PM

Nr 5/04

KEMI

KEMIKALIEINSPEKTIONEN

Survey and technical assessment of alternatives to decabromodiphenyl ether (decaBDE) in textile applications

Stefan Posner

Survey and technical assessment of alternatives to decabromodiphenyl ether (decaBDE) in textile applications

Stefan Posner

Summary

On behalf of the Swedish Chemicals Inspectorate, IFP Research has surveyed and carried out a technical assessment of flame-retardant alternatives to decabromodiphenyl ether (decaBDE) currently available for textile applications.

Coated textile materials, furniture and similar seating and bedding products but also other technical textile items are common textile applications for decaBDE. The protection against flames is based on the synergy between antimony and bromine, usually in the form of decabromodiphenyl ether, applied in the ratio of *one part antimony to three parts bromine,* which has historically proved to be the most effective synergetic molar ratio to achieve the best possible flame-retardant properties.

The market for flame retardants has grown principally because of increasingly stringent international and national safety requirements. This trend has been pushed ahead in particular in the United Kingdom, Ireland and the United States, especially California. Customers' requirements are absolute, whether they are public institutions, international organisations or businesses active in the market. If the fire requirements are not met, there is no market for the individual supplier and the manufacturer. On the other hand, there are no descriptive fire requirements at all stipulating that particular flame retardants have to be used for the requirements to be met. The choice of flame retardant is left entirely to the manufacturer. In some cases the requirements are so strict that the alternatives are not economically feasible or the environmental requirements in that part of the world do not make the alternatives possible. Inferior quality characteristics, such as a deterioration in the comfort and durability of the textile product, may also be limiting factors in the manufacturer's choice of flame retardant.

As well as statutory and safety requirements for these products, the focus on the environmental impact of flame retardants and their impact on human health has led the major manufacturers of flame retardants around the world to add non-halogenated products to their traditional ranges of halogenated flame retardants in recent years.
There are established flame-retardant materials and potential new variants based on other synergistic combinations as possible substitutes for antimony-decaBDE. These may be organic phosphorus compounds or phosphorus-chlorine compounds, aluminium and zinc hydrate, swelling (intumescent) systems, new synergistic combinations, for example antimony – bromine/phosphorus – silicon, surface-active fibre systems and systems with graft copolymers. Some of these alternatives have been established on the market for decades. The fact that organic bromine compounds continue to be used instead of halogen-free alternatives is due to a number of factors, only a few of which are technical in nature. Together with low price, one of the most common reasons why the alternatives do not always become accepted is that the market prefers to make use of tried-and-tested flame retardants.

The types of flame protection likely to entirely replace antimony-decaBDE, with the backing of clear rules and regulations, are the intumescent systems and phosphorus chemistry. The flame-resistant fibres combined with combustible fibres will probably also be used successfully in some applications. However, a number of fire-related problems remain to be solved in some applications, for example for polyurethane foam, but this trend too will accelerate when the

halogenated alternatives no longer have a role to play in the international sustainable society. It is now up to the legislators to create this incentive. The technology already exists.

Contents

Foreword

On behalf of the Swedish Chemicals Inspectorate, IFP Research has surveyed and carried out a technical assessment of flame-retardant alternatives to decabromodiphenyl ether (decaBDE) currently available for textile applications.

The assignment comprises
⇨ An analysis of the alternatives available at present
⇨ A description of what functional requirements have to be met in different applications
⇨ A description of applications in which the alternatives can be used
⇨ A technical assessment of whether the alternatives fulfil the requirements set for flame-retardant properties in the applications in which they are used
⇨ A brief description of trends in the development of flame retardants

Introduction

Why are flame retardants used?
Fires are among the most common causes of harm to property and people around the world. A number of ***risk-benefit analyses*** based on actual fires have been performed in the last ten to fifteen years. Statistics from these risk-benefit analyses indicate a clear reduction in the number of deaths and severe injuries due to improved fire safety, which includes increased and improved applications of various forms of flame-retardant materials. These forces have driven development ahead towards functionally better and more effective flame retardants, and legislation has been tightened up at the same time. This trend has been particularly apparent in the United Kingdom, Ireland and the United States, especially California, countries which have carried out risk-benefit studies on a large scale. This has been reflected in strong legislation and extensive safety requirements for protection against fire which have given rise to tough fire standards for a number of materials handled in situations where there is a risk of fire.

The market for flame retardants has grown principally because of the increasingly stringent international and national safety requirements. The primary and ultimate function of flame retardants is to satisfy these various statutory safety requirements. As the rules and regulations are tightened up, the market for flame retardants will be increasingly affected in relation to technology, the environment and price.

As well as the safety requirements specified for various products, there is a focus on the possible environmental impact of flame retardants and their impact on human health, leading major manufacturers around the world in recent years to add non-halogenated products such as those based on phosphorus chemistry to their traditional ranges of halogenated flame retardants.

Areas of use
The production of halogenated flame retardants is equivalent to around 28% of total world production of flame retardants according to statistics from 1998. Brominated flame retardants account for about 23%, which may be regarded as a significant proportion of total world production of flame retardants.

Most present-day halogenated flame retardants are used in the area of electronics in the manufacturing of circuit boards, casings for home and office electronics, including mobile phone

equipment. The plastics industry is by far the largest user of flame retardants, the largest quantities of which are supplied to raw-material manufacturers. A smaller proportion of world production of flame retardants goes to the textile and paper industries. The aromatic polybrominated flame retardants (PBDE) enter into compounds with five, eight or ten bromine atoms in the structure. This report will focus on the compound containing ten bromine atoms under the name decabromodiphenyl ether (decaBDE), which belongs to the category of additive flame retardants. This means that the flame retardant is only physically bound to the flame-retardant material, unlike the reactive flame retardants. DecaBDE is the flame retardant produced in the greatest quantity around the world in terms of tonnes per year among the organic aromatic bromine compounds. Around 90% of world production ends up in electronics and plastics, while the other approximately 10% ends up in coated textiles and upholstered furniture and bedding products.

