APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 51–56 (1991)

A synergistic organoiron flame-retarding/ smoke-suppressing system for ABS

P Carty* and S White†

* Department of Chemical and Life Sciences, Newcastle upon Tyne Polytechnic, Coach Lane Campus, Newcastle upon Tyne NE7 7XA, and

† Cookson Minerals, Wallsend, Newcastle upon Tyne NE28 6UQ, UK

Commercial acrylonitrile butadiene styrene (ABS) polymers are among the most flammable of the currently available range of thermoplastic materials. In addition to having a rather low limiting oxygen index (LOI) value in the range 18.3–18.8, ABS polymers also produce copious amounts of smoke and hazardous gases when burning in the air. In a recent study directed towards preparing and evaluating compounds which would simultaneously reduce the flammability and smoke produced from burning thermoplastic polymers, a synergistic flame-retarding/smoke-suppressing system based on organoiron compounds has been produced, which when properly compounded into ABS/PVC [poly(vinyl chloride)] blends more than doubles the LOI and at the same time reduces smoke production significantly.

Keywords: Flame retardant, smoke suppressant, organoiron compounds, ABS polymers, polymer blends, poly(vinyl chloride), Limiting Oxygen Index, smoke production, synergism.

1 INTRODUCTION

Several patents[1-4] have been published which indicate that when ABS (a terpolymer of acrylonitrile, butadiene and styrene) is compounded with organic chlorine or bromine compounds the flammability of the resulting polymer is reduced. Commercial blends of ABS with PVC [poly(vinyl chloride)] containing up to 30% PVC are available, Cycovin[5] being a typical example, and have improved flame and chemical resistance, without the presence of PVC in the blend seriously affecting the excellent strength, stiffness and high impact resistance of the ABS component. However, the addition of organochlorine or bromine compounds on their own only marginally increases the LOI and in order to achieve a V–0 rating in the UL-94[6] flammability test, a loading of about 20% organic halogen is required together with 3% antimony trioxide as a synergist. Some of the currently used flame-retarding organobromine compounds are shown in Fig. 1.

Although these mixtures of ABS and organic halogen compounds are resistant to ignition and burning, they suffer from a major disadvantage in that the flame-retarding system dramatically increases the amount of smoke, toxic and corrosive gases which are produced when flame-retardant ABS polymers burn in real fires. There is little evidence available[7] in the open literature which quantitatively describes the amounts of smoke and fire gases which are produced when flame-retardant ABS is ignited and burned. However, in a not totally dissimilar system, namely flame-retardant semi-rigid PVC, it is known that smoke production is increased by up to 40% in the presence of 5% antimony trioxide.[8]

We have recently published[9-11] details describing the effects of compounding a wide variety of inorganic and organometallic compounds on the flammability and smoke production in semi-rigid PVC and other workers have described the effects of iron compounds on the flammability and other properties in other polymers.[12-14] It is the major purpose of this paper to report quantitative experimental data relating to a potentially useful synergistic relationship between some organoiron compounds and PVC in ABS polymer systems using compound **IX** as an exemplifier of the flame-retarding and smoke-suppressing effect.

2 EXPERIMENTAL

2.1 Compounds examined

A wide range of substituted ferrocenes were prepared in high yield and in high purity via the Aldol reaction[15] using readily available ferrocene aldehydes and ketones with reactive, mainly aromatic or pseudo-aromatic, aldehydes and

