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# Phosphorus flame retardants in thermoset resins

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## Abstract

Composites based on thermoset resins like unsaturated polyesters or epoxies are used to a wide extent in the transportation area. In the event of a fire on board a moving train, immediate evacuation of the people is not possible. Therefore, it is essential that the materials used in the construction and furnishing of coaches are such that they are not easily ignited and have a low total emission of heat, smoke and toxic fume when exposed to an ignition source.

Modern railways have to be lighter and more environmentally friendly. Production has to get faster and more inexpensive. It is shown in this work that non-halogen, phosphorus-containing flame retardants are very effective in thermoset resins. Their advantages lie in their high effectiveness, which enables very low concentrations to be used, while at the same time meeting the most stringent requirements.

The formulations can, due to the low viscosity of the resin mixture, be processed by hand lay-up, pultrusion, spray laminating, winding and resin transfer moulding. The low density of the composites makes them useful for all mass transport applications. The phosphorus compounds do not affect the curing reactions of the resins and can be used in cold and hot cured systems. © 1999 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Thermosets are, due to the irreversible curing reaction, rigid, three dimensional crosslinked plastics. The fusible, soluble starting materials can incorporate various fillers such as minerals, glass fibers, glass mats, etc. As a result of their three dimensional cross-linked structure, thermosets do not soften or flow when burning. The tendency to form gaseous decomposition products is also less than with thermoplastics. Heat may cause surface charring which can prevent ignition [1]. Important thermoset resins are unsaturated polyester resins, epoxy resins, urea and melamine resins, phenolic resins and polyurethanes. The majority of unsaturated polyester (UP) resins are reinforced with glass fibers and are used in the building industry, e.g. for facade elements, domelight crowns, in the transportation sector, in the electrical industry, e.g. for cable distribution cupboards, for boats and shipbuilding, tanks, tubes, vessels and others.

Epoxies have satisfactory mechanical properties such as suitable weather, chemical and thermal resistance. Epoxies are applied for molding compounds, surface coating and painting materials, composites, microelectronic encapsulated materials, printed circuit boards, adhesives, etc.

Unsaturated polyester resins and epoxy resins require flame retardants to meet fire protection standards. The flammability of epoxy resins is greater than comparable thermosetting plastics since they have a reduced tendency to carbonize. After removal of the ignition source they continue to burn on their own. Polyurethane casting resins need also flame retardants for electronic applications. Phenolic resins have a great tendency to char thus reducing the formation of volatiles and so they extinguish if the ignition source is removed. The high nitrogen content of urea and melamine resins acts as an inherent flame retardant. Melamine resins are even added to other plastics to reduce their flammability.

Phosphorus-containing flame retardants influence the reaction taking place in the condensed phase. Their effectivity depends on the chemical structure of the polymer, they are particularly effective in materials with high oxygen content, like polyesters, polyurethanes, epoxies or cellulose.

The phosphorus flame retardant is converted by thermal decomposition to phosphoric acid. Further thermal decomposition leads to the formation of poly-

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Norms used: DIN 5510-2 Vorbeugender Brandschutz in Schienenfahrzeugen, Teil 2 (1996); ASTM-E 662, NBS Smoke Chamber; UL 94, Standard for tests for flammability of plastic materials for parts in devices and appliances, 4th edition, 1991.

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phosphoric acid [2,3]. The polyphosphoric acid esterifies and dehydrates the pyrolysing polymer. Unsaturated compounds are formed with subsequent charring. The carbonization process occurs via several steps [4]. The non-volatile, polymeric phosphoric acids inhibit further pyrolysis reactions by providing the simultaneously forming carbonaceous layer with a glassy coating. This protective layer is resistant to even higher temperatures and shields the underlying polymer from attack by oxygen and radiant heat [1]. In addition to polyphosphoric acid being formed also reducing compounds such as phosphites can be present. They reduce carbon oxidation in favor of char. This action explains why phosphorus flame retardants are good suppressers of after glow [5]. The mechanism of ammonium polyphosphate containing intumescent flame retardant systems was studied by different spectroscopic methods [6,7]. The flame retardant formulations given in this study might work according to similiar mechanisms of action. The mechanism of an organophosphorus compound as flame retardant in thermoset epoxy resin was studied with oxygen and nitrous oxide index [8]. The parallel trend of both indices suggests a condensed phase mechanism. A shielding layer of intumescent char was also observed [8].

