Flame Retardance and Smoke Suppression of Poly(vinyl chloride) Using Multicomponent Systems

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Abstract. Metal-based organic complexes (MBO) are a class of FRSS additives that comprise a transition metal and an organic ligand that cleaves at an elevated temperature thereby releasing the metal in a reactive state. They help in the formation of char and thus act as an effective smoke suppressant. Use of MBO complexes as flame retardant smoke suppressants, phosphate ester as a flame retardant and active filler as endothermic material is reported here as multicomponent FRSS systems. MBOs used in the present study are the chelates of pentanediono. They were used alone as well as in combination with aluminum trihydrate (ATH) as filler were used to impart flame retardancy and smoke suppression to poly vinylchloride. Their performance was measured in terms of flammability, smoke generation, char formation and evolution of combustion gases. MBOs of molybdenum and chromium were found to be very efficient flame retardant smoke suppressants.

Introduction

Flame retardants make a very significant contribution in reducing the likelihood of ignition and also in limiting the growth and spread of fire, even though they are not so effective in fully developed fires. Use of flame retardant additives can decrease the overall fire hazard of the product containing them thus leading to an increase in overall fire safety. Smoke development from PVC has long been considered to be one of its weakest characteristics. The improvements in smoke suppression have played a vital role in acceptance of new PVC materials for various applications. Flame retardancy and smoke suppression in polymeric materials are usually achieved by incorporation of suitable additives. Perhaps the most critical smoke suppression has come from use of multi additive formulations comprising phosphate ester plasticizers in combination with metal based additives and hydrated oxides. Hirschler [1] has reported large-scale studies on several lining materials including PVC modified by multi compoñent systems. Modified PVC was found to produce lower levels of heat release as well as smoke generation when compared to wooden panels. Comprehensive reviews on flame retardance and smoke suppression of poly(vinyl chloride) have been published [2–4]. Of the large number of suppressants reported in the literature, it is the reactive additives that form the most widely applicable and diverse group that includes oxides and other compounds of transition metals. These additives act both in the vapor and

the condensed phase processes that include promotion of the protective char layer formation, soot oxidation or production of such species that inhibit the radical chain reactions in the vapor phase. Polymer combustion involves thermal degradation of the solid matrix to the liquid and the gaseous components. The zone corresponding to the formation of volatile decomposition products from the semi decomposed substrate is the interphase where most of the initial reactions take place, particularly the action of additives such as flame retardants and smoke suppressants.

PVC decomposes by a chain stripping mechanism to leave a polyene backbone. It is this polyene structure that gives off abundant soot via the production of cyclic, (mainly aromatic) hydrocarbons. A solid phase consisting of carbonaceous residue or char is also formed simultaneously. In flaming combustion of PVC, after the dehydrochlorination further thermal decomposition occurs resulting in small aliphatic hydrocarbons, which gradually build up, to soot or polycyclic aromatic hydrocarbons [5]. In case of plasticised PVC formulations, degradation of plasticizer and formation of HCl play an important role in the formation of smoke during thermal degradation [6]. In the presence of transition metal complexes, nearly all polyenes formed are catalytically converted to trans isomers, which in turn are converted to carbonaceous char. There are basically three mechanisms by which formation of char reduces flammability (1) part of carbon stays in the condensed phase, thus reducing the amount of gaseous combustible degradation products evolved (2) low thermal conductivity of the char layer over the exposed surface acts as thermal insulation to protect the virgin polymer underneath and (3) a dense char acts as a physical barrier to gaseous combustion products.

Although several flame-retardant systems have been developed for use in polymers, many of these are known to increase the amount of smoke and toxic gases generated by them. Kashiwagi et al. have reported use of silica gel in combination with potassium carbonate for a wide variety of polymers such as PP, PMMA, PVA, Cellulose, Nylone, PS SAN etc. They observed flame retardancy without any adverse effect on smoke and CO generation [7, 8]. Metal-based complexes have certain detrimental effects associated with them. Molybdenum compounds destabilize the color of PVC and under certain circumstances even hurt the dynamic heat stability. Zinc as borates, oxides or stannates can also reduce the thermal stability. Aluminum and magnesium containing compounds can reduce processability and affect physical properties at normal levels required for FRSS. One way to reduce the detrimental effects of the individual elements and capitalize on the fire, smoke and synergistic attributes is by the formation of complexes that have extremely good dispersion characteristics in the polymer. Metal-based organic complexes are one such class of transition metal-based chelates that have good uniform dispersion in the polymer matrix. Their use in combination with other additives (multi component System) is all the more advantageous.

