Flammability of Solid Plastics Part 2

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PUBLISHER'S NOTE

CONTENTS

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SMOKE REDUCTION STUDIES ON SELECTED VINYL POLYMERS

ABSTRACT: A number of routes have been identified and discussed which effectively reduce the amount of visible smoke generated when styrenic polymers are burned. These routs include: (1) the incorporation of organometallic compounds into the polymer, with iron based organometallics being most effective; (2) incorporation of oxygen-containing monomers via copolymerization; and (3) the use of inorganic fillers alone or in combination with the above-mentioned routes.

INTRODUCTION

IN LINE WITH the increased emphasis on fire safety in recent years, the mechanisms of smoke-particulate generation and control during the combustion of polymeric materials have been the subject of a great number of investigations [1–5]. Imhof and Stueben measured both oxygen index and smoke characteristics of many polymeric materials [6] and concluded that structures containing an all aliphatic carbon backbone such as polyolefins, nylons, acetal and polymethyl methacrylate are low in smoke generation. On the other hand, polymers containing aromatic groups in the side chain, such as polystyrene, styrene-acrylonitrile, and ABS type copolymers give higher smoke densities. Polymeric structures where the aromatic group is in the main chain (e.g., polysulfone, polycarbonate and polyphenylene oxide) are intermediate in both oxygen index values and smoke generation.

The studies summarized here deal largely with the second type of the above polymers, i.e., styrene-containing systems, and with several effective methods for reducing their smoke generation properties.

EXPERIMENTAL

Polymers: The styrene polymers used in this study were prepared as described in references 7, 8 and 9.

Compounding: The mixing of the additives with the polymers involved blending of the polymers and additives followed by melt mixing either in a small laboratory Brabender at 210-220°C for 3-5 minutes and cutting into small pieces for molding

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or extruding the dry blended samples in a two-stage screw extruder at 210-220°C.

Flammability Test: The flammability tests were carried out following the Underwriters' Laboratory Test Procedures known as UL-94 [10].

Smoke Measurements: The samples for smoke-density measurements were prepared by compression molding the melt-compounded samples into 3" X 3" X 1/32" plaques. The sample thickness was accurately measured to adjust smoke-density values to the standard (0.032"). The smoke measurements were made in a smoke density chamber, Model No. 4-5800-A, American Instrument Co., Silver Spring, Md. The measurements were made with 2.5-watt/cm^2 heat flux. Both flaming and non-flaming conditions were used as described in reference 1.

Char Level: The char level was estimated from Thermal Gravimetric Analysis (TGA) traces as measured with a duPont Model 950 Thermogravimetric Analyzer at 20°C/min. The char level is taken as the deflection point after rapid weight loss.

RESULTS AND DISCUSSIONS

Smoke Suppression with Organometallics

Table 1. Smoke Density Reduction Via Organometallics in Styrene, Acrylonitrile, Butadiene Terpolymer Systems.

Additive	Metal Weight Percent	Smoke D_m (corr.)	Smoke Density Reduction	Percent Metal Vaporized*
None	None	440	--	--
Ferrocene	5.0	130	70	100
Benzoyl Ferrocene	2.5	175	60	60
Iron Acetylacetonate	2.5	310	30	20

Note: Amounts of metal vaporized were determined by thermogravimetric and atomic absorption analyses. Smoke density measured under flaming conditions.