Some organophosphorus compounds such as triphenylphosphine oxide can also be effective in the gas phase by reducing the energy of the flame [9].

## 2. Experimental section

### 2.1. *Unsaturated polyester resins*

In the past, the flammability rating of unsaturated polyester resins could be raised by incorporating halogens. Reactive flame retardants containing halogen are hexachloroendomethylenetetrahydrophtalic acid (HET-acid) or its anhydride, tetrabromphtalic anhydride or dibromoneopentyl glycol. Ethoxylated tetrabrombisphenol A is also used as a flame retardant and antimony trioxide as a synergist. When halogenated resins burn, they generate smoke and toxic fumes, which is unacceptable for some railway applications [10]. Aluminium hydroxide can be used in halogen-free formulations. At elevated temperatures, a conversion to aluminium oxide takes place in an endothermic reaction with release of water vapour. To raise the fire properties of polyester compounds to match or better those of phenolics, relatively high loadings of aluminium hydroxide are required. Disadvantages are the increase in the viscosity of the resins and also the increase in the density of the compounds up to more than 2 g/cm$^3$.

UP-resins are processed by different methods. In the hand lay-up, spray laminating, winding, poltrusion and resin transfer molding (RTM) processes the amounts of filler are limited due mainly to the viscosity of the resins. Here some halogenated resins are used to satisfy high flame retarding standards.

The use of aluminium hydroxide as a filler with flame retarding properties is limited not only by the processing of the resins, but also when high glass contents ($>30\%$) are used. To pass high levels of flame retardancy (e.g. DIN 4102 B1, Epiradiateur M1), so high amounts of aluminium hydroxide are necessary, that deteriorate the mechanical properties of the resins. Using the flame retardants ammonium polyphosphate (type Exolit AP 422, Clariant AG) and red phosphorus (type Exolit RP 65x, Clariant AG) in combination with aluminium hydroxide, we developed formulations, which meet high flame retardancy standards at relative low levels of fillers (Fig. 1). This formulation can, due to the low viscosity of the resin mixture, be processed by hand lay-up, poltrusion, spray laminating, winding and resin transfer molding. The low density of the laminates made them useful for all mass transport applications.

Table 1
Flame retarded UP-laminate according to the German railway test

| Low smoke UP-laminate, railway applications | classification DIN 5510, part 2 S4 SR 2 ST2 |
|---|---|
| UP resin Viapal UP 403 BMT 57 | 100 parts |
| Aluminium hydroxide Martinal ON 921 | 55 parts |
| **Exolit AP 422** | **10 parts** |
| Peroxide MEKP HA-2 | 2 parts |
| Glass-continous strand mat | 30 wt % of total |
| Viscosity additive Byk W 985 | 0.65 parts |
| Cobalte-accelerator NL 49 P | 0,5 parts |
| Properties: | |
| Viscosity (formulation) (Brookfield Visc. RVT, Sp. 6, 100 r.p.m., 25°C) | approx. 1500 mPas |
| Density (compound) | 1.55 g/cm$^3$ |
| Impact strength | 55 kJ/m$^2$ |
| Tensile strength | 87 N/mm$^2$ |
| Flexural strength | 169 N/mm$^2$ |
| Gel time | approx. 20 min |

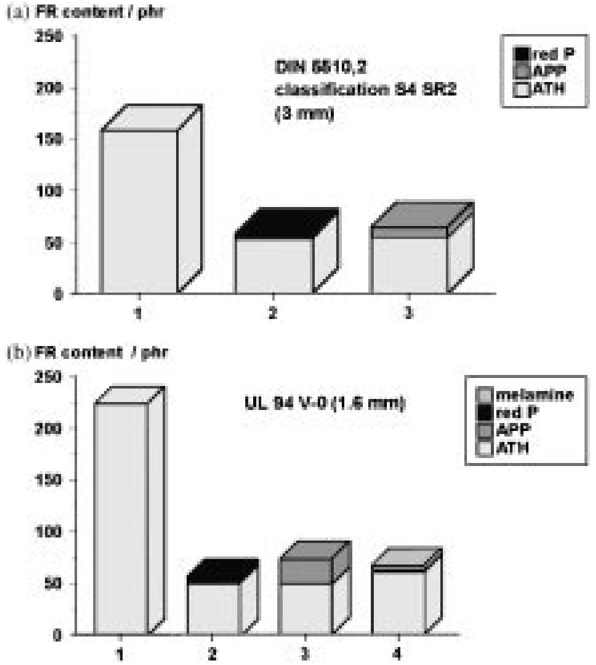

Fig. 1. Amount of flame retardant necessary to pass DIN 5510, 2 (German railway test) rsp. UL 94 V-0. Aluminium hydroxide compared to Exolit + aluminium hydroxide.

