

Fire Retardant Technologies 2009

by

Ian Holme

The highly successful international conference on the latest developments in fire retardant technologies was organised by the Royal Society Speciality Chemicals Sector and held at the University of Central Lancashire, Preston, UK. The delegates were welcomed by Dr Lee Chatfield, Head of the School of Forensic and Investigative Services, University of Central Lancashire, and Professor Richard Hull.

The initial overview session was chaired by Professor Giovanni Camino. In a comprehensive overview of plastics, flammability and flame retardancy Professor Richard Horrocks (University of Bolton, UK) pointed out that char-promoting fire retardants e.g. phosphorus compounds were polymer-specific and particularly effective on cellulosic fibres. Halogenated (especially brominated) fire retardants were universal in their action because the release of bromine atoms into the flame zone dramatically decreased the free radical reactions leading to the flame. Nanocomposites could enhance the action of fire retardants. Serious challenges to the fire retardant industry were environmental pressures and the REACH Directive which would impact on current and any new potential fire retardants.

Techniques for understanding fire retardant behaviour were described by Professor Richard Hull (University of Central Lancashire, Preston, UK) who elaborated the advantages and limitations of:

- TGA (thermogravimetric analysis)
- DSC (differential scanning calorimetry)
- FT-IR spectroscopy (Fourier Transform Infra-Red spectrometry)
- GC-MS (Pyrolysis gas chromatography – mass spectrometry)
- Rheology
- Thermomechanical analysis
- Char analysis by microscopy, spectroscopy or wet chemical analysis

Data from thermally-controlled experiments could be related to burning tests used in standard fire models such as LOI (Limiting Oxygen Index), Bunsen burner (e.g. UL 94 tests) and the cone calorimeter (ISO 5660). Professor Hull's fire research group at UCL utilised all these analytical techniques. These extensive fire research facilities were later visited by many delegates.

Dr Jürgen Troitzsch (Fire & Environment Protection Service, Germany) chaired the session on established fire retardants. Rudi Borms (ICL-IP Europe BV, Amsterdam, The Netherlands) discussed new developments in halogenated flame retardants. ICL-IP were concentrating on increasing the purity of Fyrol PCF (which was used in rigid and flexible polyurethane foams) to avoid odour in mattresses, upholstery, as well as developing more efficient anti-scorch additives (Fyrol 38). Fyrol FR2 and Fyrol A 300TB were low-fogging fire retardants that met the automotive industry requirements. Where backcoating using decabromodiphenyl ether (oxide) (DBDPO) might be visible through the fabric, low opacity formulations based on hexabromocyclododecane (HBCD) were used. This latter fire retardant could be replaced by a proprietary blend (SaFRon 9025) developed by ICL-IP.

Mineral flame retardants based upon metal hydroxides such as aluminium and magnesium hydroxides have been used in rubber, plastics and cables for many years. Professor Roger Rotheron (Rotheron Consultants, Chester, UK and Manchester Metropolitan University) pointed out that their flame retardant effect occurred because of the endothermic decomposition of the metal hydroxide at the polymer pyrolysis temperature. For aluminium hydroxide (ATH-alumina trihydrate) the flame retardant effect depended on the absorption of heat (50%) combined with the evolution of water (30%) and the production of a residual oxide layer (20%). A further advantage was that metal hydroxides were regarded as environmentally friendly because they gave rise to low levels of smoke and no evolution of acidic fumes.

A major limitation restricting their more widespread application was that high loading levels (often greater than 60% w/w) were required for a satisfactory level of flame retardancy. This clearly could impact markedly upon the mechanical properties of the composite.