Organometallic reagents have been known for some time to act as smoke suppressants in fuel oil [12, 13], particularly ferrocene and manganese compounds. Parts [14] studied the effect of several organometallic compounds in polymeric systems and identified a number of effective smoke suppressants for styrenic polymers. Our data corroborating Parts' findings is presented in Table 1. In addition to the smoke level and percent reduction, the percent of metal vaporized as determined by Thermal Gravimetric (TGA) and Atomic Absorption Analyses is also presented in Table 1. It was found that there was good correlation (Figure 1) between the level of smoke reduction and the level of metal volatilized in the organometallic suppressed styrenic systems. Ferrocene and benzoyl ferrocene which result in large amounts of volatilized metal are highly effective in reducing smoke.
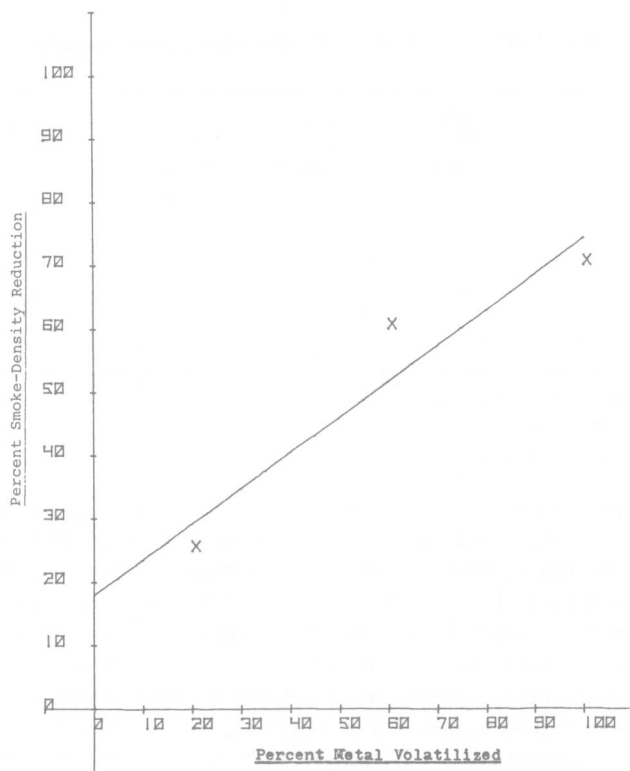
Figure 1. Percent smoke reduction as a function of iron volatilization in non-flame retardant ABS systems.

However, iron acetylacetonate which volatilizes only about 25 percent of the available iron is not as effective as ferrocene or benzoyl ferrocene indicating that the iron functions primarily in the vapor phase.

In flame-retardant ABS type systems based on polychloroprene as the elastomer the action of the organometallics appears to be different. Our data (Table 2) show that the organometallics which volatilize high percentages of metal such as ferrocene, and are highly efficient smoke suppressants in non-flame retarded systems, are ineffective smoke suppressants in flame retardant systems. However, the organometallics which volatilize low percentages of metal, such as iron acetylacetonate in non-flame retarded systems, are highly effective suppressants in the flame retardant ABS type polymers (Table 2). Thus, it appears that in flame-retardant, ABS type systems the major smoke suppressant activity takes place in the condensed phase as opposed to the non-flame retardant systems where the predominate suppressant activity appears to take place in the vapor phase.

Table 2. Smoke Reduction Via Organometallics in Acrylonitrile, Styrene, Butadiene Terpolymer (ABS) Systems.

Additive	Metal Weight Percent	Smoke D_m (corr.)	Percent Reduction	Percent Metal Vaporized
None	--	500	--	--
Benzoyl Ferrocene	5	310	38	60
Ferrocene	5	380	24	100
Iron Acetylacetonate	5	225	55	20

Note: Smoke density measured under flaming conditions.

