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# Iron-containing organometallic compounds as flame-retarding/smoke-suppressing additives for semi-rigid poly(vinyl chloride)

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**The incorporation of a range of iron-containing organometallic compounds into a cable and wire poly(vinyl chloride) (PVC) formulation has been investigated. Limiting Oxygen Index and smoke density data were obtained across a range of formulations and the effects of the compounds on flammability and smoke generation are discussed. All the organoiron compounds markedly reduce smoke formation and some of them synergistically reduce the flammability of the polymer.**

**Keywords: Flame retardant, smoke suppressant, iron-containing organometallics, poly(vinyl chloride), cable, Limiting Oxygen Index, smoke density**

## INTRODUCTION

In the interests of society generally, it is necessary to provide a reasonable level of protection against hazards, but in spite of increased legislation, fire continues to take an unacceptable toll in loss of life and damage to property in the UK and elsewhere. During the period July 1986 to June 1987 in the UK alone, there were 206 fires, each with damage costs in excess of £250 000. The total loss in these fires was £228 381 000 and the total loss in all fires in the UK during this period was £461 700 000. The cost of fires to UK society is therefore very high and if the loss in international terms were calculated, the total loss of life and property would probably be proportionately severe.

In the past antimony(III) oxide ($Sb_2O_3$) in conjunction with a chlorinated or brominated organic compound has been used as a very successful flame-retarding system for a wide range of applications, although the high cost and limited availability of the antimony ore has led many organizations to look for cheaper, more cost-effective alternatives. There has recently been an increasing concern not only for making polymeric materials less flammable, but also in reducing the smoke they produce during combustion. Three elements in particular have significant smoke-suppressing activity in the PVC system, namely zinc, molybdenum and iron, but each of these elements has problems associated with its use in commercial polymer formulations. Zinc oxide (ZnO), although having very effective smoke-suppressing properties, tends to degrade PVC rapidly at elevated temperatures. Molybdenum oxide ($MoO_3$) is also a very effective smoke suppressant in PVC but its high cost has prevented it from being used commercially in large quantities.[1] Several iron-containing compounds, especially iron(III) oxide ($Fe_2O_3$), are known to reduce the amount of smoke produced from burning PVC, but as iron oxides are coloured, commercial exploitation of these compounds has been severely restricted.

We have recently reported[2] the effects of several inorganic and organometallic iron-containing compounds on the flammability of PVC and have observed synergistic effects in several cases. It is the purpose of this paper to report on further work which we have carried out with a wider range of organometallic compounds.

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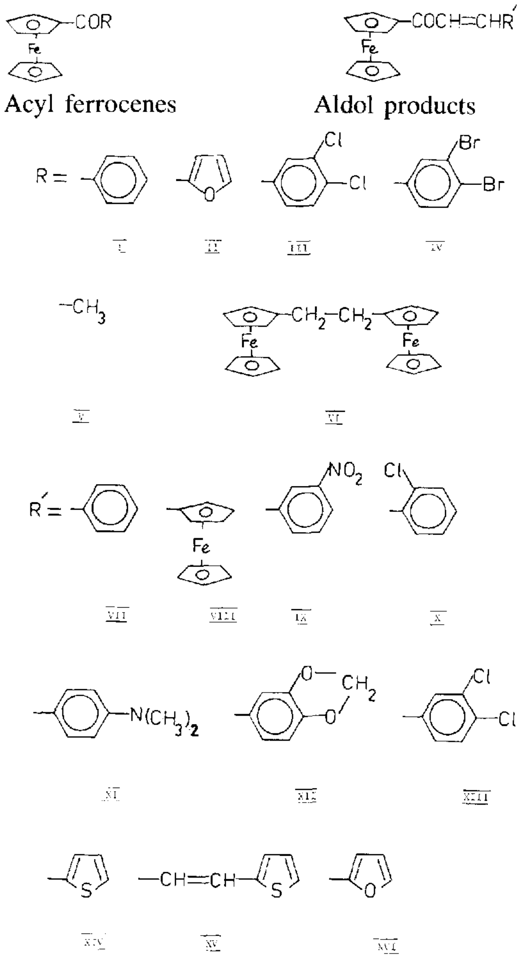
## EXPERIMENTAL

### 1 Compounds examined

The following compounds were examined in this work. Simple ferrocenyl ketones were easily prepared by Friedel–Crafts acylation of ferrocene using the appropriate acid chloride. Unsaturated ferrocenyl ketones were prepared in high yield via an Aldol reaction of aromatic aldehydes with monoacetylferrocene.[3] 1,2-diferrocenylethane was purchased from Aldrich. The acyl ferrocenes all have the general formula FcCOR, where Fc = ($\eta$-$C_5H_5$)Fe($\eta$-$C_5H_4$COR) and the Aldol products can be represented by the formula FcCOCH=CHR as shown in Scheme 1.