How do flame retardants work?
The term flame protection does not mean that the material is unable to burn but that there is a delay before the material in question catches fire or is in some other way affected by the heat generated in a fire. It is essential to differentiate between materials that delay fire, known as *flame-retardant materials,* and materials that resist fire, known as *flame-resistant materials.* The latter category includes a number of flame-resistant fibres that to some extent have replaced the flame-retardant, traditionally chemically treated textile materials. Flame-resistant fibres are generally more expensive than textiles wet-chemically treated with flame retardants, with the result that the manufacturer constantly has to maintain a balance between price, safety requirements and other quality requirements, such as design, comfort and mechanical durability, in his choice of flame protection

In order to understand the benefits and applications of different flame retardants, it is also essential to understand the process of fire in polymer and textile materials. The process, known as *pyrolysis,* can be briefly described as thermal decomposition of the material and is schematically illustrated in Figure 1 below.
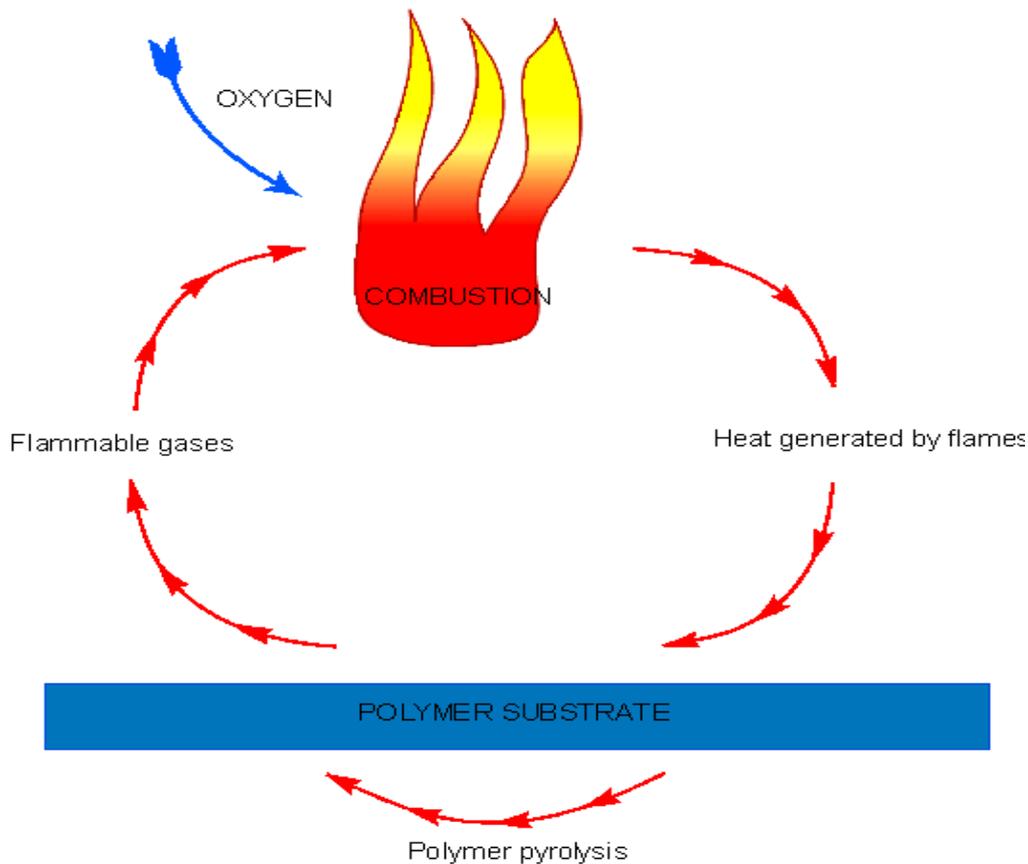
Figure 1: *Process of combustion for polymer material*

Combustion generates combustible and often toxic gases that mix with the oxygen in the air and in turn are combusted with increased heat generation. This means that the process maintains itself until all the material, which acts as a kind of fuel, is consumed. The role of the flame retardant is to interrupt this combustion process in various ways.

The traditional classification of flame retardants is often based on the predominant mechanism of the flame retardant performs in connection with the process of combustion. Flame retardants can act primarily

⇨ in the gaseous phase
⇨ in the condensed phase, also known as the liquid phase
⇨ through a physical effect

Flame retardants intended to act in the ***gaseous phase*** interact with the volatile substances formed when combustion takes place. A condition which has to be met for the flame retardants to be able to do this is that they form volatile substances that can react with the volatile substances in the combustion process in such a way that the new volatile substances formed are not combustible. Flame retardants that act in the ***condensed phase*** interfere with the process of pyrolysis so that they reduce the formation of combustible gases and change their properties so that the combustibility of the gases is reduced. Flame retardants based on ***physical effect*** on the combustion process act in both the gaseous phase and the condensed phase. Many of these flame

retardants that react through a physical process are inorganic. If they are to have the desired effect on the fire process, they need to be applied in large quantities at up to 60% by weight in the polymer material. The primary effect may be

⇨ to reduce heat generation,
⇨ to form a protective non-combustible layer
⇨ "dilution" of the organic combustible material.

Almost all commercial flame retardants in use today are active in both the condensed phase and the gaseous phase. Phosphorus-based systems are primarily active in the condensed phase, while halogen-based flame retardants primarily react in the gaseous phase, where they disrupt and finally stop the chemical reactions that occur there. The primary task of metal hydroxides is to absorb heat and in so doing lower the temperature in the combustion process. In conjunction with this thermal process, the metal hydroxide generates inert gases such as water vapour that "dilute" the gaseous phase and in so doing prevent continued progression of the fire.

The term *synergistic effects* is used in connection with the development of flame retardants. This term means that the desired effect of two or more components working together is greater than the effect of each of the components separately. Perhaps one of the most important synergistic effects historically in flame-retardant chemistry is that between halogen and antimony, where antimony reacts in the form of antimony trioxide with the formation of radicals, finally forming antimony tribromide and antimony oxybromide or their chlorinated equivalents. These flame retardants react in the gaseous phase and usually contain halogens of the chlorine or bromine type. The other halogens, iodine and fluorine, do not function at all as flame retardants. Organic iodine compounds are too unstable, while organofluorine compounds are too stable for the reactions that take place in the gaseous phase in combustion.

Textile applications with decaBDE

Coated textile materials are common applications for protection against flame and are based on the synergy between antimony and bromine, usually decabromodiphenyl ether. This construction is common in furniture and other similar seating and bedding products, but also in other technical textile items. The flame-retardant system is applied in the ratio of *1 part antimony to 3 parts bromine,* which has historically proved to be the most effective synergetic molar ratio to attain the best possible flame-retardant properties. For example, a back coating on a textile material may consist of 17 parts of antimony trioxide, 33 parts of decabromodiphenyl ether and 50 parts of resin. In terms of quantity, the flame-retarding system is applied in the order of 20 to 30% by weight of the textile system. The synergistic effect is based on the formation of antimony tribromide (Sb_2Br_3), particularly if the bromine source is aromatic, for example decabromodiphenyl ether.

Back coating

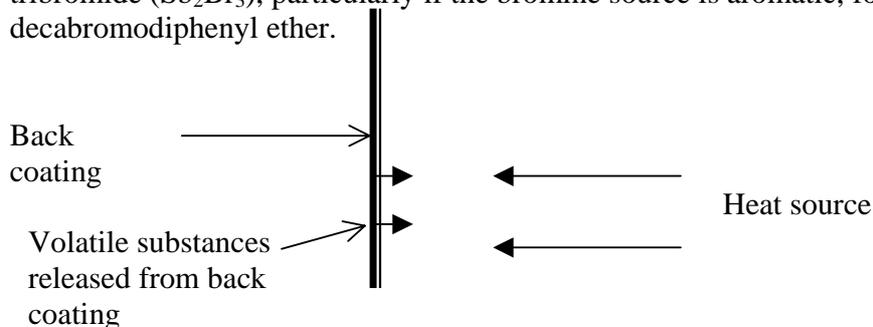Volatile substances released from back coating

Heat source

Figure 2. Simplified diagram of the effect of a heat source on the front of a back-coated textile material.

