

## **Influence of Molybdates on Char Formation and Smoke Suppression in PVC**

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### **ABSTRACT**

In recent years, the use of flexible PVC for plenum cable jackets has grown markedly. In order to meet the smoke requirement of UL910, molybdate smoke suppressants are commonly added to plenum jacket compound. It has long been recognized that molybdates act in the condensed phase by promoting the formation of protective char.

In this work we examine the influence of common molybdate additives (Kemgard 911C, AOM) on char formation in a number of PVC compounds. Various analytical methods were used to study the composition and structure of PVC char. It is seen that in addition to influencing the organic char layer, molybdates can influence the fate of other inorganic FR additives in char. Using TGA and DSC, we have also studied the interaction of smoke suppressants with FR plasticizers. Analytical and thermogravimetric results are discussed in context of apparent FR synergies seen in NBS smoke and cone calorimeter tests.

## **I. Introduction**

Today, a wide variety of thermoplastic materials are available for use in wire and cable applications. Most of these applications require some degree of flame retardancy, Certain applications must meet a low smoke requirement. The most stringent standards for wire and cable have been established for cable applications in ceiling cavity plenums.

This standard for plenum cable was established by the National Fire Protection Association (NFPA) and is based on the Underwriters Laboratory Standard UL 910. UL910 is a modified ASTM E84 Steiner Tunnel Test, with a tray for the cables placed inside the tunnel. To qualify for use, flame spread must not exceed 5 feet. In addition, peak smoke must not exceed 0.5 units and the average smoke throughout the test must be below 0.15 units

Due to the stringent requirements established by the NFPA, only fluorinated ethylene propylene (FEP) and polyvinyl chloride (PVC) have been used for plenum rated communication cable jacketing. Of these, PVC enjoys a significant cost advantage as well as processing advantages. However, a number of additives are required in order to meet the various technical requirements.

PVC is inherently fire resistant. However, in order to achieve the physical properties required for cable jacketing various additives must be added. In order to achieve flexibility, PVC jacket compounds must contain one or more plasticizers. This greatly enhances the polymer combustibility. Nevertheless, fire resistance can generally be achieved by introduction of other additives. Antimony trioxide,  $Sb_2O_3$ , is often added to PVC compounds and has been shown to enhance flame retardancy via a gas phase mechanism involving the scavenging of free radicals in the combustion process. Flame retardancy can also be improved by the use of halogenated and/or phosphate plasticizers. However, a deleterious consequence of the use of these materials is the enhancement of smoke formation, which forms when combustion is attenuated in the vapor phase.

Additional flame retardancy in PVC is often achieved by the use of metal hydrates, such as aluminum trihydrate, magnesium hydroxide, huntite/hydromagnesite etc. These flame retardant fillers decompose endothermically at temperatures ranging from 200 C to 600 C, thereby absorbing the heat of combustion. The water liberated may also have a diluting effect in the gas phase, displacing oxygen above the condensed phase. It has also been proposed that inorganic residue from metal hydrates may contribute to char formation and smoke suppression in various polymer systems.

In order to meet the smoke requirement of UL910, smoke suppressants are commonly added to plenum jacket compound. Smoke suppressants typically function in the condensed phase by promoting the formation of protective char. In addition to lowering smoke, condensed phase smoke suppressants generally also improve flame retardancy. A number of smoke suppressant chemistries are used commercially. The most common of these are zinc compounds, molybdates and borates. Phosphate ester plasticizers have also been found to lower smoke in PVC compounds.

## **II. Experimental**

PVC compound was prepared using the raw materials shown in Table 1. Compounds were prepared using a Brabender Plasti-Corder. Test plaques were prepared by compression molding using a heated Carver Press.

