

FLAME RETARDANTS. A CONCEPTUAL APPROACH

Flame retardants can be catalogued in a systematic way. There are two major types of flame retardant systems, radical quenching and barrier types. Barrier types can be further subdivided by phase of action, gas, liquid or solid.

INTRODUCTION

Table I lists the consumption and value of the various plastic additives. Flame retardants are the most prominent of the speciality additives by volume and price value used in the plastics industry. However, they are generally by specialist compounders. The range of flame retardant additives and applications can seem bewildering, however, it need not be.

The purpose of this review is to i) introduce flame retardancy for plastics, ii) to describe a method of defining flame retardants and iii) to describe recent advances in non halogen flame retardants with a special reference to phosphorus.

Any object can have one of four reactions to fire; it can be

- *Non-combustible* - will not burn when exposed to fire.
- *Flame Resistant* - Difficult to ignite when exposed to heat and/or flame, however once burning it may have no mechanism to self extinguish.
- *Flame Retardant* - Usually difficult to ignite when exposed to fire, however once burning, if the ignition source is removed, it

P.M. DAVIES

*Albright & Wilson Ltd
P.O. Box 3,
210-222 Hagley Road West
Oldbury Warley
West Midland B68 0NN, UK*

will have a mechanism to self extinguish

- *Combustible* - Will burn when exposed to fire.

The reason for adding flame retarding chemicals to plastic (or any) material for that matter is to decrease its flammability, usually to make a combustible plastic article flame retardant.

MECHANISMS OF FLAME RETARDANCY

There are only two major mechanisms of flame retardancy. These are:

RADICAL QUENCHING BARRIER METHOD

In general halogen-based systems provide radical quenching and non-halogen systems provide barrier

methods. They are not mutually exclusive and some flame retardant systems use a combination of both types.

In a fire situation, with no flame retardant present, a polymer breaks up into volatile radicals, highly excited molecules, which are self propagating leading to an avalanche of chemical reactions producing heat which continues the process. Take for a comparison, a polymerisation reaction, here for one initiation reaction there are thousands of propagation reactions, then one termination reaction. Radical quenching acts to terminate the steps at or near the initiation preventing further reaction, starved of radicals the reaction in the flame stops and the flame goes out. Free radicals are atoms, which may or may not be parts of molecules with only a single unpaired electron. The radical exists only as a highly unstable state, and it must find a partner either by stealing an electron from a stable pair or by combination with a different free radical. The unpaired electron could be thought of as an engine driving the atom to pair. If we look at various sizes of atoms, we see that the halogens bromine, chlorine and fluorine are large by comparison with the other non-metals. They all have a similar sized motor, so the halogen radicals are sluggish in comparison with other smaller radicals such as carbon or hydrogen.

Table I - Plastic speciality additives - 1985

	United States Tonnage Value (1000) (\$m)		Western Europe Tonnage Value (1000) (\$m)		Japan Tonnage Value (1000) (\$m)	
Flame Retardants	168	277	62	265	68	138
Others	156	578	246	788	140	495
Total	324	855	308	1053	208	633

SOURCE: SRI International

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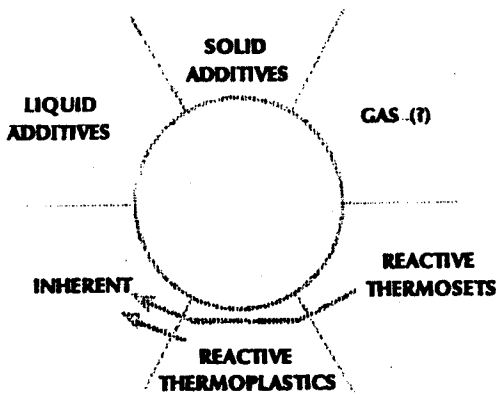


Fig. 1 - Halogen delivery systems

Moreover, the halogens are very electron rich, if the single electron has lots of couples within the atoms boundaries to be companions, this makes it less reactive.

When compared to hydrogen radicals, halogen radicals are comparatively so slow and unreactive that they are very much more likely to combine with other radicals rather than stable coupled molecules. So the halogen radicals prevent the heat producing reaction in the propagation steps shown earlier. So where do the halogen radicals come from? Fig. 1 shows the halogen delivery systems.