Recent developments included the introduction of ATH with increased stability allowing processing above 260°C for use in printed circuit boards. Magnesium hydroxide use had expanded in cables (natural form), in roofing / decking (brine form) and in automotive wire and cable (synthetic form). Nano-clays based upon alumino-silicates derived from layer clays (e.g. montmorillonite) and in the form of very thin (~1nm) high aspect ratio plates could be used at 5-10% ^{w/w} in combination with metal hydroxides to provide higher levels of flame retardancy or to decrease the overall filler level. Increased carbonaceous char formation was considered to result from catalysis by acid sites on the nano-clay as well as from decreased oxygen diffusion because of the plate-like nature of the particles.

Professor John Ebdon (University of Sheffield, UK) described the use of fire retardants based on elemental red phosphorus, as well as reactive phosphorus compounds for fire retarding polyester and polyamide fibres and also polyurethanes via copolymerisation. Phosphorus-based fire retardants could also be combined with other types of fire retardants and nanoscopic particles. Dual phase action fire retardants based on phosphorus operating in the condensed and gas phases were particularly effective e.g. in polyurethane foams.

In the next session chaired by Dr Ulrike Braun (BAM Federal Institute for Material Testing, Germany) Dr Andrew Taylor (Leighs Paints, Bolton, UK) discussed recent developments in fire resisting intumescent coatings for structural steel. Intumescent coatings (e.g. Firetex – Leighs Paints) can be applied on-site but there is now a growing tendency to apply such treatments off-site. The failure temperature of unprotected structural steel in a “British Standard” cellulosic fire is around 550°C which can be reached in 17 minutes, but when intumescent coatings are applied the time to failure can be extended to 120 minutes by using the appropriate coating formulation / coating thickness. Intumescent coatings consist of an acid source that can char a material (carbonific) together with a spumific that decomposes to evolve gas and blow / expand the char. However more complex reactions occur including the spumific reacting with the acid source and the resin binder playing a minor role in terms of softening / charring. Filler particles are incorporated to act as nucleating agents or “bubble growth sites”.

A range of solvent and water-borne technologies were approved in a wide range of countries, with third and fourth generation products now available. Current challenges included speed of drying, durability and mechanical handling as well as the increasing use of cellular beams (i.e. steel beams containing openings in the structure to allow services (e.g. electrical cables, gas and water pipes etc.) to pass through, lowering the floor height and enabling longer spans to be used. Natural fire testing standards within Europe were being harmonised under EN 13381 Part 8 for intumescent coatings and EN 13381 Part 9 for cell beams, replacing national standards such as BS476 Part 20, DIN 4102 teil 2 etc. Dramatic pictures of the effects of explosion testing demonstrated no damage to the intumescent coatings while natural fire testing at Cardington showed that intumescent coatings really did work, markedly extending the structural steel load-bearing capacity time to failure in real fires.

Professor Thomas Hjertberg (Borealis AB, Sweden) then described the CASICO low smoke halogen-free intumescent fire retardant system for cable applications. Calcium carbonate was an inert material that acted as a diffusion barrier. Ionomer formation with polyethylene copolymers increased the melt viscosity which led to a stabilised intumescent structure, decreased dripping and slower transportation of the degradation products. The five per cent PDMS (polydimethylsiloxane) formed a silicone enriched barrier layer on the surface which ultimately gave SiO_2 above 500°C . Above 700°C the calcium carbonate decomposed to calcium oxide which interacted with the silicon oxide to form Ca_2SiO_4 at 1000°C . By decreasing the melt viscosity of the polymer and increasing the interaction between the polymer and the filler by altering the comonomer content it was possible to stabilise the melt and provide increased strength to the solid char residue. Research studies had shown that the peak heat release rate in the cone calorimeter test could be decreased by more than 50 per cent, accompanied by a slower fire growth and a decreased total heat release.

Professor Giovanni Camino (Turin Polytechnic, Italy) surveyed the use of nanocomposite fire retardant materials stressing that new strategies were required to produce low fire risk, low fire hazard materials that were produced sustainably. Research was concentrating upon flame prevention by creating flame starvation conditions during polymer combustion. A most promising approach was polymer surface protection promoted by the heat of the flame. This decreased the polymer

thermal degradation rate which normally supplied fuel into the gas phase. A possible breakthrough could come about from surface ceramerisation / charring during the combustion of nanocomposites.

