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THE EFFECTS OF ZINC BORATE ADDITION ON THE FLAMMABILITY CHARACTERISTICS OF POLYESTER, VINYL ESTER AND EPOXY GLASS REINFORCED PLASTICS

Richard M. Morchat

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ABSTRACT

The effects of an inorganic fire-retardant additive, zinc borate, on flammability characteristics and smoke generation of glass reinforced polyester, vinyl ester and epoxy resins were evaluated. Information is presented on the flame spread index (ASTM E162), limiting oxygen index (ASTM D2863), density of smoke generated (ASTM E662) and toxic gases of combustion (Boeing BSS 7239).

Results indicated that the addition of 10 phr of zinc borate to the polymeric materials significantly decreased the flame spread index and increased the limiting oxygen index; however, the amount of smoke generated during pyrolytic and flaming combustion was high and unacceptable. Finally, the toxic gas evolution data indicated that the threshold limit values for some gases were exceeded.

RÉSUMÉ

On a évalué les effets d'un additif ignifuge inorganique, le borate de zinc, sur les caractéristiques d'inflammabilité et le dégagement de fumée des résines époxydiques, de l'ester vinylique et du polyester renforcés de verre. On présente des données sur l'indice de propagation de la flamme (ASTM E162), l'indice limite d'oxygène (ASTM D2863), la densité de la fumée dégagée (ASTM E662) et les gaz de combustion toxiques (Boeing BSS 7239).

Les résultats indiquaient que l'addition aux matériaux polymériques de 10 parties de borate de zinc par cent parties de résine diminuait considérablement l'indice de propagation de la flamme et augmentait l'indice limite d'oxygène; toutefois, la quantité de fumée dégagée durant la combustion accompagnée de flamme et la combustion pyrolytique était élevée et inacceptable. Enfin, les données sur le dégagement de gaz toxiques indiquaient que, dans le cas de certains gaz, la TLV était dépassée.

TABLE OF CONTENT

NOTATION

ASTM	American Society of Testing and Materials
°C	Degrees Celsius
FR	Fire Retardant
GRP	Glass Reinforced Plastic
mm	Millimeter
phr	Parts Per Hundred Resin
ppm	Parts Per Million
ZB	Zinc Borate

1. INTRODUCTION

Apart from the seas, the most terrifying enemy of the sailor is fire, the effects of which can be devastating. The April 1986 fire aboard the aircraft carrier HMS Illustrious, for example, virtually destroyed one of her main gearboxes and resulted in the ship being out of action for several months. Fire, on its own, very seldom will sink a ship, but the damage caused can be severe, especially with the incapacitating effect on the crew of the thick black smoke that is commonly associated with shipboard fires. During and after the Falklands conflict, the effects of fire became so frighteningly obvious to everyone that ship designers became intimately involved in modifications. Over the last six years, many modifications to reduce the effects of fire in RN ships have been implemented, such as fire curtains to help contain the spread of smoke, better materials for cabling and for mattresses to reduce the amount of smoke given off, and more effective fixed fire-fighting arrangements, to name but a few [1]. As a result of the experience of the USS Stark in the Persian Gulf in May 1987, the US Navy has implemented a number of fleetwide changes in fire control, including plans to increase the use of more fire-resistant materials in ship construction.

The feasibility of using a glass reinforced plastic (GRP) composite as a substitute for steel and aluminum in the construction of ships' superstructures is under active consideration by several NATO navies. When one compares GRP to the other two common structural building materials of naval vessels, obvious advantages for GRP can be identified. For example, GRP materials can be processed to have excellent thermal and mechanical properties, they have good resistance to corrosion and the marine environment, and most importantly, they have a high strength to weight relationship. However, their fire performance properties remain a serious concern.

As part of DREA's research program on fire safe materials for marine applications, we have studied several ways of improving the fire resistance of glass reinforced plastics, including the use of insulating materials on the exposed surface, the application of ceramics by plasma spray deposition technology and the addition of inorganic fire-retardant additives such as antimony trioxide. Due to its pronounced synergism with halogens, the use of antimony trioxide is a well-established method for increasing fire-retardancy with halogenated resins [2]. However, we have shown that although antimony trioxide is an excellent fire-retardant because of its ability to decrease flame spread and increase oxygen index, it is quite ineffective at decreasing the amount of smoke that is generated during burning of polyester and vinyl ester resin systems [3].