The reactive double bond is used to incorporate bromine into the polymer chain of similarly reacting double bonds at the polymerisation stage, for example in polystyrene. In the thermosets, the alcohol or anhydride groups perform a similar function (Fig. 2).

As it can be seen from Figs. 1-4 there are five (or six) major types: solid additives, liquid additives, reactive thermosets, reactive thermoplastics and inherently flame

retardant plastics. The sixth is possibly gaseous material such as CFC's.

Although CFC's are not normally considered as flame retardants they contribute to flame retardancy; for example in a polyurethane foam, if the CFC is reduced by 50% and replaced by CO₂, the flame retardancy decreases, and more flame retardant is required to achieve the same level of flame retardancy. (1)

This is not a comprehensive list. It is worth mentioning that reactive flame retardants once incorporated into the polymer in effect become part of an inherently flame

Fig. 3 - Examples of commercial halogen delivery systems: additive flame retardants

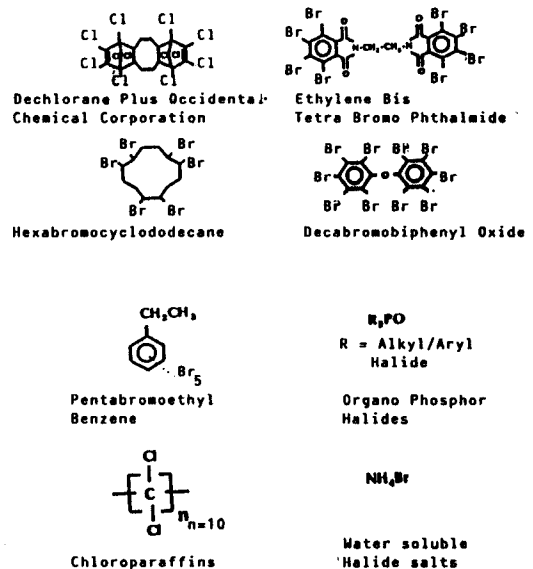
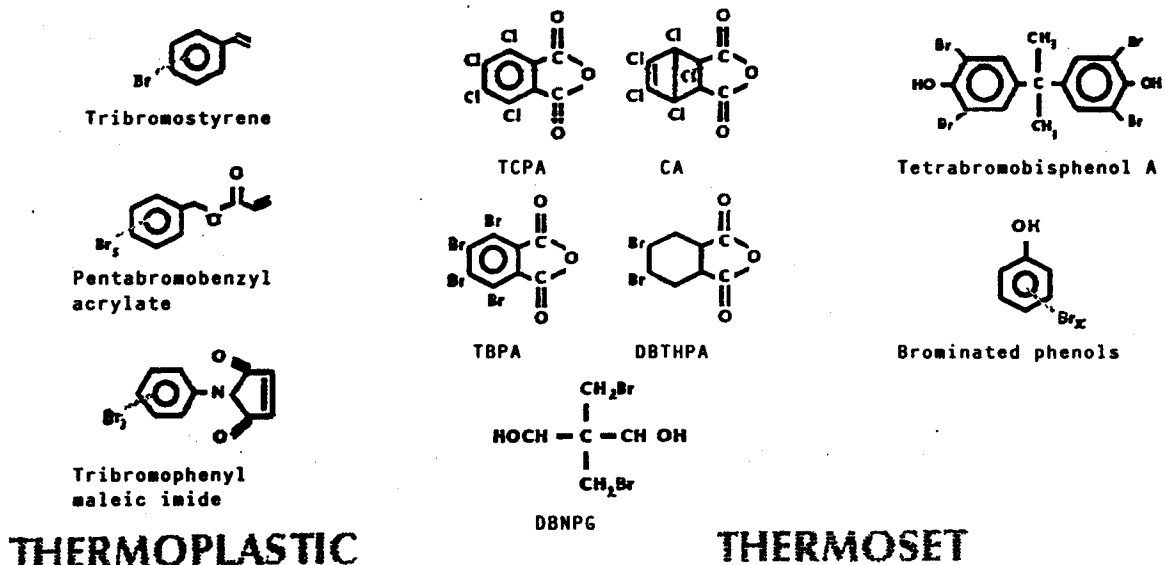


Fig. 2 - Examples of commercial halogen delivery systems: reactive flame retardants



THERMOPLASTIC

THERMOSET

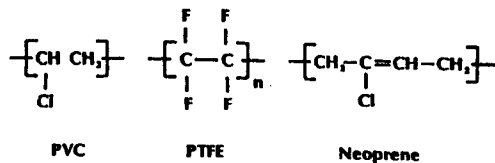


Fig. 4 - Examples of inherently flame retardant plastics

retardant polymer.