Dr Richard Lyon (Federal Aviation Administration, USA) and his coworkers had taken a novel approach to the development of fire resistant plastics for aircraft. Polymers had been screened for thermal combustion properties / char yield, heat of combustion and heat release capacity using milligram samples measured using microscale combustion calorimetry (MCC). Additive molar group contributions to the thermal combustion properties of 38 backbone and side chain chemical groups were derived by multiple linear regression of MCC data for 84 engineering polymers of known chemical structure.

The measured and calculated thermal combustion properties showed good agreement. Statistical analysis of the results of standardised flame and fire tests on 160 plastics were then conducted using their thermal combustion properties as the single independent variable. It was found that the probability of pass / fail behaviour in flammability tests for plastics used in aircraft cabins, electrical equipment, electronics and automotive applications could be predicted by using a probabilistic model of flame spread that used the heat release capacity measured by MCC as the sole explanatory variable.

In the session on emerging technologies chaired by Professor John Ebdon (University of Sheffield, UK), Nils Wenne (INCA AB, Sweden) discussed the use of expandable graphite for fire protection and said that there were three different approaches to fire safety. The pure “scientific” approach which led to long costly development, chemical solutions and theoretically correct calculations; the “standard focussed” approach which resulted in chemical solutions with a minimum of security; and the “shall not burn” approach which resulted normally in a creative protective solution.

Expandable graphite was environmentally neutral with a low heat release and low smoke emission. It was chemically stable, prevented dripping, and the emission of toxic gases. Expandable graphite was black and had a large particle size. It worked by a physical mechanism not by a chemical mechanism and could be very effective in

extending the time to ignition. However whether this would enable materials to pass specific fire ignition tests depended upon the nature of the test and the pass / fail criteria which could differ according to the national standard under consideration. He urged delegates to think creatively of new solutions rather than turn to traditional application technology.

The presentation by Dr Charafeddine Jama (École Nationale Supérieure de Lille, France) was delivered on his behalf by Professor Richard Hull. Dr Jama has studied the production of fire retardant surface coatings using cold plasma assisted deposition processes. Plasma polymerisation (PECVD) at the polymer surface could preserve the bulk properties of a polymer but it required a gaseous precursor to produce surface coatings. Deposited films from cold plasma polymerisation of 1.1.3.3-tetramethyldisiloxane (TMDS) monomer were very dense and at higher oxygen concentration larger particle sizes were observed. Durable fire retardant coatings were formed because of covalent bonds between the substrate and the growing polymer on the surface. For polyamide 6 the rate of heat release (RHR) was decreased by 30-40% with an increase in the limiting oxygen index (LOI). Similar LOI values were obtained for 2, 10 and 30 μ m thick films.

Other work on the argon plasma-induced graft polymerisation of liquid monomers such as tetrahydroperfluorodecyl acrylate (AC8), vinylphosphonic acid (VPA) and ethylene glycol methacrylate phosphate (EGMP) onto polyamide 6 was also described. AC8 on polyamide 6 gave no significant change to the degradation but still decreased the rate of heat release by 50% due to gas phase termination reactions via CF_x radicals. VPA coating imparted a lower thermal degradation onset temperature with a strong catalytic effect on char formation. EGMP imparted small increases in LOI to a range of polyester, cotton and polyester / cotton samples.

