# New Ecological Polyester Resins with Reduced Flammability and Smoke Evolution Capacity

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ABSTRACT: Smoke evolution in a smoke chamber  $750 \times 750 \times 1000 \pm 5$  mm (Polish Standard PN-91/K-02501 equivalent to UIC 561-OR 1991) was studied in, and the oxygen index flammability test (Polish Standard PN-76/C-89020) was carried out for, glass-reinforced polyester (GRP) laminates obtained with unsaturated polyester (UP) resins containing chlorine and bromine in the chain. In these studies, the effect on these properties of such additives as  $ZNSnO_3$  (ZS),  $ZnSn(OH)_6$  (ZHS),  $Al(OH)_3$ , or  $Mg(OH)_2$  and  $Sb_2O_3$  in up to 30 mass % was determined. The most efficient ignition and smoke-evolution retarder from among the investigated compounds were ZS and ZHS, and an essential reduction in smoke evolution was also observed with  $Sb_2O_3$ . GRP laminates with these additives meet the fire safety recommendations concerning smoke evolution for materials used in transportation and in the building industry. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 379–382, 1999

**Key words:** unsaturated polyester resins; glass-reinforced polyester; fire-retardant polyester resins

# **INTRODUCTION**

The smoke-forming tendency of plastics has been systematically studied, particularly for poly(vinyl chloride), presumably because this polymer has been used most extensively in appliance manufacture.<sup>1</sup> It seems that, regardless of the nature of a halogen-containing polymer, methods for reducing the optical density of smoke and the retardancy mechanisms involved may be assumed to exhibit close similarities. In the search for similarities in other polymers to unsaturated polyester resins (UPR), smoke suppression studies on thermoplastic polymers; for example, ABS, compounded with decabromobiphenyl were considered.<sup>2</sup> Burning UPR and polyester-glass laminates (GPR) produce considerable amounts of black smoke. The accompanying emission of toxic fumes (HCl, HBr, CO), especially noxious with slowburning, halogen-containing UPR, makes fire fighting difficult, if not impossible. Therefore, preparation of flame-retarded, and simultaneously, smoke-suppressed polyester resins is of considerable importance.

This goal was deemed achievable by compounding UPR with additive flame retardants. Most efficient retardants should modify UPR and GRP pyrolysis reactions toward suppressing the formation of fuliginous aromatic pyrolyzates (benzene, toluene) and increasing that of charring aliphatics. Production of smoke and emission of toxic gases from burning UPR are related to the nature and formulation of the resin. By way of illustration, styrene is more advisable at lower proportions; 1,2-propylene glycol is a more smoke component than other glycols; and so is phthalic acid as compared with isophthalic acid.<sup>3</sup> Admit-

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**Figure 1** Illuminance (E, lx) versus burning time (t, s) for laminates nos. 3 and 7, Table I.

tedly, a "specially" selected structure of the polyester resin chain does not guarantee flame retardancy in the product.

To impart flame retardancy and smoke suppression to UPR and GRP, the resins were compounded with aluminium hydroxide [Al(OH)3], which, on burning, decomposes at a temperature of 230°C to yield 34% of water: this cools the plastic and extinguishes the fire.<sup>4</sup> Again, in the pyrolysis of UPR, the hydroxide reduces smoke production and emission of HCl and HBr, but only if added in abundant amounts (up to 200 phr), prohibitively high in industrial practice. Therefore, smoke suppressants effective when incorporated into the formulation in relatively small proportions are desired.

# **EXPERIMENTAL**

### Materials

- Polimal 120 (Chemical Works "Organika-Sarzyna," Sarzyna, Poland), an isophthalicmaleic-propylene glycol UPR containing 35% styrene and no halogens
- Polimal 161 (same manufacturer), a maleicphthalic-epichlorohydrin UPR containing an incorporated bromine compound, styrene 35%, chlorine (Cl) 9.3%, and bromine (Br) 6.7%
- Polimal (same manufacturer) based on the HET acid; that is, a UPR prepared from maleic anhydride, HET acid, and diethylene gly-