0268-2605/91/010051-06$05.00

Received 8 June 1990
Accepted 29 September 1990

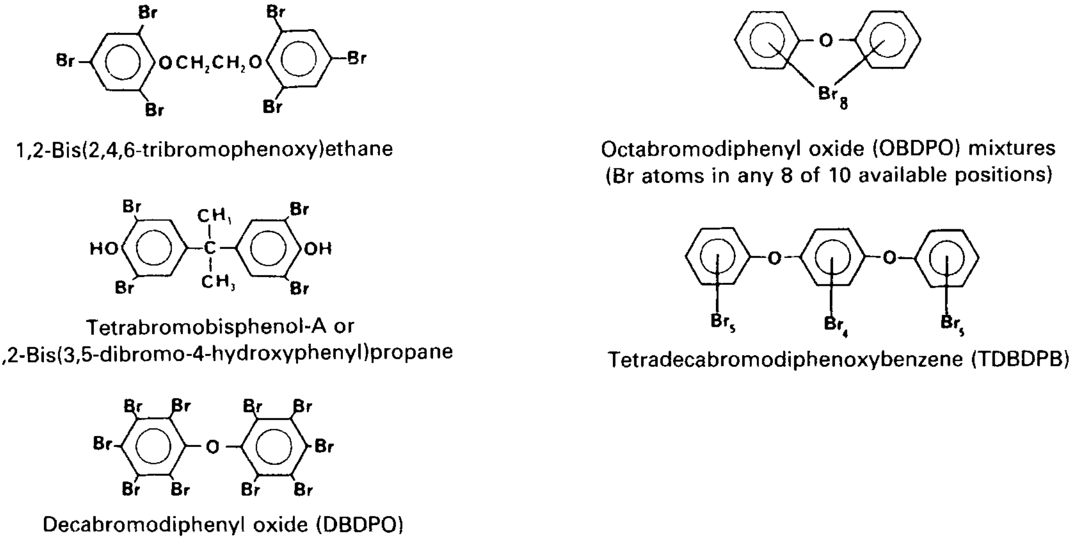


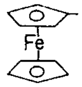
Figure 1 Commercially significant organic bromine compounds used in flame-retardant ABS polymers.

ketones. A general scheme for the reaction between a ferrocene ketone and an aromatic aldehyde can be written as shown in Eqn [1]; the possible products are shown in Fig. 2.

$$\mathrm{FcCOCH_3 + RCHO \xrightarrow[\text{EtOH}]{10\%\ \text{KOH}} FcCOCH{=}CHR + H_2O} \quad [1]$$

where

Fc =



and R = aromatic moiety

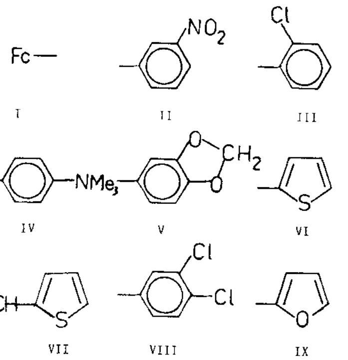


Figure 2 Aldol products formed from monoacetyl ferrocene and aromatic aldehydes, **I–IX**, all have the general formula FcCOCH=CHR, where R has one of the structures shown above (**II–IX** are aromatic aldehydes).

All the Aldol products were prepared as follows. Monoacetylferrocene was recrystallized from ethanol and the aromatic aldehydes used were reagent grade.

Monoacetylferrocene and a slight excess of aldehyde were dissolved in nitrogen-saturated ethanol and carefully added dropwise to a stirred, nitrogen-saturated solution of 10% alcoholic potassium hydroxide. When the addition of the reagents was complete the flask was stoppered and stored in a refrigerator. Dark red crystals of the Aldol product formed overnight. They were filtered off, air-dried and used without any further purification.

Before conventional compounding into ABS and ABS/PVC blends on a two-roll mill, the compounds were finely powdered and sieved so that the resulting particle size was less than 300 mesh.

2.2 Flammability and smoke density determination[16]

Limiting Oxygen Index (LOI) and NBS smoke determinations

LOI values were determined according to ASTM D-2863-77 for self-supporting specimens (BS 2782: Part 1—Method 141b) using a Standon Redcroft Flammability Apparatus. The LOI values obtained were analysed statistically by the Dixon statistical method and are quoted in the Tables to one decimal place (the accuracy of the LOI values is ±0.45 LOI units).

NBS smoke values were determined according to BS 6401 in the flaming mode and the figures quoted in the Tables represent an average value from two burns. Where two values were not in reasonable agreement (one decade), further specimens were burned in order to establish an accurate and representative value for the formulation under examination. Values quoted are D_{MAX} all corrected to 7 g of sample burned. The thickness of all specimens used for NBS smoke density determinations was 1 mm.