Metal-Based Organic Complexes

Metal-based organic complexes are a class of FRSS additives that comprise a transition metal and an organic ligand that cleaves at an elevated temperature thereby releasing the metal in a reactive state. These additives limit the polyene length, thereby restricting intramolecular cyclization. Organometallic complexes are known to affect the initial stages of polymer degradation because they release the metal in a reactive state for its action as a flame retardant

smoke suppressant (FRSS) additive. They help in the formation of char and thus act as an effective smoke suppressant. This efficacy could be ascribed to their better miscibility with the polymer. Dicyclopentanedienyl Iron (Ferrocene) was the first MBO that was widely acknowledged as a flame retardant smoke suppressant for poly(vinyl chloride). Essentially all of the effective metal-based smoke suppressants appear to work in solid phase and interfere with the normal degradation pattern of PVC. Metal based organic complexes cause incandescence of char residue left after dehydrochlorination in the temperature range of 350–450°C. This phenomenon parallels quantitative carbon monoxide and carbon dioxide formation whereas such products are normally formed at temperatures higher than 500°C for pure PVC [9].

Flame retardant smoke suppressant efficiency of MBOs is increased because they are spread much more evenly through the polymer system in a smaller amount. Being tied up to the organic ligand (in the complex) until thermal breakdown occurs at the elevated temperature of real fire or a fire test condition dramatically reduces the detrimental activity of the individual element. The efficiency of an additive is dependent on at least three factors: its ability to be well dispersed within the PVC polymer, its reaction with HCl (the concentration of which might be large inside the solid during the initial phase of the fire), and the ability of its reaction products with HCl to be oxidized to provide an efficient catalyst at the temperature where smoke formation takes place. Pentanediono complexes (acetylacetonates) have been found to be the most efficient FRSS additives for PVC. This can partially be ascribed to the better miscibility of these organometalic compounds with a polymer.

Pentanedione (acac) complexes of molybdenum, vanadium, chromium and cobalt were synthesized using 2,4 pentanedione (acetylacetone) [10]. In each case the hydrogen of the hydroxyl group of the enol form of the 1,3 diketone was replaced by metal, resulting in the formation of a chelate ring. The general formula being: $M^{+n} (C_5H_7O_2)_n$
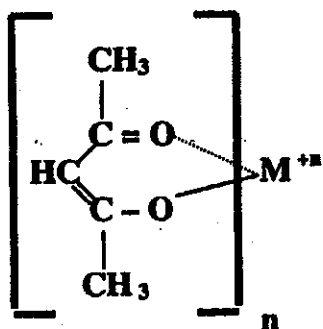
Where 'M' represents the metal (Mo, V, Cr, Co) having a valency 'n'.

Multicomponent System

Multicomponent fire-retardant systems normally take advantage of several fire retardant mechanisms. One of the most important of these is the concept of what some call chemically combined water in a dry system [11]. Well-known materials of this type are ATH and magnesium hydroxide. When raised above the decomposition temperature, the endothermic compounds with hydroxyl groups sacrificially break down; creating considerable absorption

of heat that takes away from the heat available to decompose a polymer system into the low molecular weight fuel gases that support the combustion; thus retarding the polymer burning process. The by-products of decomposition are simply anhydrous oxides and water. Advances have been made in optimizing the leading low-smoke flame retardant chemistry for PVC by combining char-forming and endothermic mechanisms. Because the metal based additive-induced type of char formation does not inhibit other fire retardant mechanisms, MBOs were used with other FR additives (like those active in gas phase and endothermic materials) to enhance their efficacy and reduce smoke. In the present communication, we have attempted the use of a flame retardant plasticizer, metal-based organic complexes and the endothermic filler ATH.
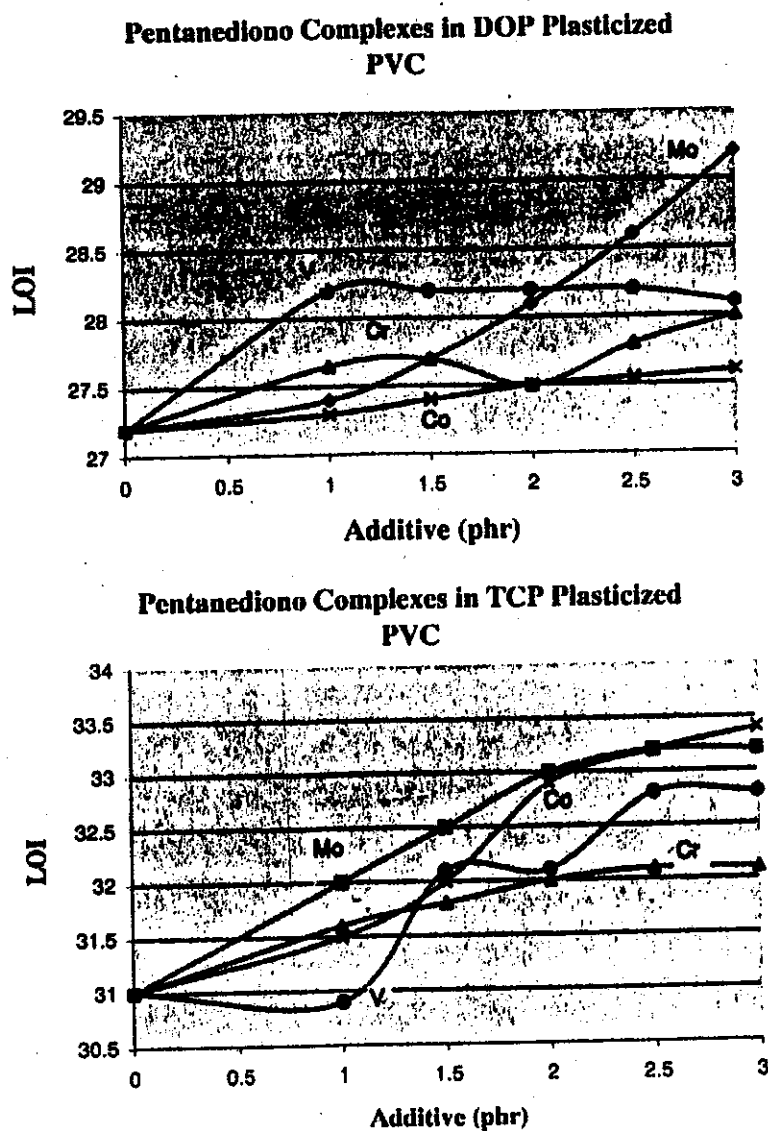
Preparation of Specimens