col, containing styrene 33% and chlorine (Cl) 21%

- A glass mat, surface density 450 g/m<sup>2</sup>, prepared from a borosilicate glass
- Aluminium hydroxide, Al(OH)<sub>3</sub> (Consulting Enterprise ADOB, Poznań, Poland)
- Antimony trioxide (PPOCh, Gliwice, Poland)
- Magnesium hydroxide,  $Mg(OH)_2$  (Merck-Schuchardt, Hohenbrunn, Germany)
- Molybdenum trioxide (PPOCh, Gliwice, Poland)
- Calcium sulfate (PPOCh, Gliwice, Poland)
- Zinc hydroxystannate,  $ZnSn(OH)_6$  (ALCAN Chemical Europe, Buckinghamshire, UK)
- Zinc stannate,  $ZnSnO_3$  (same manufacturer)
- $\bullet$  Zinc borate, 2ZnO  $\cdot$   $3B_2O_3 \times 3H_2O$  (same manufacturer)
- Methyl ethyl ketone peroxide (Ketonox), a 40% solution in dimethyl phthalate
- Cobalt naphthenate, a 1% Co solution in styrene

# Scope of Study

An overview of the literature and this institute's past research works made the following resins advisable for study: an isophthalic UPR; and halogen-containing resins; namely, a maleicphthalic-epichlorohydrin resin, a maleic-phthalicepichlorohydrin resin compounded with a boron compound, and a UPR prepared from hexachloroendomethylenetetrahydrophthalic acid (HET



**Figure 2** Illuminance (E, lx) versus burning time (t, s) for laminates nos. 4, 9, 10 of Table I.

Sample No.	UPR Used in GRP Laminate	Smoke Suppressant	Smoking Intensity $(lx \times s)$	<i>OI</i> (vol. %)
1	X-free <sup>a</sup>		9100	19.1
2	Cl		4706	25.8
3	Cl/Br		5100	26.1
4	Cl(HET acid)		6363	30.4
5	Cl/X-free		8700	24.1
6	Cl/X-free	$Al(OH)_3$ , $CaSO_4$ , $MoO_3$	8247	26.2
7	Cl/Br/X-free	$ZnSn(OH)_{6}$ , $Al(OH)_{3}$	9204	28.5
8	Cl/Br/X-free	$ZnSnO_3$ , $Sb_2O_3$	9523	26.1
9	Cl(HET acid)/X-free	$ZnSnO_3$ , $Mg(OH)_2$	12,159	38.7
10	Cl(HET acid)/X-free	$ZnSn(OH)_{6}$ , $2ZnO 3B_{2}O_{3} \times 3H_{2}O$	17,500	44.4

Table I Smoking Intensities and Oxygen Indices Determined for GRP Laminates

<sup>a</sup> X: halogen; Cl: epichlorohydrin's chlorine incorporated into resin formulation; Br: bromine incorporated into resin formulation.

acid). The resins were compounded with selected metal oxides, metal hydroxides, and mixtures thereof to benefit by synergism. Synergism occurs between tin, zinc, antimony, molybdenum, calcium, and magnesium compounds. For halogencontaining UPR, tin and zinc compounds; namely, ZnSnO<sub>3</sub> and ZnSn(OH)<sub>6</sub>, seem particularly promising.

Indigenous UPR and selected smoke suppressants were used for investigations. Each composition examined included 100 weight parts of resin and 5-30 weight parts of additive(s). The curing compound was a mixture of methyl ethyl ketone peroxide (3 phr) and the (1% Co) cobalt naphthenate (0.4 phr). From each composition, a laminate was prepared involving three layers of a  $\sim 30\%$  glass mat (surface density, 450 g/m<sup>2</sup>). The laminate was conditioned at room temperature, relative air humidity 50%, for 24 h and then cured up at 353 K (80°C). The laminate was cut into strips,  $120 \times 100$  mm in size. Samples identical in composition, 2 to 3-mm thick, were examined in triplicate. Smoke tests were carried out at the Polish State Railway Research Institute's Laboratory for Plastics, Warsaw.

#### **Smoking Intensity**

Smoking intensity was studied in conformity with the Polish Standard PN-91 K-02501, Rolling Stock, "Intensity of Smoking of Materials on Burning; Requirements and Tests." The method is to measure the quantity of light passing through the smoke and falling upon a surface during the initial period of the 4-min period of burning time. A special smoke chamber made of heat-insulated material,  $(750 \times 750 \times 1000 \text{ mm}) \pm 5 \text{ mm}$  in internal size, was used. The chamber was equipped with an ignition system, an illuminance measuring system, and a ventilation system.