Effect of Polymer Oxygen Content

Earlier smoke generation data on common polymers [2, 4] suggests that the presence of oxygen, chemically bound in the polymer reduces the amount of smoke particulates produced during flaming combustion. Similar findings have been reported for monomeric fuels [1]. A variety of vinyl-type polymers was prepared and tested in an attempt to quantify the effect of oxygen content on their smoke generation behavior. The results are presented in Figure 2. All the polymers were flame retarded with 20 weight percent polychloroprene rubber and 9 weight percent antimony oxide; and exhibited V-0 flammability rating [10]. The polymer systems in Figure 2 encompass a wide variety of vinyl polymer structures, i.e., methyl methacrylate, dimethylitaconate, vinyl phenylacetate, vinyl benzoate, 4-methoxy styrene, etc. [7, 8]. Thus, a general relationship between smoke-density level and oxygen content in vinyl polymer systems is evident. Maleic anhydride is one of the high, oxygen-containing vinyl monomers (48.9% oxygen). The random copolymers of styrene/maleic anhydride were, therefore, prepared [7] and the smoke-density levels of these copolymers were measured (Figure 3). Copolymers of methyl methacrylate and styrene were also prepared [8, 9], and their smoke properties were measured (Figure 4). When these copolymers were then formulated into flame retardant products (V-0 rating), they showed substantially higher smoke levels. When the smoke values of these flame-retarded, styrene-methyl methacrylate copolymers are recalculated based on available oxygen in the polymer and are replotted as shown in Figure 5, the two lines come very close to each other. The difference in smoke levels at a given oxygen level may be attributable to the effects of additives used. In the case of styrene-methyl methacrylate, smoke-density reduction was directly proportional to the methyl methacrylate concentration. However, for maleic anhydride, its effect is not linear. When one compares maleic anhydride with methyl methacrylate in terms of smoke level vs. oxygen content as shown in Figure 6, it is noted that maleic anhydride becomes increasingly more effective than methyl methacrylate in reducing smoke at concentrations above 7% oxygen.
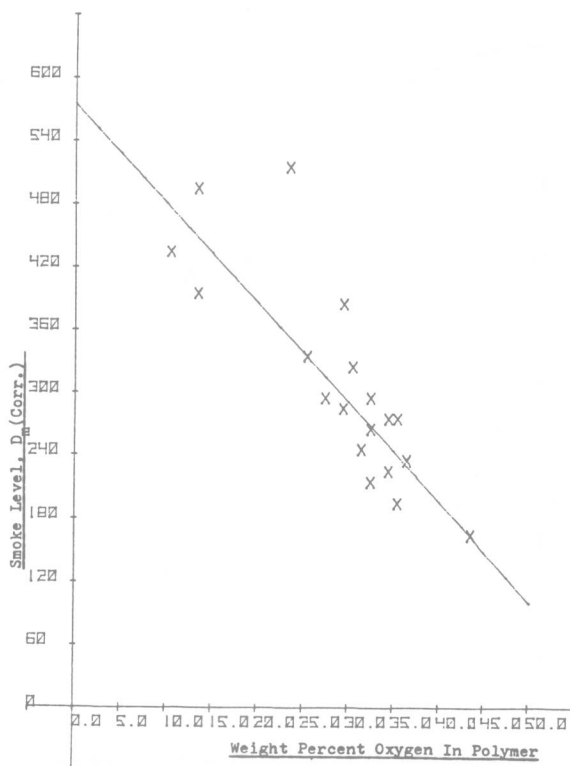
Figure 2. Weight percent oxygen in polymer vs. smoke level (Dm).

Examination of themogravimetric analysis curves of styrene-methyl methacrylate copolymers and those of styrene-maleic anhydride (Figure 7) reveals that the styrene/maleic anhydride copolymers produce noticeable amounts of residue while styrene/methyl methacrylate copolymers are completely volatilized. These "char" deposits are increasingly apparent in styrene/maleic anhydride copolymers containing over 10% maleic anhydride when they are tested for smoke generation in the NBS smoke chamber.

Effects of Inorganic Fillers

There are many commercial flame retardant grades of vinyl polymers available, which exhibit UL-94, vertical-ignition resistance ratings of V-1 or V-0. Most of them contain halogenated compounds and synergists (e.g. Sb_2O_3) as flame-retardant additives. However, the smoke generation characteristics of these polymers generally are not improved. In most cases, they tend to generate more smoke than
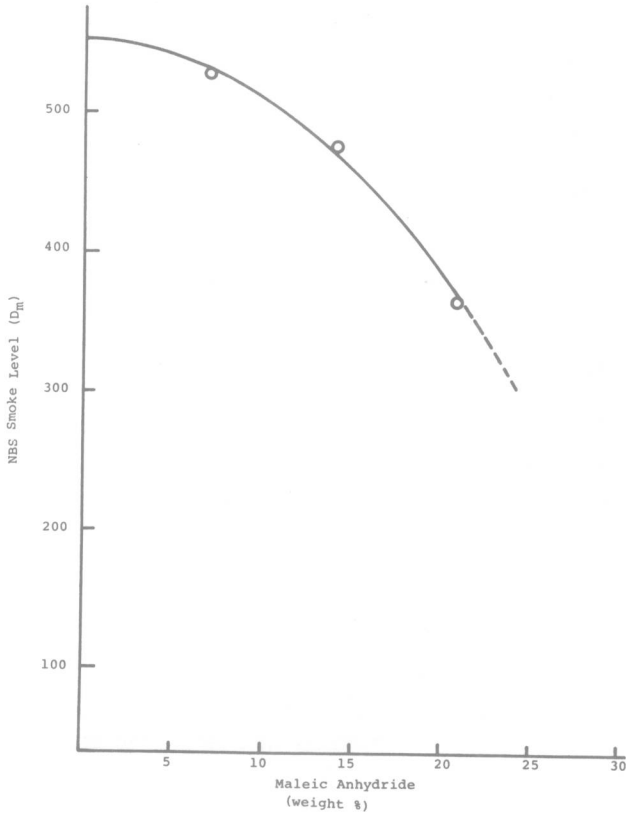
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Figure 3. Maleic anhydride content vs.
smoke level (D_m).