Figure 2 shows in diagrammatic form the difficulty with back coating (and intermediate-layer coating). The effect of antimony-decaBDE resides in its ability to release active volatile substances, such as $SbBr_3$ and antimony oxybromides, when the fabric is heated from the front. These volatile substances diffuse from the back, where they are released, through the fabric to the front, where they extinguish the incipient fire through their activity in the gaseous phase. The alternative flame retardants active in the liquid phase have a serious drawback in that they do not act directly on the flame. They can, however, lead to the release of non-combustible gases such as water vapour, ammonia or carbon dioxide, which can reduce the risk of ignition by diluting the combustible mixture of volatile substances and air. The question to be answered is how flame retardants that work in the liquid phase can transfer their activity from the back of a fabric through the fabric to its front, which may be a significant question in the further development of mature alternatives to antimony-decaBDE synergy.

Polymer materials given flame-retardant protection with antimony:halogen, for instance decaBDE, are:
⇨ polyester
⇨ polyamides
⇨ polyolefins, for example polypropene
⇨ polyurethanes
⇨ polyacylonitriles
⇨ polystyrene

In textile contexts, all these materials are relevant in various applications, with the exception of polystyrene. In the earlier literature up to the 1970s, cellulose-based applications with antimony:halogen synergy are described, but these were based on chlorine sources, for instance in the form of chloroparaffins.

Functional requirements and rules for textile applications

Tightened legislation and tougher fire requirements are the major forces that have driven forward development towards functionally better and more effective flame retardants. This trend is particularly clear in the English-speaking countries, ***the United Kingdom, Ireland and the United States, especially California,*** countries that have carried out extensive large-scale risk-benefit studies. In the light of this trend, a large number of specific fire standards with unique fire requirements have been developed internationally for various widely differing situations. The overview of international fire requirements presented in Table 3 of this report is not intended to be complete, but is an attempt to present the most important and most prominent international requirements occurring in the area of textiles.

Customers' requirements are absolute, whether they are public institutions, international organisations or businesses in the market. If the fire requirements are not met, there is no market for the individual supplier and the manufacturer. On the other hand, there are no descriptive fire requirements at all stipulating that particular flame retardants have to be used for the requirements to be met. The choice of flame retardant is left entirely to the manufacturer. In some cases the requirements are so strict that the alternatives are not economically feasible or the environmental requirements in that part of the world do not make the alternatives possible. Inferior quality characteristics, such as a deterioration in the comfort and durability of the textile product, may also be limiting factors in the manufacturer's choice of flame retardant.

There are wide-ranging rules in Europe regarding protection against flame for personal protective equipment. These regulations cover a broad range of occupational categories in which personnel are exposed to the risk of fire at work. Some of these standards are summarised in Table 1 below.

Table 1: *EU standards covering personal protective clothing*

Type of risk	Example of risk	Corresponding EU standard
Small flames	All activity in the vicinity of flames	EN 533
Larger flames and convective heat	Proximity to small fires	EN 531 level B1
Radiated heat	Proximity to ovens	EN 531 level C1
Heat and flames	Fire-fighting	EN 469
Drops of molten metal	Welding and cutting work with oxygen	EN 470-1
Splashes of molten metal	Foundry, smelting plant	EN 531 levels D1 and E1

The United Kingdom and Ireland have excelled themselves among other European countries with their very strict statutory safety requirements against fire. The "UK Furniture and Furnishings Fire Safety Regulations" have been in force in the United Kingdom since 1988. This legislation contains far-reaching fire regulations, with requirements relating to safety labelling in the sale of the following products
⇨ beds, bed heads and mattresses
⇨ sofa-beds and equivalent
⇨ furniture for children's rooms
⇨ garden furniture
⇨ caravan furnishings
⇨ cushions and pillows
⇨ furniture and bedding

This British legislation is multifaceted and extensive in a similar way to the Flammable Fabrics Act (FFA) in the United States, which was adopted by the US Congress as long ago as 1953. The meaning of the American legislation is that the sale of all forms of items/clothing regarded as highly flammable and combustible that pose a risk to the wearer is prohibited. The Act describes three classes of combustibility in textile fabrics, as shown in Table 2.

Table 2: *Classification of textile fabrics according to the FFA.*

Class		Time for spreading of flame
Class 1	Normal flammability	4 seconds or more
Class 2	Intermediate flammability	Between 4 and 7 seconds before fabric ignites
Class 3	Rapid and intense burning	Less than 4 seconds. Dangerous and flammable. Unsuitable for clothing.

The US Occupational Safety & Health Administration (OSHA) has laid down strict rules relating to safety equipment worn by personnel at risk of being exposed to fire or electric discharges.

These rules make it clear that this category of personnel must not wear protective clothing that can contribute to any form of injury in the event of an accident. The regulations state in particular that certain types of fibre at 100% or in combinations must not be present in protective clothing unless they are treated with flame retardant. Some of these types of fibre are acetate, polyamide, polyester and viscose. The OSHA also regulates the use of natural fibres such as cotton and wool with weight per unit area of less than 409 g/m^2, unless they are treated with flame retardant. New legislation comes into force in California at the beginning of 2005, the "California Assembly Bill 603", which entails substantially tougher rules for protection against flame in mattresses on sale in California. The new rules require the mattress to withstand an open flame for 30 minutes instead of the present-day requirement of 3 minutes. Equivalent rules for upholstered bedding products are also under discussion in California. Other federal states are expected to follow suit.

However, international discussions are being held to set limit values and requirements and to look at the consequences the requirements would have on an unwanted increase in the use of flame-retardant chemicals. Work is in progress, for example, to draw up a European document within CEN for fire requirements to be met by nightwear. Many countries have opposed the increased requirements for fire safety, as they realise that with currently known technology this will inevitably lead to increased use of flame retardants. It is said that the benefits gained are not sufficient to outweigh the drawbacks. It was also mentioned at an early stage of this work that there was talk of having to list which flame retardants would be used. However, this has been removed from the draft standard. The members of this CEN working group soon realised that flame-retardant chemistry had to be treated separately.

