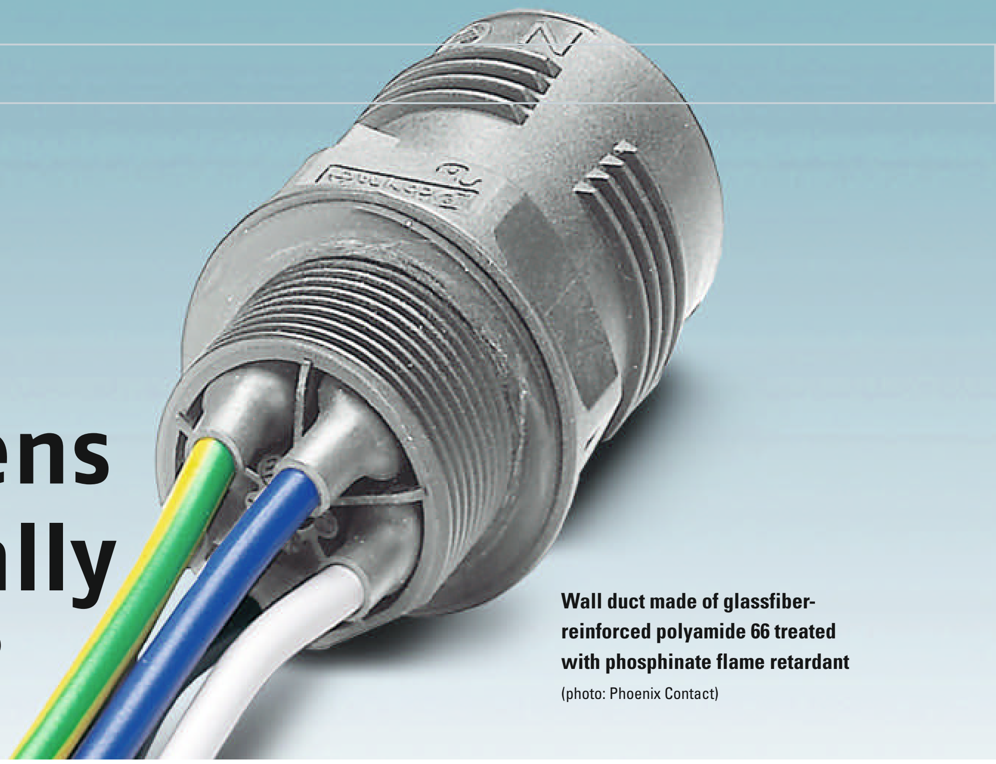
Are Halogens Really Necessary?



Wall duct made of glassfiber-reinforced polyamide 66 treated with phosphinate flame retardant (photo: Phoenix Contact)

Flame Retardants. Sophisticated plastic components that must meet high safety and fire protection requirements can be producted without halogenated flame retardants. Environmental friendly alternatives offer comparable effectiveness combined with a competitive price-performance ratio. This has been revealed by extensive studies and reviews conducted by twelve universities, institutes and companies.

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Preventing fire is a better way to protect life, limb and property than fighting it. Design engineers and manufacturers of electrical and electronic equipment, systems and components are tasked with ensuring that high safety standards are met. That is not easy given the plethora of polymers specified by designers and the seemingly unstoppable urge to miniaturize and integrate functions. Notebooks and smart-phones, electrical household appliances, electrical systems for industrial and residential construction, photovoltaics and not least automotive and aircraft construction increasingly require polymers that reliably prevent a fire from starting and spreading in the event of a fault.

For many years, a range of additives based on different working principles have been used to prevent components from going up in flames in the event of an electrical short, an encroaching external source of ignition, or overheating. Unfortunately, these additives also change the properties of the base polymers and compounds, along with their processing behavior, in different ways and to varying degrees. Added to which, a substantial number of the additives have a reputation for releasing harmful, brominated or chlorinated gases when heated, a fact which also considerably hampers thermal recovery at the end of a product's life cycle.

As a result of the need to ensure that the highest demands imposed on mechanical, optical and thermal properties of the material are met, while taking account of processing parameters, the effectiveness of the fire protection, environmental compatibility and economy, different perspectives and different assessments of possible solutions present themselves to the experts. The importance of this prompted the European Union in 2009 to set up the ENFIRO project to study and evaluate the modes of action and consequences of using fire-protection alternatives in plastics.

Full-fledged Alternative Methods Available

Proceeding from the finding that some BFRs are not only directly harmful, but also accumulate in the food chain, the University of Amsterdam, home to the Institute for Environmental Studies, collaborated with twelve project partners over the course of three years on intensive studies aimed at collecting data and facts on possible alternatives. They looked at 15 commercially available, non-halogenated flame retardants of different composition and applications. Their goal was to be able to make credible pro-

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nouncements about potential health hazards and environmental compatibility, including beyond the end of the useful life of flame-retarded components, as well as the processability of the polymers, and other criteria.