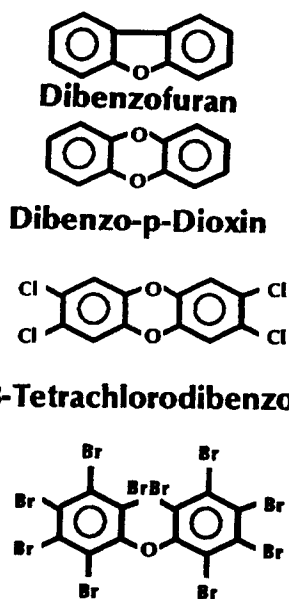
Another factor that can assist radical stabilisation is delocalisation of the radical electron. The delocalisation of various organohalides gives rise to the generally observed effectiveness of these flame retardants: aryl > vinyl > alkyl (halides).

The radical reactions are all gas phase reactions, so that any system which aids halogens to become volatile improves the halogens efficiency of flame retardancy. Antimony oxide falls into this category. Antimony oxide produces antimony trihalides in the presence of the halogen compounds which are volatile gases. Antimony oxide is only used as a flame retardant in combination with halogen compounds to produce volatile gases. On its own antimony oxide only acts as a mineral filler.

The gas phase nature of these reactions is where their nemesis lies, being considered environmentally unfriendly, as they give off caustic gases such as HCl during fire. In the special case of the halogenated phenol ethers some give off gases which can be toxic.

Fig. 5 shows the relationships between dioxins and a commonly used halogenated flame retardant. Dibenzofurans and -p-dioxins are the basic toxic compounds. There are many isomers of these products with

Figure 5



Decabromo bis phenol ether

halogens, the most lethal being the chlorine compound which is simply known as dioxin. These compounds are under intense scrutiny and increasing registration. For this reason, an enormous research effort is now being directed towards barrier-type flame retardants which are non-halogen.

THE BARRIER CONCEPT OF FLAME RETARDANTS

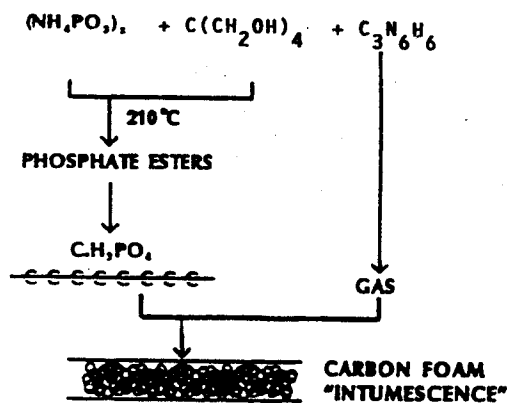
As a contrast to radical quenching, barrier flame retardants seek to place chemical barriers in between the fuel (unburnt polymer) and the fire. Barriers can be external (e.g. an aluminium foil coating or a flame retardant paint) or internal i.e. additives. Flame retardant plastic additives are internal, their delivery systems stem from chemicals which under normal conditions are an inert part of the plastic article, however, under fire conditions these chemicals become active and form a flame retardant barrier (Table II).

Table II - The physical states the barrier can take.