We expanded our study to include a fire-retardant where the mechanism is based on release of "water of hydration" during decomposition, with the accompanying absorption of a considerable amount of heat. The fire-retardant chosen was alumina trihydrate, also known as hydrated alumina. This fire-retardant is unique in having a high proportion (35%) of chemically combined water and is a readily available refined mineral filler that shows the unique and desirable properties of imparting significant fire retardant and smoke suppressive qualities to reinforced polyester plastics. Our investigation [4] showed that the addition of the inorganic material, alumina trihydrate, affected the flammability characteristics and smoke generation of polyester, vinyl ester and epoxy GRP panels. In fact, the smoke density was the one parameter that was affected the most by the alumina trihydrate addition. There were measured decreases as high as 57% as well as increases of 35%; nevertheless, the maximum value for smoke density was high for all resins tested and thus unacceptable. A fire-retardant that also exhibited smoke suppression abilities needed to be evaluated.

Zinc borate is a unique multifunctional fire-retardant [5]. It can function as a flame-retardant and smoke suppressant. It is claimed to act as an efficient synergist of organic halogen sources, and in certain halogen containing resin systems such as unsaturated polyester and epoxy, the zinc borate can outperform antimony oxide. In halogenated polymers the zinc borate markedly increases the amount of char formed during combustion. The zinc species remain in the condensed phase and alter the pyrolysis chemistry by catalyzing the dehydro-halogenation and promoting cross-linking. This results in increased char formation and a decrease in both smoke production and flaming combustion. In addition, due to its unique glass forming ability zinc borate acts as an afterglow suppressant.

In the study reported herein, we investigated the effect that the addition of the inorganic fire retardant/smoke suppressant additive, zinc borate, to several polyester, vinyl ester and epoxy resins has on both the amount of smoke generated and on the time delay to reach the maximum allowable concentration of smoke. In addition, the effects of this additive on other fire properties were monitored, such as the flame spread index, the oxygen index, and toxic gas evolution.

2. EXPERIMENTAL PROCEDURE

2.1. Resins Evaluated

Five resins were evaluated in this study; Hetron 197AT, Hetron 27196, Hetron 692TP25 (Ashland Chemicals), Derakane 510A (Dow Chemical Canada Inc) and Epon 813 (Shell Canada). Information from the resin manufacturers' product data sheets indicated that: Hetron 197AT is a Class 1 fire-retardant, chemical resistant, heat resistant, unsaturated polyester; Hetron 27196 and Hetron 692TP25 are low viscosity, thixotropic, promoted, halogenated, flame retardant polyester resins; Derakane 510A is a corrosion resistant, chemical resistant, fire resistant vinyl ester; and Epon 813 is a low viscosity, chemically resistant bisphenol-A based epoxy resin. All the resins, with the exception of the Epon, were catalyzed with 0.15 phr (parts per hundred resin by weight) of the accelerator cobalt naphthenate (Nuodex DMR, Nuodex Canada Ltd) and 1.0 phr of methyl ethyl ketone peroxide catalyst (Lupersol DDM-9, Pennwalt). The Epon 813 was cured by the addition of 15 phr of the epoxy resin hardener Ancamine 1638 (Pacific Ancor Chemical).

Except for the epoxy resin (Epon 813), the other four resins (Hetron 197AT, Hetron 27196, Hetron 692TP25 and Derakane 510A) contained proprietary halogenated materials, and they derived their fire-retardancy characteristics through the chemical action of chlorine and/or bromine molecules in the solid and gas phases.

2.2. Laminate Fabrication

Panels, 1200 x 1200 x 6 mm nominal thickness (4 ft x 4 ft x 0.25 inch), were manufactured by the custom contact molding method (also known as hand lay-up method). The panels were constructed using 6 layers of 450 g/m^2 (1.5 oz/ft^2) chopped strand mat "E-glass" cloth (FC M751-450, Fiberglas Canada Inc). The inorganic fire-retardant component, Firebrake® ZB from US Borax ($2ZnO \cdot 3B_2O_3 \cdot 5H_2O$) was added to the resin at 10 phr.

3. RESULTS AND DISCUSSION

The evaluation of the fire performance of the GRPs containing the selected fire-retardant was conducted using four standard fire test procedures. These included an evaluation of the ability for flames to spread over the material, an evaluation of the minimum oxygen concentration required to support combustion of the panels, an evaluation of the amount of smoke and the associated visual obscuration created by a flaming and non-flaming panel, and an evaluation of toxic gas evolution.

3.1. Surface Flammability

The radiant panel surface flammability test (ASTM E162)[6] provides a procedure for measuring and comparing the surface flammability of materials when exposed to a prescribed level of radiant heat energy. The rate of travel of a flame front along the surface depends on the physical and thermal properties of the material, the method of mounting and orientation of the specimen, the type and magnitude of fire and heat exposure, the availability of air and the properties of the surrounding area [7]. The rate of flame spread is a very important property in the history of a fire in that it controls the time after ignition when a fire has grown to a "dangerous size." The ability to detect, fight or escape from a fire depends on the time before the fire reaches a "dangerous size," and thus the lower the flame spread, the greater the time for escape becomes [8].

