
Surface Coating and Metal-Based Organic Additives—Approaches for FRSS PVC Cables

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ABSTRACT: Polyvinyl chloride (PVC) is one of the most widely used polymers today. One of its major applications is in electrical and control cables. Although PVC is intrinsically self-extinguishing, it supports flame spread along its length because of the additives used during processing. The spread of fire along electrical cables may be alleviated either by using flame-retardant smoke-suppressant (FRSS) additives or by applying fire-retardant intumescent coatings to the surface of the cable sheath. The intumescent coating also acts as a fire-protective barrier for electrical cables. Plasticized PVC compositions incorporating a molybdenum-based organic (MBO) complex were prepared and evaluated for their fire performance. Excellent smoke suppression was observed in the specimens modified using the complex, which acts as an FRSS additive. The limiting oxygen index (LOI) was also found to be fairly high, particularly when the PVC samples were plasticized with a phosphate plasticizer. FRSS intumescent coatings were applied on PVC-sheathed electrical cables. Their fire performance was evaluated using national and international standard procedures. Significantly low levels of smoke generation was observed along with zero flame spread when the coated cables were exposed to standard test conditions. The formulations used in both the treatments – coating as well as additive – offer improved resistance to ignition, flame spread and smoke generation.

KEY WORDS: flame retardant, smoke suppressant, metal-based organic complex, intumescent, cable, coating, smoke, PVC, molybdenum.

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INTRODUCTION

THE EXTENSIVE USE of plastics has multiplied many folds the problem of fire and smoke. Many plastics that are combustible in nature burn rapidly, and some produce copious amounts of smoke. Polyvinyl chloride (PVC) is one of the most widely used polymeric materials today. It finds a wide range of applications in buildings and industries because of its many desirable properties. PVC has long been the base material of choice for insulating wires and cables. Large quantities of cables are being used because of the modern trends in construction and the growing need for electronic communication, as well as in industrial applications. Modern production facilities demand long runs of power and control cables all over the plant area. Any fire incidence in the vicinity of a cable may result in the initiation of fire at the cable surface, and the flames spread along it. Fire at the La Spezia power station in Italy in 1967 was a major accident, that drew attention towards the problem of fire protection of cables. It highlighted the fact that high cable densities with their larger fuel load of polymeric insulation and sheathing required much more protection than mere PVC.

Although it is intrinsically self-extinguishing, large amounts of smoke and other combustion products are evolved when PVC is forced to burn [1]. Rapid and unrestrained propagation of fire can be checked either by the addition of flame-retardant smoke-suppressant (FRSS) additives during the preparation of PVC sheets or by the application of an effective fire-retardant coating on the PVC-sheathed cables [2,3]. FRSS additives are mainly used during polymer processing, while coatings can be applied to the existing cable systems. Many FRSS systems for PVC have been reported in the literature [4-6]. PVC is combined with a variety of additives to improve upon the performance of several properties necessary for wire and cable sheathings. However, many of these additives result in a compromise in its fire performance.

Fire-retardant coatings can safely be grouped under two categories, the non-intumescent and the intumescent coatings. While the fire-retardant non-intumescent coatings comprise additives such as borax, boric acid, antimony trioxide, zinc oxide and chlorinated compounds that do not support combustion [3,6-8], the fire-retardant intumescent coatings are those that swell up on heating, due to the evolved gases. The resulting expanded residual carbonaceous matter forms a toughened insulating layer over the substrate, which protects it [6,9-12]. Several researchers have studied various fire-retardant coatings to find their efficacy for retardation of the burning of cellulosic

materials such as wood and wood-based products [3,6-13]. However, sufficient attention has not been paid toward the use of suitable coatings to impart fire protection to PVC-sheathed electric cables. This article deals with studies on the efficacy of FRSS additives in intumescent coatings for PVC-sheathed electrical cables and FRSS-modified PVC sheets, using cone calorimeter and other standard methods.