Table 3: *Some examples of fire requirements and corresponding building standards based on FFA, UK Furniture and Furnishings Fire Safety Regulations and the fire–safety requirements of other European countries and international transport organisations*

Product type	Type of fire source	Example of risk	Standard or equivalent
Seating	Smouldering cigarette	Smoking in furniture	Testing according to EN 1021-1. National requirements in several EU Member States
Seating	Smouldering cigarette	Smoking in furniture	Testing according to UFAC (*The Upholstered Furniture Action Council*) Voluntary industry requirements, followed by many manufacturers in the US
Seating	Ignition with small gas flame	Carelessness with open fire	Testing according to EN 1021-2. National requirements in some EU Member States. Requirements for low flammability in purchasing for example for hotels.
Seating etc.	Ignition with burning wood	Carelessness with fire	Testing according to BS 5852, fire source 5. Requirements for consumer environment for upholstery materials for furniture, mattresses and cushions in the UK. Medium risk level for public environment in the UK according to BS 7176
Seating	Ignition with	Carelessness with	Testing according to BS 5852, fire source 7.

	burning wood	fire/arson	High and very high risk level for public environment in the UK according to BS 7176
Seating, ships	Smouldering cigarette and small gas flame	Smoking, carelessness with fire	Testing according to IMO Resolution A.652 (16): 1989. Requirement for low flammability
Seating, trains	Ignition with burning wood	Carelessness with fire/arson	Testing according to BS 5852, fire source 7. Requirement for seats in X2000 trains
Seating, trains	Ignition with burning paper	Carelessness with fire/arson	Testing according to UIC 564-2, app. 13. Used by Central European train companies
Seating, aircraft	Ignition with oil burner	Fire on board	Testing according to FAA 23.853. Requirement for self-extinguishing is applied by most airlines
Mattresses, beds	Ignition with cigarette	Smoking in bed	Testing according to EN 597-1. Requirement for low flammability in several European countries
Mattresses, beds	Ignition with cigarette	Smoking in bed	*Code of Federal Regulations* (CFR) Testing according to 16 CFR part 1632 (USA) General requirements for low flammability in the USA
Mattresses etc., ships	Smouldering cigarette and small gas flame	Smoking, carelessness with fire	Testing according to IMO Resolution A.688 (17):1991. Requirements for low flammability
Mattresses, beds	Ignition with burning wood	Carelessness with fire	Testing according to BS 6807, fire source 5. Medium risk level for public environment in the UK according to BS 7177
Mattresses, beds	Ignition with burning wood	Carelessness with fire/arson	Testing according to BS 6807, fire source 7. High and very high risk level for public environment in the UK according to BS 7177
Mattresses, beds	Ignition with gas burner	Carelessness with fire/arson	Testing according to California Technical Bulletin 603. Requirement for limited heat and smoke generation from 2005. Other states are expected to follow suit.
Curtains and drapes	Gas flame + heat radiator	Carelessness with fire	Testing according to EN 1101, EN 1102 and EN 13772 and classification according to EN 13773. These standards are expected to gradually replace existing national standards. The requirements are not expected to be commonly adopted in the various countries.
Curtains and drapes	Large gas flame	Carelessness with fire	NFPA *(National Fire Protection Association)* NFPA 701 (USA). Requirement for self-extinguishing
Curtains and drapes, ships	Gas flame	Carelessness with fire	Testing according to IMO res. A.471 (XII), 1981 Requirement for self-extinguishing products.
Interior materials in	Gas flame	Carelessness with fire	Testing according to ISO 3795 and equivalent. Requirement for limited rate of flame spread is specified

cars			in FMVSS 302 (USA), Directive 95/28/EC and by individual car manufacturers.

Alternatives to decaBDE
There are established flame-retardant substances and potential new variants based on different synergistic combinations as possible substitutes for antimony-decaBDE. These may be
⇨ organic phosphorus compounds or phosphorus chlorine compounds
⇨ aluminium and zinc hydrate
⇨ swelling (intumescent) systems
⇨ new synergistic combinations, for example antimony - bromine/phosphorus - silicon
⇨ surface-active fibre systems
⇨ systems with graft copolymers
Alternatively the effect of the flame retardant can be maximised by developing surface-active fibre systems, for example systems with graft copolymers which may have low flammability in themselves. At present there are no established commercial effective total replacements, although the concentrations of antimony:decaBDE can be reduced by partially replacing them with phosphorus-based systems. In recently published papers it has been hypothesised that total replacement may be possible with phosphorus-based systems *if they become liquid,* either when they melt or by decomposing into liquid substances during the initial pyrolysis. This would mean that the textile substrate is wetted and the flame-retardant effect is transferred to the front of a back coating, for example.

Some examples of commercial alternatives to antimony:decaBDE synergy
This section describes some of the dominant commercial alternatives to antimony:decaBDE on the market for different textile materials, and is a more detailed description of the general overview contained in Table 4.

Table 4 .*Commonly occurring permanent wet-chemical flame-retardant treatments and*
       flame-resistant fibres

FIBRE	PROTECTION AGAINST FLAME	TREATMENT
Natural fibre		
Cotton	Organophosphorus and nitrogen-containing monomers or reactive groups.	F
	Antimony-organo-halogen systems	F
Wool	Zirconium hexafluoride complex	F
Regenerated		
Viscose	Flame-retardant additives: organophosphorus and nitrogen/sulphur-containing; polysilicic acid complex	A
		A
Synthetic		
Polyester	Organophosphorus components	C/A
Modacrylic	Halogenated compounds (35-50 % w/w)	C
Polypropene	Halo-organic compounds usually as bromine derivative	A
Flame-resistant:		
Polyhaloalkenes	Polyvinyl chloride	H
	Polyvinylidene chloride	
Polyaramides	Poly(m-phenylene isophthalamide)	Ar
	Poly(p-phenylene terephthalamide)	
Poly(aramide-arimide)		Ar
Polybenzimidazole		Ar
Carbonised acrylic		Ar

Note:
F : chemical post-treatment
A : additive in fibre melt spinning
C : modified copolymer. Copolymers are made up of two or more different monomers.
H : homopolymers constructed as a single type of monomer.
Ar : aromatic homo- or copolymer

Intumescent (swelling) systems
Intumescent systems have existed since the 1940s, principally in paints. Several intumescent systems linked to textile applications have been on the market for about 20 years, and have successfully shown their great potential.

Most textile applications with flame retardants are designed to reduce the risk of flammability and of fire spreading in the material. In addition to their ability not to ignite and spread fire, flame-retardant materials are intended to act as a barrier for underlying layers of materials, so that

the fire does not propagate through the whole structure. Typical applications today with a need for these properties are mattress covers, furniture upholstery and protective clothing. In these contexts and for other applications of textile materials, swelling or intumescent systems, as they are sometimes known, can be advantageously used as alternatives to other flame-retardant treatments based for instance on antimony:decaBDE synergy.