Figure 1 shows the results of the radiant panel surface flammability test for the 10 panels tested (five resins, without and with fire-retardant). The flame spread index for the polyester and vinyl ester resins were relatively low (12-43), while the flame spread index value for the epoxy resin was high at 60. The addition of the fire-retardant lowered the flame spread index in varying degrees (8-42%) depending on the resin system evaluated. In most cases the addition of 10 phr zinc borate was sufficient to lower the flame spread index below the established guideline of 25 maximum. The one anomaly was the Epon 813 where the fire-retardant addition had a minimal effect on the flame spread index.

These observations can be rationalized by examination of the mechanisms at play. For example, the four polyester/vinyl ester resin systems contained proprietary halogenated fire-retardant organic resins. These halogen containing fire-retardant resins (RX) act by interfering with the burning process taking place in the gas phase. The combustion process comprises a series of free radical chain reactions that generate the high energy OH• and H• radicals by chain branching. These radicals are removed by the halogen containing fire-retardant [9].

The halogen radical, X•, reacts to form the hydrogen halide HX that interferes in the gas phase with the free radical chain branching and propagation reactions associated with the key radicals responsible for the propagation of the combustion as follows:

$$RX \quad \text{--------->} \quad R\bullet + X\bullet$$

$$X\bullet + RH \longrightarrow R\bullet + HX$$

$$HX + H\bullet \longrightarrow H_2 + X\bullet$$

$$HX + OH\bullet \longrightarrow H_2O + X\bullet$$

In this way the highly reactive chain propagating species (H• and OH•) are replaced by the relatively unreactive halogen radicals, X•, which may themselves regenerate HX by hydrogen abstraction from the fuel as follows:

$$RH + X\bullet \longrightarrow HX + R\bullet$$

The observed decreases in flame spread index values, upon addition of zinc borate, for the resin systems with the proprietary halogenated fire-retardants, results from the additional interference to the radical chain mechanism caused by physical action. The mechanisms by which zinc borate is believed to operate are several fold. It is assumed that this additive performs as a flame retardant by forming a protective glass matrix at the burning surface of a flammable substrate. The hydrated zinc borate combines with halogen from the halogenated resin during pyrolysis to generate zinc oxychloride and zinc chloride, both known flame retardants [10]. In addition, this unique form of zinc borate releases 14% by weight water in the temperature range of 290-450°C.

3.2. Limiting Oxygen Index

The oxygen index determination (ASTM D2863)[11] measures the ignitability of materials by measuring the minimum concentration of oxygen in a mixture of oxygen and nitrogen flowing upwards in a test column that will just support flaming combustion measured under equilibrium conditions of candle-like burning. A small propane gas flame, which is inserted into the open end of the column, is used to ignite the test specimen. As the sample is burned, the energy feedback from the flame to the burning surface maintains the surface temperature required for pyrolysis of the polymer, and this supplies gaseous fuel to form a combustible mixture with the oxygen/nitrogen stream. As the oxygen concentration is decreased, the flame temperature decreases, resulting in a reduction to the heat feedback and the supply of fuel to the flame zone. The limiting oxygen index (LOI) is defined as

$$LOI = \frac{[O_2]}{[O_2]+[N_2]}$$

where [ ] is the volume concentration of each gas in the combined gas stream. At the critical oxygen concentration (the LOI), a sudden transition from active burning to extinction occurs.

In the standard test, the sample burns downward with a small laminar flame and the energy is quickly dissipated to the cool surroundings with little energy feed-back to support the combustion of the sample. This is in sharp contrast to the hot turbulent environment characteristic of most real fires. Thus, it has been suggested [12] that the oxygen index should be measured as a function of temperature and the temperature at which the limiting oxygen index equals 20.9 should be taken as a measure of material flammability. This variation to the ASTM procedure was not currently measured due to unavailability of a modified test instrument, but will be considered when such an instrument is available.

Figure 2 shows the results of oxygen index determination for the 10 panels tested. The data was grouped by resin type. The oxygen index for all five resins evaluated was above the value of 20.9. With no added fire retardant, the oxygen index values were in the range of 22-30. The addition of zinc borate raised the oxygen index values in varying degrees (11-43%) depending on the resin system evaluated. Similar results were reported when 4-8 phr of zinc borate was added to halogenated polyester resins. The LOI was observed to increase from 27 to 40 [13].

3.3. Smoke Density

The smoke evolution test (ASTM E662)[14] measures the degree of light or sight obscuration by photometrically measuring the specific optical density of smoke generated by a solid material under specific exposure conditions. The values obtained are important since they can be used to provide a measure of fire hazard. Escape from a burning enclosure is enhanced if the occupant can see the exits. Firefighters also have a better chance of fighting and extinguishing a fire if visibility is not limited.

