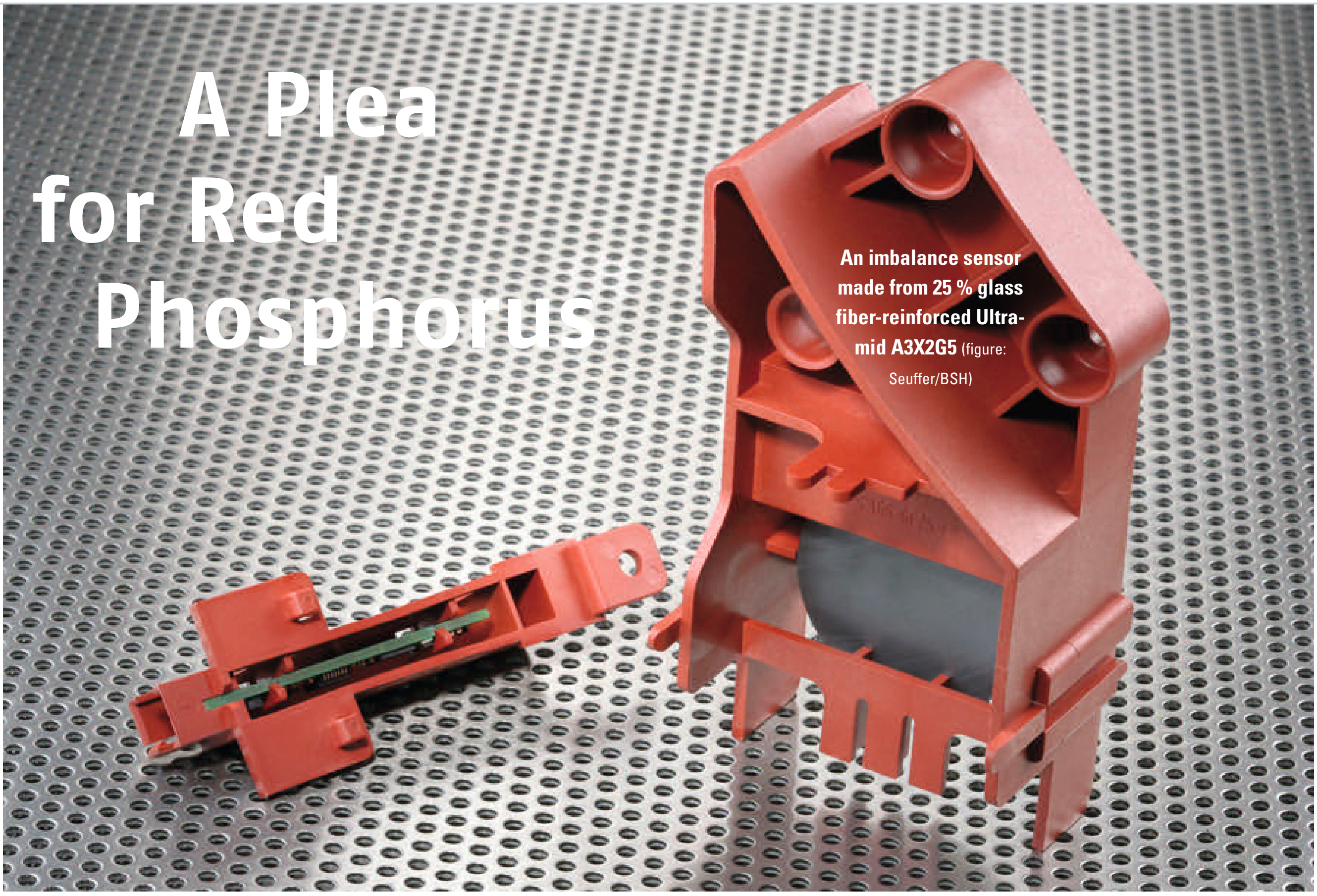
A Plea for Red Phosphorus



An imbalance sensor made from 25 % glass fiber-reinforced Ultramid A3X2G5 (figure: Seuffer/BSH)

Flame-Retardant Polyamides. Polyamides flame-retardant-modified with red phosphorus have better flame retardancy and are more environmentally acceptable than is commonly assumed. This is confirmed, for example, by a report from the German Federal Environmental Agency and other comprehensive studies. The article discusses the key results.