The system is based on the formation of expanded coal tar, which partly acts as an insulating barrier against heat but also as a smoke-fume trap.
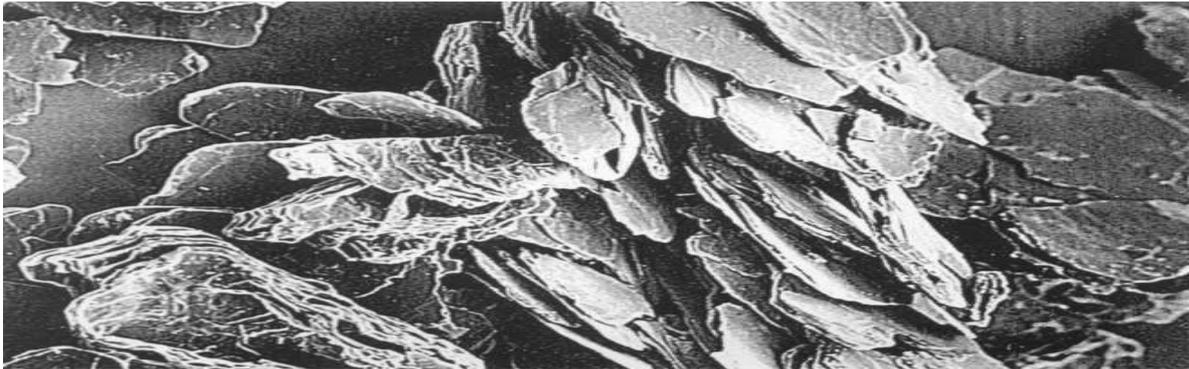

Figure 1: *Expandable graphite – on heating, the graphite expands 150 to 200 times and acts as a very effective smoke-fume trap.*
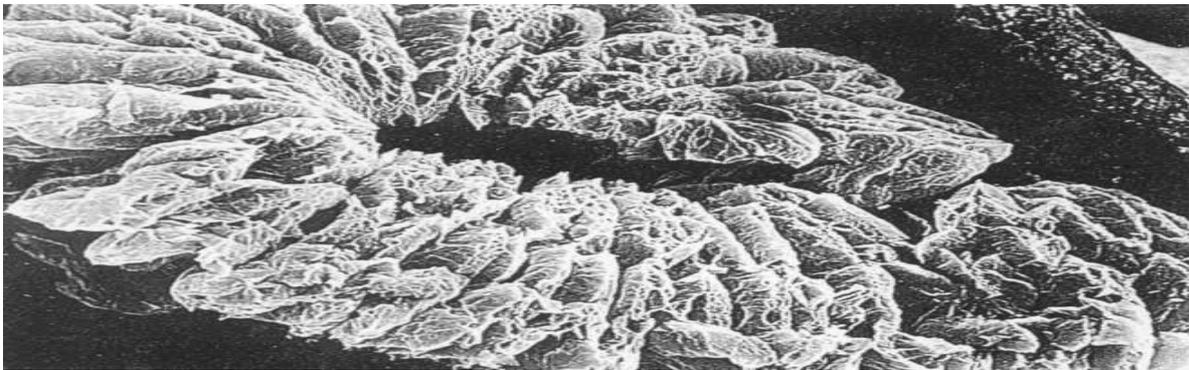

Figure 2: *Expanded graphite – reflects 50% of the radiated heat in fire and is a good insulator.*

The effect of intumescent systems in connection with fire depends on the type and added quantity of intumescent system. Intumescence does not just relate to specific systems based on expanded graphite. This property also exists in a number of fibres present in textiles. Wool is an example. Figure 3 below illustrates the formation of tar in the combustion of wool.

Figure 3: *Tar formation on a woollen rug.*

Flame-resistant fibres in principle behave in the same way as wool, in that they do not undergo pyrolysis at temperatures of around 450°C and above, and gradually form a tar-like insulating layer, unlike conventional textile fibres which are already ignited at these temperatures.

How do intumescent systems work?
Intumescent systems consist of three components:
⇨ acid source
⇨ carbon source
⇨ gas source
The acid probably acts as a catalyst when the carbon source decomposes with the formation of gas, for example water vapour. The acid may also be a compound that forms acid in contact with heat. The carbon source consists of polyols (polyalcohols) that lose their hydrogen and form a "***carbon foam"*** of suitable density and thickness to create good safety against continued spread of fire.

INCIDENT RADIANT HEAT
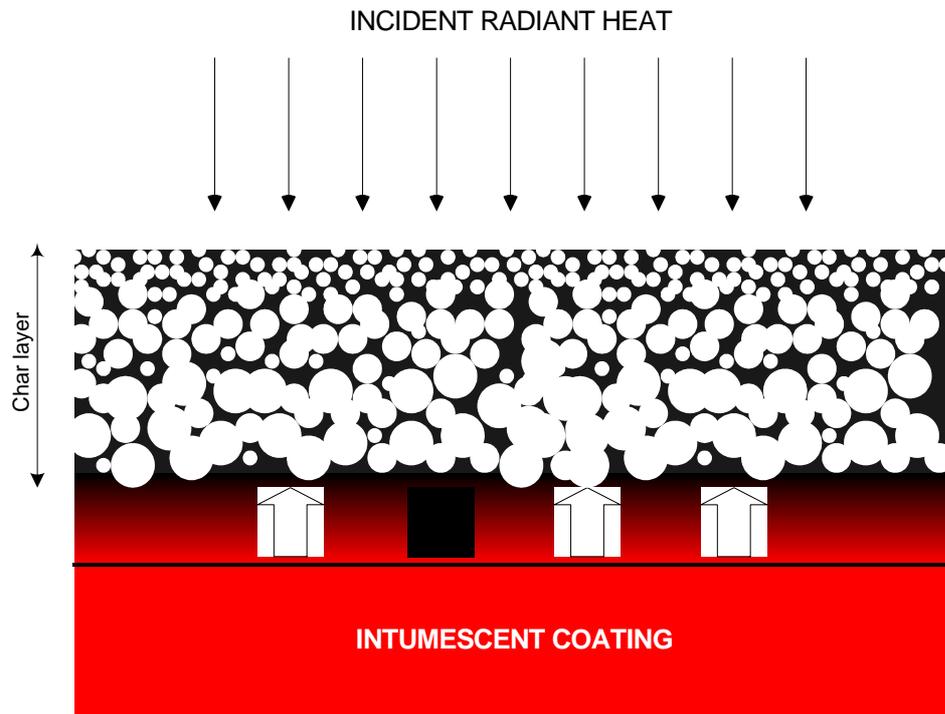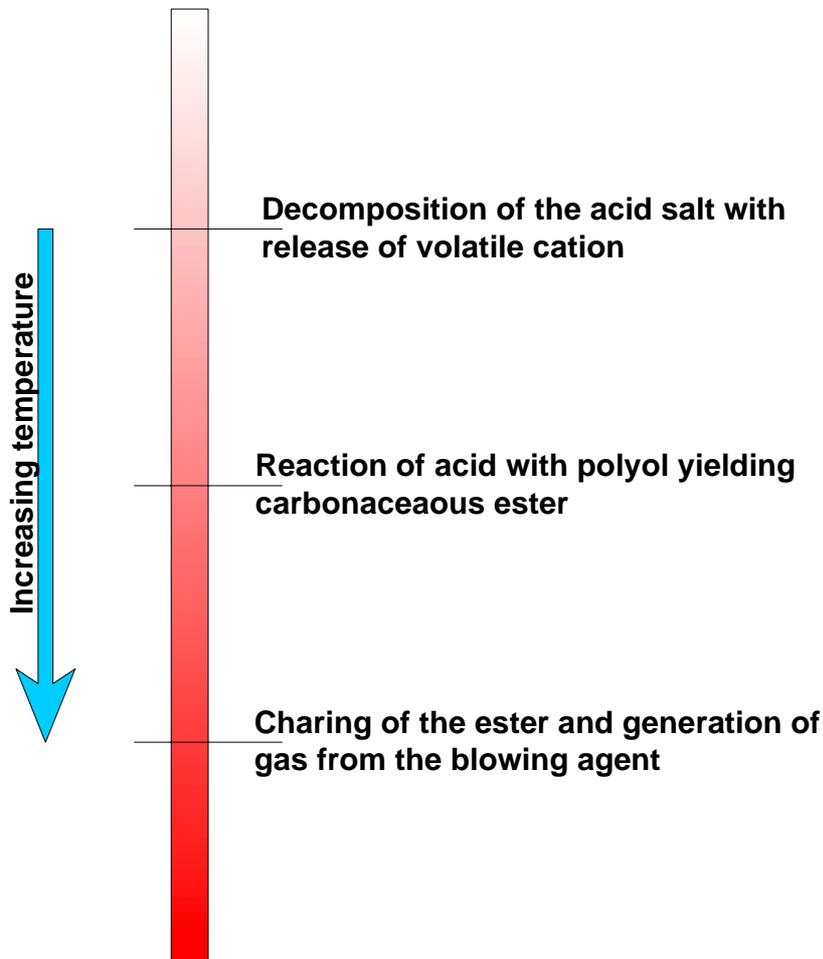
Char layer