The smoke density generated by the GRP samples was followed by the measurement of the specific optical density using the NBS Smoke Chamber. Among the parameters normally reported are:

$Ds_{1.5}$ - Specific optical density after 1.5 minutes,

$Ds_{4.0}$ - Specific optical density after 4.0 minutes, Dm - Maximum specific optical density anytime during the 20 minute test, and

$Dm_{(corr)}$ - Dm corrected for incidental deposits on the optical surfaces.

The specific optical density values of $Ds_{1.5}$, $Ds_{4.0}$, Dm and $Dm_{(corr)}$ for the five resin systems during the flaming (F) and non-flaming (NF) modes were plotted as Figures 3-7. It can be seen that, all five resin systems yielded relatively similar results. The $Ds_{1.5}$ values were all below 200; however, the four minutes maximum optical density, $Ds_{4.0}$, values were between 300 and 600 in the flaming mode and between 10 and 50 in the non-flaming mode. The maximum smoke density $Dm_{(corr)}$ values of the five systems, for both the flaming and non-flaming modes were quite high. In the majority of samples tested the addition of zinc borate resulted in a lowering of the specific optical density values in varying degrees (12-60%) depending on the resin system evaluated (Table 1). The one anomaly was Hetron 692TP25 in the flaming mode where the specific optical density actually increased by 32%. The lowest value measured approached 200; however, the guideline level of 200 maximum used by the transit industry was exceeded for most of the samples.

The lowest $Dm_{(corr)}$ value was observed for Epon 813 (Table 1) even though this resin had the highest value for flame spread index (Figure 1). This can be rationalized because as flaming combustion is favored, the amount of smoke generated usually decreases.

3.4. Toxic Gas Analysis

Toxic gases are an important cause of casualties in fires. A wide variety of toxic gases are produced in a fire, at levels that can be extremely hazardous, both as single gases and in combination of gases [15]. The composition of these gases varies considerably with types of resin used, additives used, and with varying fire conditions. When a polymer is heated, sufficient energy can be introduced into the polymer system to cause thermal degradation by breaking the bonds along the polymer chain. Gaseous molecules are released. The combustible gases, in the presence of an oxidizing agent (air), will ignite and produce a flame. Other gases may also be produced that are not combustible (eg. H_2O, CO_2 and SO_2). Particles, primarily carbon, may also be emitted, leading to smoke production. These three components (unburned gases, burned gases and smoke) will be responsible for the direct toxic effects generated in a real fire situation.

The use of a flame-retardant additive may tend to increase the toxic emission problems by chemically changing the composition of the gases released in the fire situation. For example, a chlorine-containing additive will generate chlorine radicals which in an oxygen-rich condition can result in the formation of toxic phosgene. This would result in a completely different type of emission profile, with the evolution of new toxic compounds. In fact, many of the flame-retardant additives are themselves toxic at normal operating temperatures, and it is not expected that they will lose their toxicity at the higher temperatures experienced in a fire. Consequently, a study of the hazardous gases released by these resin systems when thermally degraded was conducted.

The last test conducted on the ten GRP panels involved the Boeing BSS 7239 toxic gas sampling [16]. In this test, the gases generated during the NBS Smoke Chamber evaluation are sampled at various intervals for the following components: Carbon Monoxide (CO), Hydrogen Bromide (HBr), Hydrogen Chloride (HCl), Hydrogen Cyanide (HCN), Hydrogen Fluoride (HF), Nitrogen Oxides (NO_x) and Sulphur Dioxide (SO_2). The results for Carbon Monoxide (CO), Hydrogen Bromide (HBr) and Hydrogen Chloride (HCl) are shown in Table 2. The values for CO_{max}, the maximum concentration of CO in parts per million (ppm), as a function of resin without and with fire retardant are plotted in Figure 8. The transit industry guideline for carbon monoxide concentration is set at 3500 ppm. As can be seen from Figure 8, several of the resin systems have maximum CO levels near the 3500 ppm guideline, and this level is only slightly reduced through the addition of zinc borate. The two anomalies were the Hetron 27196 and Hetron 692TP25, where the CO_{max} values actually increased upon addition of zinc borate.

High concentrations of two acid gases, HCl and HBr, were detected from the four resins that were known to contain proprietary halogenated fire-retardants. The values for HCl_{max}, the maximum concentration of HCl in ppm, as a function of resin without and with fire retardant are plotted in Figure 9. It can be seen (Table 2) that Hetron 197AT and Hetron 27196 are heavily loaded with a chlorinated additive, while Derakane 510A contains a brominated species. Epon 813, which was known not to contain any fire-retardant, did in fact generate small quantities of these two gases.

The other gases monitored were produced in very low concentrations and would not be significant contributors to the overall toxicity of the fire gases.

It was apparent from the results that smoke density was the one parameter that was affected the least by the zinc borate addition. This parameter still remains too high to be acceptable and further studies will be aimed at lowering the smoke. "New and improved" polyester resins, other fire-retardants and smoke-suppressants, and other thermoset resins such as phenolics will be investigated as a means by which smoke generation can be lowered.