EXPERIMENTAL PROCEDURE

Preparation of Intumescent Coatings

Flame-retardant intumescent coatings were prepared by using different types of phosphates such as diammonium phosphate (Merck) and ammonium polyphosphate (Exolit AP 422, Clariant Produkte GmbH, Germany), amide dicyandiamide (Loba), polyol pentaerythritol (BDH, India) and binder (vinyl acetate/vinyl versatate copolymer emulsion from Vam Organics Chemicals Limited, India) in different weight ratios with a pentanediono complex of molybdenum (molybdenum acetylacetonate) (Table 1). The coatings were prepared by mixing ingredients of 325-400 mesh size with 2-5% solution of thickener along with appropriate quantity of wetting (Fynol EDA, Fine Organics, India), anti-setting (Antisett 117, Fine Organics, India)

Table 1. Compositions of Fire-retardant Intumescent Coatings.

Ingredients	Parts by weight for formulation numbers			
	1	2	3	4
Phosphate	14.0	12.0	15.5	17.0
Dicyandiamide	12.0	10.0	9.0	11.0
Pentaerythritol	10.0	12.0	14.0	8.0
Pigment	5.0	3.0	6.0	4.0
Thickener	0.30	0.30	0.24	0.24
Filler	8.0	9.0	6.0	10.0
Co-polymer emulsion	33.0	35.5	33.0	33.0
Molybdenum complex	2.0	2.0	2.0	2.0
Antifoaming, wetting and antissetting agents	0.20	0.20	0.26	0.16
Water	15.5	16.0	14.0	14.6

*Details of ingredients are given in the text.

and anti-foaming (Antifon-NXZ, Fine Organics, India) agents. The binder was modified by reacting with dimethyloldihydroxyethylene urea (DMDHEU) (HICOFOR, HICO Products, India) and a polymeric plasticizer (Reoplex 400, Hindustan Ciba-Geigy Ltd, India) to increase the adhesion to PVC as well as to improve the flexibility of the coating. An adequate quantity of the modified binder was added to the above contents to make a homogeneous mixture. A sufficient quantity of water was added to obtain brush consistency. The mix was stirred vigorously for 1 h with a heavy-duty stirrer.

The developed intumescent coating was applied by brush on a glass plate. A number of layers were applied to obtain a dry paint film thickness of 5 mm. The paint film was peeled off and cut into specimens of 100 mm × 100 mm for exposure to test conditions by a cone calorimeter. For all other tests on the coating, a sufficient number of coats was applied with a brush on PVC-insulated electrical cables to obtain different film thicknesses.

Preparation of PVC Specimens

Specimens were prepared by mixing virgin resin (having <math><0.1\text{ ppm}</math> of vinyl chloride monomers and glass transition (T_g) of 78°C —obtained from Shriram Chemical, India—with different ingredients including heat stabilizers and lubricants such as Ba-Cd stabilizer, dibutyl tin dilaurate and stearic acid. Dioxobis-(2,4-pentanedione) Molybdenum VI (molybdenum acetylacetonate) was synthesized by replacing the hydrogen of the hydroxyl group of the enol form of the 1,3-diketone by metal (Molybdenum VI), resulting in the formation of a chelate ring, adopting the method described by Moeller [14]. This complex was used as FRSS in the preparation of PVC specimens, and magnesium hydroxide was used as filler. The quantity of ingredients used was dependant on the design of the experiments (Table 2).

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 at $165\text{--}170^\circ\text{C}$ for 5–10 min, depending on the formulation. The masticated mix was molded into sheets of 300 mm × 150 mm using a compression-molding machine at 175°C , followed by slow cooling. Specimens were cut from the molded sheets (100 mm × 100 mm) for calorimetric studies using a cone calorimeter and 52 mm × 140 mm for flammability studies using a limiting oxygen index (LOI) apparatus.

Table 2. Recipe and processing conditions for plasticized poly (vinyl chloride) samples.

Ingredients	Composition (phr ^a)				
	1	2	3	4	5
PVC	100	100	100	100	100
Plasticizer	50	50	50	50	50
DBTDL	0.5	0.5	0.5	0.5	0.5
Pb _x (SO ₄) _y ^b	3	3	3	3	3
Stearic acid	0.1	0.1	0.1	0.1	0.1
Mg(OH) ₂	70	70	70	70	70
FRSS	0.0	0.5	1.0	2.0	3.0

Processing Conditions
 Dry blending at room temperature for 20 min
 Mastication on two-roll mill at 165°C for 10 min
 Compression molding at 175°C

^a Phr: parts per hundred parts of resin
^b x and y may or may not be equal

PERFORMANCE EVALUATION

Fire performance of the PVC sheet and intumescent coating was evaluated using Cone Calorimeter (ASTM E 1354, ISO 5660), NBS Smoke Density Chamber (ASTM E662), LOI (ASTM D 2863) and circuit failure time for electrical cables (IEC 331).