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The use of flame retardants is increasingly entering public consciousness and is a continual subject of controversial debate. The fact that flame retardants not only protect material goods but can save human lives is quickly forgotten in such discussions. Besides their use in textiles, adhesives, paints & coatings, and products for the paper industry, flame retardants are primarily used in plastics for electrical and electronic applications. In this field, achieving the required property profile and meeting the relevant product standards of the energy, electronics, and household appliance industries are equally important. A variety of different standards and guidelines are specified by, for example, Underwriters Laboratories (UL), IEC or EN and the complexity of requirements for the electrical and electronics industries is very challenging.

In electrical and electronic articles, plastics provide electrical insulation and therefore also ensure protection during contact. Today, it would no longer be possible to manufacture highly insulated switch parts and housings, power distribution systems **(Fig. 1)**, cable ducting, contactors **(Fig. 2)**, circuit breakers, connectors, electrical components for computer hardware or electrical parts for large domestic appliances such as washing machines and dishwashers **(Title figure)** without making them flame retardant. In these electrical and electronic components, thermoplastics modified with a wide range of different flame retardant systems are used. In Europe, polyamides are protected mainly by brominated flame retardants, red phosphorus, organophosphorus compounds, and melamine-based flame retardants, as well as by metal hydroxides to a lesser extent [1]. Red phosphorus is one of the most important flame retardant systems.

Starting in the early 1970s, BASF SE, based in Ludwigshafen, Germany, was one of the first manufacturers to develop flame retardant polyamides based on red phosphorus. The high efficiency of red phosphorus, especially in polyamide 66, remains unsurpassed. Only a low addition of this flame retardant is needed and so the exceptionally good mechanical and electrical properties of polyamide are largely retained. The flame-retardant

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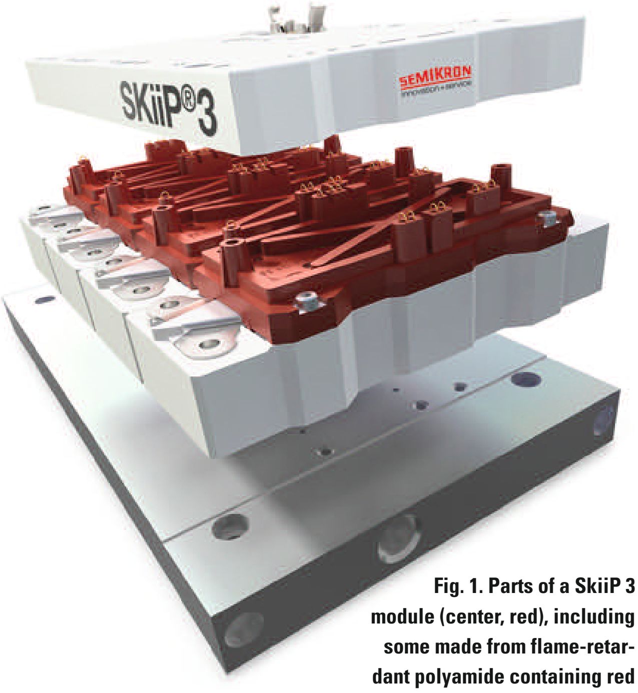

Fig. 1. Parts of a SkiiP 3 module (center, red), including some made from flame-retardant polyamide containing red phosphorus (figure: Semikron)

plastic so produced also represents an optimum solution from the cost viewpoint. This makes red phosphorus a "state-of-the-art" solution for PA66. With its Ultramid A3X2 range, BASF offers high-quality PA66 grades that not only have a highly effective flame retardant system but also fulfill their technical function without any problem in many different applications.

Although flame-retardant products are intended first and foremost to guarantee the highest possible safety of humans and the environment, the public is becoming increasingly concerned about the environmental effects of certain product contents. For example, many consumers fear that the flame retardant system will emit toxic gases in the event of fire, will be leached out of the plastic in contact with water or can be released as a result of wear and tear. And, last but not least, the recyclability and long-term sustainability of the products are called into question. These and other aspects of flame-retardant polyamides are examined in more detail as follows.

No Risk to Humans and the Environment

For various reasons, a distorted picture of red phosphorus as a flame retardant has emerged in recent years. This results partly from the poor product quality of red phosphorus in some cases in the past, due to impurities and other factors. But misleading regulatory classification has also contributed to the negative public image.