In order to closely reflect industrial practice, the studies addressed flame retardants in different classes of materials, from PA6 to PBT and PET through to HIPS and epoxy resins. Various production methods were employed to ensure that typical applications were represented, too.

Although the detailed assessments of the studies are not yet available in their entirety, some key findings have already been made. These include:

- For all polymer systems, full-fledged, non-halogenated treatments with flame retardants are available as replacements for traditional brominated variants **(Fig. 1)**.
- Non-halogenated flame-retardant formulations were found to match or outperform their brominated counterparts in injection molding **(Fig. 2)**.
- Non-halogenated additives can impart the specified technical and statutory levels of flame retardance **(Fig. 3)**. Non-halogenated systems typically emit much less smoke and the smoke contains less harmful substances **(Fig. 4)**.

Improper disposal or recycling of brominated additives can lead to release of toxic compounds. The level of discharge from a polymer (leaching, migration) is determined critically by the polymer itself.

Phosphinates for Demanding Cases

Consequently, then, there are hardly any arguments in favor of using classical halogenated flame retardants in polymers. This is due in no small measure to phosphinates, which can also be used in applications involving elevated processing temperatures. Flame retardants based on aluminum salts of diethylphosphinic acid (DEPAL) have been on the market since about 2004. The German subsidiary of Clariant International Ltd., Pratteln, Switzerland, produces such additives for various classes of base polymers, and sells them under the name Exolit. These are now widely used in products for telecommunications and consumer electronics, as well as in electrical applications **(Title photo)** and cable sheathing. In most cases, a relatively small dose is sufficient to meet the stringent fire safety standards in force in these market segments, such as UL 94 V-0 for 0.4 mm wall thickness and GWFI 960 °C (glow wire flammability index) while still complying with environmental regulations, including the European Directive 2011/65/EU on the Restriction of Hazardous Substances (RoHS) in electrical and electronic equipment, and the European Directive 2012/19/EU on Waste Electrical and Electronic Equipment (WEEE).

For many users, the main reason to use Exolit is likely to be the scope for incorporating reliable, non-halogenated flame retardance even into engineering thermoplastics, some of which are processed at temperatures exceeding 300 °C.

The ENFIRO studies show that polyamides and polyesters, as well as thermoplastic elastomers (TPEs) and thermosetting resins can be treated with Exolit. Despite the absence of bromine, Exolit can impart to these polymers a level of fire safety that can otherwise only be achieved with expensive high-performance polymers, which are more difficult to process. Besides the variant Exolit OP, which specifically targets thermoplastic

Fig. 1. Core question for the ENFIRO project: How good in reality are the non-halogenated flame retardants in plastics – during the fire test (left) and after passing the test (right) (photos: Clariant)

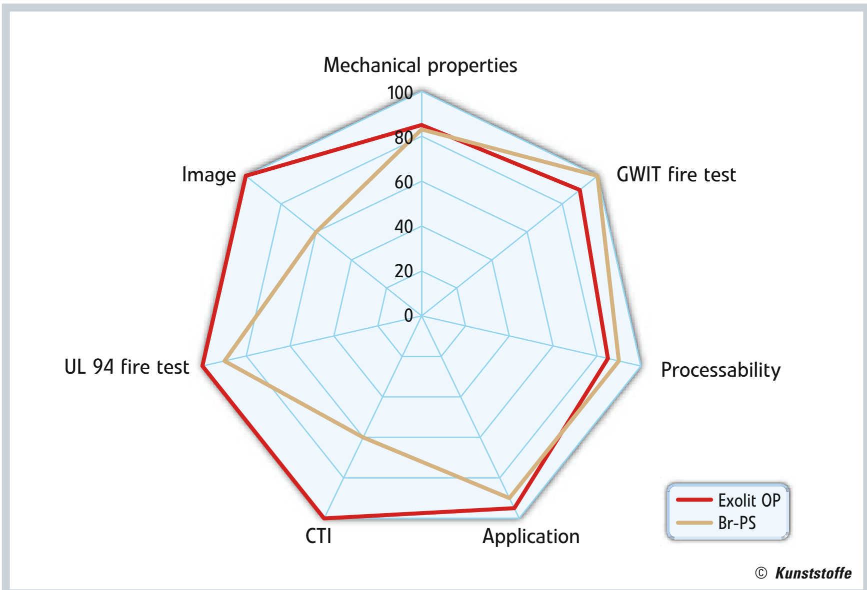

Fig. 2. In addition to fire protection, the ENFIRO project evaluated other parameters of relevance to the processing of non-halogenated materials and compared them with brominated materials (figure: Clariant)