Gas	Liquid	Solid
H ₂ O	H ₃ PO ₄	C (soot)
NH ₃	H ₂ SO ₄	SiO ₂
CO	B(OH) ₃	CaCO ₃
CO ₂	(HNO ₃)	MgO) also smoke ZnO) suppressants

The delivery systems can involve a combination of different states, as an example, the classic intumescent reaction. In this reaction system, there are three important ingredients, ammonium polyphosphate

Fig. 6 - The intumescent reaction



(AMGARD MC), pentaerythritol and melamine (Fig. 6). Generally:

- 1) A catalyst: A material that produces a dehydrating acid such as phosphoric acid (H₃PO₄) upon absorbing heat, e.g. ammonium polyphosphate ((NH₄PO₃)_x)
- 2) A carbonific: A material that produces carbon and water upon contact with dehydrating acid (this can be a polyol such as for coatings or cellulose for

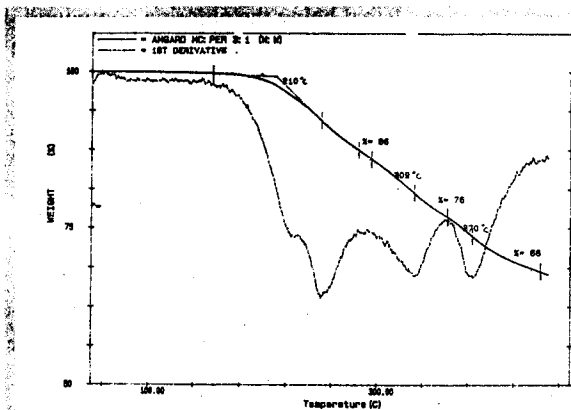


Fig. 7 - The thermogravimetric analysis of an APP/PER blend

- 3) textiles, wood or paper.
 A blowing agent - A material that produces inert gases (at the required temperature) upon absorbing energy (heat). This can be melamine or urea derivatives, even chloroparaffins.

Albright & Wilson produce a wide range of flame retardants with its AMGARD(r), RETARDOL(r) and PROB'AN(r) range of products for a wide variety of substrates for textiles, paper, timber, polyurethanes and plastics which use similar principles.

Looking more closely, the phosphate reacts with the polyol to produce a phosphate ester, which eventually breaks down further to give the three basic components: carbon, a phosphorus acid and water, i.e. a solid, a liquid and a gas. This can be clearly seen by thermal analysis (Fig.7).

If a mixture of an ammonium polyphosphate and pentaerythritol is heated, it loses weight. However, differential analysis shows that it is in four steps, each step represents a loss of water as steam, phosphoric acid plus alcohol gives ester plus water. These esters break down further to give carbon, water and phosphoric acids.

So there is a sticky carbon char produced from a phosphate and polyol on contact with heat (this reaction may also be thought of as a heat sink). The melamine is added so that at higher temperatures it will decompose to gases. It decomposes at a temperature approaching 300°C to cause the sticky flowable carbon char to bubble and foam.

The effects of intumescent reaction are dramatic: an

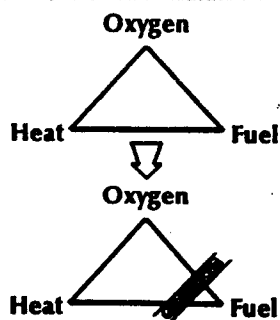


Fig. 8 - The flame retardant action of intumescence

intumescent paint can expand from 100 μm to 14 mm. However, similar charring effects are seen in polyolefins where phosphates can also be used.

The carbon char acts as an insulating barrier between the unburnt or unaffected substrate (textile, paper, wood, steel, plastic) and the fire. There is a barrier formed in between the fuel (polymer) and the heat and oxygen. In fact these three elements form the basis of the so called fire triangle (Fig. 8). Intumescence comes between the fuel and the other two elements; in fact, practically all barrier flame retardants could be thought of as acting on or near the unburnt substrate to form a barrier in between the substrate and the fire.

TYPICAL NON HALOGEN FLAME RETARDANTS, THEIR APPLICATION, LIMITATIONS AND MODES OF ACTION

Nitrogen based flame retardants

The broad class of these materials fall into various chemical types (Table III) (2), the most important of

Table III
Melamine Melamine salts Melamine derivatives
Guanidine Guanidine salts Guanidine derivatives
Urea Urea salts Urea derivatives
Dicyandiamide Dicyandiamide salts Dicyandiamide derivatives

which for plastics are melamine and melamine cyanurate. Melamine is used as a flame retardant in polyurethane (and a synergist with phosphates in polyolefins and coatings). Melamine cyanurate is used as a flame retardant in nylon. The others are only used in cellulose materials. Their mechanism of the action is not fully understood. What is clear is that in a fire situation they release inert volatile gases which may act as a diluting gas, i.e. a gas barrier near the flame/substrate interface. However, in producing the gas, heat is required, i.e. the most important action could be as a heat sink. All flame retardants act as heat sinks by effectively changing the reaction profile from energy releasing to energy absorbing, i.e. from exothermic to less exothermic or even endothermic. The melamine materials seem to be unique in that after absorbing the energy they may not have a subsequent flame retardant action.