In the risk assessment by the European Union [2], chemicals – including elementary phosphorus – are assigned so-called risk phrases (R). Phosphorus occurs in two modifications, which have a very different risk potential. White (or yellow) phosphorus is classified with risk phrases R26/28 and R50 as "very toxic by inhalation and if swallowed" and "very toxic to aquatic organisms". In addition, this phosphorus modification is very reactive (R17, "spontaneously flammable in air") and therefore difficult to handle. However, the red phosphorus used as a flame retardant has a much less critical classification with risk phrase R52/53 "harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment". On the other hand, if red phosphorus is part of a formulation, e.g. embedded in the matrix of a polyamide, it represents no risk to the environment at all and so the formulation does not require classification with a risk phrase.

CAS numbers (Chemical Abstracts Service, American Chemical Society) and EINECS numbers (European Inventory of Existing Commercial Chemical Substances) are used for the registration and identification of chemical substances by the regulatory bodies. Originally red and white phosphorus were listed under the same number.

Since then, the fact that the two phosphorus modifications exhibit considerable differences in terms of reactivity and toxicity has been taken into account by the European Commission. Red phosphorus now has its own EINECS number EC 918-594-3. In the CAS system, a similar change has not yet been implemented and at the present time both white and red phosphorus are listed under the same CAS registration number 7723-14-0. So on this point, the CAS system continues to be misleading for the time being.

In addition to quoting classifications under the relevant chemical guidelines, many market leaders have taken to publishing lists of substances that are undesirable for a wide variety of reasons. Note is taken of these lists across regional and industry boundaries and they are sometimes adopted unchanged. A good example of this is the Apple "Regulated Substances Specification" 069-0135. Red phosphorus was included in this list until recently. Since the last revision at the start of 2013 (revision G), red phosphorus is no longer contained in the Apple product list [3].

The WEEE Directive (2012/19/EU, Waste Electrical and Electronic Equipment) [4] regulates how waste electrical and electronic equipment should be handled; the ROHS Directive (2002/95/EC, Regulation on Hazardous Substances) [5] serves to restrict the use of certain hazardous substances in electrical and electronic equipment. Red phosphorus is not mentioned in either directive and so is not subject to any restrictions.

In a report by the German Federal Environment Agency, it is stated that the red phosphorus used in polymers can only be released into the environment at the plastic interfaces, where it reacts with water to form phosphorus oxides and phosphoric acids [6]. Phosphorus compounds in environmental samples deriving from the use of flame retardants are indistinguishable from naturally occurring phosphorus compounds. Health risks due to the release of toxic phosphine at plastic interfaces are negligible because of the low doses involved. Normal use of injection molded components with red phosphorus therefore poses no risk. For this reason, the German Federal Environment Agency – taking into account the ecological priorities – includes red phosphorus as one of its recommended alternatives to halogenated flame retardants [7]. →

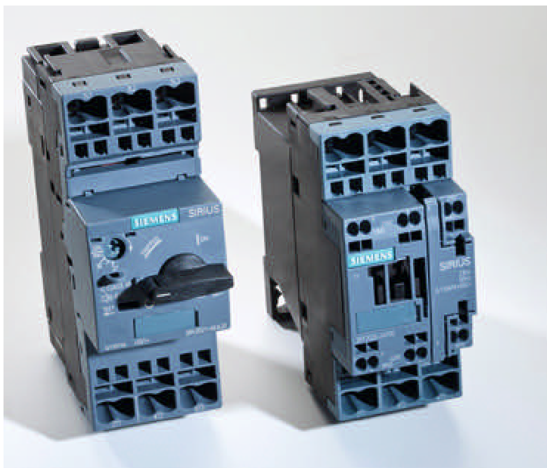

Fig. 2. Typical applications of flame-retardant polyamides include industrial switchgear and contactors (figure: BASF)