INTUMESCENT COATING

Figure 3: *Probable process with an intumescent system exposed to heat*

The gas source is the third component. Gases are formed that are not combustible, for example hydrochloric acid, ammonia, water or carbon dioxide depending on what the chemical system is like. The most common intumescent systems are listed in Table 5 below.

Table 5: *Suitable chemical substances for intumescent systems*

			Decomposition temperature (°C)
Dehydrating substance	Monoammonium phosphate	$NH_4H_2PO_4$	147
	Diammonium phosphate	$(NH_4)_2HPO_4$	87 and 147
Carbonising substance	Ammonium polyphosphate	$(NH_4PO_3)_2$	215
that releases acid for	Melamine phosphate	$C_3H_6N_6 \cdot H_3PO_4$	300
esterification of hydroxyl	Guanyl urea phosphate	$C_2H_6N_4O \cdot H_3PO_4$	130
groups	Urea phosphate	$CO(NH_2)_2 \cdot H_3PO_4$	
	Diammonium sulphate	$(NH_4)_2SO_4$	
	Ammonium tetraborate	$(NH_4)_2B_2O_7 \cdot 4H_2O$	
Carbonising substances	*Polyols*		
	Erythritol	$C_4H_6(OH)_4$	
Contain large quantities	Pentaerythritol	$C_5H_8(OH)_4$	
of carbon	Pentaerythritol dimer	$C_{10}H_{16}(OH)_6$	
Thermal decomposition	Pentaerythritol trimer	$C_{15}H_{24}(OH)_8$	
which results in carbon	Arabitol	$C_5H_7(OH)_5$	
skeleton	Sorbitol	$C_6H_8(OH)_6$	
	Inositol	$C_6H_6(OH)_6$	
	polyhydrophenols		
	resorcinol	$C_6H_8(OH)_2$	
	sugars		
	Glucose	$C_6H_{12}O_6$	
	Maltose	$C_{12}H_{22}O_{11}$	
	Arabinose	$C_5H_6C_4$	
	Dextrin	$(C_6H_{10}O_5)_n$	
	Starch	$C_6H_{10}O_5)_n$	
Gas sources	*Ämne*	*Gases formed*	Decomposition temperature (°C)
	Dicyandiamide	NH_3, CO_2, H_2O	
Produce non-combustible	Melamine	NH_3, CO_2, H_2O	300
gases in connection with	Guanidine	NH_3, CO_2, H_2O	160
thermal decomposition	Glycin	NH_3, CO_2, H_2O	233
	Urea	NH_3, CO_2, H_2O	130
	Chloroparaffins	HCl, CO_2, H_2O	160-350

The fire process in connection with intumescence can be illustrated as shown in Figure 4 below.

Increasing temperature ↓

Decomposition of the acid salt with release of volatile cation

Reaction of acid with polyol yielding carbonaceaous ester

Charing of the ester and generation of gas from the blowing agent

The composition of intumescent systems depends on each specific situation, for example
⇨ desired flame-retardant properties
⇨ polymer composition in application concerned
⇨ any presence of fillers and additives in the polymer systems concerned

After all the positive things that have been said about intumescent systems, the question arises as to whether there are any problems as applications in textiles are still under development. The principal reason for this concern is that these systems require special handling in application, for example on a back coating, so that the system works as intended. As the three-component system is stable and in solid form, it is important to find the best conditions and combinations of the three different components in an evenly and well distributed dispersion in the textile application for desired flame protection.

Flame protection of cellulose
Cellulose-based fibres dominate in the textile industry. Cotton is by far the most widely used fibre globally in the textile industry. It accounts for just under 50% of world production or around 25 million tonnes per year; this is largely due to the high content of cellulose in cotton, around

94%. The global trade trend, however, suggests that the total proportion of natural fibres will decrease over the next few years in favour of synthetic fibre alternatives, principally polypropene and polyester.

Antimony:decaBDE synergy could theoretically be applied to provide protection against flame for cellulose, for example cotton. This type of obsolescent application is very sparsely described in the literature. Today phosphorus chemistry dominates. Some of these phosphorus-based chemicals will be briefly described in the following sections.

Dimethylphosphono (N-methylol) propionamide has been used in a number of commercial cellulose-based applications for several decades and is one of the most widely used flame-retardant chemicals for cellulose. The molecule is chemically bound to the cellulose through a resin, for example melamine resin, so that the flame retardant is regarded as being [1]wash-resistant, which may be an important requirement in certain applications, for example work wear and protective clothing, provided the usual washing recommendations are followed.
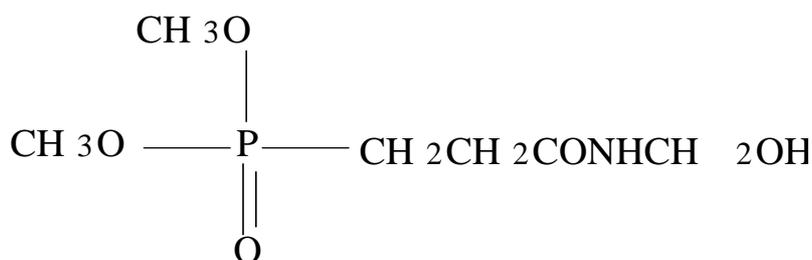
$$CH_3O \cdots P \cdots CH_2CH_2CONHCH_2OH$$

(with CH_3O above and O double-bonded below the phosphorus)

Figure 5: Dimethylphosphono (N-methylol) propionamide

The cellulose is modified through the chemical reaction in such a way that it becomes more difficult to burn, and the proportion of emitted smoke fumes in combustion is reduced at the same time. A drawback with this chemical wet treatment is the emission of formaldehyde from the resin in connection with the chemical reaction between resin, flame retardant and cellulose polymer. In recent times the market has developed resins that emit very low concentrations of or no formaldehyde.