their non-flame retardant equivalent grades when tested in the NBS smoke chamber. Several inorganic filler materials have been found to be effective in reducing smoke generation and flammability of plastics when added in large amounts [15, 16]. However, large amounts of such fillers tend to adversely affect physical properties. Accordingly only small amounts of filler can be tolerated.

G. L. Nelson [17] investigated the effect of hydrated alumina on smoke generation in polystyrene and polyethylene. He noted changes in the amount of H_2, CO_2 and CH_4 produced and especially an increase in toluene. He concluded that polystyrene's mode of degradation appears to have been altered by the hydrated alumina leading to less smoky fuel. Sobolev and Woychesin reported that hydrated alumina in polystyrene and polymethyl methacrylate increased the oxygen index but there was no significant reduction in the burn rate [16]. They also noticed that there was no effect on smoke reduction. They attributed the results to the inherent
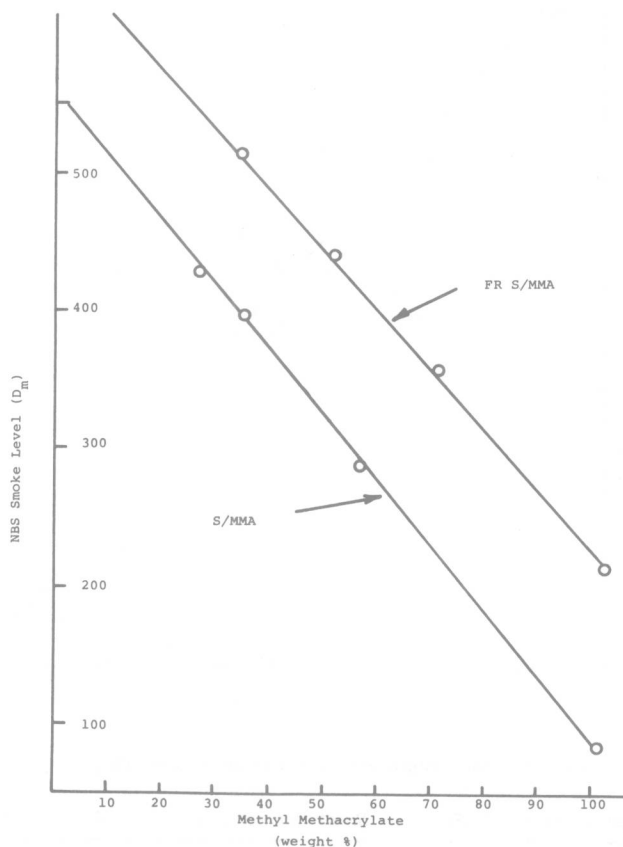
Figure 4. Effect of flame retardant additives on smoke level (D_m) of styrene/methylmethacrylate.

low pyrolysis temperature of the polymers relative to the endothermic decomposition temperature of the hydrated alumina. These results suggested that endothermic fillers with a lower decomposition temperature than alumina hydrate, such as ammonium Dawsonite could be more effective in reducing smoke generation and flammability properties of such polymers.

