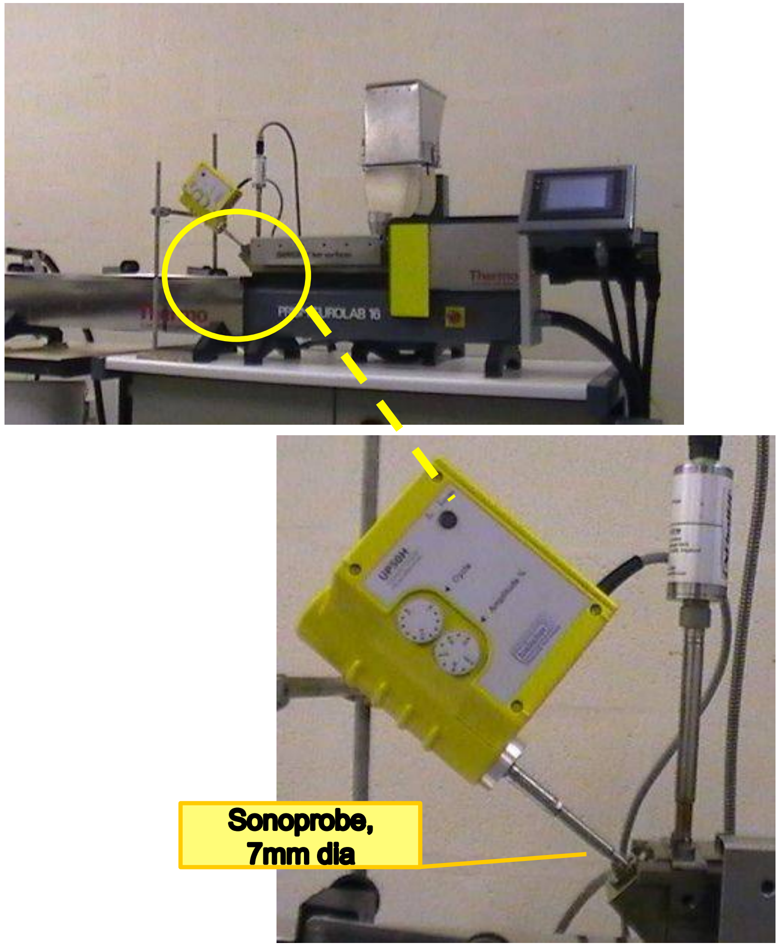
In presence of FRs, reduce rate of flame spread

Sample	Flame spread		
	60mm, t_1 (s)	120mm, t_2 (s)	Flame out (s)
PP	3	59	71
PP-clay	4	-	26
PP- clay-FR1 (P-contg)	8	-	34
PP-clay-FR2 (Halogen contg)	14	-	45

Nanocomposites in Synthetic Fibres – Bolton work

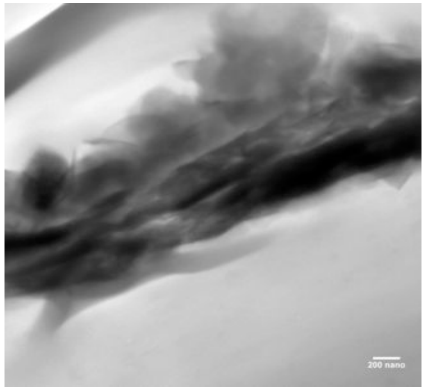
University of Bolton

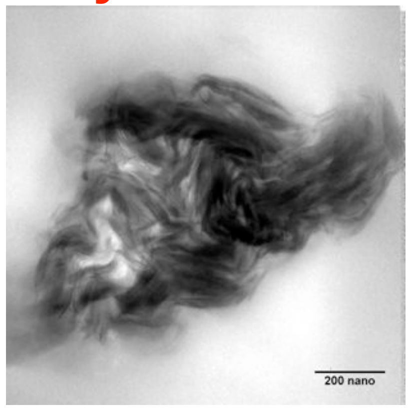
The use of ultrasonification in thermoplastic polymer melts to improve nanodispersion and efficiency of flame retardants



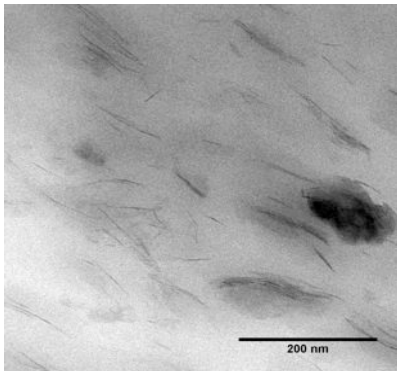
Hielscher ultrasound generator (30kHz) attached to the head of the extruder barrel.

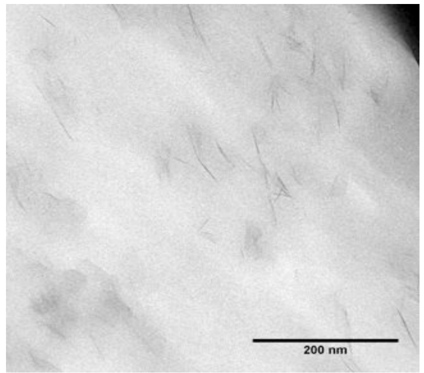
TEM : PP/ 1.3T clay





No sonification | **U/s 90% 100W**





TEM : PA6/ 25A clay

Nanocomposites in Synthetic Fibres – Bolton work

Flammability of fabrics: Vertical strip test based on BS5438 Test 1

Sample	Area density of fabric (g/m^2)	Rate of flame spread (mm/s)	No.of drops	Total mass loss (%)	Mass of the molten /burnt drops (%)
PP	110	1.5	98	100	**74**
PP/1.3T	100	1.4	95	100	**77**
PP/1.3T - U/S	90	1.6	45	**71**	**34**
PP/APP	80	5.8	18	77	**10**
PP/1.3T/APP	70	2.3	41	100	**94**
PP/1.3T/APP – U/S	120	2.2	44	**63**	**37**