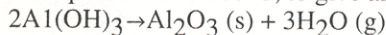
Further studies of the charring effect of the residue and volatile acids from these compounds (cyanuric, prussic, cyanic) would prove useful. Incidentally as the

melamine cyanurate works by producing an inert gas, it is not suitable in glass reinforced nylon where flow of flame retardant chemical is internally restricted (3).

Melamine can also be found as melamine phosphates: Albright & Wilson's AMGARD NH and AMGARD ND where the synergistic effects of phosphates and nitrogen are combined. There are other examples of such materials (4).

Hydrated mineral fillers

There are a range of these materials, for example aluminium trihydrate, magnesium hydroxide and magnesium carbonate. The most important of these and of all flame retardants is aluminium trihydrate (ATH). Its estimated consumption in Western Europe is approximately 50,000 metric tonnes per year (5). It is inexpensive, non-toxic and suppresses smoke. However, if ATH is used without a synergist, a high loading is required (60-70%), and it has limited stability (<200°C). Its main use is in thermosets, rubbers and cables. ATH can be written as aluminium hydroxide, this decomposes above 200°C, to give alumina and water.



This conversion acts as a heat sink, but additionally, the water vapour given off dilutes any combustible gases and hinders the access of oxygen to the surface of the polymer, thereby suppressing ignition. This area is widely documented and analogous reactions can be written for the other hydrated mineral fillers (6, 7). Basically, these materials breakdown by absorbing heat to give gas and ash. Both the inert gases and the residue ash dilute the unburnt substrate (polymer) at or near the surface.

There are many other polymer fillers eg. minerals (carbonates, silicates, sand, glass, carbon) which are not flame retardant, but help to make the polymer flame resistant by in effect diluting the proportion of combustible polymer. In the case of carbon compare the ease of igniting paper or cotton to coal, carbon char can be described as flame resistant material. One effect of this must be realised that although plastic compounds of flame resistant material may be difficult to ignite, once

burning they may have no mechanism to self extinguish.

One flame retardant filler type additive CEPREE from ICI used in thermosets works by solid action alone by sealing the polymeric surface by a glass cap. (8)

Borate based flame retardants

There appear to be no boron based flame retardant except hydrated boron phosphate ($\text{BPO}_4 \cdot \text{H}_2\text{O}$), which only releases water, so is in fact a hydrated mineral filler. Generally all the flame retardant additives in this group are borates. They decompose to produce boric acid which chars in a similar fashion to phosphorus based flame retardants. Boric acid is not as potent/efficient as phosphoric acid and so a higher loading is required. Borate compounds are not particularly thermally stable, simple borates (especially boric acid) are only useful in cellulosic materials. Compounds of borates with metal smoke suppressants, eg zinc borates ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$), are widely used in PVC cable compounds.

Phosphorus based flame retardants

Phosphorus based flame retardants have a wide range of applications; textiles, paper, coatings, polyurethanes, timber and plastics (liquid and solid additives), in nearly all of these areas, phosphorus chemicals and Albright & Wilson have major or dominant roles. The sole exception to that list is the use of solid inorganic additives to plastics, where phosphorus chemicals have been neglected due to halogens dominance and for reasons that will be explained later. For convenience it is easier to split this subject into two sections, liquid organo phosphorus and inorganic phosphates.

Organo-Phosphorus Flame Retardants

There are a large number of organo phosphorus based flame retardants. They have been very well summarised in other discussions. (9)

Albright & Wilson produce a large range of organo-phosphorus halogenated and non-halogenated materials for use in polyurethanes, thermosets and plasticizers in certain polymers. Organo-phosphorus chemicals are the most important phosphorus based flame retardant chemicals for plastics. For plastics however, they suffer from limited thermal stability and volatility in the extruder coupled with a sometimes unwelcome plasticisation precluding their use in many applications.