4. CONCLUSION

This investigation showed that the addition of the inorganic material, zinc borate, affected the flammability characteristics and smoke generation of polyester, vinyl ester and epoxy GRP panels. For example, the addition of 10 phr zinc borate to resins containing halogenated fire-retardant additives lowered the flame spread index to values below the transit industry's upper acceptable guideline. The limiting oxygen index increased with all resin systems upon addition of zinc borate. The smoke density was the one parameter that was affected the most by the zinc borate addition. There were measured decreases as high as 60% as well as increases of 32%; nevertheless, the $Dm_{(corr)}$ values were high for most resins tested and thus unacceptable. Finally, the toxic gas evolution data indicated that the threshold limit values for some gases, in particular the acid gases, were exceeded.

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Table 1. The Effect of Added Zinc Borate on $Dm_{(corr)}$ Values and the Measured % Decrease.

RESIN	FLAMING MODE		NON-FLAMING MODE	
(with 10 phr ZB)	$Dm_{(corr)}$	% Decrease	$Dm_{(corr)}$	% Decrease
Derakane 510A	673	12	396	30
Hetron 197AT	414	36	445	22
Hetron 27196	386	37	440	25
Hetron 692TP25	746	-32	330	-3
Epon 813	232	60	203	34

Table 2. Toxic Gas Concentrations by Volume (ppm) as a Function of Added Fire Retardant - Flaming Mode (BSS 7239/ASTM E662).

RESIN	phr ZB	$CO_{1,5min}$	CO_{4min}	CO_{max}	HCl	HBr
Derakane 510A	0	245	1010	3056	60	62
	10	120	805	2926	72	76
Hetron 197AT	0	320	1160	3328	450	28
	10	180	620	2544	650	10
Hetron 27196	0	160	700	1760	870	7
	10	170	555	2164	4310	3
Hetron 692TP25	0	105	615	2545	150	16
	10	156	630	2866	16	46
Epon 813	0	50	260	870	26	4
	10	32	104	600	8	1

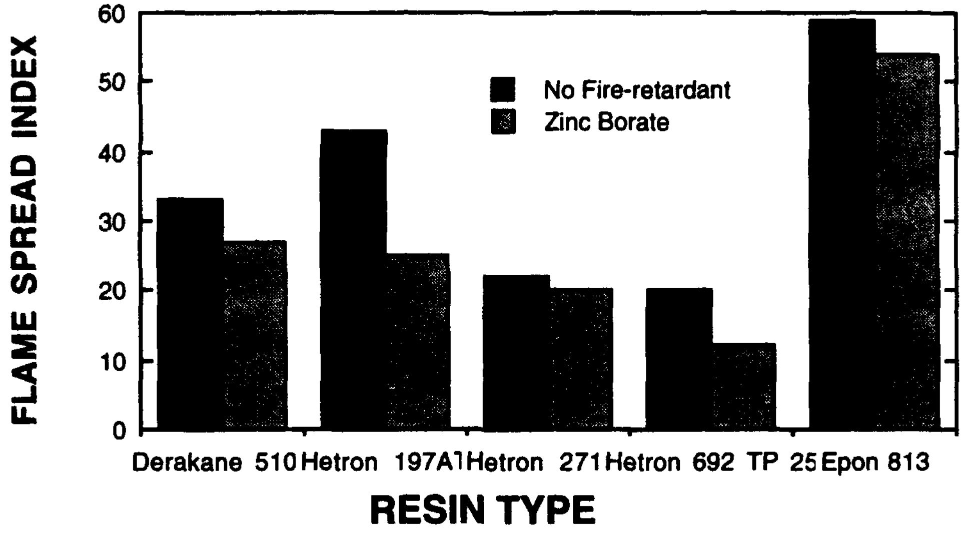

Figure 1. Effect of Added Fire Retardant on the Flame Spread Index (ASTM E 162).