Evaluation of Coating

Different quantities of the developed coating were applied on PVC cables to achieve varying thicknesses and thus the effect of coating thickness on fire performance. Standard procedures were followed to determine the characteristics of the intumescent coating.

Physical Properties

Standard procedures were followed for the determination of physical properties such as color, specific gravity and flexibility of coatings. The results are reported in Table 3.

Cone Calorimetric Studies

The cone calorimeter used had a cone heater to provide irradiance levels of 10-100 KW/m². The hood and duct section ensured thorough

Table 3. Physical properties of coatings.

Color	Off white
Odor	Faint odor
Specific gravity	1.2-1.36
pH	6-8
Flexibility (As per IS:10810)	No cracking observed
Solid binder ratio	2.6-2.8
Volatile contents	30-32%
Covering capacity	2.25 kg/m ²

mixing and enabled continuous oxygen sampling and flow measurements the two measurements essential for estimating of the rate of heat release. Smoke density measurements were made by using helium-neon laser beam across the duct. Combustion products were estimated with the help of different gas analyzers. Multiple layers of the intumescent coating were applied on a glass plate to achieve dry film thickness of 5 mm. On drying, the film was peeled off, and samples of 100 mm × 100 mm were prepared from it. Samples were exposed in horizontal orientation at an irradiance level of 50 KW/m². The irradiance level used represent severe fire conditions. The various parameters measured are reported in Table 4.

Circuit Failure Time (as per IEC-331 Method)[15]

The fire-retardant intumescent coatings were applied on PVC insulated electric cables of different diameters. Specimens coated with different thicknesses were subjected to tests in order to assess the effect of coating thickness on fire retardancy. Circuit failure time was evaluated by the IEC 331 method. Three and a half core aluminum conductor PVC insulated armored cable specimens of length 1200 mm and having an outer diameter of 31 mm were used to determine the circuit failure time. The cables were coated with different amounts of coating to achieve 1.0 mm-3.0 mm dry coating thickness. A 100-mm sheath of outer covering of the cable was removed from each end of the specimens. At one end of the cable, the conductor wires were suitably connected for electrical connections and, at the other end, the exposed cores were spread apart to avoid contact with each other. The cable specimen was held horizontally by means of suitable clamps at each end of the sheathed portion. The middle portion of the cable was supported by two metal rings, placed approximately 300 mm apart, and all the metal parts of the supporting apparatus were properly earthed.

Table 4. Cone calorimeter results of FR coating.

Property	Average	Peak	Time, s
Time of ignition, ^a s	Does not ignite	Does not ignite	-
Flame out, s	0	0	-
Specific extinction area, (m ² /kg)	257.56	2784.13	55
Burning rate, (kg/M ² s × 10 ⁻²)	1.69	2.26	-
Heat release rate (KW/M ²)	5.63	10.20	48
Effective heat of combustion (MJ)	2.81	35.38	55
Mass loss rate (g/s)	0.022	0.0149	31
CO yield (kg/kg)	0.0012	0.0140	60
CO ₂ yield (kg/kg)	0.97	8.8	60

^aNo ignition here means flaming ignition was not observed.

The cores of the cable under test were connected to separate phases for obtaining three sets of connections to the three phases. Adjacent conductors were connected to different phases. The test was carried out in a chamber provided with proper means for disposing of gases resulting from the burning cable. A Tubol-type gas burner of 610 mm length was used to ignite the specimen. A thermocouple was fixed parallel to the burner and 75 mm above it to measure the temperature of the flame. Liquefied petroleum gas was used as the fuel. The air supply and flame height were so adjusted that a temperature of 750°C was obtained throughout the test.

A 440-V, 3-phase electric supply was connected to the cable specimen, kept parallel to and 75 mm above the burner, through a 3-A fuse in each phase and a 5-A fuse in the neutral phase, which was earthed. The cable remained energized with rated voltage throughout the fire test. The flame temperature, 75 mm above the burner, was maintained at 750°C. The flame and rated voltage were applied continuously till the failure of the 3-A fuse. A few specimens were exposed at 750°C for 20 min, and then a re-energized test, using rated voltage (as above), was carried out 12 h later to check the continuity of the electric cable. Observations made during the evaluation with four different compositions are recorded in Table 5. The effect of coating thickness on fire performance was studied for the composition found most effective in the earlier experiments. The results for the same are recorded in Table 6.