All specimens of Poly(vinyl chloride) used in this study were prepared in the laboratory. Virgin PVC resin having less than 0.1 ppm of vinyl chloride monomer and glass transition (T_g) temperature of 78°C was used. Specimens were prepared by mixing virgin resin with different ingredients including phthalate or phosphate esters as plasticizers [50 phr (Parts per hundred parts of resin)] Ba-Cd stabilizer, dibutyl tin dilaurate [1 phr] and epoxidised soya bean oil and stearic acid as heat stabilizers and lubricants [2 phr] and FRSS [0–3 phr]. A sample without any additive was used as the control or the reference sample and its results were used for computation of smoke suppression index (SSI). Based on earlier experiments, 60 phr of aluminum trihydrate (ATH) was found optimum and thus used in the present study for preparation of specimens incorporating multi-component systems.

Dry chemicals were mixed thoroughly in a dry blender. Liquids such as lubricants, stabilizers and plasticizers were then added slowly and the mixing continued till a uniform consistency of the mix was obtained in the form of a free flowing powder. The dry mix thus obtained was masticated on an electrically heated two-roll mill, having rollers of 6-inch diameter and length of 12 inches. The temperature and duration of mixing was dependent on the formulation. However, a temperature in the range of 140–150°C and the duration of 5 to 10 minutes was found optimum for most of the cases. Masticated mix was obtained in the form of sheets of non-uniform dimensions. These were molded into sheets of 300 mm × 150 mm using a compression-molding machine at 175°C, followed by slow cooling.

Methodology

The effect of FRSS additives on the combustion of the polymer was studied in terms of flammability (Figure 1), smoke generation (Figure 2) and char formation (Figure 3). Flammability was studied using the Limiting Oxygen Index (LOI) test apparatus as per ASTM D 2863. The smoke generation and hence the effect of FRSS additives on smoke suppression was estimated in terms of a smoke suppression index (SSI—a dimensionless quantity) using a dynamic method employing LOI apparatus for combustion of the test specimen [12]. Specimen was burnt for three minutes at an oxygen concentration that was 2% higher than the LOI value of that specimen. The smoke evolved was allowed to flow