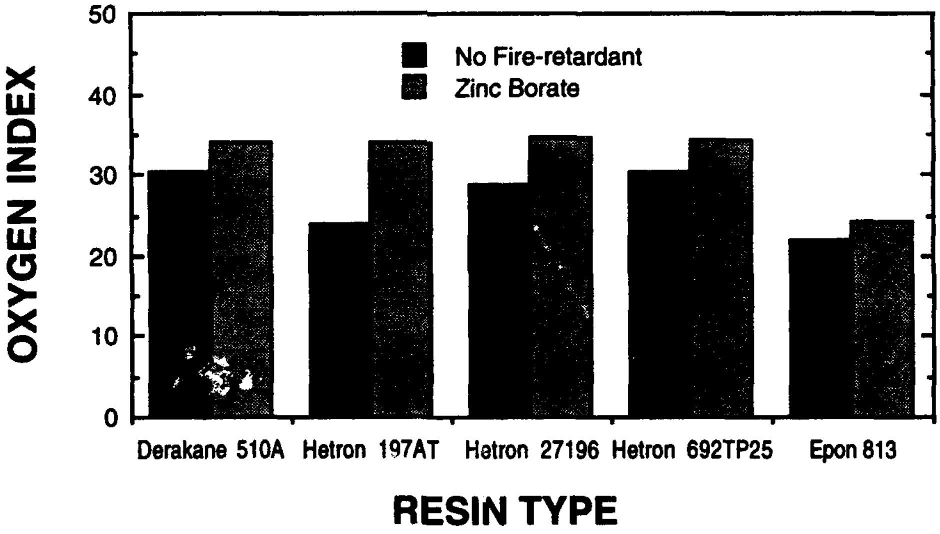

Figure 2. Effect of Added Fire Retardant on the Oxygen Index (ASTM D 2863).

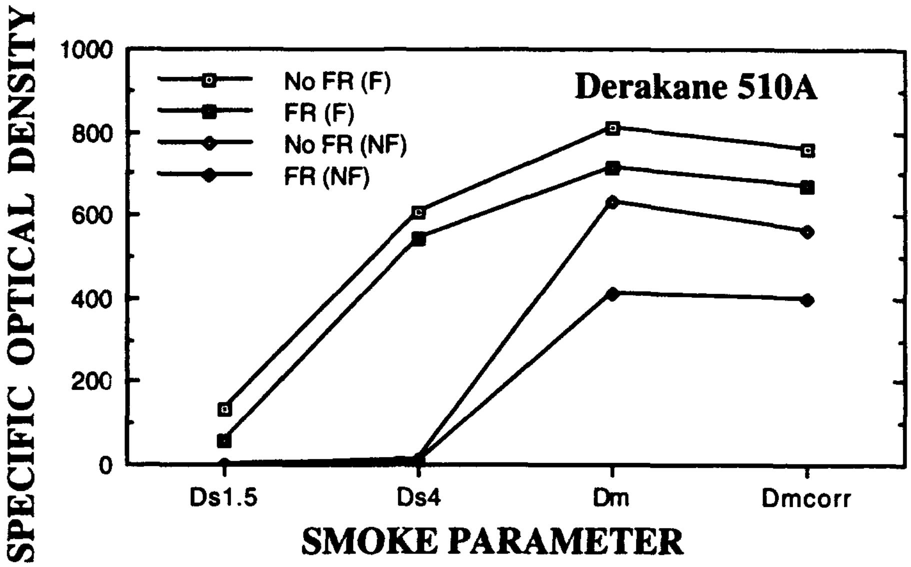

Figure 3. Effect of Added Fire Retardant on the Specific Optical Density (ASTM E 662).

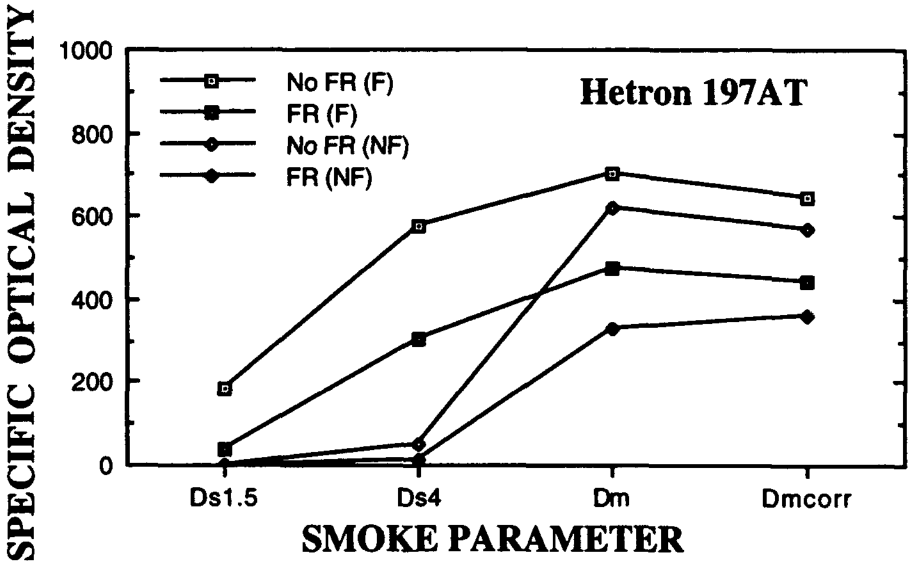

Figure 4. Effect of Added Fire Retardant on the Specific Optical Density (ASTM E 662).