Smoke Generation Characteristic

Smoke generation from coatings was studied as one of the aspects by cone calorimeter; however, it was also studied by using the

Table 5. Results as per IEC-331.

Composition	Cable diameter (mm)	Coating thickness (mm)	Failure of circuit time (min:s)
1.	31	1.64	12.60
2.	31	1.60	11.80
3.	31	1.62	10.80
4.	31	1.61	13.90
Uncoated	31	-	3.35

Table 6. Effect of coating thickness (results as per IEC-331 composition—4).

Cable diameter (mm)	Coating thickness (mm)	Circuit failure time (min:sec)	Re-energize test results
31	Uncoated	5.1	Fail
31	1.5-1.8	14.7	Fail
31	2.0-2.2	21.5	Fail
31	2.2-2.5	22.3	Pass
31	2.5-3.0	23.0	Pass
31	3.0-3.5	27.1	Pass

National Bureau of Standards (NBS) Smoke Density Chamber, as described in the ASTM E 662 method [16]. Since the developed coating is especially designed for PVC, 76 × 76 × 3 mm sheets of polyvinyl chloride were coated with four different compositions to obtain a 2-mm-thick (dry) film. The coated specimen was mounted vertically. The light transmittance measurements were used to calculate the specific optical density of smoke for 20 mins. The following parameters were determined:

D_m = maximum specific optical density

$t_{90\%}$ = time in which 90% of D_m is reached (in minutes)

D_{90s} = optical density at 90 s

SoN = sum of specific optical densities at 1 min, 2 min, 3 min and 4 min,

a measure for the rate of smoke development

V_{max} = maximum rate of smoke generation estimated every 30 s and

expressed in density of smoke per minute (D_s /min)

The results are listed in Table 7. LOI of the paint film was found to be in the range of 98.8-100.0.

Table 7. Smoke density results in NBS chamber (smoldering test conditions).

Composition No.	Values of*			
	D_m	$t_{90\%}$	D_{90s}	SON
1.	32.0	18.0	2.2	14.6
2.	35.0	16.8	2.8	16.0
3.	34.6	17.5	2.6	15.2
4.	31.2	18.8	2.0	14.1
Uncoated	632	2.4	127	986
				301

Note: Lower value of D_m , D_{90s} , SON, V_{max} and higher value of $t_{90\%}$ indicate the better performance of a material.

Evaluation of PVC Sheet

The effect of FRSS additives on the combustion of polymer was studied in terms of flammability, smoke generation, char formation and generation of combustion gases.

LOI

Flammability was studied using the LOI test as per ASTM D 2863 [17]. LOI is the value at which the material just supports flaming combustion. The minimum concentration of oxygen in a mixture of oxygen and nitrogen flowing upward in a test column that will just support combustion is determined under equilibrium conditions of candle-like burning. The LOI of a material is determined as:

$$LOI = 100 \times \frac{[O_2]}{[O_2] + [N_2]} \quad (1)$$

Where [] is the volume concentration of each gas in the airstream. A Stanton Redcroft FTA flammability unit was used to determine the oxygen index of different compositions. A PVC sheet of size $52 \times 140 \times 5$ mm was used to determine the LOI.

Smoke Suppression Index

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 the combustion of test specimen [18]. Specimen was burnt for 3 min at an oxygen

concentration that was 2% higher than the LOI value of that specimen. The smoke that evolved was allowed to flow through a duct. An He-Ne laser source and receiver were employed to measure the density of smoke flowing through the duct. The efficacy of smoke suppressant systems was calculated in terms of the SSI, as follows:

$$\text{SSI} = \frac{S - S_t}{S} \times 100 \quad (2)$$

where S = area under the time versus smoke density curve for the untreated sample, and S_t = area under the time versus smoke density curve for the treated sample.

Since the initial weight as well as the weight loss for each sample may not be identical, A (area under the time versus smoke density curve for the untreated sample/weight loss of the sample) and A_t (area under the time versus smoke density curve for the treated sample/weight loss of the sample) may be used in place of S and S_t . Positive values of SSI (i.e., $S > S_t$ or $A > A_t$) indicate a reduction in the amount of smoke generated, whereas a negative value represents an increase.