Accurate determination of D_{MAX} for the ABS and ABS/PVC blends proved to be particularly difficult using an Aminco smoke density chamber. ABS burns very quickly and is also a very high smoke-producing polymer. The intense heat and high levels of smoke produced in the flaming mode of the test frequently resulted in the 'blow out' panel in the floor of the smoke box developing leaks which prevented the accurate determination of specific optical density. The relationship between smoke density and sample thickness is not linear[17,18] and as all our earlier work with PVC[10,11] has been carried out with standard samples 1 mm thick we decided to carry out smoke density determinations in the usual way (i.e. as previously). Values of D_{MAX} (corr.) for 100% ABS, the ABS/PVC blends and the ABS/PVC/Sb_2O_3 formulations were all very high.

2.3 Polymers used

ABS	
ABS polymer (Cycolac GSM)	100 phr*
PVC (for blending with ABS)	
Corvic ICI PVC grade S67/111)	100 phr
Tribasic lead sulphate (stabilizer)	5 phr
Calcium stearate (lubricant)	1 phr

3 RESULTS

The results are shown in tabular form in Tables 1–3.

4 DISCUSSION

Analogous work, carried out using the same organometallic compounds but in semi-rigid PVC, has been described elsewhere.[11] However, as excellent results had been obtained in the PVC system using the easily prepared organometallic compound derived from **IX**, i.e. the Aldol product from monoacetylferrocene and furfural, it was decided to investigate the effects of adding varying levels of the compound to 100% ABS and to ABS/PVC blends of varying composition. The LOI values and D_{MAX}(corr.) data are shown in Tables 1–3. LOI data are complete for all the formulations prepared but values for the smoke density are not complete. The reasons for this have been mentioned earlier.

4.1 Synergism between compound derived from (IX) and PVC in ABS

Tables 1–3 clearly show that there is a particularly effective synergistic interaction between the organometallic compound and PVC. There is a similar effect with the chlorinated alkane Cereclor 70 but Dechlorane Plus appears not to interact synergistically. Dechlorane Plus may not easily decompose to liberate hydrogen chloride at the temperatures experienced during the LOI test and consequently there may be little chemical interaction with the iron compound.

High LOI values (in the middle-to-high thirties) cannot easily be achieved using antimony oxide as a synergist with PVC in ABS. Even with 30 parts of PVC in a blend with ABS, 5 parts of antimony trioxide gave an LOI value of only 26.6.

Table 2 shows that the observed and calculated LOI values for the ABS/PVC/**IX** blends are markedly different. In every case the experimental LOI value is about twice the calculated value assuming an additive interaction between PVC and the organometallic compound. This synergism may be closely related to the very well known and thoroughly studied synergistic reaction between antimony oxide and the halogens chlorine and bromine generated *in situ* from the decomposing halogen retardant. In this case the active species in the flame are antimony trichloride (or tribromide), antimony oxychloride and particulate antimony trioxide. It is highly likely that the ABS/PVC/organometallic blends promote char formation by cross-linking and the active flame-retarding species is either hydrochloric acid or volatile organoiron species produced when the blend is thermally decomposing. Little is known about the route of decomposition of ABS and more research is required to examine the chemistry operating in this system.

---

* phr = parts per 100 parts of polymer.

Table 1 LOI and D_{MAX} data for ABS, ABS/PVC with organoiron compound derived from **IX**