Dr Ulrike Braun (BAM Federal Institute for Materials Testing, Germany) discussed research work on the fire retardant mechanisms of phosphinates in thermoplastics e.g. glass fibre reinforced-poly(butylene terephthalate) (PBT-GF) and polyamide (PA66-GF, PA6-GF). Aluminium diethylphosphinate and zinc diethylphosphinate were used separately and in combination with melamine polyphosphate. A VO performance using aluminium diethylphosphinate was achieved with PBT-GF, but for

PA6-GF and PA66-GF it was necessary to combine this with melamine polyphosphate and melamine polyphosphate / zinc borate respectively. A battery of flammability, fire behaviour and pyrolysis analysis tests was used to determine the decomposition mechanism of the phosphinate salt. The interaction of the latter with the flame retardants and the decomposition mechanism in the different polymer matrices were also evaluated.

In the session on flammability and toxicity chaired by Dr Richard Lyon (Federal Aviation Authority, USA), Dr Jürgen Troitzsch (Fire and Environment Protection Service, Germany) in discussing fire safety regulations and testing said that many new developments would impact on the use of flame retarded polymers. The European harmonised reaction to fire classification and testing system was increasingly substituting the old national systems for buildings. New voluntary classification criteria included smoke, burning drips and acidity for cables. Rail vehicles will be classified and tested to the new European technical specification CEN / TS 45545 which will become a European standard in 2010. For ships the IMO Fire Test Procedures (FTP) Code was under revision leading to new requirements to become effective in 2010. In electrical engineering and electronics the glow wire test for appliances will probably be revised for better reproducibility. IEC / TS 62441 describes external ignition sources for consumer electronics and IT equipment and may be introduced in the new standard IEC 62368 after redrafting. Since 2006 mattresses for use in private homes in the USA have to meet a nationwide stringent open flame fire test standard. However upholstered furniture in private homes in the USA only require a low fire safety level cigarette test.

Professor Patrick van Hees (Lund University, Sweden) discussed the complex nature of the interpretation of fire retardant behaviour from flammability test data. He pointed out that new materials / products e.g. nanocomposites / technical textiles have brought new challenges in flammability testing. Tests could be used for different purposes and the effect of the flame retardant needed to be investigated for each specific purpose. A fire test could be used to obtain a certain fire class within a prescriptive regulation which was satisfactory for dealing with products and product development. The fire performance-based approach designed an objective without specifying how this might be achieved. For example, safe evacuation from a stadium or building within a

specified time, or structure stability within a specified time. This option allowed more flexible solutions, especially for large public areas.

The fire safety engineering approach for establishing a safe evacuation time would typically involve:

- Selection of the appropriate fire scenario and design fire;
- Calculation of smoke and fire spread by means of a zone model or by the computational fluid dynamics approach; and
- Calculation of the available evacuation time by means of evacuation models.

In fire safety engineering applications the effectiveness could thus be demonstrated in the overall process by an improvement in performance e.g. longer evacuation time, while for prescriptive testing of products the improvement of the class obtained in the flammability test was more appropriate.

The important relationships between fire retardants and fire smoke toxicity were discussed by Dr Anna Stec (University of Central Lancashire, Preston, UK) who has been designated as the UK's Principal Expert on fire chemistry. She emphasised that interest in the toxic effects of fires had been rapidly increasing and a number of international standards for its assessment had been developed. The majority of fire deaths resulted from the inhalation of toxic gases (usually carbon monoxide), the fire toxicity being dependent upon both the material and the fire conditions, the latter being difficult to replicate on the laboratory scale.

One recent significant development had been the steady state tube furnace (ISO TS 19700 : 2006) which had been demonstrated to replicate the toxic product yields corresponding to the individual stages of fires. Another had been the acceptance of performance-based fire design as an alternative to prescriptive fire regulations. Thus architects can now specify the components within a building based on a safe escape time within which toxic / irritant gas concentrations must not approach a lethal level (ISO 13571 : 2007).

Fire hazard was a combination of flammability and fire toxicity. Many fire retardants can affect fire toxicity in unpredictable ways dependent upon the nature of the polymer and fire conditions. Halogen-based flame retardants generally increased the fire toxicity because of increased yields of carbon monoxide and hydrogen halides. However in most halogen-free fire retarded systems that they had studied no large increases in fire toxicity had been observed.