- U/s reduces burn rate and number of drops
- U/s increases residue and
- reduces mass% of molten drips

Kandola, Horrocks et al, 2012

Nanocomposites in Synthetic Fibres – Bolton work

University of Bolton

Flammability of fabrics: Vertical strip test based on BS5438 Test 1

Sample	Area density of fabric (g/m^2)	Rate of flame spread (mm/s)	Number of drops	Total mass loss (%)	Mass of the molten /burnt drops (%)
PA6	60	2.8	17	42	19
PA6/AlPhos	50	3.9	7	14	11
PA6/25A	100	1.3	**89**	33	17
PA6/25A - U/S	90	2.8	**36**	34	21
PA6/25A/AlPhos	90	1.7	7	**65**	**41**
PA6/25A/AlPhos – U/S	70	3.4	8	**45**	**26**

- **PA6/25A – U/s increases burn rate?**
- **U/s reduces number of drops**
- **PA6/25A/AlPhos – U/s reduces total mass loss and mass of molten drops**
- **Area density variations?**

Kandola, Horrocks et al, 2012

Nanoparticles on the surface

- Potential for:
  - Formation of a heat reflective layer
  - Nanoceramic surface as a flame shield
  - Applied to any fibre/textile substrate
  - Minimise effect on other textile or substrate properties
  - Use known chemistry

Nanoparticle, plasma-activated surface treatments for improving flash fire resistance of textiles

Sept 2005, Iraq

- Heat flux of 75-100 kW/m^2 incident on a target for up to 3 seconds
- US std: NFPA 2112; *Standard on Flame-Resistant Garments for Protection of Industrial Personnel Against Flash Fire (published in 2000)*
- Expose 84 kW/m^2 for the duration of 3 seconds with a pass /fail rate of 50% under the testing protocols set in ASTM F1930

Recent work in our laboratories

(Horrocks A R, Kandola B K, Nazaré S and Price D, Flash fire resistant fabric, *UK Patent Application 0900069.6, 5 January 2009*).

Fabrics:
100% Cotton
Proban® cotton
Nomex® aramid

- Use an experimental atmospheric argon plasma torch to activate FR textile substrates in the presence of a silicon-containing monomer and functional nanoparticles.
- Si monomer: hexamethyldisiloxane (HMDSO)
- Nanoclay: Na-MMT and quaternary phosphonium salt functionalised MMT

Plasma etch fabric under Ar for 15 min → *Introduce* :

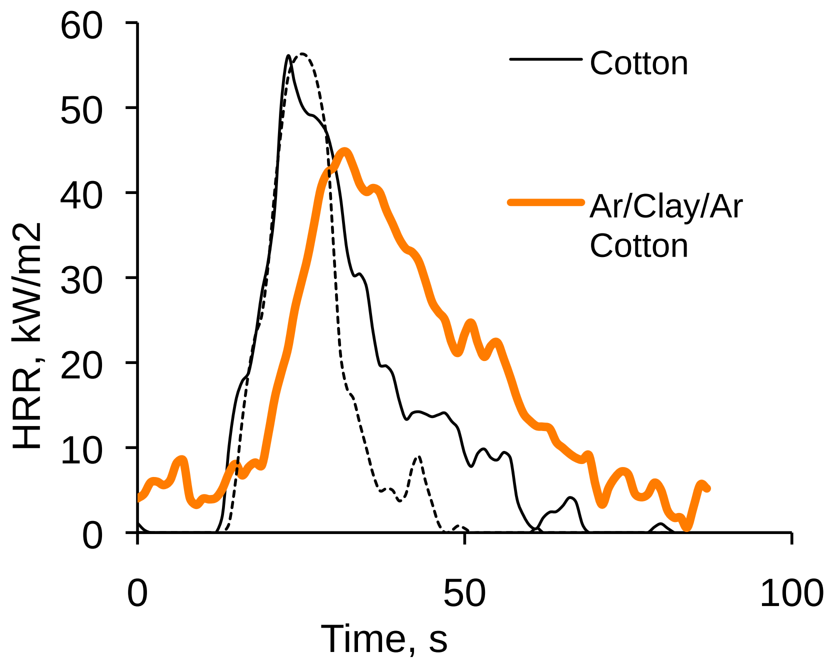
HMDSO or

Nanoclay (NC) or

HMDSO + NC

Plasma treat for 15 min

Cone results for Cotton at 35 kW/m²



Plasma treatment	TTI, s	TTP, s	PHRR, kW/m²
Untreated cotton	14	23	56
Ar	19	25	58
Ar/Clay/Ar	27	32	45
Ar-HMDSO	15	21	58
Ar/Clay/Ar-HMDSO	22	23	54

TTI and TTP increase

Cone results for Nomex at 60 kW/m²

Plasma treatment	Mass change, %	TTI, s	TTP, s	PHRR, kW/m²
Nomex only	-	13	16	83
Ar	-2.8	16	20	73
Ar/Clay/Ar	-0.6	NI*	-	-
Ar-HMDSO	1.6	NI*	-	-
Ar/Clay/Ar-HMDSO	3.5	NI*	-	-

NI = "No ignition"

Durability

Effect of an accelerated wash removes plasma effect with 100% cotton but increases TTI/reduced PHRR retained for Proban® and Nomex® fabrics

Conclusions

- challenges

- New chemistry?
- Environmental acceptability: *halogen acceptability?…Risk-benefit?*
- Make current chemistry work harder
- Char-promotion in thermoplastics
- Smart FR/HR systems
- Nanocomposite fibres