Scheme 1

### 2 Polymer system

A typical semi-rigid PVC wire and cable formulation was employed. Proportions are stated as phr (parts per hundred PVC resin).

| | |
|---|---|
| Breon (BP PVC grade S110/10) | 100 |
| Dioctyl phthalate<br>[di-(2-ethylhexyl)phthalate] (plasticiser) | 30 |
| Tribasic lead sulphate (stabilizer) | 5 |
| Calcium stearate (lubricant) | 1 |

### 3 Limiting Oxygen Index (LOI) and National Bureau of Standards (NBS) smoke determinations[4]

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

Smoke values were determined using an Aminco smoke density chamber to ASTM E-662-83 (BS 6401) in the flaming mode and the figures quoted in Table 1 represent an average value from two burns; wherever two values were not within one decade on the recorder further samples 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.

Standard samples were used for NBS smoke density determinations throughout with a thickness of 1 mm. As the relationship between smoke density and sample thickness is not linear, every attempt was made to standardize sample dimensions in all of these tests.

## RESULTS

Table 1 shows:

(i) the formulations investigated with varying levels of additives present.

(ii) The LOI and $D_{\max}$ (corr.) smoke values and the changes ($\delta$) in LOI and smoke values with respect to a control formulation containing no additives.

Table 1

| Compound | Formulation | LOI | $\delta$LOI | $D_{\text{max}}$ (corr.) | $\delta D_{\text{max}}$ (corr.)(%) |
|---|---|---|---|---|---|
| | Control | 27.7 | – | 460 | – |
| **I** | Control + 1 phr **I** | 32.6 | +4.9 | 304 | −34 |
| | Control + 5 phr **I** | 32.8 | +5.1 | 308 | −33 |
| **II** | Control + 1 phr **II** | 31.0 | +3.3 | 239 | −48 |
| | Control + 5 phr **II** | 30.8 | +3.1 | 253 | −45 |
| **III** | Control + 1 phr **III** | 28.9 | +1.2 | 239 | −48 |
| | Control + 5 phr **III** | – | – | – | – |
| **IV** | Control + 1 phr **IV** | 29.9 | +2.2 | 258 | −44 |
| | Control + 5 phr **IV** | – | – | – | – |
| **V** | Control + 1 phr **V** | 29.8 | +2.1 | 294 | −36 |
| | Control + 5 phr **V** | 28.9 | +1.2 | 258 | −44 |
| **VI** | Control + 1 phr **VI** | 32.0 | +4.3 | 317 | −31 |
| | Control + 5 phr **VI** | 32.0 | +4.3 | 354 | −23 |
| **VII** | Control + 2 phr **VII** | 30.4 | +2.7 | 313 | −32 |
| | Control + 5 phr **VII** | 31.5 | +3.8 | 327 | −29 |
| **VIII** | Control + 1 phr **VIII** | 29.9 | +2.3 | 253 | −45 |
| | Control + 5 phr **VIII** | 30.5 | +2.9 | 290 | −37 |
| **IX** | Control + 1 phr **IX** | 29.9 | +2.2 | 279 | −41 |
| | Control + 5 phr **IX** | 29.7 | +2.0 | 238 | −50 |
| **X** | Control + 1 phr **X** | 30.8 | +3.1 | 288 | −39 |
| | Control + 5 phr **X** | 31.7 | +4.0 | 273 | −43 |
| **XI** | Control + 1 phr **XI** | 31.6 | +3.9 | 354 | −25 |
| | Control + 5 phr **XI** | 30.2 | +2.5 | 312 | −34 |
| **XII** | Control + 1 phr **XII** | 30.5 | +2.8 | 274 | −42 |
| | Control + 5 phr **XII** | 30.7 | +3.0 | 241 | −49 |
| **XIII** | Control + 1 phr **XIII** | 30.5 | +2.8 | 268 | −44 |
| | Control + 5 phr **XIII** | 30.8 | +3.1 | 219 | −54 |
| **XIV** | Control + 1 phr **XIV** | 30.8 | +3.1 | 233 | −51 |
| | Control + 5 phr **XIV** | 31.7 | +4.4 | 232 | −51 |
| **XV** | Control + 1 phr **XV** | 30.9 | +3.2 | 298 | −37 |
| | Control + 5 phr **XV** | 31.6 | +3.5 | 250 | −47 |
| **XVI** | Control + 1 phr **XVI** | 31.8 | +4.1 | 234 | −40 |
| | Control + 5 phr **XVI** | 31.1 | +3.4 | 233 | −50 |