Several inorganic fillers in the 5-20% concentration were tested as smoke-density suppressants in flame retardant polystyrene formulation. Most of them, however, were found unsatisfactory in yielding smoke reduction plus flame retardance (Table 3). Although Dawsonite is observed to be the most effective smoke-suppressing filler (Figure 8), as little as 5 pts of it in FR HIPS resulted in a loss of the flame retardant properties. On the other hand, $MgCO_3$ has little effect either on smoke or FR properties. In most cases, presence of the fillers reduces or eliminates the
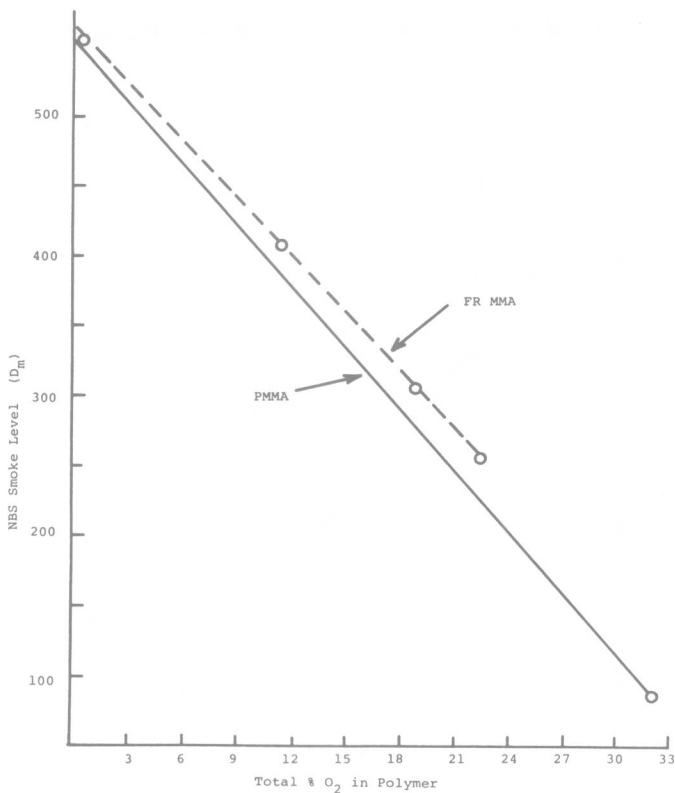
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Figure 5. Total oxygen in polymer vs smoke level (D_m).

Table 3. Effect of Inorganic Fillers on Smoke of FR High Impact Polystyrene (HIPS).

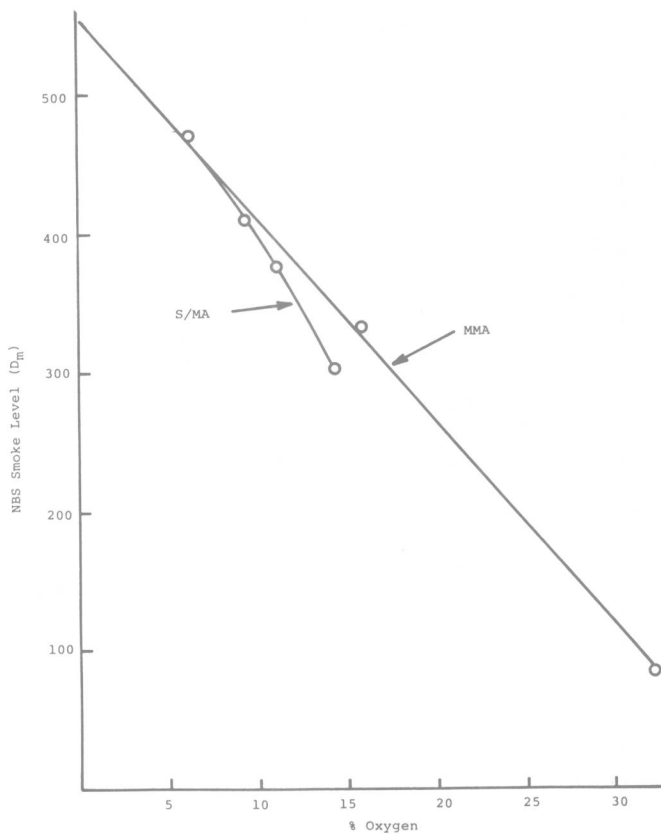| Amount of Filler	10 pts.		20 pts.	
	Smoke (D_m)	UL-94	Smoke (D_m)	UL-94
FR HIPS	675	V-0 (V-2)	550-700	V-0 (V-2)
Dawsonite	425	FAIL	335	FAIL
Al_2O_3	653	FAIL	695	FAIL
$Al(OH)_3$	555	V-2	551	FAIL
Na_2CO_3	546	FAIL	432	FAIL
$MgCO_3$	557	V-0	493	V-0
$ZnCO_3$	576	FAIL	496	FAIL
$MgCO_3/ZnO$ (1:1)	510	FAIL	450	FAIL

