Halogen-free flame-retardant cable sheaths of thermoplastic polyurethane (photo: BASF)

Flame Retardants. Plastics used in building, electrical and electronic engineering or transportation have to satisfy the fire protection demands in the respective segment of industry. Innovations are being made especially in environmentally safe products which contain polymeric or halogen-free flame retardants. The synergistic effect of these additives is also becoming an increasingly important aspect.

Demands and Innovations

JÜRGEN TROITZSCH

The fire protection demands made on plastics differ widely, depending on the field in which the plastics are to be used. If plastics are to be used in building **(Fig. 1)**, electrical and electronic engineering (E&E) or transportation, innumerable very different regulations and tests for fire protection have to be observed. The majority of fire tests today are international, so that the "small state mentality" with national tests is steadily decreasing. In the European Union, classifications and tests for fire protection in building have been harmonized for about 10 years. This has finally been achieved also for rail transportation: The EN 45545 standard on fire protection in railway vehicles that has been undergoing development since 1998 will be adopted in 2013, harmonizing tests and classifications in the EU. The European classifications and testing procedures have become generally more stringent and more comprehensive. Apart from the class fire parameters flammability, flame propagation and heat release, parallel fire phenomena such as flaming droplets, smoke development and toxicity of the combustion gases are playing an increasingly important role. That is the case particularly for the transportation sector, as there are only limited possibilities of escape in trains, aircraft and ships.

This has naturally also led to a rethinking with respect to the flame retardant systems to be used in plastics: Today systems are demanded with a lower smoke development and those which release less of the decomposition products such as CO, CO_2, NO_2, SO_2, HCl, HBr, HF and HCN declared as toxic. That is why the formerly predominant brominated flame retardants are now facing growing pressure from flame retardant systems based on phosphorus, nitrogen and inorganic components.

In the E&E sector, the demands and tests for flammability have always been distinctly international, so that by contrast with building and parts of the trans-

Fig. 1. Films in the construction industry have to satisfy strict demands on fire prevention and protection (photo: Thor)

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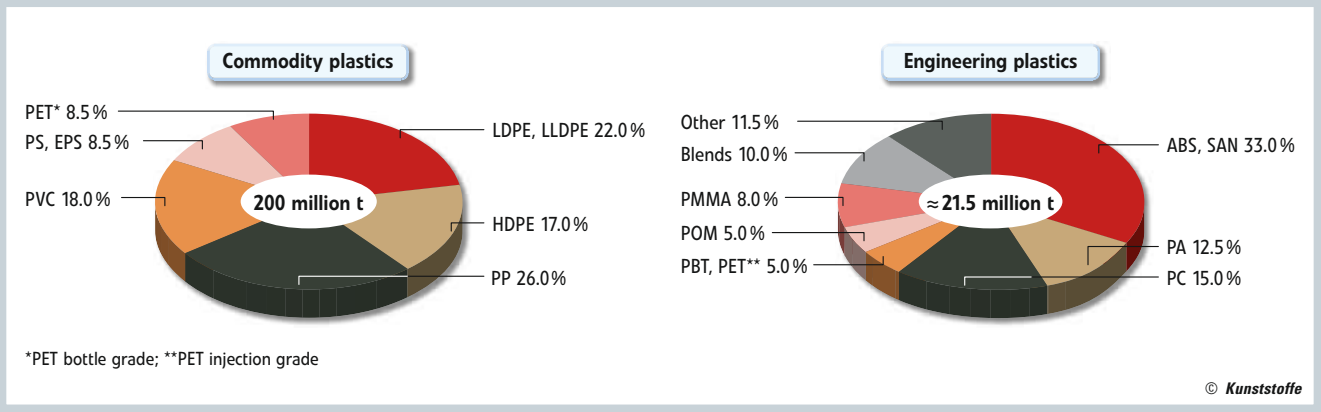

Fig. 2. Estimated demand for thermoplastics in 2011 (source: PlasticsEurope Market Research Group (PEMRG)/Consultic Marketing & Industrieberatung GmbH)

portation sector they have worldwide rather than purely regional applicability. The demands on fire protection, however, are lower, as here it is predominantly a question of protecting a device from the attack of a small ignition source (inside: overheated parts, short-circuit and electric arc; outside: cigarette, match and candle) and thus of preventing the development of a fire. By contrast with the building and transportation sectors, larger ignition sources and the more advanced initialing fire do not play a major role here.