Flame-retardant treatment, mostly due to the resin, may also tend to discolour the textile product, which may be a problem from the design point of view. Another very important phosphorus-based flame-retardant chemical is *tetrakis (hydroxymethyl)phosphonium urea ammonium salt.* Applications using this salt require a market licence, as a special ammonia-based preparation is included. This has resulted in it not being as widely used as treatment with dimethylphosphono (N-methylol) propionamidene. The tetrakis salt is polymerised with ammonia in the cavities of the cellulose fibre and is held so firmly that the treatment is regarded as wash-resistant. Its

---

[1] A textile product treated with a flame retardant which is classified as wash-resistant has to withstand at least ten wash cycles without losing its flame-retardant properties.

function from the point of view of fire is the same in principle as for dimethylphosphono (N-methylol) propionamidene.

$$\left[\begin{array}{c} CH_2OH \\ | \\ HOCH_2 \text{———} P^+ \text{———} CH_2OH \\ | \\ CH_2OH \end{array} \right] \quad X^- \qquad X^- \text{ is a counterion}$$
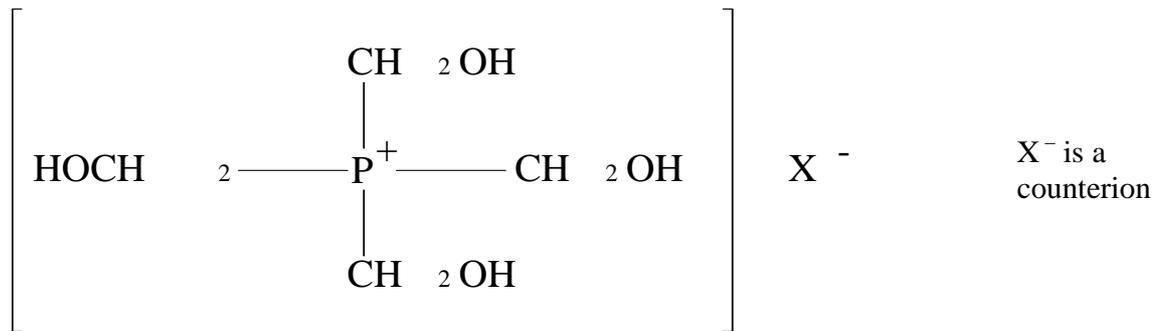
Figure 5: *Tetrakis(hydroxymethyl)phosphonium urea ammonium salt*

The tetrakis molecule has a broad range of textile applications, from clothing to interior products. There are also a number of semi- and non-wash-resistant treatments for cellulose-based textiles. These are based on different inorganic salts and metal compounds with boron. They are not regarded as providing as good protection against flame as the wash-resistant treatments but are regarded as adequate in certain applications where washing does not need to be carried out particularly often. In addition, they are generally cheaper than the wash-resistant treatments.

Flame protection of wool
Like all protein fibres, wool is, in itself, flame-resistant. In certain applications in transport, for example on board aircraft, this inherent property is not sufficient. Carpets intended for aircraft, where particularly strict fire-safety requirements apply, made of 100% wool or predominantly made of wool, are often given a flame-retardant coating with *zirconium hexafluoride salts,* the primary function of which is to increase the ability of the wool to char and reduce emissions of its usually highly toxic smoke fumes.. Chlorine-based flame-retardant alternatives are described in older literature from the 1970s and earlier, but it is not clear in later sources whether they are used today and to what extent.

Flame protection of polyester
Polyester is one of the most commonly used textile fibres around the world. It accounts for about 30% of world fibre production. It is employed in a very wide range of textile applications, in clothing, technical applications and interiors. The fibre also occurs in all imaginable applications where a high degree of fire safety is required. Untreated polyester is a powerful fire source. The material causes injuries due to melting on the user in the event of a fire and burns with a "dripping" flame, rather like a wax candle. By far the most common flame-resistant application today is based on a modified version of the most common polyester, polyethylene terephthalate, with built-in phosphorus.
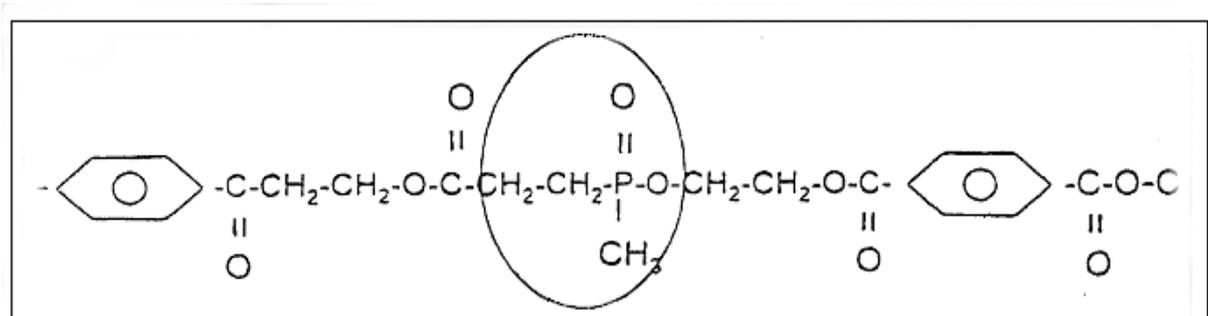
21

Fig. 6: *Flame-resistant modified polymer of polyester*

The modified polyester is used in the majority of textile applications in which there are strict requirements for flame-retardant treatment and can be said to be a good substitute for antimony:decaBDE synergy.

Flame protection of polyurethane
Polyurethane (PUR) is a unique group of polymer materials that are difficult to beat from the point of view of comfort and is found in both upholstered seating and bedding products and in coated textile products. A number of research projects are under way around the world to find suitable alternatives to polyurethane from the point of view of comfort, These have mixed success, as there are problems in connection with the final disposal of PUR. Polyurethane foam is one of a category of materials that necessitate strict fire-safety requirements, as they have a high oxygen content. Some of the flame retardants used as substitutes for antimony:decaBDE are now based on chlorinated phosphate esters. Some of these are:
⇨ Tris(1-chloro-2-propyl) phosphate (TCPP)
⇨ Tris(1,3-dichloro-2-propyl) phosphate (TDCPP). As well as in PUR, it is used in latex and resins.
⇨ Tris(2-chloroethyl) phosphate (TCEP). This is used in coated textile applications.
As well as the chlorinated phosphate esters described above, the intumescent systems are mature alternatives to antimony:decaBDE synergy in particular for coated applications. A good knowledge of intumescence and associated technology for application in the product is required if intumescent systems are to be used successfully.

Flame protection of polyamide
There are no explicit fire-safety requirements in the majority of applications. The fibre usually occurs in various forms of lightweight clothing, where these requirements are uncommon. In cases where fire-safety requirements are specified, polyamide normally copes with fire without the addition of flame retardant. In unusual cases in which flame retardants are present, they are usually based on additive phosphorus chemicals that are added at the time of fibre spinning and are thus built into the polyamide from the start.