Pentanediono Complexes in DOP Plasticized PVC

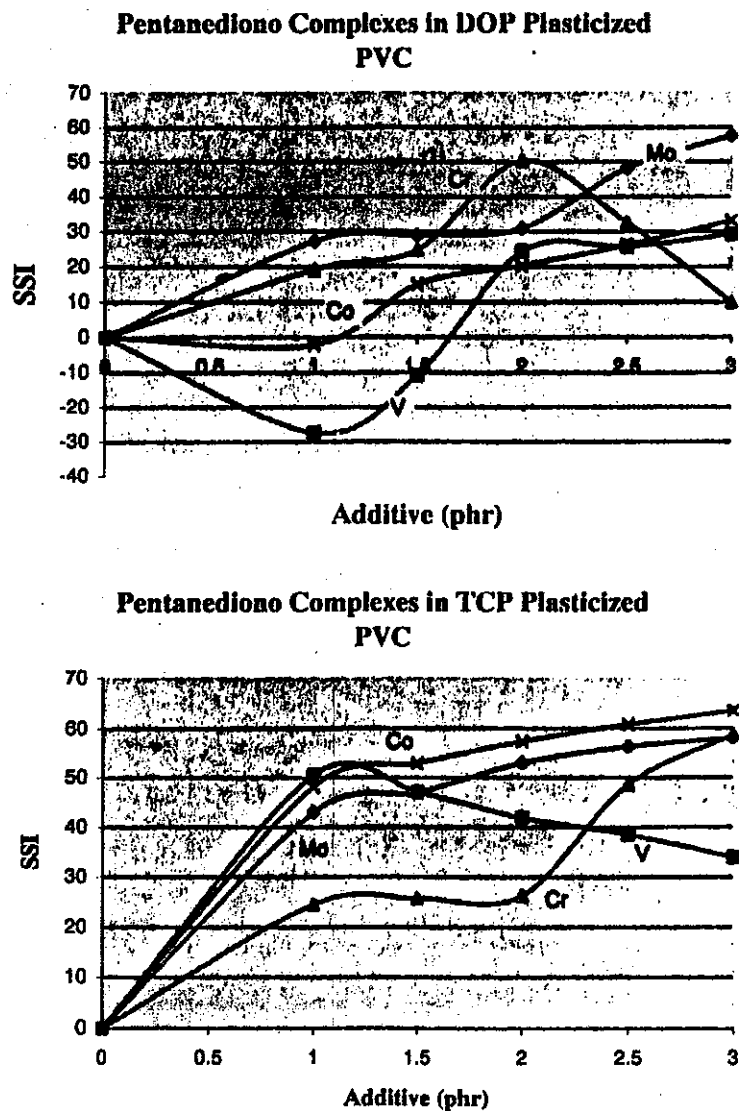

Pentanediono Complexes in TCP Plasticized PVC

Figure 1. Effect of organometallic complexes on limiting oxygen index in plasticized PVC.

through a duct. A He-Ne laser source and receiver were employed to measure the density of smoke flowing through the duct. Efficacy of smoke suppressant systems was calculated in terms of the Smoke Suppression Index (SSI) as follows:

$$SSI = \frac{A - A_t}{A} \times 100 \qquad (1)$$

Where

A = Area under the time vs. smoke density curve for the untreated sample/weight loss of the sample, and

A_t = Area under the time vs. smoke density curve for the treated sample/weight loss of the sample
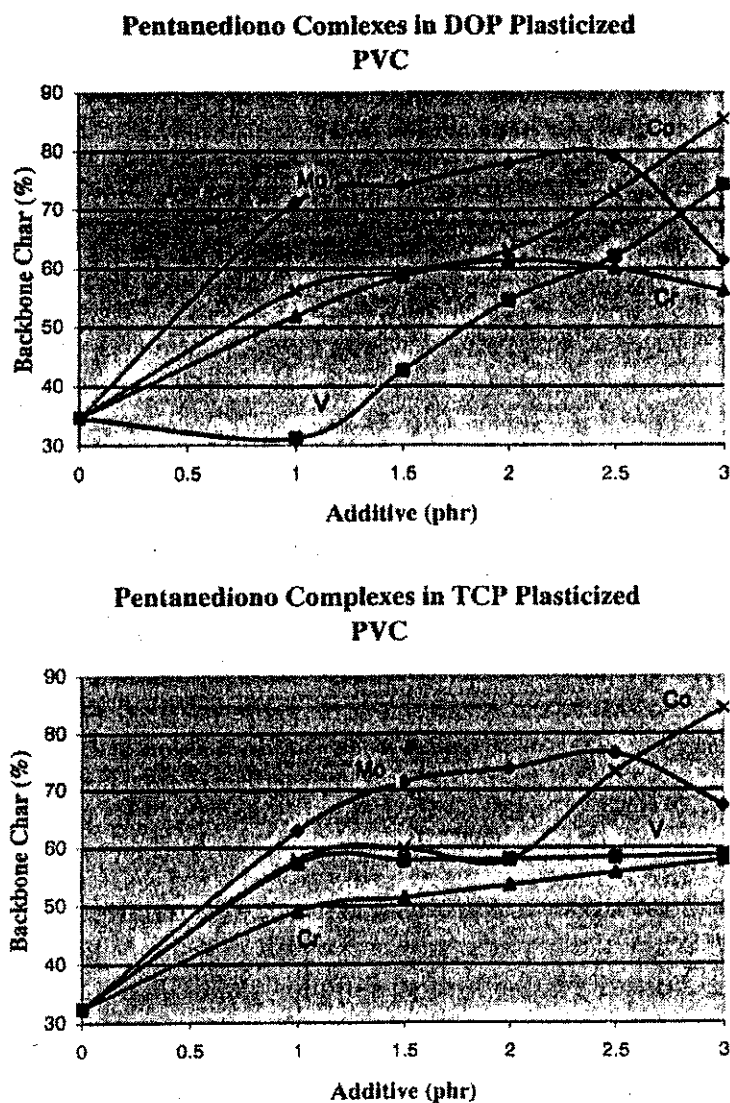
Pentanediono Complexes in DOP Plasticized PVC

Additive (phr)

Pentanediono Complexes in TCP Plasticized PVC

Additive (phr)

Figure 2. Effect of organometallic complexes on smoke suppression index in plasticized PVC.