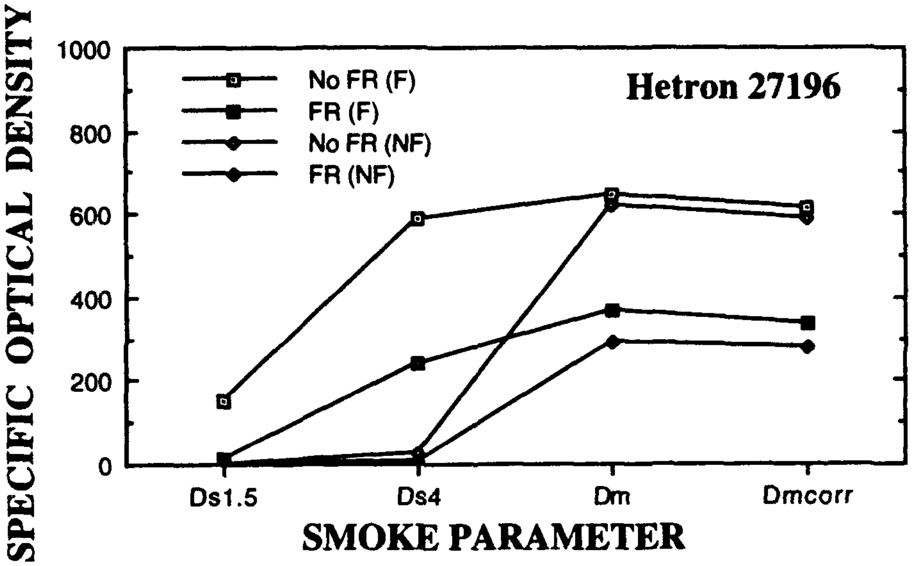

Figure 5. Effect of Added Fire Retardant on the Specific Optical Density (ASTM E 662).

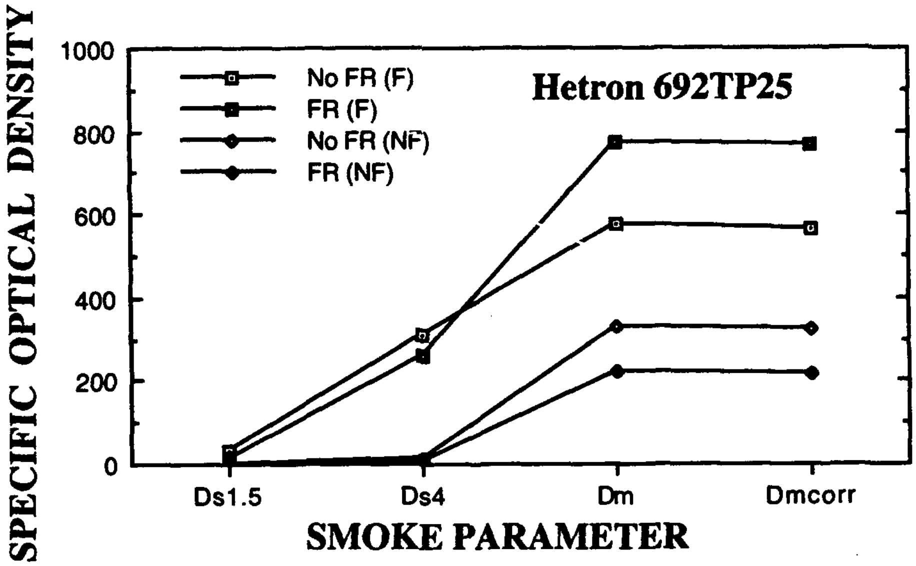

Figure 6. Effect of Added Fire Retardant on the Specific Optical Density (ASTM E 662).

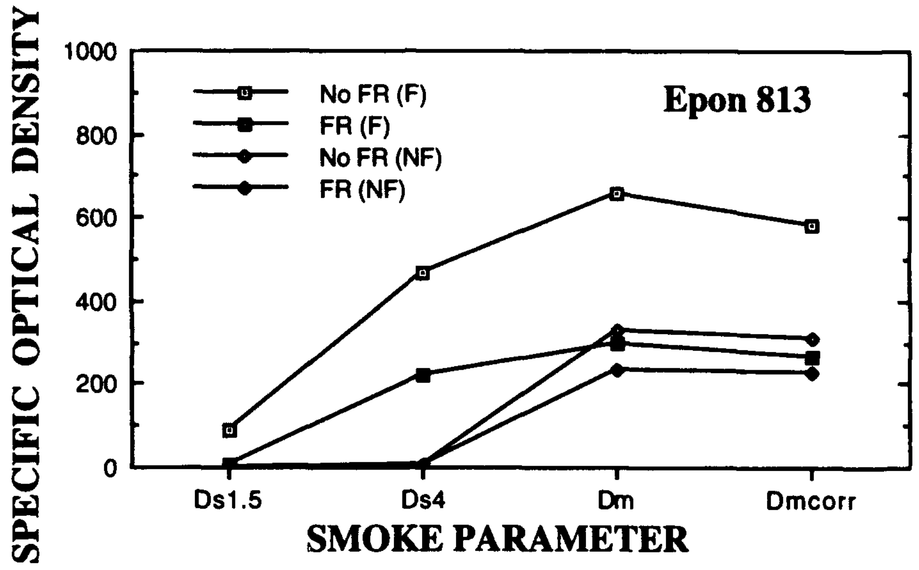

Figure 7. Effect of Added Fire Retardant on the Specific Optical Density (ASTM E 662).