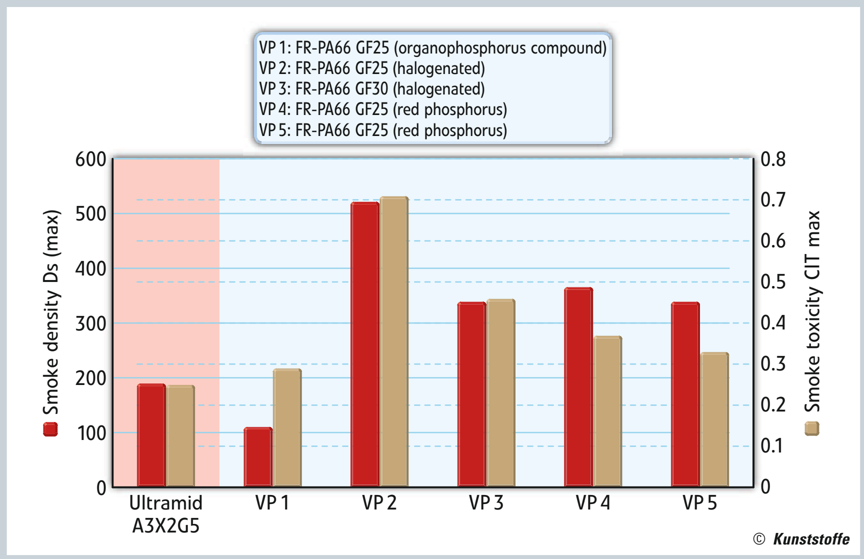

Fig. 3. Emissions in a fire: smoke density Ds (max) (left) and smoke toxicity CIT (max) (right) of polyamides with different flame retardants; (RP: reference product) (source: [8])

Less Smoke and Toxic Gases in the Event of Fire

In comprehensive studies by the German Fraunhofer Institute for Environmental, Safety, and Energy Technology (Umsicht), the flammability of glass fiber-reinforced PA66 grades with different flame retardant systems was examined. Besides products with red phosphorus, polyamides containing halogenated flame retardants and organophosphorus compounds were also tested. The tests were based on European railroad vehicle standard CEN/TS 45545-2 (2009-07). The test specimens were exposed to a 25 kW/m^2 radiant heat source in a test chamber and the released smoke gases were collected over a period of 20 min. The optical density of the smoke was determined by light transmittance measurements, while the toxicity of the smoke gases was assessed by FTIR-spectroscopy and calculation of the CIT value (Conventional Index of Toxicity) [8].

The smoke density value Ds (max) of 188 determined for Ultramid A3X2G5 is relatively low. The BASF polyamide performed with shortest extinguishing time and lowest mass loss as compared with other materials. Its smoke density value was slightly higher than that of reference product 1 **(Fig. 3, left)**; but in comparison with the other products, significantly better values were obtained. Regarding smoke toxicity (CIT max value) **(Fig. 3, right)**, Ultramid A3X2G5 achieved the best rating: in smoke gas analysis with a Dräger tube to detect phosphine, concentrations below 25 ppm were found in all cases. Concentrations of less than 1 ppm were even measured for the BASF product [8].

Lowest Toxicity to Aquatic Organisms

In these studies, the Fraunhofer Institute tested not only the fire behavior of flame-retardant polyamides but also their behavior in aquatic media. Once again, glass fiber reinforced and flame retardant PA66 grades containing red phosphorus, organophosphorus compounds and halogenated flame retardants were compared. The leaching test shows how the materials behave when in constant contact with water. In this test, specially prepared standard test bars were immersed for 100 days in hot deionized water at a temperature of 60°. Then, the separated eluate was evaluated in a Daphnia test according to DIN 38412 L 30. Here, the number of immobilized Daphnia magna (large water fleas) was measured in several eluate dilutions. In a dilution of 1:1, Ultramid A3X2G5 immobilized 30 % of the Daphnia. At higher dilutions, no significant toxic effect was recorded [8]. The reference products tested, on the other hand, continued to exhibit a significant immobilization rate, even in high dilutions **(Fig. 4)**. So because red phosphorus is well embedded in the polymer, long-term immersion of Ultramid A3X2G5 in water has only a slight adverse effect on the aquatic organisms.