So if we take this background as our framework, what new trends are there for flame retardants, flame retardant plastics and in environmental questions?

Growing Markets for Flame Retardants

First we have to observe that the markets for plastics and flame retardant are continuing to grow. According to the "Plastics – Facts and Figures" presented at the trade press day of PlasticsEurope on 28 March 2012 in Frankfurt, Germany, the worldwide demand for plastics rose from 83.6 million tonnes in 1990 to 225 million tonnes in 2010. The forecast for 2016 reaches an estimated 292 million tonnes, corresponding to an annual growth of 4.4 % **(Table 1)**.

The worldwide demand for thermoplastics for 2011 is estimated at 200 million tonnes for standard plastics and at 21.5 million tonnes for engineering plastics, a segment particularly important for the flame retardants market. **Figure 2** shows the breakdown of their most important representatives by market shares.

One of the largest markets for flame retardants is the E&E sector. Its most important segment – printed circuit boards – is continuing to show strong growth: According to the Central Association of the German Electrical and Electronics Industry (ZVEI) in Cologne, the world market for printed circuit boards will grow from USD 58.8 billion in 2011 to an estimated USD 62.7 billion in 2012, an increase of 6.6 %. The Asia/Pacific region with an estimated USD 38 billion and a growth of over 8 % makes the major contribution to this, while all other regions of the world – with the exception of Japan – are left trailing well behind **(Fig. 3)**.

According to various market studies in the last 18 months, a market volume of almost 2 million tonnes of flame retardants is expected for 2012, corresponding to sales of around USD 5 billion. The estimates for the future annual growth of the flame retardants market for the next 5 years lie between 6 and 7 %. A slightly more conservative estimate of 4 to 5 % for the coming years is assumed in a new market study by Townsend Solutions, Houston/USA **(Fig. 4)**: Behind aluminum hydroxide (ATH), the brominated flame retardants still lie ahead of the phosphorus-based retardants.

In 2011, the Asia/Pacific market accounted for almost 48 % of the world market sales of flame retardants, thanks in no small part to a flame retardant consumption of 400,000 t in China. Together with the emerging market in India, the market in this region of the world will grow at an above-average rate in the coming years, with an annual growth forecast of more than 10 %.

The flame retardants industry can therefore look forward to a growing market and good prospects. That has induced several companies to expand their production.

New Capacities and Products

First Clariant, Muttenz/Switzerland, has built a new plant in Hürth-Knapsack due to the great success of the Exolit OP range with metal phosphinates as an alternative →

Demand 1990-2016e for plastics type	1990 [million t]	2010 [million t]	2016e [million t]	Growth p.a. 2010–2016e [%]
LDPE, LLDPE	18.8	39.2	49.2	3.9
HDPE	11.9	34.9	45.4	4.5
PP	12.9	50.9	68.3	5.0
PVC	17.7	35.1	44.2	3.9
PS	7.2	10.8	13.7	4.0
EPS	1.7	5.2	7.0	5.1
ABS, ASA, SAN	2.8	7.3	9.1	3.7
PA	1.0	2.6	3.5	5.1
PC	0.5	3.4	4.6	5.2
PET	1.7	15.5	20.8	5.0
PU	4.6	11.9	15.1	4.0
Other thermoplastics	2.8	8.3	10.9	4.6
Total	83.6	~225	~292	4.4

e = estimated

Table 1. Worldwide demand for plastics in the period 1990 to 2016 (source: PEMRG)