Positive values of SSI (i.e. $S > S_t$) indicate reduction in amount of smoke generated whereas a negative value represents an increase.

The char formation was assessed using the oxygen index apparatus [13]. Since use of higher oxygen concentration for burning does not affect the burning of specimen appreciably. Thus the samples modified by the FRSS additives, which gave the best results in terms of flame retardance and smoke suppression, were exposed to burning conditions in an 'Oxygen Index' apparatus so as to produce char. The duration of exposure was three minutes and the oxygen concentration employed was 2% higher than the LOI value for that specimen. A wire gauge was placed beneath the specimen for collection of char. The specimen and char were carefully weighed before and after burning. The backbone char percentage (BC%) was computed as follow·

$$BC\% = \frac{Weight \quad char}{Wt \ of \ sample - Wt \ of \ non\text{-}PVC \ component - Wt \ of \ HCl} \times 100 \qquad (2)$$

Pentanediono Comlexes in DOP Plasticized PVC

Pentanediono Complexes in TCP Plasticized PVC

Figure 3. Effect of organometallic complexes on backbone char percentage in plasticized PVC.

Combustion gases i.e. carbon monoxide and carbon dioxide were measured by using infra red spectroscopic technique. Hydrocarbons were measured by employing a flame ionization detector.

Results and Discussions

Dioxobis(2,4 pentanediono) Molybdenum (VI)

The oxygen index values of samples modified by dioxobis(2,4 pentanediono) molybdenum (VI) indicate (Table 1) that the improvement in flame retardancy is directly proportional to the amount of additive used when the plasticizer was DOP. However, it is interesting to note that a maximum value for LOI (33.2) in the case of TCP plasticized samples was obtained when 2.5 phr of the additive was used. A further increase in its concentration does not cause any appreciable improvement in the fire retardancy of the sample.

TABLE 1
**Effect of Dioxobis(2,4 Pentanediono) Molybdenum (VI)
on Flame Retardance and Smoke Suppression of
Plasticized Poly(vinyl chloride)***

Sample	Phr	LOI	SSI	BC%	CO	CO$_2$
		SET I—DOP Plasticized Specimens				
Control	0.0	*27.2*	–	*34.79*	–	–
M$_1$	1.0	27.4	27.27	71.25	17	1150
M$_2$	1.5	27.7	28.88	74.31	17	1150
M$_3$	2.0	28.1	30.90	78.07	16	1150
M$_4$	2.5	28.6	48.18	79.11	22	1100
M$_5$	3.0	29.2	57.57	61.38	12	600
		SET II—TCP Plasticized Specimens				
Control	0.0	*31.0*	–	*32.45*	–	–
M$_6$	1.0	32.0	43.00	62.94	33	1250
M$_7$	1.5	32.5	46.99	71.40	40	1150
M$_8$	2.0	33.0	52.98	73.87	40	1100
M$_9$	2.5	33.2	56.30	76.49	62	1050
M$_{10}$	3.0	33.2	58.08	67.21	80	900

*The concentrations of CO and CO$_2$ reported are the peak concentrations over a three-minute test duration and are over and above the base line i.e. the concentrations observed in case of control samples. V acac, M acac, Cr acac and Co acac are the acetylacetonates (MBOs) of vanadium, molybdenum, chromium and cobalt respectively.

Smoke results indicate a constant decrease in smoke generation; i.e., an increase in SSI from 27.27 to 57.57 when the plasticizer used was DOP (Figure 2). Comparatively higher values of smoke are observed in the case of samples plasticized with the phosphate plasticizer. The SSI increased from 43.00 to 58.08 when the loading of the molybdenum complex was increased from 1 to 3 phr. This interesting feature tempts us to correlate this behaviour in terms of char formation (BC%) and evolution of combustion gases. Quantity of char is found to increase with the addition of additive upto 2.5 phr after which it shows a decrease. An increase in CO and CO$_2$ evolution was observed. Surprisingly the CO$_2$ concentration remained low, which goes unexplained. The amount of unsaturated hydrocarbons (C$_1$ to C$_5$) in the combustion gases was found to have increased from 10 ppm to 42 ppm in the case of DOP and from 12 ppm to 60 ppm in the case of TCP plasticized samples when the quantity of additive used is increased from 1 phr to 3 phr. A change in the degradation process, which results in lower aliphatics (C$_1$ to C$_5$) instead of crosslinking seems to be the reason for lower values of char when more than 2.5 phr of additive was used. Fire retardant behaviour (estimated in terms of LOI) and smoke suppressant behavior (estimated as smoke suppression index—SSI) of the molybdenum complex reveals that although the additive acts as a FRSS with both the plasticizers its overall performance is superior in the case of TCP plasticized PVC.