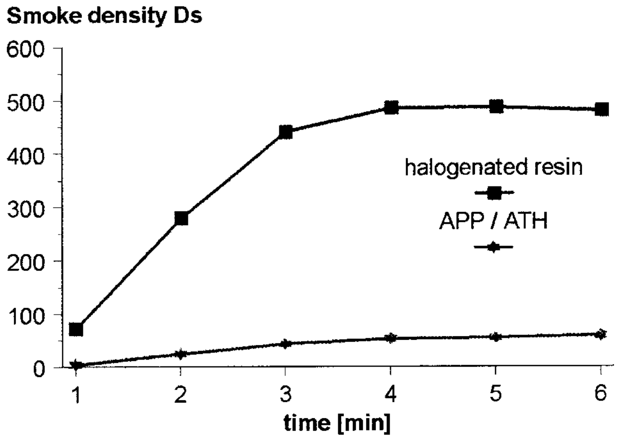

Fig. 2. Smoke density (NBS Smoke Chamber ASTM-E 662, flaming conditions) of the APP/ATH system compared to a halogenated resin.

Table 2
High flame-retarded SMC-formulations

| | A | B |
|---|---|---|
| Palapreg P1803 | 50 | 50 |
| Palapreg H85203 | 50 | 50 |
| Byk W 996 | 3 | 3 |
| Glass content | 25% | 25% |
| Aluminium hydroxide | 360 | 200 |
| Exolit AP 422 | – | 25 |
| Properties: | | |
| Oxygen index | 100% | 100% |
| Densitiy | 2.2 g/cm$^3$ | 1.7 g/cm$^3$ |
| Viscosity | 32.8 mPa*s | 10.6 mPa*s |

For German railway applications, fire performance and secondary fire effects are tested in the DB Brandschacht. Five specimen 500×190 mm and usual thickness are vertical burned. The ignition source is a Bunsen burner with fishtail jet, the flame temperature is 950°C and the flame application is 3 min. The afterburning time, the smoke development and the dripping of the materials are classified. Table 1 gives a typical formulation for the German railway test according to DIN 5510, classification S4 SR2, which means afterburning times of less than 10 s after 3 min flaming and a smoke density integral of less than 50%.

Fig. 2 shows the lower smoke density of the halogen-free ammonium polyphosphate/aluminiumoxide con-

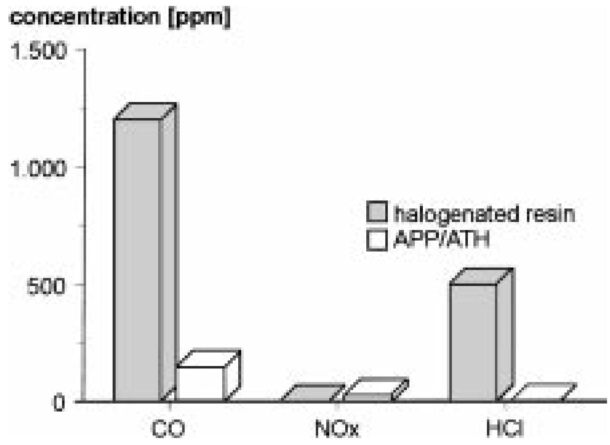

Fig. 3. Measurement of toxicity acc. ABD 0031 (NBS Smoke Chamber ASTM-E 662, flaming conditions) of the APP/ATH system compared to a halogenated resin.