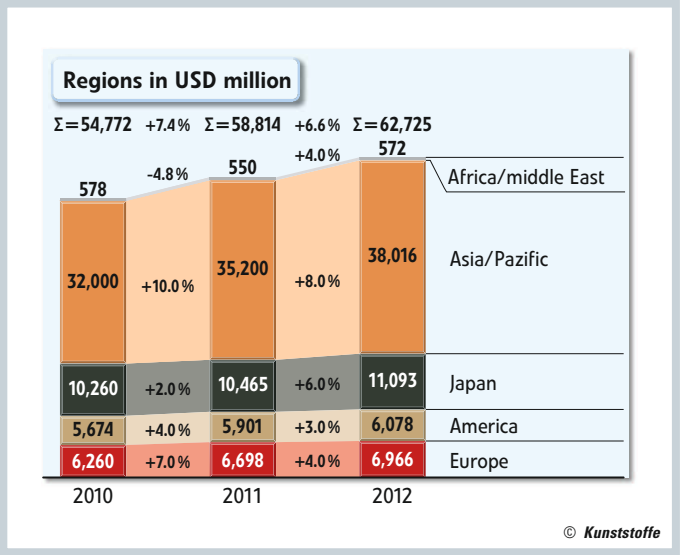

Fig. 3. World market for printed circuit boards in the period 2010 to 2012 (source: ZVEI)

to brominated flame retardants in engineering plastics, such as glassfiber-reinforced polyamides (PA) and polybutylene terephthalate (PBT); this plant is scheduled to go into production this fall and will double the existing Exolit OP capacities. Parallel to that, Clariant has developed a new family of flame retardants for thermoset plastics applications in E&E, transportation and building. Exolit EP 150 and EP 200 are phosphorus-based reactive flame retardants that in small doses give epoxy resins and laminates highly effective flame protection. Currently still in the test phase, the Exolit EP grades have very high phosphorus contents of 25 and 29% respectively, so that they only have to be used in small quantities to satisfy specific fire protection requirements. In the E&E sector it is to be seen that UL 94 V0 is already achieved with only 50 % of the quantity of conventional flame retardants. Exolit EP 150 and EP 200 do not migrate as they are integrated reactively into the polymer and therefore have little influence on the material properties.

In response to the growing demand for polymeric flame retardants and blends with high phosphorus content, FRX Polymers Inc., Chelmsford, USA, founded in 2007, is now building its first commercial plant for polyphosphonates on a site leased from Bayer in Antwerp, Berlgium. Construction started in August 2012 and the plant is scheduled to go into production in the 4th quarter of 2013. The most important products are homopolymers which are currently used mainly in flame-retardant polyester fibers. Parallel to that they are offered together with polycarbonate as transparent copolymers in the E&E sector and as reactive oligomers in epoxy resins and laminates.

In October 2011 Lanxess Deutschland GmbH, Leverkusen, Germany, acquired the American polymer additive producer, Unitex, thus expanding the Lanxess range of flame retardants. The most important new products are Uniplex FRP 45, an effective thermostable flame retardant for rigid PUR foam applications that can also be used in combination with phosphates, Uniplex FRX 4494S (an EDAP/melamine blend) for polyolefins and Uniplex FRP-64 (poly-2,6-dibromophenylene oxide), a brominated flame retardant for PBT, PA6 and PA66. The Disflamoll range with the classic phosphate esters includes an interesting new flame retardant, Disflamoll TP LXS 51036, developed specially for imitation leather. In the Levagard range which is particularly suitable for flame retarding polyurethane rigid foams, Levagard DMPP (dimethylpropane phosphonate) is outstandingly suitable also for unsaturated polyester resin applications thanks to its high phosphorus content and low viscosity. Finally an intumescent Bayfomox coating gives PU insulating panels good thermal insulation, high fire resistance and at the same time acoustic insulation properties to DIN EN ISO 10534-2 in a single production step. Insulating panels coated with the Bayfomox system achieve a fire resistance of F45-F60 for floors, walls and pitched or flat roofs.

Apart from the phosphorus/nitrogen-based flame retardants Aflammit PCO 700 and 800 already on the market for polyolefin films, Thor GmbH, Speyer, Germany, is now launching a new range of intumescent flame retardant systems, the Aflammit PPN series. New here is that apart from further developed ammonium polyphosphate-based (APP) products, some types now require no APP: Aflammit PPN 903 has higher thermal stability (>270 °C), lower solubility and better acid resistance than APP-based products. UL94 V0 is achieved in PP homopolymers with 30 % PPN 903. In addition there is also Aflammit TL 1365 as a trial product. It is particularly effective (PP: 20 to 22 % for UL 94 V0), has good flow properties and is thermally very stable (270 to 280 °C). Both products are also outstandingly suitable for thermoplastic elastomers such as TPS-S (PP/SEBS block copolymers).