**Table 1**

<b>Material</b>	<b>Product Name</b>	<b>Supplier</b>
PVC	OxyVinyl 240	Oxyvinyls
Antimony Oxide	Fireshield L	Laurel Industries
Aluminum Trihydrate	Micral 9402	J.M. Huber
Magnesium Hydroxide	Zerogen 50 SP	J.M. Huber
Phosphate Ester Plasticizer	Santicizer 2148	Solutia Inc.
Brominated Phthalate Plasticizer	Uniplex FRP-45	Unitex Chemical
Zinc Molybdate/Talc	Kemgard 911C	Sherwin-Williams Chemicals
AOM	Ammonium Octomolybdate	Climax Minerals

NBS (Fire Testing Technology) testing was performed according to ASTM E662. All results presented were obtained in the flaming mode of the test method. In this test a 3" x 3" x 1/8" test plaque is exposed to a radiant heat source (25 kW/m<sup>2</sup>). A small flame also impinges on the bottom of the sample to promote ignition. Smoke accumulates in the test chamber and is measured by light transmittance. Smoke density, reported at various times, and the maximum smoke density, D<sub>max</sub>, are calculated from the percent transmittance.

Cone Calorimetry work was performed at Solutia Inc. according to ASTM E1354. Radiant heat flux was 70 kW/m<sup>2</sup>. Samples (4" x 4") were prepared on a two roll mill, followed by compression molding in a heated press.

Several chars formed in NBS tests were analyzed. All samples were run for 20 minutes, which was generally 10 minutes past the time for maximum smoke density. X-ray diffraction analysis of char was performed by first grinding the char in a mortar and pestle. Diffraction patterns were obtained using a Siemens D5005 and compared with ICDD powder diffraction files. Chemical analysis of the chars were performed by digestion in a HNO<sub>3</sub>/HF solution using a using a 950 W CEM MDS-2100 Microwave Sample Preparation System (CEM Corporation, Matthews, NC). Elemental analysis of the digest was performed an IRIS Advantage Radial ICAP Solid State Spectrograph (Thermo Electron, Franklin, MA).

Differential scanning calorimetry measurements were performed using a Perkin Elmer DSC-7 Differential Scanning Calorimeter. Blends of smoke suppressant and plasticizer were heated at a rate of 20°/min and data was analyzed using Perkin Elmers Pyris Software.

### **III. Molybdate Smoke Suppressants**

There are a number of smoke suppressants commercially available. These are frequently based on zinc and/or molybdenum compounds. In this study two molybdate based smoke suppressants were examined. Ammonium Octomolybdate, obtained from Climax Minerals, is available in various particle sizes and contains approximately 61% Mo. Kemgard 911C is one of several molybdate based smoke suppressants manufactured by Sherwin-Williams Chemicals. Kemgard products are structured materials produced by a patented process in which molybdates are precipitated on to the surface of an inert mineral core. This approach makes more efficient use of the molybdate species by maximizing the active surface area. The active component of Kemgard 911C is zinc molybdate whereas the core material is a fine (typically 4 micron) talc. The use of a "coated core" structure provides smoke suppression at a cost much lower than pure molybdate chemicals. Both Kemgard 911C and AOM are widely used in low smoke PVC applications.

#### IV. Results

##### NBS Results

The effectiveness of both AOM and Kemgard 911C in lowering smoke is demonstrated by NBS smoke chamber results. Table 2 (columns 1-3) shows the effect of 20 phr smoke suppressant on smoke density and LOI in compound containing 40 phr halogenated plasticizer. As a control, a third system is shown with CaCO<sub>3</sub>, an inert filler, replacing the smoke suppressant. In this system, Kemgard 911C and AOM show comparable reductions in smoke density and also appear to increase the LOI slightly. Previous authors have proposed that molybdates may suppress the formation of volatile aromatic compounds during combustion, which could account for the observed increase in LOI.