Flame protection of polyolefins
The use of polyolefins in the world of textiles is increasing, principally due to the low weight of polymers. As all these polymers can be regarded as condensed oil, they are to be viewed as powerful sources of fire. The most common polyolefin with a textile connection is polypropene

(PP). Wallpapers are an example of common PP applications. There are several different technical options for protecting PP against flame, both with and without halogens, where the additive flame retardant is added to the polyolefin melt at the time of fibre spinning.

Flame-resistant fibres
There are a number of fibre materials in this category that are used where the requirements for fire safety are very strict. They often occur in connection with fire requirements for suits for firefighters and other occupational groups with equivalent exposure. The flame-resistant materials can be divided into polyhaloalkenes and polyaramides. The group of polyhaloalkenes includes polymers that consist of halogens, for examples PVC.
The second category of flame-resistant fibres is that of polyaramides. These are used where exceptional fire requirements have to be met, for example for firefighters. They are generally more expensive than other flame-retardant materials but otherwise have superior fire-retardant properties. The polyaramides rarely occur in applications with more modest fire requirements such as public interior environments.

Conclusions
There is nothing in standards or other documents containing fire-safety requirements that describes or calls for particular flame-retardant treatments for the requirements to be met. On the other hand, it is an absolute requirement and an indisputable fact that the product has to comply with the fire standard or standards cited in the statement of requirements for it to be sellable at all. According to experienced gained by IFP Research and its many years of involvement in European standardisation in relation to fire-safety requirements, it is up to the manufacturer to solve this problem, while at the same time having to take account of various regulations that prohibit or advise against the use of certain chemical products.

There have for decades been many alternatives to antimony:bromine synergy, including the use of decabromodiphenyl ether. The trend over the last 20 years with new environmental requirements for flame retardants has led to the large international chemical manufacturers becoming interested in halogen-free alternatives.

The fact that organic bromine compounds are still used instead of their halogen-free alternatives is due to a number of factors, only a few of which are technical in nature.
Combined with low price, one of the most common reasons why the alternatives do not always make a breakthrough is that the market prefers to use tried-and-tested flame retardants. In the event that the flame-retardant protection does not meet specified fire-safety requirements according to applicable standards cited by the market and to some extent by parties in society, this can lead to catastrophic fires, with fatalities. It will therefore take many years until the phase-out of halogen-based systems is complete, unless international legislation comes about in the near future together with customer requirements that take account of environmental and fire-safety requirements on a broad front. Only then will there be an incentive for the market players to use the commercially available halogen-free alternatives, which are not currently regarded as economically and traditionally attractive in the international market.

The flame retardants that ultimately are likely to completely replace antimony:decaBDE with the backing of clear rules and regulations are the intumescent systems and those based on phosphorus chemistry. Flame-resistant fibres combined with combustible fibres will also be used successfully

23

in certain applications. However, a number of fire-related problems remain to be solved in some applications, for example for polyurethane foam, but this trend too will accelerate when the halogenated alternatives no longer have a role to play in the international sustainable society. It is now up to the legislators to create this incentive. The technology already exists.

Terms and abbreviations used

IMO, International Maritime Organisation, previously (1948-82) IMCO, Inter-Governmental Maritime Consultative Organisation, an organisation set up by the United Nations in 1948 with the aim of providing a form of international co-operation on rules and practice governing safety at sea. A convention was drafted and came into force in 1958. The organisation's highest policy-creating forum, the Assembly, met for the first time the following year. It has since met once every two years. A Council meets twice a year to take decisions on new provisions and guidelines, which are drawn up by the organisation's committees. The IMO deals with issues relating to design and equipment, freeboard, tonnage measurement and stability, radio communication, rescue equipment, *fire safety,* transport of hazardous goods and protection of the marine environment. There is close collaboration with classification societies and national shipping authorities.

UIC, **Union Internationale des Chemins de fer, International Union of Railways**. The organisation has its headquarters in Paris and in 1999 had 142 members, including the Swedish National Rail Administration and Swedish State Railways. The UIC was formed in 1922 with the aim of promoting co-operation between the various railway administrations, representing railway interests in international organisations and initiating and disseminating research in the area of the railways. The UIC formulates and issues standards, regulations and recommendations.

CEN, Comité Européen de Normalisation, the European body for standardisation, issues European standards (EN) in all areas except electricity. The Swedish member organisation is SIS. The international equivalent of CEN is ISO.

BSI, **British Standards Institution,** the central standardisation body of the United Kingdom, a member of CEN, CENELEC, ISO and IEC. BSI was formed in 1901 under the name of the British Engineering Standards Association and is the world's oldest national standardisation body. It issues British Standards (BS)

ISO, International Organisation for Standardisation, the international standardisation body for all areas except electrical engineering. It came into existence in 1946 and has its headquarters in Geneva. ISO co-ordinates its work with the IEC and co-operates on standardisation matters with a large number of international and regional bodies, and like the IEC issues international standards. The Swedish member organisation is SIS.

References

1. M. Lewin, S.B Sello (1983), *Handbook of Fiber Science and Technology: Vol II,* "Chemical processing of fibres and fabrics-Functional Finishes- Part B", pages 3- 141.
2. L. Muran, (2003), *Technical Textile Markets 3rd-4th quarter* "Flame Resistant Fibres and Fabrics", pages 11 – 34.
3. M. Carole, d. André, V. Moise,D. René, P. Franck (2003), *Journal of industrial textiles*, "Behaviour of an intumescent system for flame retardant materials coated of polypropylene textiles", vol 32, No 4, pages 255 – 266.
4. G.C Stevens, A.R Horrocks ((2003), *Journal of industrial textiles*,"Textile back-coating challenges for the UK furnishing fabrics industry; release and exposure of flame retardant species", vol 32, No 4, pages 267 – 279.
5. M. Cole (June 2004), *Flame resistance,* "Race is on in bedding industry to meet stringent new flammability standards". Pages 19 – 24.
6. R. Horrocks, S. Zhang, (2004), *Textile Research Journal,* "Char formation in polyamides (Nylons 6 and 6.6) and wool keratin phosphorylated by polyol phosphoryl chlorides", pages 433 – 441.
7. J. Laperre, T. Demeyere, T. Meyvis, B van der Beke, (2002) "Intumescent flame retardant coatings for textiles. An overview", a paper presentation from Centexbel in Belgium.
8. Bromine Science and Environmental Forum, www.bsef.org, "Fact sheet - Brominated Flame Retardant –Deca-BDE"
9. D. Drohmann, (2001), Seminar "Moderne Flammschutzmittel für Kunststoffe", Haus der Technik , Great Lakes Chemical Corporation.
10. UK Furniture and Furnishings Fire Safety Regulations, Stautory Instrument1988 No 1324, "The Furniture and Furnishings (Fire)(Safety) Regulations 1988"
11. S. Posner (2000), *IFP report,*"Flamskyddsmedel – förekomst och användning".
12. Nationalencyklopedien, www.NE.se

KEMI

KEMIKALIEINSPEKTIONEN