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New Generation of Fire Retardant Polyester Resins

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Summary: Smoke evolution [in a smoke chamber (750 x 750 x 1000) ± 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 an amount of up to 30 mass-% was determined. The most efficient ignition and smoke-evolution retarder from among the investigated compounds was ZS and ZHS, whereas an essential reduction in smoke evolution was observed also with Sb_2O_3. GRP laminates with these additives meet the fire-safety recommendations concerning smoke evolution from materials used in transportation means and in the building industry.

Keywords: FR additives, oxygen index, polyester resins, smoke evolution

Introduction

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.[1]

It appears 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, e.g., ABS, compounded with decabromobiphenyl were taken into consideration.[2]

Burning UPR and polyester - glass laminates (GPR) produce black smoke in considerable amounts. The accompanying emission of toxic fumes (HCl, HBr, CO), especially noxious with

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slow - burning halogen - containing UPR, makes fire - fighting difficult or even 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 smoky component than other glycols; so is phthalic acid compared with isophthalic acid.[3] Admittedly, 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 have been 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.[4] 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. Smoke suppressants are therefore desired which are effective when incorporated into the formulation in relatively small proportions.

Experimental

Materials

- Polimal 120 (Chemical Works "Organika - Sarzyna", Sarzyna, PL), an isophthalic - maleic - propylene glycol UPR containing 35% of styrene and no halogens;
- Polimal 161 (same manufacturer), a maleic - phthalic - 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, i.e., a UPR prepared from maleic anhydride, HET acid and diethylene glycol, containing styrene 33% and chlorine (Cl) 21%;
- A glass mat, surface density 450 g/m^2, prepared from a borosilicate glass;
- Aluminium hydroxide, $Al(OH)_3$ (Consulting Enterprise ADOB, Poznań, PL);

- Antimony trioxide (PPOCh, Gliwice, PL);
- Magnesium hydroxide, $Mg(OH)_2$ (Merck - Schuchardt, Hohenbrunn, Germany);
- Molybdenum trioxide (PPOCh, Gliwice, PL);
- Calcium sulfate (PPOCh, Gliwice, PL);
- Zinc hydroxystannate, $ZnSn(OH)_6$ (ALCAN Chemical Europe, Buckinghamshire, GB);
- Zinc stannate, $ZnSnO_3$ (same manufacturer);
- Zinc borate, $2ZnO.3B_2O_3 \cdot 3H_2O$ (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:

(i) an isophthalic UPR;

(ii) halogen - containing resins, viz., a maleic - phthalic - epichlorohydrin resin, a maleic - phthalic - epichlorohydrin resin compounded with a boron compound, and a UPR prepared from hexachloroendomethylenetetrahydrophthalic acid (HET 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 halogen - containing UPR, tin and zinc compounds, viz., $ZnSnO_3$ and $ZnSn(OH)_6$, appear to be 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 ~30% glass mat (surface density, 450 g/m^2). The laminate was conditioned at room temperature, relative air humidity 50%, for 24h and then cured up at 353K (80°C). The laminate was cut into strips, 120 x 100 mm in size. Samples identical in composition, 2-3 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 x 750 x 1000 mm) ±5 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 (Figs. 1, 2) against the experimental burning time (t, s) and the luminous energy (S, lx•s) transferred during the initial period, t = 4 min, of experiment duration was evaluated as the surface beneath the curve E=f(t), viz.,

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

where: S - exposure, E - illuminance (exposure intensity), t - exposure time.

The above terminology is consistent with that of the PN-91-/K-02501.

Smoking intensity was thus 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 respectively flame - retarded and unretarded UPR laminates, C = the retardant content, %, in a UPR resin.

Discussion and Conclusion

Tables 1 and 2 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 1) 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 appears to be associated[5, 6] with the HET acid residues which 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 favouring the formation of char rather than of volatile aromatic pyrolyzates.[13]

Table 1. Smoking intensities and oxygen indices determined for GRP laminates.

Sample No.	UPR used in GRP laminate	Smoke suppressant	Smoking intensity, lx•s	OI, vol.%
1	[1] X-free	-	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	$ZnSnO_3$, $Mg(OH)_2$	12159	38.7
10	Cl(HET acid)/ X-free	$ZnSn(OH)_6$, $2ZnO\ 3B_2O_3 \circ 3H_2O$	17500	44.4

[1] X = halogen, Cl = epichlorohydrin's chlorine incorporated into resin formulation, Br = bromine incorporated into resin formulation.

The OI data (Table 1) 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, the laminates Nos. 4, 7, 9 and 10 are non-flammable, whereas Nos. 2, 3, 5, 6 and 8 fall in slow - burning class (Table1). Smoke intensity data are given in Table 1, 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 1, Figs. 1, 2) show that a suitable combination of smoke suppressants results in a smoking intensity successfully lowered.

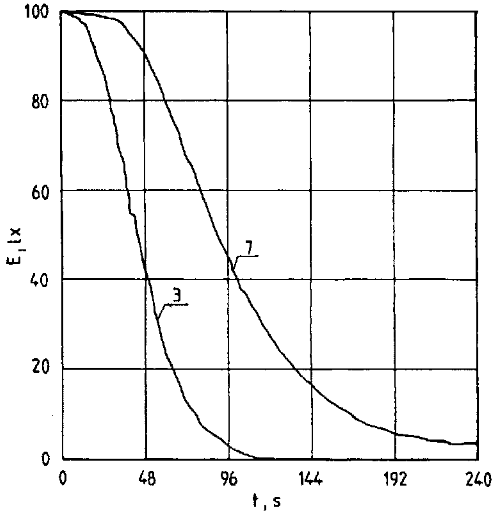

Fig. 1. Illuminance (E,lx) vs. burning time (t,s) for laminates Nos.3 and 7 Table 1.

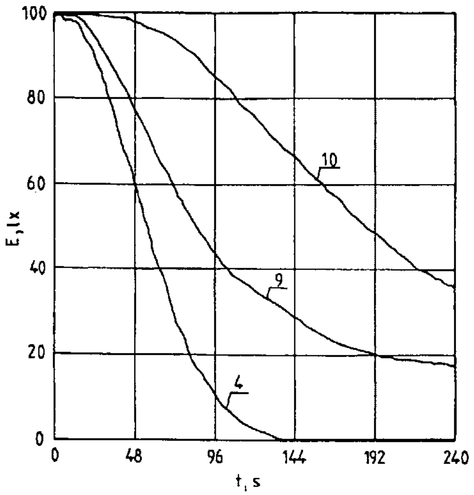

Fig. 2. Illuminance (E,lx) vs. burning time (t,s) for laminates Nos.4, 9, 10 of Table 1.

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.[12] 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 1) show that some laminates fall in the medium intensity class, D2 according to PN-91/K-02501. These are the laminates Nos. 1, 7, 8, 9, 10 with luminous energies ranging from $9 \cdot 10^3$ to $1.35 \cdot 10^4$ lx •s (Table 1).

Table 2. Relative efficiencies, e_r, of flame retardants in GRP Laminates.

	$ZnSn(OH)_6$, $2ZnO\ 3B_2O_3 \circ 3H_2O$	$ZnSnO_3$, 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)/$^{1)}$X-free	0.72	0.58	0.24

$^{1)}$ X = halogen

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

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