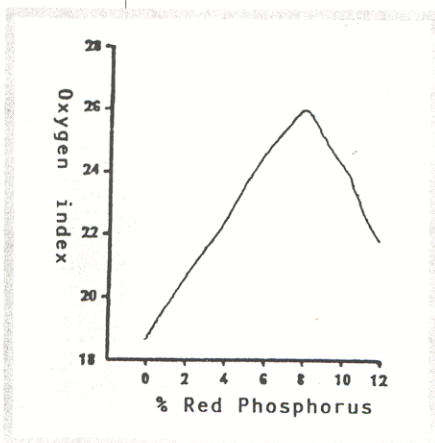
Due to the very significant synergy between phosphorus and halogens organic compounds containing phosphorus and halides are widely used. These phosphor-halide compounds work with both radical quenching and barrier method and are consequently very effective.

Inorganic Phosphorus Flame Retardants

Water soluble phosphates are used exclusively in cellulose materials and hence fall outside the scope of this paper.

There are two main groups of water insoluble materials used to flame retard plastics namely phosphates and phosphorus. Phosphates act in the manner previously described. Typically ammonium polyphosphate can be used in polyolefins. However, its thermal stability is low and is only really suitable for polyethylene. Albright & Wilson have launched a further advancement in non-halogen flame retardants, AMGARD EDAP. This

Fig. 9 - Flame retardancy of polyethylene with added phosphorus. Source: E.N. Peters; *J. Appl. Polym. Sci* 24 1457 (1979)



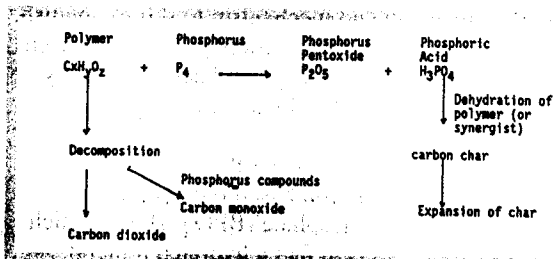


Fig. 10 - The flame retardant action of phosphorus

product will enjoy a limited launch in Europe in the near future.

The efficiency of all phosphorus based flame retardants is directly related to their phosphorus content. So the most efficient flame retardant chemical is the one with the highest phosphorus content. The chemical with the highest phosphorus content is red amorphous phosphorus, which is 100% phosphorus.

This material has an unusual property in that its flame retardant effect is not additive, but reaches a maximum at around 8% as shown on Fig. 9. At higher concentrations, the material has no flame retardant effect until at higher concentrations (>50%) it becomes flammable itself. It sounds like an exotic chemical, however most people have regular contact with it: Red Amorphous Phosphorus (RAP) is widely used on the sides of safety match boxes. If you look carefully a reddish colour can be seen, this can be masked, the skill of Albright & Wilson has been to make this flammable material safe to handle. Red amorphous phosphorus is made safe to handle by the plastics processor by two major actions. The first action is to coat the material with an impervious layer. Typically this will comprise of an amphoteric mineral and an organic outer skin. These layers mop up trace acidity and prevent moisture and oxygen ingress. The second action is to put the coated red amorphous phosphorus into a masterbatch (for thermoplastics) or paste (for thermosets).

Albright & Wilson now have a range of masterbatches and pastes:

Carrier	
AMGARD CPC 100	Polyethylene
AMGARD CPC 200	Polypropylene
AMGARD CPC 300	Ethyl vinyl acetate
AMGARD CPC 400	Polyamide
AMGARD CPC 500	High impact polystyrene
AMGARD CPC 700	Epoxy resin
AMGARD CPC 725	Unsaturated polyester resin

These materials are composed of 50% coated red phosphorus, with 50% host polymer. These masterbatches of phosphorus are now classed as non-hazardous and can be processed in the extruder as with any other masterbatch. They are extremely stable. As an example, the thermogravimetric analysis of AMGARD CPC 400, the nylon masterbatch, shows that the material is stable to above 400°C. Processability is good and indeed we have been unable to detect any corrosion of our extruders even after 10 years of processing this material.