Char Formation

The char formation was assessed using the oxygen index apparatus. Samples modified by the FRSS additives that gave the best results in terms of flame retardance and smoke suppression were exposed to burning conditions, to produce char, in an LOI apparatus. The duration of exposure was 3 min, and the oxygen concentration employed was 2% higher than the LOI value for that specimen. A wire gauge was placed about 15 mm below the specimen, for the collection of char. The specimen and char were carefully weighed before and after burning. The backbone char percentage (BC%) was computed as described by Kroyenke [19] and results reported in Table 8.

Combustion Gases

Combustion gases, i.e., carbon monoxide and carbon dioxide, were measured by using the infrared spectroscopic technique. Hydrocarbons were measured by employing a flame ionization detector. The concentrations reported in Table 8 are averaged over a 3-min test duration and those in Table 9 are the peak concentrations. These are

Table 8. Effect of dioxobis-(2,4-pentanedion) 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	27.2	—	34.79	—	—
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

M₁-M₁₀ Samples 1-10

DOP Diocyl 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, ppm

CO₂ Carbon dioxide, ppm

control samples.

over and above the base line, i.e., the concentrations observed in case of

Cone Calorimeter

Samples of PVC modified with different quantities of flame-retardant smoke-suppressant complex as well as the unmodified sample (control) were evaluated for time of ignition, flammability, heat release rate (HRR), total heat release (THR), smoke density as well as generation of combustion products using a cone calorimeter (Table 9). The samples were exposed to an irradiance level of 40KW/m² in a horizontal orientation. The irradiance levels used in the present study represent severe fire conditions.

Since the maximum effectiveness of MBO additives in suppressing smoke emission is obtained at relatively small concentrations, it was decided to use the pentanedion complex of molybdenum (VI) up to

Table 9. Cone calorimeter results of FRSS PVC.

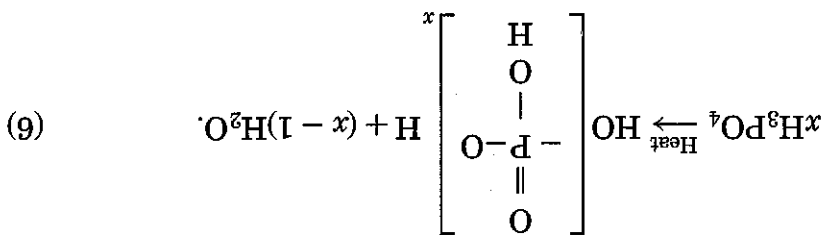
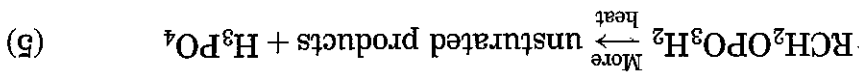
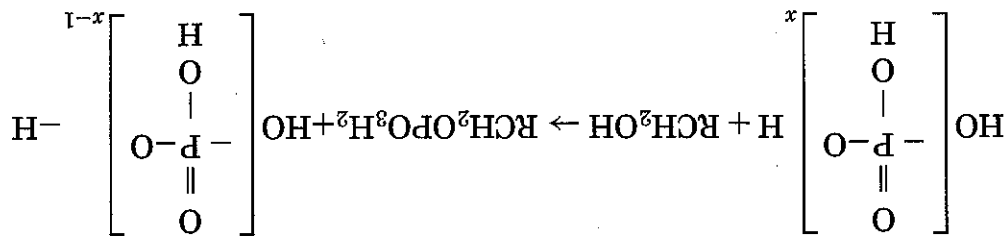
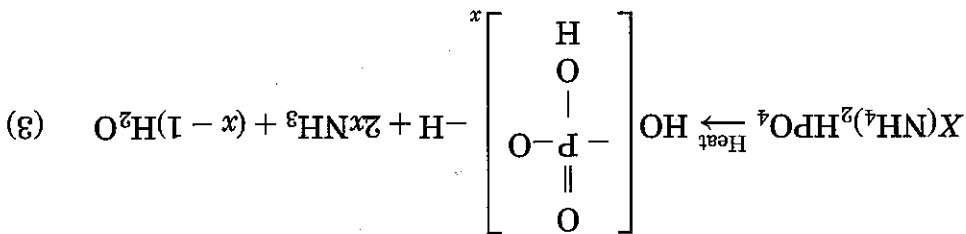
Property	Specimens				
	1	2	3	4	5
Time of ignition, s	94	96	99	97	106
Oxygen index	31.55	31.65	31.70	31.80	31.90
Smoke density, %	62.0	72.2	73.0	71.6	72.8
Burning rate, (Kg/M ² s × 10 ⁻²)	2.36	2.31	1.54	1.32	1.44
Heat release rate (KW/M ²)	180.96	175.33	163.99	169.45	173.49
Total heat release (MJ)	21.99	21.04	16.29	16.65	15.45
CO (ppm)	120	159	185	111	180
CO ₂ (ppm)	2794	2838	2642	2711	2762
Hydrocarbons (ppm)	81.45	88.96	91.14	88.89	84.16
					227.04
					1702
					279
					18.02
					165.62
					1.57
					32.0
					34.6
					128