Bis(2,4 pentanediono) oxo Vanadium (IV)

This organometallic complex of vanadium (VO acac) has been reported [2] to be moderately effective in unplasticized PVC. However, it revealed interesting behavior when used in plasticized PVC. Samples of plasticized PVC (50 phr of DOP and TCP) were prepared by

TABLE 2
Effect of Bis(2,4 Pentanediono) Vanadium (IV) on Flame Retardance and Smoke Suppression on Plasticized Poly(vinyl chloride)*

Sample	Phr	LOI	SSI	BC%	CO	CO_2
SET I—DOP Plasticized Specimens						
Control	*0.0*	*27.2*	–	*34.79*	–	–
M_1	1.0	28.2	–27.30	31.29	13	850
M_2	1.5	28.2	–10.74	42.67	15	1050
M_3	2.0	28.2	24.37	54.60	18	1150
M_4	2.5	28.2	25.77	62.08	20	1200
M_5	3.0	28.1	39.13	74.29	23	1350
SET II—TCP Plasticized Specimens						
Control	*0.0*	*31.0*	–	*32.45*	–	–
M_6	1.0	30.9	50.59	57.31	8	850
M_7	1.5	32.1	47.09	57.56	9	850
M_8	2.0	32.1	41.90	57.97	12	950
M_9	2.5	32.8	38.57	58.30	14	1050
M_{10}	3.0	32.8	33.95	58.73	16	1100

*The concentrations of CO and CO_2 reported are the peak concentrations over a three-minute test duration and are over and above the base line i.e. the concentrations observed in case of control samples. V acac, M acac, Cr acac and Co acac are the acetylacetonates (MBOs) of vanadium, molybdenum, chromium and cobalt respectively.

incorporating 1–3 phr of the additive. The additive exerted no influence on the flammability of DOP plasticized PVC samples (Table 2) when used alone. The effect of the additive on flame retardancy in TCP plasticized samples was also marginal (LOI increases from 30.9 to 32.8) as shown in Figure 1.

Enhanced smoke generation, rather than smoke suppression, was observed when the additive was used in DOP plasticized PVC (Figure 2). However, further addition of the organometallic complex resulted in a corresponding increase in smoke suppression (Table 2). The effect on smoke suppression is not very different from that due to V_2O_5. This means that at least in the present case, the oxidation state of the metal is not important, even though the local environments around the vanadium atom in the two additives are very different. Char formation increased with the increase in quantity of the additive used. A predominantly condensed phase smoke suppression mechanism is thus indicated. Higher quantities of unsaturated hydrocarbons (90 ppm) indicate a change in the thermal decomposition mechanism. This is presumably the reason for the negative SSI at low additive levels.

Initially, when 1 phr of organometallic complex is employed in TCP plasticized samples, the SSI increases from 0 to 50.59 (Figure 2). Additional quantities of the complex result in a steady increase in smoke generation. Increasing the concentration of this additive does not seem to influence char formation (Figure 3). Afterglow, representative of the oxidation of char, is observed in all samples. Oxidation of char is also indicated by a concurrent increase in CO and CO_2 evolution from all the specimens, thereby suggesting a change in the decomposition process. Increasing the loading of the additive beyond 1 phr seems to have resulted in auto ignition of the mixed gases thereby resulting in an increase in the evolution of CO, CO_2 and smoke [14].

TABLE 3
**Effect of Tris(2,4 Pentanediono) Chromium (III) on
Flame Retardance and Smoke Suppression on
Plasticized Poly(vinyl chloride)***

Sample	Phr	LOI	SSI	BC%	CO	CO_2
		SET I—DOP Plasticized Specimens				
Control	*0.0*	*27.2*	–	*34.79*	–	–
M_1	1.0	27.6	19.19	51.93	20	1200
M_2	1.5	27.7	24.85	58.62	18	1300
M_3	2.0	27.5	50.30	61.43	20	1450
M_4	2.5	27.8	32.52	60.00	21	1400
M_5	3.0	28.0	09.09	56.27	24	1450
		SET II—TCP Plasticized Specimens				
Control	*0.0*	*31.0*	–	*32.45*	–	–
M_6	1.0	31.6	24.59	49.13	14	1150
M_7	1.5	31.8	25.80	51.30	17	1050
M_8	2.0	32.0	26.37	53.58	23	1000
M_9	2.5	32.1	48.57	55.71	20	900
M_{10}	3.0	32.1	58.75	57.79	18	850

*The concentrations of CO and CO_2 reported are the peak concentrations over a three-minute test duration and are over and above the base line i.e. the concentrations observed in case of control samples. V acac, M acac, Cr acac and Co acac are the acetylacetonates (MBOs) of vanadium, molybdenum, chromium and cobalt respectively.