Great Lakes Solutions, West Lafayette, USA, and in the meantime also ICL-Industrial Products, Beer Sheva, Israel, and finally Albemarle Corporation, Baton Rouge, USA, have taking out licenses from Dow Global Technologies LLC, Midland, USA, for a new polymer flame retardant. It is intended as a flame retardant in insulating foams of expandable and extruded polystyrene (EPS and XPS) as a substitute for hexabromocyclododecane (HBCD) which has recently come under attack. Due to environmental concerns, HBCD was included in the approvals procedure under the new European chemicals legislation (REACH) and placed on the list of substances subject to

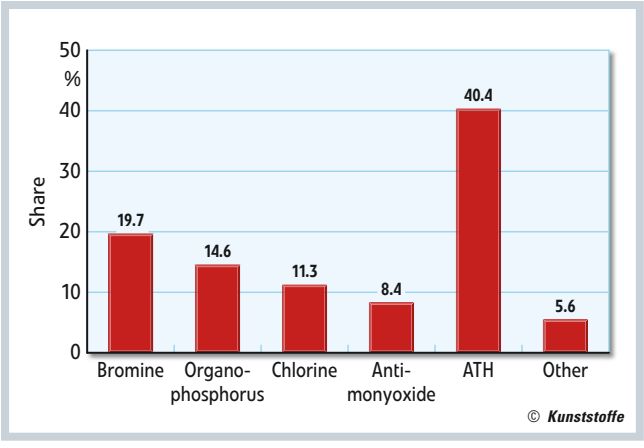

Fig. 4. World consumption of flame retardants in plastics in 2011 (source: Townsend Solutions)

authorization in Annex XIV of REACH. If no application for authorization is made to the ECHA (European Chemicals Agency) for HBCD by February 2014 – as is not to be expected – this substance will no longer be available in the EU from August 2015 (sunset date).

The new polymer flame retardant which offers significantly better environmental properties than HBCD with the same flame-retardant effect is already commercially available today from the first Dow licensee, Great Lakes Solutions (29.3.2011), as Emerald 3000. As second licensee (25.1.2012), ICL-IP aims to make the new flame retardant available commercially under the name FR122P by 2014 through the construction of a 10,000 t plant. Sample quantities can already be ordered. The third in the group, Albemarle, finally took the last license on 12 April 2012 and plans to market the product commercially under its Earthwise platform in 2014.

ICL-IP has furthermore introduced two new halogen-free flame retardants. Fyrol P26 is an additive flame retardant with high phosphorus content (26 %) which is recommended for polyolefins such as EVA and PP where it achieves the classification UL 94 V2 in 3.2 mm thickness with additions of 4 and 6 % respectively and allows transparent formulations. In glassfiber-reinforced PBT it achieves the classification UL 94 V0 with 0.8 mm as a substitute for antimony trioxide together with brominated flame retardants. A halogen-free formulation with melamine phosphate also achieves UL94 V0 with 1.6 mm. The second product, FR-1120, is a synergist (borate/calcium on silicate carrier) that can be used as a substitute for zinc borate and in some cases antimony trioxide. In formulations with brominated flame retardants, it can replace up to 50 % of antimony trioxide in polyolefins and up to 90 % in PBT and PA.

Improvements in Flame-retardant Plastics

There are no breathtaking innovations from the major plastics producers, masterbatch manufacturers and compounders, but steady further developments of the products with the main focus on halogen-free formulations. BASF Polyurethanes GmbH, Lemförde, Germany, for example, is introducing new flame-retardant, halogen-free thermoplastic polyurethanes for cable sheathings **(Title photo)**. They combine good mechanical properties with improved flame-retarding (high limiting oxygen index (LOI) and low heat release in the cone calorimeter), low smoke development and flue gas toxicity. The new Elastollan 1185 A 10 HFFR (halogen-free flame-retardant) grade with an additive of aluminum hydroxide – a grade with magnesium hydroxide additive is also available – is particularly suitable for applications in railway vehicles according to the European fire protection standard EN 45545-2. Further applications are the offshore sector, ships, aircraft and e-mobility.