3 parts per hundred parts of resin (phr) loading. Samples were prepared as described earlier, using both the phthalate (dioctyl phthalate, DOP) and the phosphate (tricresyl phosphate, TCP) plasticizer at 50 phr. Magnesium hydroxide was used as the filler. A sample containing 0.0 phr of the FRSS additives was used as the control or the reference sample for the computation of SSI.

RESULTS AND DISCUSSION

The main constituents of fire- and smoke-retardant intumescent coatings under study are amides, polyols phosphates and propane-dione complex of molybdenum. When this combination is exposed to fire, the phosphate decomposes to produce phosphoric acid, which acts as a dehydrating agent. The polyol is dehydrated by the acid, forming a large amount of carbonaceous char that produces a noncombustible barrier to protect the substrate. The amide gives off non-flammable gases, causing the carbon to swell up and produce a honeycomb blanket, resulting in highly effective insulation. The binder, on softening, forms an expandable skin over the carbonaceous char to resist the escape of gases produced by amides. All these reactions take place within the coating, thereby protecting the material from heat. The above mechanism may be expressed by the following equations [7,11,20]. The smoke retardant performed through increase in char formation as well as through change in pyrolyzates generated. The resulting species are abundant in CO and CO₂ instead of volatile vapors that help in

accelerating the combustion process. This results in slower burning and lower smoke generation.



Specimens of 5-mm-thick dry film of the developed intumescent paint were exposed to test conditions as per ASTM E 1354 in a cone calorimeter. The irradiance level of 50 kW/m² was used, and the specimen was placed in horizontal orientation. It was observed that, in spite of the severe test conditions, the specimens did not ignite at all. At 13 s, a granular formation was observed on the paint surface, which turned blackish in color by 21 s. The paint film started swelling at 29 s. By 60 s, an increase in weight of the specimen was observed. This is erroneous by conventional wisdom, but could be explained as the result of the swelled up char touching the ignition rod that partially added the weight of the ignition rod to the weight of the specimen. The actual mass loss was estimated to be only 1.8 g, as against the initial mass of

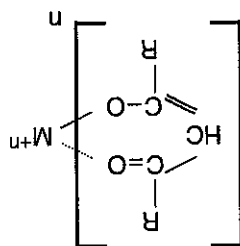
61.58 g of the paint film exposed to the test conditions. The total heat release (0.3 MJ/m^2) as well as the total smoke evolved ($25.3 \text{ m}^2/\text{m}^2$) were very nominal. These results indicate that the paint films contribution to fire was very insignificant. The combustion gases and smoke generation was found to be insignificant, and their peak values were found to have occurred at an early stage (Table 4). This was expected because, once the char formation starts, it provides a heat-protective sheath that does not allow the material to come in direct contact with the heat, thereby slowing down combustion of the underlying material.

It is evident from the fire tests that the paint formulations under discussion were very effective in reducing the burning characteristics of electric cables. The circuit failure time increased significantly (from 3.35–13.9 min) when cable specimens were coated with different compositions, up to $\sim 1.6 \text{ mm}$ coating thickness (Table 5). The studies also revealed that fire performance is dependent on coating thickness. In the re-energize test, the specimen was considered as "Pass" when no failure of any 3-A fuse occurred even after 12 h of exposure. Specimens, that did not meet the above criteria were considered as "Fail". In order to pass this test after 20 min exposure as per IEC-331, the cables of 31-mm diameter required a coating thickness of greater than 2.2 mm (Table 6).