# Results

Illuminance (E, lx) averages of the triplicate measurements were plotted (Figures 1, 2) against the experimental burning time (t, s) and the luminous energy  $(S, lx \times s)$  transferred during the initial period, t = 4 min, of experiment duration was evaluated as the surface beneath the curve E= f(t); namely,

Table II	Relative	Efficiencies	е.	of Flame	Retardants	in	GRP	Laminates

	$\begin{array}{c} {\rm ZnSn(OH)_6,\ 2ZnO}\\ {\rm 3B_2O_3\times 3H_2O} \end{array}$	$\rm ZnSnO_3,Sb_2O_3$	$Al(OH)_3$ , $CaSO_4$
Cl	0.12	0.15	0.14
Cl/Br	0.28	0.21	0.18
Cl/(HET acid)/X-Free <sup>a</sup>	0.72	0.58	0.24

 $^{\mathrm{a}}X = \mathrm{halogen}$ 

$$S = \int_0^t E \, dt$$

where: *S*: exposure; *E*: illuminance (exposure intensity); and *t*: exposure time.

The above terminology is consistent with that of the PN-91-/K-02501. Thus, smoking intensity was expressed in terms of the luminous energy that was transferred throughout the initial burning time (t = 4 min) of the material examined.

### Flammability

Flammability tests were carried out in conformity with the Polish Standard PN-76/C-89020 "Flammability Tests by the Oxygen Index Method." The method is to establish the minimum oxygen concentration in a nitrogen–oxygen mixture that sustains combustion of a material sample fixed vertically inside the measuring chamber.

The relative efficiency  $e_r$  of a flame retardant was expressed as  $e_r = (OI - OI_O)/C$ ; where OI,  $OI_O$  = the oxygen indices (% by vol.) of flameretarded and nonretarded UPR laminates, respectively, C = the retardant content, %, in a UPR resin.

# DISCUSSION

Tables I and II show, respectively, the OI indices determined for the laminates examined and the relative efficiencies evaluated for the retardants studied. In the series of the flame-retarded halogenated resins, flammability is seen (Table I) to decrease almost rectilinearly. The OI of the HET acid-based resin is higher than could be expected from the amount of incorporated chlorine. This fact seems to be associated<sup>5,6</sup> with the HET acid residues that decompose in the course of polyester pyrolysis to revert to starting diene synthesis reactants. The resulting hexachlorocyclopentadiene (HEX) provides a protective barrier against the access of oxygen. The other chlorine-containing UPR released chloride or chlorine. HEX can affect thermal degradation of the original polyester chain by favoring the formation of char rather than of volatile aromatic pyrolyzates.<sup>7</sup>

The *OI* data (Table I) for the GRP laminates examined allow simple flammability class assignments. According to the Polish Standard PN-84/ K-02500, the laminate characterized by an *OI* value of 21 to 28% (determined in conformity with PN-76/C-89020) belongs to the slow-burning material class and the one with OI > 28% belongs to the non-flammable material class. By this definition, laminates nos. 4, 7, 9, and 10 are nonflammable; whereas, nos. 2, 3, 5, 6, and 8 fall into the slow-burning class (Table I). Smoke intensity data are given in Table I, column 4. They confirm the fact that any halogen-free resin produces less smoke than does a halogen-containing resin.

A desirable smoking intensity (as determined in conformity with PN-91/K-01501) could be achieved by blending a halogen-free resin with a chlorine-containing resin. An optimum OI was obtained. The observed smoking intensities (Table I, Figures 1, 2) show that a suitable combination of smoke suppressants results in a successfully lowered smoking intensity.

Zinc hydroxystannate  $[ZnSn(OH)_6]$  and zinc stannate  $[ZnSnO_3]$  have been found to be particularly effective as smoke suppressants, especially when used in chlorinated and brominated resins.<sup>8</sup> The present data confirm the synergism between these suppressants and the halogens incorporated into the polyester chain in the Polish UPR examined. The observed smoking intensities (Table I) show that some laminates fall in the medium intensity class D2 according to PN-91/K-02501. These are laminates nos. 1, 7, 8, 9, and 10 with luminous energies ranging from  $9 \times 10^3$  to  $1.35 \times 10^4 lx \times s$  (Table I).

Such laminates are suitable for rolling stock construction and/or repair applications, including floors, walls, ceilings, and toilets. Thus, Plywood and hardboard can be eliminated. This replacement would result in prolonged service life, improved external appearance, and, most importantly, enhanced fire safety of railway carriages.

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