Tris(2,4 pentanediono) Chromium (III)

Samples were prepared as before using 50 phr plasticizer and 1–3 phr of chromium based organometallic complex. The fire behaviour of samples plasticized with DOP and TCP and modified by the additive is reported in Table 3.

Samples plasticized by either of the plasticizers revealed an increase in flame retardancy with an increase in concentration of the chromium additive. While LOI for the DOP plasticized samples was found to have increased from 27.65 to 28.00 the increase in the case of TCP plasticized specimens was from 31.60 to 32.10 (Figure 1).

Smoke generation shows an overall trend of suppression vis a vis quantity of the complex used for both the DOP (Figure 1) and TCP plasticized samples (Figure 2). Phthalate plasticized samples reveal a maximum smoke suppression at 2 phr loading of the organometallic complex. A further increase in the additive concentration results in higher char formation, CO and CO_2 evolution but also higher smoke generation. An increase in smoke suppression was also observed in the case of TCP plasticized samples. The largest SSI values were at 2.5 phr and 3.0 phr levels.

. The reason for the above behavior could be that the complex interacts with phosphate (from TCP) to result in greater crosslinking while the phthalate plasticizer results in increased char in its own right. In DOP plasticized samples the char formation due to the additive (through crosslinking) seems to have been replaced (Figure 3) by a change in pyrolyzates reflected in an increased CO, CO_2 and hydrocarbon evolution.

FRSS performance of this additive was also studied using a cone calorimeter [15]. In this case DOZ (dioctyl azelate) was used as the plasticizer. The additive was found to be

effective in terms of ignition time, burning rate, heat release, combustion gas evolution (including CO, CO_2 and hydrocarbons) and smoke generation at 1 phr loading. The oxygen index was found to increase with the increase in the quantity of the additive used. However, further discussion of its performance will be out of context here as the formulation recipe used was different from the one reported here.

Tri(2,4 pentanediono) Cobalt (III)

Samples of plasticized PVC modified by tri(2,4 pentanediono) cobalt (III) were prepared using DOP and TCP plasticizers. The concentration of additive employed was 1–3 phr. The fire performance of these samples indicate that the organometallic complex has little effect on the flammability of the substrate, particularly in the presence of DOP plasticizer (Table 4). However, a steady increase in flame retardancy i.e. an increase in LOI from 31.5 to 33.4 was observed in the case of samples plasticized by TCP (Figure 1).

At 1.0 phr a slight increase in the smoke generation (SSI = −2.10) was perceived in the case of DOP plasticized samples. However, higher levels of additive lead to consistently lower smoke generation (Figure 2). An increase in SSI and char formation indicates a condensed phase mechanism. No afterglow was observed, hence it may be concluded that the complex did not act as a precursor to an oxidation catalyst. This conclusion is also supported by CO and CO_2 evolution data that indicate a lower amount of gaseous evolution.

It was observed that this organometallic complex induces oxidation of char (Table 4) when used in the presence of phosphate ester (TCP). The quantity of CO and CO_2 evolved was found to increase with the loading of the additive employed. Afterglow was observed

TABLE 4
Effect of Tris(2,4 Pentanediono) Cobalt (III) on Flame Retardance and Smoke Suppression on Plasticized Poly(vinyl chloride)*

Sample	Phr	LOI	SSI	BC%	CO	CO_2
SET I—DOP Plasticized Specimens						
Control	*0.0*	*27.2*	–	*34.79*	–	–
M_1	1.0	27.3	−2.10	56.22	10	1000
M_2	1.5	27.4	15.07	59.34	16	1050
M_3	2.0	27.5	20.40	63.08	23	1000
M_4	2.5	27.5	26.26	72.96	18	950
M_5	3.0	27.6	33.13	85.49	11	950
SET II—TCP Plasticized Specimens						
Control	*0.0*	*31.0*	–	*32.45*	–	–
M_6	1.0	31.5	48.24	57.97	20	900
M_7	1.5	32.0	52.90	59.77	22	950
M_8	2.0	32.9	57.35	57.86	25	1000
M_9	2.5	33.2	60.81	73.21	30	1050
M_{10}	3.0	33.4	63.54	84.43	34	1050

*The concentrations of CO and CO_2 reported are the peak concentrations over a three-minute test duration and are over and above the base line i.e. the concentrations observed in case of control samples. V acac, M acac, Cr acac and Co acac are the acetylacetonates (MBOs) of vanadium, molybdenum, chromium and cobalt respectively.

for a small duration and the amount of char formed was relatively high (57.97% to 84.43%). High levels of smoke suppression and char formation were observed (Figures 2 and 3) when increasing amounts of the cobalt based complex were used in the TCP plasticized PVC.