Fig. 5. Plastic coil in which the metal wires previously used are replaced by laser direct structuring on the plastic surface (LSD technology) (source: DSM)

DSM Engineering Plastics Europe, Sittard,Netherlands, has introduced the new flame-retardant, halogen-free grades Stanyl HFX and Stanyl CR for the E&E sector as part of its Stanyl (PA46) product range. The flame-retardant Stanyl CR grades are particularly to be recommended as high temperature-resistant polyamides, as they exhibit very good flame-retardant properties in the glow wire test and to UL94, good flowability and extremely low corrosiveness. In the glow wire test for finished parts (GWT), the 850 °C demands (flame must be extinguished after 2 s) are satisfied. Furthermore for railway vehicles, the French specification I2/F2 to NFF 16-102 and strict requirements of the new European standard EN 4545-2 for the fire protection of railway vehicles are satisfied. **Figure 5** shows an application example for the E&E sector.

Lanxess also has new products to offer for the E&E sector: Since the market is still demanded non-reinforced polyamides with halogen-based flame retardants, Durethan B30SF30 – a PA6 – has now been introduced which guarantees stable values in the glow wire test (GWT: no flame at 750 °C), satisfies UL94 V0 at 0.4 mm, exhibits a comparative tracking index (CTI) value of 300 V and can be easily processed. Pocan BFN4231 was developed as a new halogen-free, glassfiber-reinforced PBT grade with P/N-based flame retardant. UL94 V0 is achieved with 0.4 mm thickness, combined with improved mechanical properties and higher color and UV stability.

The Engineering Plastics Division (MEP) of Mitsubishi International GmbH, Düsseldorf, Germany, promises high transparency with good flame protection for two new polycarbonate grades for injection molding of thin-walled parts for the E&E sector. According to MEP, the Lupilon grades EMT3100 (UL94 V0 at 1.0 mm) and EMT3120 (UL94 V0 at 1.2 mm) and also other grades from the EFT range have flame-retardant properties without the use of bromine or phosphorus. MEP highlights LEDs and lenses as potential applications, as EMT3100 and 3120 have a light transmissivity of 88 % at thicknesses up to 3 mm and an opacity <1 %.

Sabic Innovative Plastics, Bergen-op-Zoom, Netherlands, offers new flame-retardant polycarbonate grades for the E&E sector: The Lexan CFR (Clear Flame Retardant) copolymer and three new Lexan LUX polymer grades. The Lexan CFR copolymer satisfies the growing demands of manufacturers in the entertainment electronics, household technology and →

sun collector industries for a transparent, flame-retardant (FR) material. Lexan CFR achieves UL 94 V0 at 1 mm and UL94 5VA at 3 mm. It is halogen-free, contains no phosphates and no fluorinated anti-drip additives. Further applications are thin parts in consumer and office electronics, transparent covers for refrigerators and other household appliances and charging stations for electric vehicles.

The new Lexan LUX polymers are suitable for LED applications in the automotive sector (optical waveguides, interior lights and general lighting). They achieve UL94 V2 at 0.8 mm and satisfy the glow wire flammability index (GWFI) for 850 °C at 1 mm.

Outlook

What does the future have in store? First, the flame retardant market will continue to expand globally, as the standard of living and – hence – the consumption of plastics in the emerging countries of Asia, South America and Africa rise sharply. At the same time, the emerging countries will also increasingly adopt international flame retardant requirements, which will greatly enlarge the market for flame retardants in building, transportation and the E&E sector with the main focus on insulating materials, expansion of the railway network, information technology and household appliances.

As far as the trend towards new flame retardants is concerned, not only high effectiveness and compatibility with polymers, but also questions of environmental and health protection will play a role. An important development is therefore moving away from low-molecular chemicals to high-molecular compounds and polymer flame retardants – the latter are non-bioaccumulative and non-toxic. Thanks to their high molar mass, they also do not contribute to emissions (e.g. in room interiors). Here is the chance for bromine-based flame retardants, many of which have come under attack.

The second development focal point is on flame retardant systems with synergistic effect – these have been known for bromine-based systems for many years – which is now increasingly moving towards systems based on phosphorus, nitrogen, organic and inorganic salts and metal hydroxides. ■

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