**Table 2. Test Results**

<b>Formulation</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
OxyVinyl 240	100	100	100	100	100
Zerogen 50 SP	40	40	40	40	40
Uniplex FRP 44-57	40	40	40	30	30
Santicizer 2148				10	10
H-695 Stabilizer	7	7	7	7	7
CaCO <sub>3</sub>	20				
Kemgard 911C		20		20	
AOM			20		20
<b>NBS Smoke (ASTM E662)</b>					
<b>Flaming Mode</b>					
D90	51+/-6	28 +/- 3	37 +/- 4	21+/-3	34 +/- 4
D4.0	305 +/-15	183 +/- 5	182 +/- 7	143 +/- 8	200 +/- 12
Dmax	455 +/- 24	302 +/- 15	271 +/- 16	255 +/- 16	263 +/- 17
<b>LOI</b>	46	51	50	50	48

In order to achieve necessary physical and performance properties, two different plasticizers are commonly used in PVC plenum cable jacket compound. In particular, phosphate ester plasticizers are used to both lower smoke and improve mechanical properties, particularly low temperature flexibility. Columns 4 and 5 in Table 2 show the effect of replacing 25% of the plasticizer system with the phosphate ester, Santicizer 2148. Again it appears that both molybdate smoke suppressants are equally effective in terms of the maximum smoke density. However, there are significant differences in smoke density early in the test, at both 90 seconds and 4 minutes after exposure to the radiant heat. During this time period it is observed that the samples containing Kemgard 911C begin to char more quickly, and that char appears to be quite lustrous.

This phenomenon of reduced smoke at short times was also observed in numerous other systems containing phosphate ester plasticizer. Table 3 shows data for systems using a combination of phosphate ester and brominated phthalate plasticizers in a 1:1 ratio. The series shown in columns 1-3 contain ATH rather than Mg(OH)<sub>2</sub> as the metal hydrate flame retardant. This system also included antimony oxide as an additional flame retardant. Again it is observed that both AOM and Kemgard 911C effectively lower the maximum smoke density, but the sample with Kemgard 911C yields much lower smoke early in the test, particularly at 90 seconds. The lowering is still significant at 4 minutes. Both smoke suppressants increase LOI significantly, with a slight advantage to AOM.

The data shown in columns 4 and 5 represent a system containing Mg(OH)<sub>2</sub> but no antimony oxide. Removal of antimony oxide from the system significantly lowers the LOI, an indication of its effectiveness as a vapor phase flame retardant. The maximum smoke densities are also lower than seen in the first system, again because the vapor phase action of antimony oxide promotes smoke. The data in columns 4 and 5 reinforce the previous observations – AOM and Kemgard 911C are comparable in lowering the maximum smoke density, but Kemgard 911C delays the onset, giving lower smoke at shorter times.

**Table 3 Test Results**

<b>Formulation</b>	<b>1</b>	<b>2</b>	<b>3</b>		<b>4</b>	<b>5</b>
OxyVinyl 240	100	100	100		100	100
Fireshield L	3	3	3			
H-695 Stabilizer	7	7	7		7	7
ATH 9402	30	30	30			
Zerogen 50 SP					40	40
Uniplex FRP-45	20	20	20		20	20
Santicizer 2148	20	20	20		20	20
<b>Variables</b>						
CaCO <sub>3</sub>	30	10	10			
Kemgard 911C		20			20	
AOM			20			20
<b>NBS Smoke (ASTM E662)</b>						
<b>Flaming Mode</b>						
D90 (ave)	41	33	69		15	34
D4.0 (ave)	259	133	195		94	139
Dmax (ave)	481	257	249		196	199
<b>LOI</b>						
	40	47	50		39	40

### Cone Calorimeter

In order to determine the influence of heat flux on the relative performance of AOM and Kemgard 911C, formulations 2 and 3 from Table 3 were analyzed by cone calorimetry. Testing was performed at a heat flux of 70 kW/m<sup>2</sup> (compared to only 25kW/m<sup>2</sup> for the NBS smoke test). In addition to smoke parameters, cone calorimetry also provides heat release data, which has been related to flammability. Average values obtained in these tests are shown in Table 4.