Note: Smoke density measured under flaming conditions.

Figure 6. Total oxygen content of polymer vs smoke level (D_m).
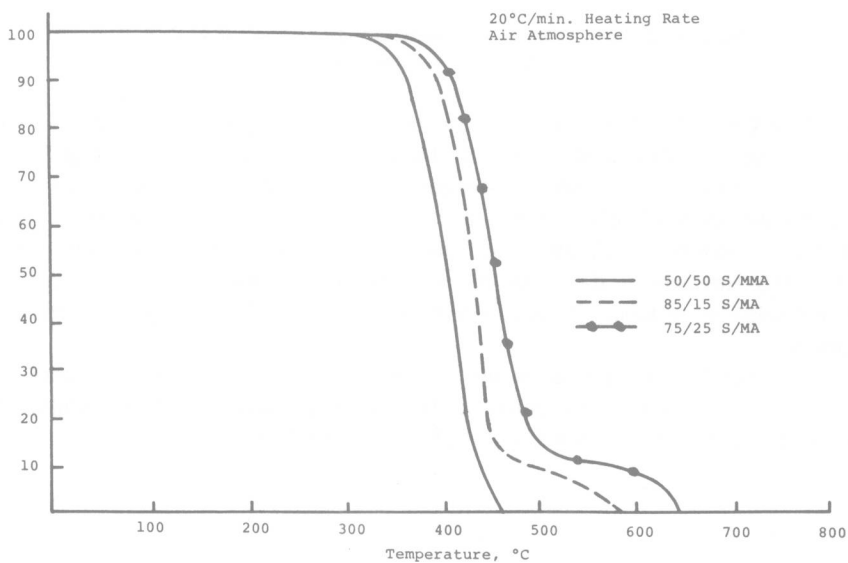

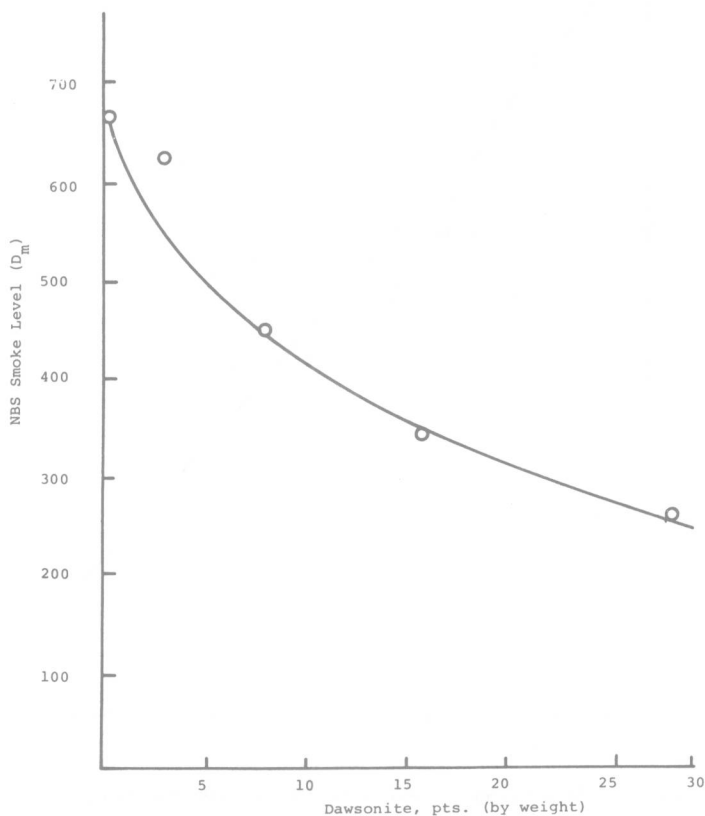Figure 7. Thermogravimetric analysis of oxygenated polymers.