Formulation		LOI	δLOI[a]	NBS D_{MAX}(corr.)	δNBS[b] (%)
ABS (100)	—	18.3	—	>1000	—
	IX (phr)				
	1	20.0	+1.7	716	≥28
ABS(100)/**IX**	2.5	21.1	+2.8	—	—
	5	23.4	+5.1	677	≥32
	10	23.2	+4.9	—	—
ABS(70)/PVC(30)	—	22.2	+3.9	>1000	—
	IX (phr)				
	1	28.6	+10.3	758	≥24
ABS(70)/PVC(30)/**IX**	2.5	32.7	+14.4	—	—
	5	35.0	+16.7	—	—
	10	34.7	+16.4	659	≥34
ABS(67.5)/PVC(32.5)/**IX**(5)		35.3	+17.0	—	—
ABS(70)/PVC(30)/**IX**(5)		35.0	+16.7	652	≥35
ABS(72.5)/PVC(27.5)/**IX**(5)		34.8	+16.5	—	—
ABS(75)/PVC(25)/**IX**(5)		32.8	+14.5	—	—
ABS(77.5)/PVC(22.5)/**IX**(5)		36.0	+15.7	—	—
ABS(80)/PVC(20)/**IX**(5)		33.9	+15.6	—	—
	Sb_2O_3 (phr)				
ABS(70)/PVC(30)/Sb_2O_3	2.5	25.0	+6.7	>1000	—
	5	26.6	+8.3	>1000	—
ABS(70)/Dechlorane Plus[c](30)/**IX**(5)		22.6	+4.3	—	—
ABS(70)/Cereclor 70[d](30)/**IX**(5)		35.5	+17.2	—	—

[a] δLOI is the difference in the LOI values between the value obtained for a specimen of 100% ABS and the specimen under investigation. [b] δNBS(%) is the percentage difference in NBS D_{MAX} values (corr. 7 g) between the value obtained for a specimen of 100% ABS and the specimen under investigation. [c] Dechlorane Plus is an organochlorine flame retardant available from Occidental Chemical Corporation, New York. It is a proprietary product based on an alicyclic chlorocarbon. [d] Cereclor 70 is a partially chlorinated alkane which is available from ICI Ltd in the UK. It is a proprietary product based on a chlorinated polyethene derivative.

4.2 Smoke suppression

Although we experienced difficulty in determining D_{MAX} values for all the ABS formulations it is quite clear that the smoke-suppressing activity of the organoiron/PVC system is a real and experimentally reproducible effect. It was clearly visible during the experimental determinations of smoke density that the blends containing the organoiron compounds produced significantly less smoke than the blends which contained ABS and PVC only. Experience using the Smoke Density Chamber has shown that compounds which suppress smoke production up to levels of about 20% do not visibly appear to be producing less smoke during the determination of D_{MAX} in the flaming mode. However, smoke suppressants which reduce smoke by more than 20% do visibly show less smoke being produced during burning. In this work it has been established that the smoke-suppressing activity of the organoiron/PVC combinations is at a minimum of 30% when compared with a control sample which has no organometallic present. Because the control samples produced smoke density values which were higher [D_{MAX}(corr.) $\geq$ 1000] than the optical system in the Smoke Chamber could cope with, we cannot report strictly accurate values for the smoke-

Table 2 Synergism between aldol product **IX** and PVC in ABS

Formulation	ABS(100)	ABS(70) PVC(30)	ABS(100) **IX**(1)	ABS(100) **IX**(2.5)	ABS(100) **IX**(5)	ABS(30) **IX**(10)	ABS(70) PVC(30) **IX**(1)	ABS(70) PVC(30) **IX**(2.5)	ABS(70) PVC(30) **IX**(5)
LOI	18.3	22.0	20.0	21.1	23.4	23.3	28.6	32.7	35.0
δLOI	—	+3.9	+1.7	+2.8	+5.1	+5.0	+10.3	+14.4	+16.7
LOI (theor.)[a]	—	—	—	—	—	—	+5.6	6.7	+9.0

Formulation	ABS(70) PVC(30) **IX**(10)	ABS(77.5) PVC(22.5)	ABS(72.5) PVC(27.5)	ABS(67.5) PVC(32.5)	ABS(77.5) PVC(22.5) **IX**(5)	ABS(72.5) PVC(27.5) **IX**(5)	ABS(67.5) PVC(32.5) **IX**(5)	ABS(75) PVC(25) **IX**(5)
LOI	34.7	21.0	21.5	22.1	34.0	34.8	35.3	32.8
δLOI	+16.4	+2.7	+3.2	+3.8	+15.7	+16.5	+17.0	+14.5
LOI (theor.)[a]	+8.9	—	—	—	+8.9	+8.3	+8.9	+7.8

[a] LOI (theor.) values are calculated using the LOI value of a sample of ABS.