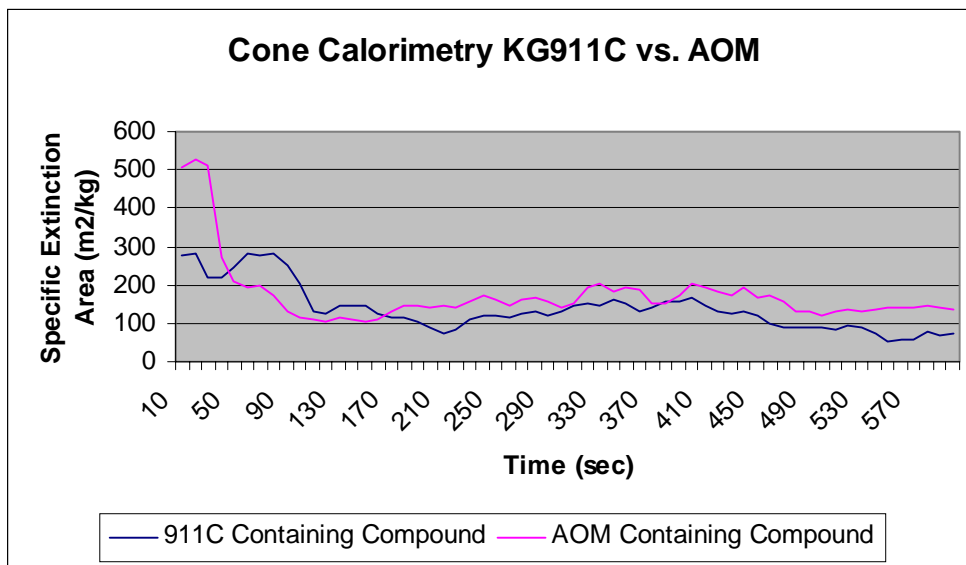
**Table 4. Cone Calorimetry Data**

<b>Cone Calorimetry Data</b>	<b>Compound 2 (Kemgard 911C)</b>	<b>Compound 3 (AOM)</b>
Peak Heat Release (kJ)	3.95	4.38
Peak Heat Release Rate (kW/m <sup>2</sup> )	74.7	76.65
Average Heat Release Rate (kW/m <sup>2</sup> )	52.01	50.04
Peak Smoke (m <sup>2</sup> )	0.095	0.125
Average Smoke	0.052	0.052

It can be seen that both samples yielded comparable heat release numbers. The peak heat release rate was slightly lower for the Kemgard containing compound, whereas the average heat release rate was slightly lower with the AOM containing compound. In terms of smoke generation, both compounds yielded the

same average smoke value. However the peak smoke with Kemgard was slightly lower. Peak smoke normally occurs early in the cone calorimetry test. Figure 1 is a plot of specific extinction area vs. time for one of the replicate runs. The AOM containing compound showed a peak extinction area within the first minute of the test and was much higher than the Kemgard containing compound. In contrast, the peak extinction area for the Kemgard containing material was approximately 90 seconds after the test, and the peak was broader, but not as high.

Figure 1.