The smoke retardant based on the pentanedione complex of molybdenum was also found quite effective in reducing the rate and amount of smoke formed. The value of $t_{90\%}$ increased from 2.4 min to 18.8 min, indicating that the smoke generation time was increased significantly on using these coatings. Further, it was also found that during the standard exposure, the amount of smoke was noted in the range of $31.2\text{--}35.0 \text{ D}_m$, whereas the value for the uncoated specimen was 632 D_m when evaluated as per ASTM E-662 (Table 7).

PVC sheets were prepared using resin, stabilizers, lubricants and plasticizers, along with dioxobis-(2,4-pentanediono)-molybdenum (VI) as the FRSS complex. The plasticizers used were di-*o*-cetyl phthalate (DOP) and tri-cresyl phosphate (TCP) as a flame-retardant plasticizer. Thus, the performance of FRSS-modified PVC samples has been reported in terms of the MBO complex and the plasticizers used. The metal complex appears to function as a smoke suppressant through gas-phase destruction of soot or by preventing the formation of soot particles. However, an effective smoke suppressant may contribute in the vapor phase, condensed phase or in both through different processes.

MBO complexes are chelates of transition metals having an organic ligand that can cleave at an elevated temperature, thereby releasing the metal in a reactive state for its action as an FRSS additive. These additives limit the polyene length, thereby restricting intramolecular cyclization and hence resulting in lower amounts of smoke generation. Their efficacy in suppressing smoke generation could be ascribed to their better miscibility with the polymer. Essentially, all of the effective metal-based smoke suppressants appear to work in solid phase, resulting in increased char formation and thus reduced flammability of the polymer. They also interfere with the normal degradation pattern of PVC [21]. The efficacy of MBOs is superior to that of the transition metal alone. This is ascribed to its better miscibility with the polymer [22]. The pentanedione complex was found to be a very effective FRSS additive for PVC. The general formula of MBOs is:



Where M represents the transition metal, n is the valency of the transition metal used and R represents a $-\text{CH}_3$ group. The oxygen index values of samples modified by dioxobis-(2,4-pentanediono)-molybdenum (VI) (molybdenum acetylacetonate) indicate that the improvement in flame retardancy is directly proportional to the amount of additive used when the phthalate plasticizer (DOP) was used. However, it is interesting to note that a maximum value for LOI (33.2) in the case of the phosphate (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 9).

A constant decrease in smoke generation, i.e., an increase in SSI from 27.27 to 57.57, was observed when the plasticizer used was DOP (Figure 1). 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