Table 3 LOI data for ABS/PVC blends

ABS/PVC blend	LOI	δLOI
67.5/32.5	22.1	+3.8
70.0/30.0	22.2	+3.9
72.5/27.5	22.5	+3.2
75.0/25.0	21.0	+2.7
77.5/22.5	21.0	+2.7
80.0/20.0	20.7	+2.4

suppressing activity of the PVC/organometallic system. In a US patent[19] it was recorded that ABS samples less than 1 mm thick gave D_{MAX}(corr.) values of 1297. In another publication, ABS samples ($\frac{1}{8}$ inch = 3.18 mm thick) gave a D_{MAX} value of 1230.[18] Using these data, calculations indicate that the PVC/organometallic synergists may reduce smoke by about 45% in an ABS(70)/PVC(30)/**IX**(5) formulation.

It is hoped to establish similar synergism between organobromine compounds and organometallics and to investigate the effects of the PVC/organometallic flame-retarding/smoke-suppressing system in other polymers.

Acknowledgements We would like to thank Dr F J Fletcher, Mr G Henderson and especially Mr M Savage at Cooksons Minerals Ltd who helped with the preparation of the formulations and with the LOI and smoke density determinations. Professor A J Carty of the University of Waterloo, Ontario, Canada kindly supplied samples of monocetyl- and monoformyl-ferrocene. Dr B Adger of Great Lakes Chemical (Europe) Ltd kindly supplied copious quantities of the aromatic aldehydes used in the synthesis of the organometallic compounds. Finally we thank Dr D Booth and Dr M S Byrne of Newcastle Polytechnic without whose help, encouragement and support this work would not have been possible.

REFERENCES

1. Toyooka, Y, Deguchi, A and Kimura, A Japan Kokai Tokkyo Koho JP 63/210155 A2 [88/210155], August 1988
2. Kolesov, S V, Neboikova, I V, Akhmetkanov, R M, Ableev, R I and Minsker, K S *Plant. Massy*, 1988, 11: 26
3. Mishima, Y, Shibata, T and Takao, N F Japan Kokai Tokkyo Koho JP 62/39653 A2 [87/39653], February 1987
4. Coleman, J F and Dannis, M L Canadian Patent CA1014690, July 1977
5. Crawford, R J *Plastics Engineering*, 2nd edn, Pergamon Press, Oxford, 1987, p 347
6. Troitzsch, J *International Plastics Flammability Handbook*, Carl Hanser Verlag, 1983, p 349
7. Hirschler, M M *J. Fire Sciences*, 1987, 5: 289
8. Confidential Research Report, Cooksons Minerals, 1987
9. Carty, P, Grant, J and Simpson A *Appl. Organomet. Chem.*, 1988, 2: 277
10. Carty, P and Docherty, A *Fire and Materials*, 1988, 12: 109
11. Carty, and Adger, B M *Appl. Organomet. Chem.*, 1990, 4: 127
12. Markezich, R L Int. Prog. Fire Saf. Paper 17–27. Fire Retard. Chem Assoc., Lancaster, PA, 1987
13. Brauman, S K *J. Fire Retardant Chem.*, 1980, 7: 161
14. Krishnan, S, Price, R J European Patent Application EP 212411, 1986
15. Rosenblum, M *The Chemistry of the Iron Group Metallocenes*, Wiley, New York, 1965, p 81

16. Troitzsch, J *International Plastics Flammability Handbook*, Carl Hanser Verlag, Munchen, 1983, pp 183, 394
17. Standard test method for specific optical density of smoke generated by solid materials. American Society for Testing and materials (ASTM) Publication E662-83, p 28
18. Maahs, G and Schuler, R *J. Fire and Flammability*, 1981, 12: 281
19. Parts, L P, Dayton, P and Miller, J T US Patent US 3766157, 1973
20. Jacobs, M I *J. Fire and Flammability*, 1975, 6: 347