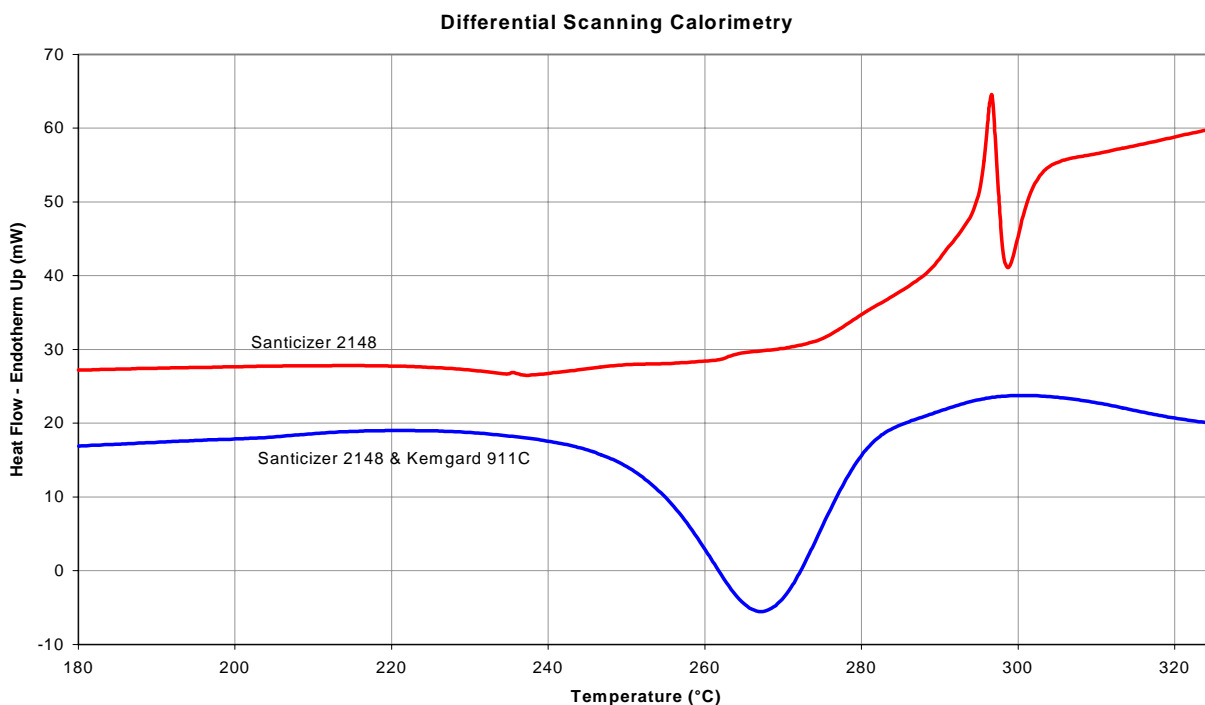


Both the NBS data, and the limited cone calorimetry tests appear to indicate that although both AOM and Kemgard 911C lower total smoke (Dmax for the NBS test and Average Smoke in the Cone Calorimeter), the time course of smoke generation differs. Kemgard 911C favors lower smoke during the onset of combustion, while smoke suppression with AOM appears to be delayed. This is principally observed in compounds formulated with phosphate ester plasticizer. In the absence of phosphate ester, both differences between the two smoke suppressants are minor. This suggests that Kemgard 911C may influence the action of the phosphate ester differently than does AOM.

#### Differential Scanning Calorimetry

To examine the possible interactions between Kemgard 911C and phosphate ester plasticizer, physical blends of the two were analyzed by differential scanning calorimeter. This was compared to runs for the individual components. As shown in Figure 2, the DSC profile for Solutia 2148 phosphate ester exhibits a very broad, weakly exothermic peak beginning at a temperature above 200 C. This is followed by a very sharp endothermic peak at 296C. The sharp endothermic peak corresponds closely with published decomposition temperature, determined by TGA. The DSC profile for Kemgard 911C (data not shown) shows only a very minor endothermic peak, beginning at around 280C, which corresponds to loss of bound water.

In contrast the DSC results for a 1:1 blend of Kemgard and Santicizer 2148 exhibit an exothermic peak centered at 268C, followed by a weak endothermic peak at 300C. This is also shown in Figure 2. The presence of the strong exothermic peak is evidence of chemical interaction between the two components. The nature of the chemical interaction has not yet been determined.



Using the same DSC technique, no interaction between AOM and Santicizer 2148 was observed. Similarly, no interactions were observed for either Kemgard 911C or AOM with the brominated phthalate plasticizer Uniplex FRP-45. Clearly interactions between flame retardants in a burning polymer matrix may be very complex and apparent synergies are often reported. In this case it is clear that in a simple two component system, Kemgard 911C and Santicizer 2148 do interact. It is possible the interaction between the two may help promote char formation, which may account for the lower smoke formation in the early stages of combustion.

### Char Analyses

In PVC compound containing the phosphate ester plasticizer, the choice of smoke suppressant appears to influence the time course of smoke generation in both NBS smoke and cone calorimetry tests. Although peak smoke (cone calorimeter) and Dmax (NBS smoke) were similar using either AOM or Kemgard 911C, faster char formation and lower smoke were observed with Kemgard. This appears to be related to an interaction between Kemgard and the phosphate ester. We therefore decided to chemically analyze the char formed during NBS smoke testing. Both XRD and elemental analysis (ICP) were used to examine the fate of the various inorganic additives in PVC char.