Table 3
Flame retarded EP-laminate according to the German railway test

| EP formulation, railway applications | Classification DIN 5510, part 2 S4 SR 2 ST2 (3 mm) |
|---|---|
| Liquid epoxy resin Beckopox EP 140 | 100 parts |
| Polyamine hardener Beckpox EH 625 | 39 parts |
| **Exolit AP 422** | **30 parts** |

Table 4
Flame retarded epoxy resin solution for printed circuit boards

| Epoxy resin solution for printed circuit boards | UL 94 V-0 (1.6 mm) |
|---|---|
| Solid epoxy resin Beckopox EP 301 | 100 parts |
| Dicyandiamide Dyhard SF | 4 parts |
| Accelerator dyhard MI | 0.4 parts |
| **Exolit RP 650** | **12 parts**<br>**(6 parts if V-1 is required)** |
| Solvent dimethylformamide DMF | approx. 30 parts |

Table 5
UL 94 V-0 (1.6 mm) formulations with epoxy resins and PU casting resins

| Epoxy resin | UL 94 V-0 | Polyurethane resin | UL 94 V-0 |
|---|---|---|---|
| Liquid epoxy resin epicote 828 | 100 parts | polyetherpolyole baygal K 55 | 100 parts |
| Curing agent methylhexahydrophtalic anhydride M-HHPSA | 89 parts | MDI Baymidur K 88 | 100 parts |
| Benzyldimethylamine BDMA | 1 part | benzyldimethylamine BDMA | 1 part |
| Aluminium hydroxide Apyral 2 | 50 parts | aluminium hydroxide Apyral 2 | 100 parts |
| **Exolit RP 650** | **10 parts** | **Exolit RP 652** | **20 parts** |

taining laminate compared to a halogenated UP-resin without any fillers. This increases the available escape time in the event of fire.

Since inorganic phosphorus flame retardants act in the solid phase in the fire [1,8], the combustion gases are not contaminated with additional corrosive gases (HCl, HBr) from the flame retardant.

Table 2 shows a SMC (sheet molding compound) formulation with oxygen indices of 100%. By combination of APP and ATH, the amount of filler can be reduced again so that the compounds have lower densities and the formulation lower viscosities Fig. 3.

### 2.2. Epoxy resins

Epoxy laminates are also used in railway applications. Due to the high class contents of such laminates, the amount of fillers is limited. By the addition of only 30 parts of ammonium polyphosphate Exolit AP 422 laminates pass the German railway test DIN 5510 with the best classification S4 SR2 Table 3.

All materials employed in electronic equipment operating under voltage stress have to be flame retardant. Flame retarded epoxy resins for printed circuit boards are produced by reacting tetrabrom-bisphenol A into the liquid resins. To comply with the flame retardancy specification UL 94 V-0, the resins contain about 20% bromine (Table 4). In case of fire or smoldering, brominated epoxies evolve highly corrosive decomposition products that can damage the surrounding electronic equipment. This is not the case when phosphorus flame retardants are used [11].

It was found that the flame retardancy of printed circuit boards can be attained by the addition of finely divided red phosphorus [12]. The thermal and electrical properties of the laminates are not affected by the incorporation of red phosphorus. Table 2 shows formulations, which pass the UL 94 classification V-1 rsp. V-0 at 1.6 mm.

### 2.3. Phenolic resins

In the few cases where phenolic resins require fire retardant treatment (e.g. paper composites), reactive flame retardants like tetrabrombisphenol A or additive flame retardants like organo-phosphorus compounds are used. Ammoniumpolyphosphate is also an effective flame retardant in phenolic resins.

### 2.4. Polyurethane-casting resins

Polyurethane casting resins require in many cases the addition of flame retardants [1]. High amounts of aluminium hydroxide are added to the polyol. To pass the UL 94 V-0 classification at 1.6 mm material strength, about 300 php (parts per hundred polyol) are necessary. The addition of red phosphorus and aluminium hydroxide is much more effective and does not affect the insulating properties of the resins. Such low filled formulations can be used in each application, where low viscosity resins are required (Table 5).

## 3. Conclusion

It is shown in this work that ammonium polyphosphate and red phosphorus are excellent halogen-free flame retardants for all types of thermoset resins. In most cases, the combination of red phosphorus with aluminium hydroxide pass high levels of flame retardancy at relativeley low amounts of fillers (e.g. 50–70 parts per hundred resins compared to 150–250 php using ATH alone). The low filler levels reduce the viscosity of the formulations and the density of the laminates.

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