Figure 8. Effect of dawsonite content on smoke level (D_m) on high
impact polystyrene (HIPS).

melt-dripping problem associated with polystyrene when they are burned in the vertical mode. Mathis & Morgan [18] have found that a mixture of $MgCO_3$ and ZnO is a very effective smoke suppressant in halogenated polymers but this combination was only marginal in polystyrene. The styrene/methyl methacrylate copolymers were affected by these inorganic smoke suppressant additives very similarly to HIPS. However, in the S/MA copolymer systems it was found that these fillers are effective in reducing smoke and maintaining satisfactory ignition-resistance properties.

It is believed that the tendency of the S/MA systems to char enhances the effectiveness of these fillers which contribute to the amount of noncombustible char and to a reduction in the amount of combustible fuel.

CONCLUSIONS

Organometallics which volatilize high percentage of metal, such as ferrocene, are highly effective smoke-density suppressants in non-flame retarded systems. Organometallics which volatilize low percentages of metal, such as iron acetylacetonate, are highly effective suppressants in the flame-retarded, ABS-type polymers.

The presence of chemically bound oxygen in the polymer chain reduces the amount of smoke produced during combustion, and there is a general relationship between smoke-density level and oxygen content in vinyl polymer systems. Copolymerization of styrene with oxygenated monomers such as methyl methacrylate and maleic anhydride greatly reduces the smoke-density level of styrene polymers. Most of the inorganic fillers studied in the 5-20% concentration have a marginal effect on smoke reduction and some of the hydrated fillers adversely affect ignition resistance of the flame retardant grades of styrene polymers based on halogen/Sb_2O_3 additive systems.

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REFERENCES

1. A. E. Clark. T. G. Hunter and F. M. Gardner, J. Institute of Petroleum, *32,* 627 (1946).
2. J. R. Gaskill, J. Fire and Flamm, *1,* 183 (1970).
3. C. J. Hilado, Fire and Flammability, 217 (1970).
4. J. R. Gaskill and C. R. Veith, Fire Technology, *4,* 185 (1968).
5. C. J. Hilado, University of Detroit Polymer Conference Series, June, 1970.
6. L. G. Imhof and K. C. Stueben, Polymer Eng. and Science *13,* No. 2, 146 (1973).
7. M. Baer, U. S. Pat. 2,971,939 (Monsanto) February 14, 1961.
8. G. L. Deets, U. S. Pat. 4,065,428 (Monsanto), December 27, 1977.
9. Y. C. Lee, U. S. Pat. 4,051,311 (Monsanto), September 27, 1977.
10. Underwriters Laboratory Test Procedures, "Test for Flammable Plastics Materials for Parts in Devices and Appliance", 2nd Ed., September 1973 (Revised February, 1974).
11. Smoke Density Chamber, Model No. 4-5800-A, American Instrument Co., Silver Spring, Md.
12. B. S. Chittawadi and A. N. Noinov, Indian J. Technol. *6,* (3), 83 (1968).
13. K. S. B. Addleott and C. W. Nettl, Am. Chem. Soc. Div. Petrol. Chem. Preprints, *14,* (4), A-69 (1967).
14. L. P. Parts and J. T. Miller, Jr., U.S. Pat. 3,766,157 (Monsanto), October 16, 1973.
15. E. A. Woycheshin, et al, U.S. Pat. 3,878,166 (Kaiser Aluminum & Chemical Corp.) 1975.
16. I. Sobolev and E. A. Woycheshin, Div. of Org. Coatings and Plastics Chem., Am. Chem. Soc., 172nd Meeting (August 30-September 3, 1976).
17. G. L. Nelson, J. Fire and Flammability, *5,* 125 (April 1974).
18. T. C. Mathis and A. W. Morgan, U. S. Pat. 3,869,420 (Monsanto), March 4, 1975.