## DISCUSSION

The data in Table 1 represent a summary of the LOI and smoke density results which have been obtained. A detailed examination of Table 1 shows some interesting variations but we will only discuss those results which either have potential commercial significance, or which may be of interest because of the fundamental chemistry involved.

### Flammability

Benzoyl ferrocene (**I**) (Scheme 1), 1,2-diferrocenylethane (**VI**) and the Aldol products **X, XIV** and **XVI** raise the LOI of this wire and cable formulation by between four and five LOI units, some of the compounds being particularly effective at the lower (1 phr) level. The Aldol product prepared from monoacetylferrocene and furfural (**XVI**) benzoyl ferrocene (**I**) and 1,2-diferrocenylethane (**VI**) are as effective as the widely used antimony trioxide flame retardant for PVC. Antimony oxide at 2.5 phr will raise the LOI in this formulation by about five LOI units (for comparisons see Table 1). It is also pertinent to this discussion to mention that iron(III) oxide itself has little effect on the LOI. At 1 phr, iron(III) oxide has no effect on polymer flammability and at the higher level the effect is minimal, raising the LOI by 2–2.5 LOI units.[2]

It is interesting to speculate how these organometallic iron-containing compounds are acting as flame retardants in this PVC system. From our results it would appear that by modifying the structures of the organometallic compounds, both positive and negative flame-retarding effects can be observed. For example, the Aldol compound **XVI** is rather more active than the simple ketone **II**, but in the case of the benzoyl derivatives **I** and **VII** the reverse is true; here the Aldol compound **VII** is markedly less effective as a flame retardant than the simple benzoyl derivative **I**. With the halogen-containing compounds we also obtained unexpected results. The fact that chlorine is a flame retardant can be readily deduced from the fact that chlorine-containing polymers have low flammability and in most systems the bromine compound is more effective than the equivalent chlorine-containing compound. A single chlorine atom *ortho* to the point of attachment of the benzene ring to the ferrocenyl moiety (i.e. compound **X**) is more active than similar compounds which contain two chlorine atoms in the 3- and 4-positions on the benzene ring, i.e. compounds **III** and **IV** respectively, but the 3,4-dichloro Aldol compound **XIII** is more effective than the ketone **III** which also has a 3,4-dichloro pattern of substitution. Obviously in these compounds the chemical nature of the environment surrounding the halogen atoms is important. Organometallic compounds which contain five-membered rings in the side chain are particularly effective flame retardants in PVC. They generally raise the LOI by more than three LOI units at a loading of 1 phr and greater than four LOI units at 5 phr.

Brauman[5] has investigated the effect of iron compounds in rigid PVC and Cullis[6] has examined the flame-retarding effects of ferrocene and Cereclor (ICI Ltd) in polypropylene. Markezich[7] has published data on potential commercial application of iron oxides as flame retardants in polyamide formulations. Hirschler has recently reviewed the effects of metal oxides acting as smoke suppressants[8] in a range of polymers, and other work with iron compounds in related polymers[9,10] suggests that the active species is iron(III) chloride ($FeCl_3$) generated from the iron compound reacting with hydrogen chloride (HCl) produced from the decomposing PVC. Although iron oxides have been positively identified as being present in the char residues from fire tests and also as the final product formed during Differential Thermal or Thermogravimetric Analysis (DTA/TGA) experiments on some related iron organometallics,[11] the role of iron(III) chloride as the active flame-retardant species has been questioned. Cullis[6] has unequivocally established that in polypropylene, maximum flame retardancy is not achieved when the chlorine:iron ratio is 3:1 in the formulation; indeed, he has found that a very much higher chlorine:iron ratio is required (i.e. 40:1) to maximize the flame-retarding effect of these two elements. We established that when anhydrous iron(III) chloride is carefully compounded into this semi-rigid PVC system the effect on the LOI is marginal. At 1 phr the LOI is 28.5 and at 5 phr the LOI is raised by about 3.5 LOI units.[12]