In the final session on fire retardants and the environment (chaired by Professor Patrick van Hees (Lund University, Sweden) Dr Adrian Beard (Clariant Corporation, Huerth, Germany) said that the prevention of accidental fires through using flame retardant materials saved both lives and property but there were concerns related to chemical release into the environment and potential health effects. Flame retardants based on halogens, phosphorus and nitrogen were widely used. Halogenated flame retardants had been the focus of public scrutiny and other flame retardants needed to prove their environmental benefits.

Dr Beard focussed on a study of the release of flame retardant and degradation products over the key stages of the life cycle of various plastics containing a new class of phosphinate-based flame retardants (Exolit OP) from Clariant Corporation. This was compared with brominated systems in processing by extrusion, use phase, accidental fires, incineration and end of life disposal for flame retarded polyamide 6 and 6.6, high temperature nylon and polybutylene terephthalate. It was considered that the methodology developed could be utilised to evaluate the environmental profile of other flame retardants / plastics additives within the context of the implementation of the European chemicals regulations (REACH). REACH would change the whole chemical industry within Europe. It required all chemicals “new and old” to be registered and is based on the principle of “no data, no market”. A brief update of recent developments and projects on environmental aspects of flame retardants was then presented.

Dr Rudi Borms delivered the lecture for Pierre Georlette (ICL-IP, Israel) on the environmental benefits of brominated flame retardants (BFRs). Non-governmental organisations (NGOs) and green activists often issued misleading information on BFRs while ignoring the available scientific information and positive risk assessments.

Life cycle assessments conducted by renowned academic researchers put forward the environmental value of a high level of fire safety brought by BFRs as determined by significant reductions in the emissions of toxic gases e.g. polyaromatic hydrocarbons (PAH), polychlorinated biphenyls, chlorinated and brominated dibenzodioxins and furans, CO, CO₂, HCl, HBr, volatile organic compounds and HCN.

Plastics containing BFRs had been shown to be more preferable in the mechanical recycling of electrical and electronic (E&E) plastics waste with respect to hydrolytic stability and process safety. Much valuable information on the health, safety and environmental aspects of the production / use of BFRs from voluntary programmes (OECD Voluntary Industry Commitment (VIC)), the US High Production Volume (HPV) Initiative as well as under EU Risk Assessment (Council Regulation 793/93) is expected to correct many misleading perceptions regarding BFRs.

The Voluntary Emission Control Action Programme (VECAP) introduced by the BFRs industry in 2004 had introduced a code of good practice that had proved so successful in decreasing waste and environmental emissions that it could serve as a model for management of chemicals in many other industries.

ICL-IP was following its policy of Responsible Care and was now promoting the use of reactive and polymeric BFRs which were not expected to be subject to leaching, nor be readily absorbed by biological tissues and were thus relatively non-toxic.

The theme of the environmental concerns of brominated flame retardants was discussed by Professor Åke Bergman (Stockholm University, Sweden). He pointed out that some flame retardants used in the past like penta- and octabromodiphenyl ethers were still in the environment and were bioaccumulative. Exposure pathways and dose assessments particularly in children were under way. The CHARGE research program (Childhood Autism Risk from Genetics and the Environment) had studied the bioaccumulation of pentabromodiphenyl ethers in Californian children (2-5 years old) and a number of brominated compounds had been detected at median concentrations of 10-90mg/g lipid weight.

Decabromodiphenyl ether (BDE-209) was persistent. It had a very low solubility in water, very low volatility and high adaptivity. This led to high concentrations in sediment and indoor dust. The bioaccumulation was species-dependent and there had been no increase in human milk. Hexabromocyclododane had been detected in Swedish and Japanese mother's milk at pmol/g fat levels. Professor Bergman was presently concerned about the less well known neutral, lipophilic brominated flame retardants and halogenated phenolic compounds.