materials, Clariant has also developed new reactive phosphorus-based flame retardants, which are especially suitable for printed circuit boards because the influence of the additive on the glass transition temperature of the plastic material is minimized – this is a crucial aspect of epoxy resin chemistry in this demanding application area. A further consequence is that the requisite amount of flame retardant can be reduced by up to 50 %, as compared with conventional products. Meanwhile, Exolit AP, based on ammonium polyphosphate, can be used to confer flame resistance on polyolefins for use in electrical and electronic products. The ENFIRO project also confirmed that ammonium polyphosphate has a very good toxicity and environmental profile.

The Cost Issue

The non-halogenated alternatives studied in the ENFIRO project are all commercially available and can be added in doses similar to those for brominated additives, and in some cases – e.g. polyamides – in even lower amounts, and they offer a competitive price-performance ratio. A further plus is the resultant gain in safety and the long-term risk reduction: avoiding even just one claim for damage can lead to tremendous savings for a company, both financially and for its image. These arguments boost the case for using non-halogenated flame retardants.

Industries such as consumer electronics and telecommunications, along with electrical engineering, photovoltaics, household appliances and others, seek the optimal technological and economical solutions to – literally – burning issues. The non-halogenated products do not contain any of the hazardous substances listed in the RoHS Directive. The flame retardants have little adverse effect on the properties of the end products and, in the event of fire, do not generate any corrosive smoke, a fact which reduces the risk of fire damage. Such products are also eligible for eco-labels such as the Blue Angel, TCO and the EU Ecolabel. Western Europe is not the only region in which this is a major selling point.

Clariant is responding to growing global demand by continually devising new application-specific, optimized flame-retardant formulations from the additives in all their different variants. The focus of development is currently on polyesters, polyamides and bio-plastics.

How Fire Protection Works

Polymers treated with Exolit intumesce in the event of a fire, rapidly creating a charred protective layer that will not burn further. This provides a heat shield for polymer that has not yet been attacked, and wards off atmospheric oxygen, too. Some of the flame retardant also acts in the gas phase by blocking chemical reactions in the flame. These two effects ensure that the fire has no further source of fuel and so extinguishes. Thanks to this technology, polymers can attain the highest flammability ratings. ■

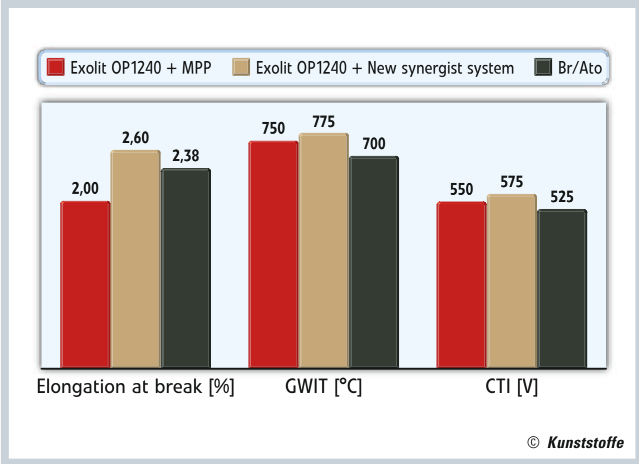

Fig. 3. Technical data for a PBT grade with glassfiber reinforcement, treated with two variants of a non-halogenated fire retardant as an alternative to one treated with a brominated PBT. Optimization of the synergist with the new Exolit formulation led to a further improvement (figure: Clariant)

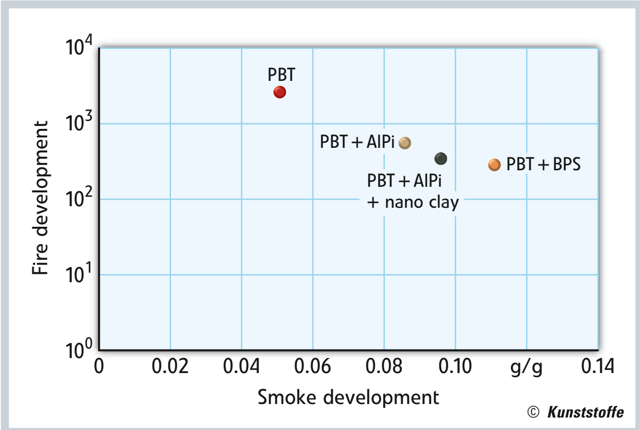

Fig. 4. Non-halogenated systems typically emit much less smoke and the smoke has low contents of harmful substances (source: University of Ulster, Prof. M. Delichatsios)

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