Hirschler[8] has also mentioned that iron(III) oxide has limited effectiveness as a flame retardant and also that iron(III) chloride is involatile in polymer formulations. If iron(III) chloride itself is not the major flame-retarding species it is likely that hydrogen chloride, organic or organoiron species could be responsible for the flame-retarding effect of these organometallic compounds. We reported[11] the results of some thermal analysis work on a related ferrocenium species (albeit in the absence of PVC) and we identified cyclopentadiene ($C_5H_6$, cpH) as being one of the major decomposition products. Volatile cyclopentadiene and possibly $(Cl)_x$Fecp species are likely to be formed in burning or thermally decomposing PVC when these additives are present. However, it is still far from clear that either iron(III) chloride, hydrogen chloride, organic or organoiron species are responsible for the flame-retarding effect observed with these compounds.

Several years ago, using thermal analysis methods, Smith[13] proposed that iron(III) chloride initiated cross-linking reactions in PVC. High concentrations of iron(III) oxide in PVC produced inactive iron(II) chloride, ($FeCl_2$) but at low concentrations (down to 0.1%) iron(III) chloride ($FeCl_3$) and hydrogen chloride are formed. These conclusions lend support to our data. At 5 phr the flame-retarding effect of the organometallic compounds is only marginally better than at 1 phr. Calculations confirm that in a 7 g sample of polymer containing iron(III) oxide at 1 phr, 50 mg of iron(III) chloride will be produced (assuming a 100% conversion). The effects of the iron(III) chloride must therefore be catalytic and be active in condensed-phase reactions only. This effect would explain some of Brauman's observations (see below). We would propose that in this polymer system the flame-retarding entity is hydrogen chloride, its formation being promoted by the organometallic compounds themselves or by some derived organoiron species formed during decomposition of the PVC.

### Smoke suppression

Examination of Table 1 shows quite a wide variation in the values of $D_{max}$ obtained. All these compounds reduce the amount of smoke produced during the burning of PVC as measured in the NBS smoke density chamber. The smoke-suppressing effect may be a purely physical one. Volatility of the compounds and thermal decomposition effects also must be taken into account. Ferrocene, which is itself highly volatile, is not the most effective organometallic smoke suppressant[2] and mechanisms of smoke/particle generation during the combustion of polymers have been the subject of much research work. Polymer structure is important; structures containing aliphatic backbones, e.g. polyolefins, polyamides and poly(methyl methacrylate) etc., generate low levels of smoke during burning. Polymers with aromatic groups in the side chain (or which generate aromatics during decomposition) give high smoke densities. When the aromatic groups are present in the main chains, smoke values are intermediate. Cross-linking and char formation in condensed-phase reactions are also very important features and those compounds which promote cross-linking and enhance char formation have been identified by many workers. Brauman suggested that char formation by metal halides or oxyhalides tends to correlate fairly well with Lewis acid strength. In an earlier paper we reported that iron(III) oxide is as effective as other iron-containing compounds in reducing the smoke produced from burning PVC in flaming conditions but, as we have outlined earlier, iron(III) oxide has no effect in reducing the flammability of this formulation. The Aldol organometallics investigated in this work are undoubtedly good smoke-suppressant additives and they probably act by promoting char formation. Char formation by cross-linking involves the reaction of unsaturated systems in PVC[15] but the high values of smoke suppression shown by compounds **II**, **III** and **IV**, which do not contain carbon–carbon double bonds, is inconsistent and compound **XV**, which has a conjugated system spread over at least five carbon atoms, is only moderate-to-good in its smoke-suppressing action in this system. It is actually no better than those compounds which do not contain unsaturated groupings. More work needs to be done to explain these findings.

## CONCLUSION

This work has identified several organoiron compounds which will synergistically improve the flame retardancy and reduce the level of smoke produced during burning of PVC. Whether or not these compounds will be used commercially is a matter of economics. The colours of these compounds also make them unsuitable for use in plastics which need to be transparent or to be available in white, but it is possible to mask the colours of the compounds in the formulation by using white pigments with a high tinting strength. In line with increased emphasis on fire safety by governments throughout the world these organometallic compounds should be investigated further in order to establish the mechanism of their effects on burning and smoke-producing reactions in this polymer system.

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