Phosphorus is extremely potent as a flame retardant, its flame retardant action is as in Fig. 10. Phosphorus is

able to strip out oxygen and/or elements of water of a polymer such as nylon and epoxy resin where phosphorus is most effective, as the polymer acts as a synergist to phosphorus.

Coated red phosphorus has two other properties that are very valuable. The first is its hydrolytic stability: it will pass flame retardant test after soaking in warm water for many months. It has little effect on electrical properties and so has been in use in nylon for transformer cases, switchgear and circuit boards. It is widely used in epoxy potting compounds in combination with aluminium trihydrate. Phosphorus is very synergistic with ATH and is normally used in thermoset resins to reduce the ATH loading to give lower viscosity. This synergism is very useful, and although phosphorus works fairly well in EVA (and not so well in polyethylene) on its own it is envisaged that AMGARD CPC 300/100 will find more use in cables.

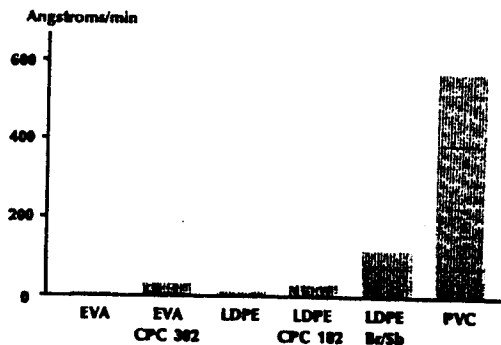
There are advantages in using ATH/CPC combinations. Comparative tests have been carried out in America to examine the corrosive effects of smoke (10, 11) from PVC cables compared to flame retarded polyethylene and EVA based cables. Test pieces were burned and exposed to copper plates. The rate and amount of loss of metal through corrosion was measured. Fig. 11 and 12 show a clear order of corrosivity of smoke:

PVC >> FR LDPE(Br) >> FR EVA (P) > FR LDPE (P) > PE ~ EVA

The reduction in corrosivity is not the only positive effect of using phosphorus. When the smoke evolution of a reactive halogen (chlorine) is compared against an ATH/phosphorus system, an advantage in smoke production is also seen in the quoted case of the polyester. Smoke production from polyester flame retarded with (i) reactive halogenated flame retardant acid and (ii) and ATH/AMGARD CPC 700 system was measured. All test pieces, flame retarded to the same extent, were heated and the smoke density examined against time.

The halogen system produced a large quantity of smoke reaching obscurant level (~100-500) after about one minute. However the ATH/red phosphorus did not reach this level for over 2.5 minutes thus demonstrating the low smoke producing benefits of ATH/CPC systems.

Fig. 11 - Maximum rate of metal loss of various polymers



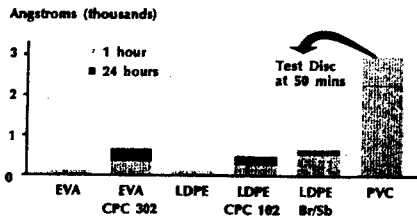


Fig. 12 - Total metal loss of various polymers.

Phosphorus is synergistic with: hydrated mineral fillers, halogen-based flame retardants, nitrogen, phosphates, antimony oxide and maybe more. This area of synergy is a very active area of research in Albright & Wilson.

Other flame retardants

Two other elements which require further inspection are sulphur and silicon. At present only the water soluble ammonium sulphamate is widely used as a flame retardant for cellulose, its propensity to decompose to dehydrating acid deserves further inspection in the search for new flame retardants. Silicones which are highly flame resistant are finding favour in some areas of the cable industry, but they are very expensive. It is interesting to note that all the materials described are based on non-metals, the other non metals exclude themselves on the grounds of toxicity (e.g. arsenic) or low volatility (e.g. iodine) or inertness (inert gases). The one exception could be oxygen itself, however if a material is already fully oxidised, it will not burn.

THE FUTURE

There will be a concerted drive to non halogen alternatives, especially in the reactive area to produce non-halogen inherent flame retardants. More systems will be developed rather than just additives, which will rely on more than one mode of action.

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