On the strength of the above results, it may be concluded that pentanediono complexes are generally effective smoke suppressants in the presence of phosphate plasticizer. ·

Multi-Component Systems

Metal based organic complexes of vanadium, molybdenum and chromium were used at 1 and 2 phr loadings along with 60 phr Aluminum trihydrate and 50 phr of tri cresyl phosphate (TCP) for preparation of samples. The above loadings of the MBO were selected as they are known to act as effective FRSS at low concentrations of 1–2 phr [10]. Fire performance of the samples thus modified was compared with reference to a 50 phr TCP plasticized sample without FRSS and ATH used as a control sample. Though addition of MBO results in a slight decrease in the LOI, the values are not very different from that of the control sample. A very important level of flame retardance and smoke suppression is observed in case of chromium and molybdenum complexes. All the specimens exhibited after glow there by indicating a condensed phase oxidation reaction. This results in lower quantities of char (Table 5) compared to the control sample. The carbon thus lost may account for either an increase in CO, CO_2 generation or ash formation or both. An associated increase in CO, CO_2 is also observed. However, as the experiments were carried out in an oxygen enriched atmosphere, resulting in more complete combustion of the samples, the amount of CO, CO_2 evolved was lower than what would have been otherwise. Although vanadium based MBO also acted as FRSS the efficacy of molybdenum and chromium based MBOs was definitely superior.

TABLE 5
Effect of Multi Component System of MBO and ATH on Flame Retardance and Smoke Suppression on Plasticized Poly(vinyl chloride)*

Sample	Phr	LOI	SSI	BC%[#]	CO	CO_2
Control	*0.0*	*40.1*	*67.74*	*141.25*	*5*	*700*
V acac	1.0	38.0	64.80	103.49	18	1050
V acac	2.0	38.2	72.65	111.38	14	950
M acac	1.0	38.3	81.07	99.81	15	1450
M acac	2.0	38.5	82.59	103.64	10	1400
Cr acac	1.0	38.4	82.70	121.58	15	1000
Cr acac	2.0	38.8	82.70	121.58	12	950

*The concentrations of CO and CO_2 reported are the peak concentrations over a three-minute test duration and are over and above the base line i.e. the concentrations observed in case of control samples. V acac, M acac, Cr acac and Co acac are the acetylacetonates (MBOs) of vanadium, molybdenum, chromium and cobalt respectively.

[#]BC% in case of samples filled with ATH appear to be > 100%. This is because the weight of the non-PVC components is much higher and so the denominator in Equation (2) above becomes very small, thus resulting in higher BC%.

As expected the use of multi component systems transformed an exothermic (fire propagating) system into an endothermic (fire retardant) one without any adverse consequences.

Conclusions

Multi component systems comprise of more than one active ingredient. These systems take advantage of more than one mechanism for achieving the end results. The only care one has to take while choosing the various components of the system is that the effect of one component should not be nullified by the other component; rather a synergistic effect is desirable. In the present study use of phosphate ester as flame retardant, metal-based organic complexes as smoke suppressants and active filler as endothermic material has been made. Advantage of char forming characteristic of MBOs and phosphate ester were exploited in presence of endothermic behavior of aluminum trihydrate. MBOs comprise a transition metal and an organic legend that cleaves at an elevated temperature thereby releasing the metal in a reactive state. These additives help in the formation of char and thus act as effective smoke suppressants. They are effective as flame retardant smoke suppressants because they act in condensed phase via char formation as well as precursors of oxidation catalyst for char. The presence of phosphate plasticizer has been found to play a definite role in enhancing the efficiency of the additive that acts in the condensed phase. Generally speaking, pentanediono complexes are effective smoke suppressants in the presence of phosphate plasticizer. Tris(2,4 pentanediono) cobalt (III) that revealed only a moderate improvement both in flame retardancy and smoke suppression when used with phthalate plasticizer was found to be very efficient smoke suppressant when phosphate plasticizer was used. As expected the use of multi component systems transformed an exothermic (fire propagating) system into an endothermic (fire retardant) one without any adverse consequences. Excellent smoke suppression (SSI ~ 83) was achievable.

Nomenclature

FRSS	Flame retardant smoke suppressant
MBO	Metal based organic complexes
ATH	Aluminum trihydrate
M_1–M_{10}	Sample 1 to 10
DOP	Dioctyl phthalate plasticizer
TCP	Tri cresyl phosphate plasticizer
Phr	Parts per hundred parts of resin
LOI	Limiting oxygen index
SSI	Smoke suppression index
BC%	Backbone char percentage
CO	Carbon monoxide gas
CO_2	Carbon dioxide gas
ppm	Parts per million
acac	Acetylacetonate (pentanediono) complex of the metal whose symbol precedes it

Acknowledgment

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