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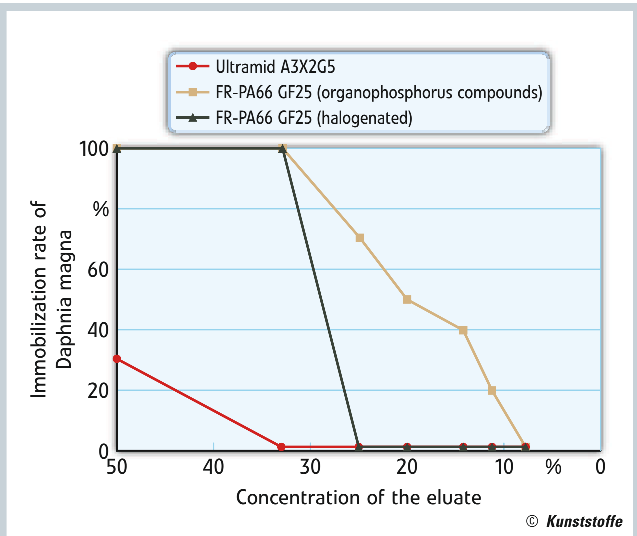

Fig. 4. Behavior of Ultramid A3X2G5 compared with other flame-retardant polyamides in aquatic media (Daphnia test) (source: [8])

Exceptional Phosphorus Stability

Besides the ecological aspects, the stability of phosphorus in the polyamide compound is crucial. To ensure a long-term flame-retarding effect, it is important for the flame retardant to remain in the plastic for the entire utilization phase of the component, even when exposed to thermal stress or environmental influences. Inadequate phosphorus stability could also cause decomposition products to diffuse out of the plastic, leading to failure of electrical contacts.

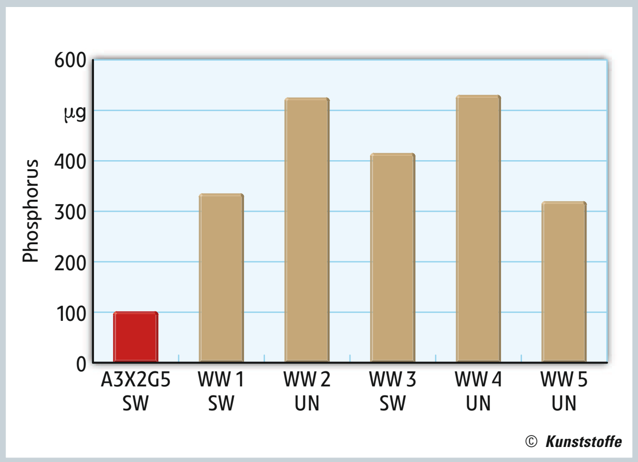

Fig. 5. Phosphorus deposits on metal contacts after 28 days' storage at 70 °C [9] (sw: black; un: uncolored; WW1 to WW5: PA66 GF25 competition products with red phosphorus) (source: [9])

A practical test to determine phosphorus stability involves storing plastic components together with silver contacts at 70 °C for 28 days at 100 % relative humidity. The amount of phosphorus deposited on the metal at the end of the test period is then assessed. Compared with competition products of the PA66 GF25FR type (red phosphorus), the BASF polyamide has by far the lowest deposits on the silver strip and therefore the most effective phosphorus stabilization [9] **(Fig. 5)**.

No Processing Problems

In terms of their behavior in the injection molding process, the Ultramid A3X2 products flame retarded with red phosphorus according to the current state of the art differ only negligibly from standard PA66-GF molding compounds, provided that certain precautionary measures are taken.

The main reason for the reluctance of some processors to use this very efficient flame retardant is the disproportionation of the red phosphorus to phosphine and phosphoric acids that occurs in the presence of moisture at elevated temperatures. This means, however, that significant disproportionation can only take place in the injection molding process if the residual moisture content in the polyamide is too high. Efficient pre-drying is therefore a necessary and generally sufficient countermeasure.

Another reason for the good processing behavior of the Ultramid A3X2 grades lies in the high-quality raw materials used in their production, which are very gently incorporated and additionally stabilized. In this way, BASF has succeeded in considerably reducing the formation of phosphine in injection molding. With adequate pre-drying and under typical injection molding conditions, it is often no longer possible to detect phosphine with the instruments normally used [9], so that compliance with occupational exposure limits (0.14 mg/m^3) [10] is reliably guaranteed.

A Whole Portfolio

BASF's glass fiber-reinforced PA66 grades with red phosphorus achieve flammability rating UL 94 V-0 at 0.8 mm thickness. These products also satisfy the requirements of glow wire test IEC 60695-2-12 and the HWI and HAI ignitability tests according to UL 746 C from 0.6 mm. The PA66 range includes the 25, 35, and 50 % glass fiber (GF)-reinforced grades Ultramid A3X2G5, A3X2G7, and A3X2G10 as well as the 25 % GF-reinforced and additionally impact-modified grade Ultramid A3XZG5. ■

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