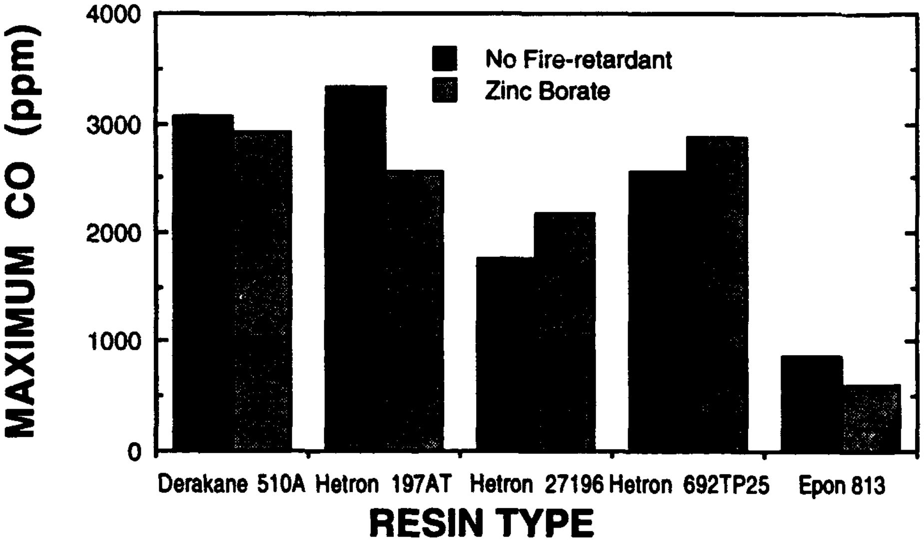

Figure 8. Effect of Added Fire-Retardant on the Concentration of CO_{max} (ppm).

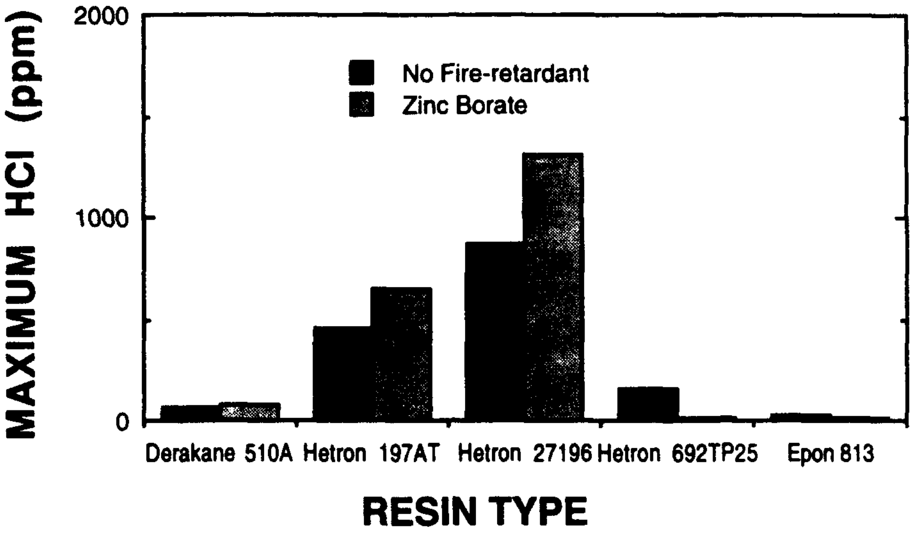

Figure 9. Effect of Added Fire Retardant on the Concentration of HCl_{max} (ppm).

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The effects of an inorganic fire-retardant additive, zinc borate, on flammability characteristics and smoke generation of glass reinforced polyester, vinyl ester and epoxy resins were evaluated. Information is presented on the flame spread index (ASTM E162), limiting oxygen index (ASTM D2863), density of smoke generated (ASTM E662) and toxic gases of combustion (Boeing BSS 7239).

Results indicated that the addition of 10 phr of zinc borate to the polymeric materials significantly decreased the flame spread index and increased the limiting oxygen index; however, the amount of smoke generated during pyrolytic and flaming combustion was high and unacceptable. Finally, the toxic gas evolution data indicated that the threshold limit values for some gases were exceeded.

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