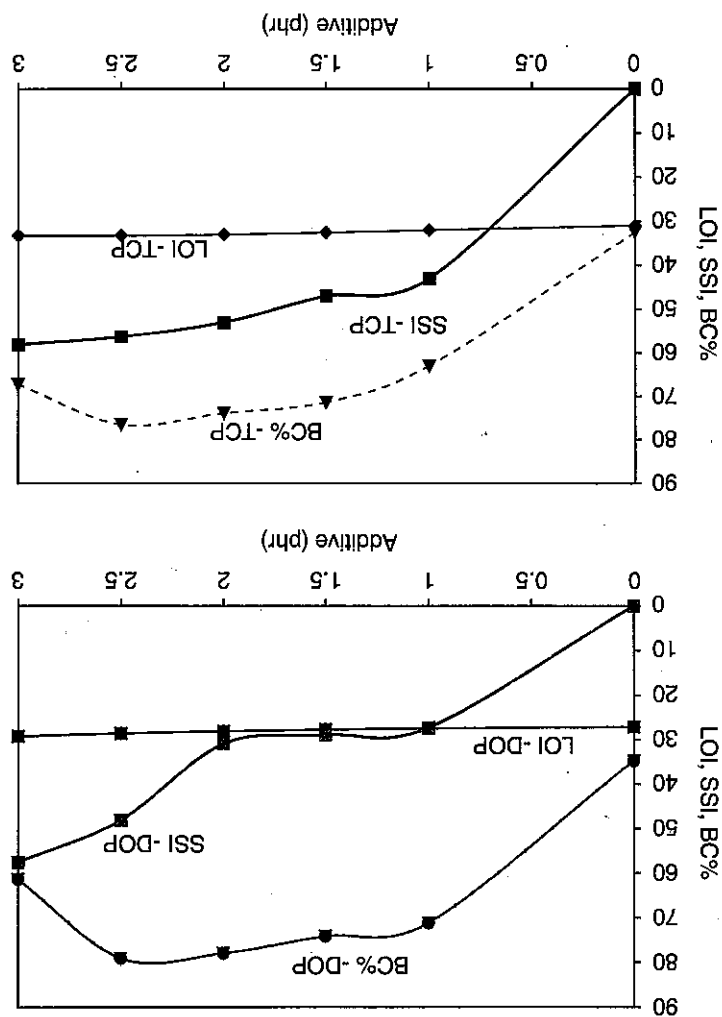


Figure 1. Effect of dioxo bis (2,4 pentanedione) molybdenum (VI) on FRSS characteristics of plasticized PVC.

us to correlate this behavior in terms of char formation (BC%) and evolution of combustion gases. The quantity of char is found to increase with the addition of additives up to 2.5 phr, after which it shows a decrease. An increase in CO and CO₂ evolution was observed (Table 9). The amount of unsaturated hydrocarbons (C₁-C₅) in the combustion gases was found to have increased from 10 to 42 ppm in the case of DOP and from 12 to 60 ppm in the case of TCP-plasticized samples when the quantity of additive used is increased from 1-3 phr. A change in the degradation process, which results in lower aliphatics 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 behavior (estimated in terms of LOI) and smoke-suppressant behavior (estimated as SSI) of the molybdenum complex reveals that, although the additive acts as an FRSS with both the plasticizers, its overall performance is superior in the case of TCP-plasticized PVC.

PVC sheets were exposed to the irradiance level of 40 kW/m^2 in a horizontal orientation in a cone calorimeter. The performance was compared to a commercially available fire-retardant PVC sheet of equivalent thickness. The recipe of the specimen included 70 phr of magnesium hydroxide used as filler. The specimens were prepared by using the recipe given in Table 2. It releases inert gases, which dilute the fuel in the gas phase; also, the spent magnesium hydroxide has higher heat capacity as compared to the polymer, which reduces thermal energy to degrade the substrate [23].

The effect of the FRSS additive on burning characteristics and combustion products was studied. The combustion gases were analyzed in the duct section of the calorimeter. Only the peak values are reported here. The specimen modified by using the FRSS MBO took 106 s for ignition, as compared to 82 s for the specimen without FRSS. Although the time of ignition is not important for a deterministic scheme for the first item to ignite, it is important for items burning subsequently. The FRSS used did not effect the time of ignition significantly. When a commercially available fire-retardant PVC was compared with the FRSS-modified specimen, it took considerably longer (128 s) to ignite; however, smoke generation was found to have reduced very appreciably when the FRSS additive was used (Table 8). It was observed that the rate of burning was influenced by the quantity of FRSS additive used, which was found to be most effective at ~ 2 phr. Observations of heat release rate (HRR) and total heat release (THR) also support this observation, since the increase in these parameters, if any, was not appreciable at the concentrations used. The analyses of combustion gases reveal that, while generation of CO increased, generation of CO_2 was found to have decreased. Lower levels of oxygen in the exhaust gases also support this observation. Although the peak values of CO, CO_2 and O_2 appear earlier in case of FRSS specimens, they were significantly lower than those for commercial FR PVC. Hydrocarbons were generated in large quantities and much earlier in case of FR PVC, and the higher levels of smoke generated by it also matched this (Table 8). These observations strengthen our claim that the complex used reduced smoke generation as well as the rate of burning, and thus acted as an FRSS.

CONCLUSIONS

A few fire-retardant and smoke-suppressant intumescent coatings based on indigenously available chemicals were developed, and a molybdenum-based organic (MBO) complex (molybdenum acetylacetonate) was synthesized for use as FRSSs in polyvinyl chloride. The intumescent coatings as well as the MBO were found to be quite effective in reducing the flammability as well as smoke generation characteristic of PVC. In case of PVC-sheathed cables, the developed coatings resulted in significantly increased circuit breaking time. When the rated voltage was given to coated cables after exposing them to standard fire conditions, the cables were found to be in workable condition. The formulations were also found to be quite effective in reducing the amount of smoke and its rate of generation.

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