The only identifiable phase determined by XRD in the char produced from the AOM containing compound was MoO<sub>2</sub>. This is consistent with reports suggesting that molybdenum oxide may promote char formation through a complex set of reactions involving the reduction/oxidation of various oxides/oxychlorides. On the very outer surface of the char, a white powdery ash was formed and found to contain the oxidized molybdenum oxide, MoO<sub>3</sub> as well as an aluminum molybdate, presumably formed by reaction of MoO<sub>3</sub> with ATH or its decomposition product.

The chemical analysis of the AOM containing chars are shown in Table 5. These are compared to the calculated composition for the PVC compound, as formulated. One would expect that the inorganic content of the char would be greater than that of the unburned sample, simply because the combustion reaction would removed organic matter. This was the observed result for molybdenum, lead (originating from the stabilizer) and P (originating from the phosphate ester plasticizer). Again this result is very consistent with early work by Moore and others, which showed that molybdenum flame retardants remain and function in the solid phase. Similarly, phosphate esters are known to promote char formation and would be expected to remain in the solid phase.

In contrast, the antimony levels in the char were quite low, much lower than the original levels. Antimony synergists are known to function in the gas phase; so again this result is not unexpected.

Perhaps the most surprising result was the very low level of aluminum found in the char. This would indicate that during the burning of PVC, volatile aluminum species, possibly reduced oxychlorides are formed. This could account for “white smoke” which has often been observed in PVC studies.

**Table 5. Analysis of Char of AOM Containing Compound**

Element	Oxide	Calculated		Char Analysis	
		Wgt. Percent	Percent Oxide	Weight Percent	Percent Oxide
Al	Al <sub>2</sub> O <sub>3</sub>	5.20	9.80	1.30	2.46
P	P <sub>2</sub> O <sub>5</sub>	0.80	1.80	1.10	2.50
Pb	PbO	1.80	2.10	3.20	3.50
Sb	Sb <sub>2</sub> O <sub>3</sub>	1.25	1.50	0.20	0.20
Mo	MoO <sub>3</sub>	6.10	9.15	11.80	17.70
Total		15.15	24.35	17.60	26.36

In the char produced from the Kemgard 911C containing compound, the only identifiable phase determined by XRD was talc, the mineral support for zinc molybdate in Kemgard 911C. No molybdate phase was detected. However, this is not surprising because the XRD peaks for zinc molybdate are weak and the molybdate concentration in the compound is relatively low.

The chemical analysis for the Kemgard containing char are shown in Table 6. As with the previous sample, the concentration of antimony is significantly lower in the char than in the starting compound. Concentrations of Zn, Mo, Pb and P were higher in the char as was Si (which originates from the talc). The magnesium concentration is somewhat low, based on the chemical structure of talc. This is an artifact of the analysis, because Mg formed insoluble fluorides during the digestion and these were not picked up by ICP. The biggest difference in this and the previous analysis is the aluminum content. Here the aluminum appears to remain in the char. Possibly differences in char structure influence the volatilization of aluminum species. Similar analyses were conducted using compound with higher ATH levels, and similar results were found.

**Table 6. Analysis of Char of Kemgard 911C Containing Compound**

Element	Oxide	Calculated		Char Analysis	
		Initial Wgt. Percent	Percent as Oxide	Weight Percent	Percent as Oxide
Al	Al <sub>2</sub> O <sub>3</sub>	5.2	9.8	7.5	14.2
P	P <sub>2</sub> O <sub>5</sub>	0.8	1.8	1.3	3
Pb	PbO	1.8	2.1	3.4	3.7
Sb	Sb <sub>2</sub> O <sub>3</sub>	1.25	1.5	0.2	0.2
Mg	MgO	1.54	2.54	1.5	2.48
Si	SiO <sub>2</sub>	2.37	5.06	5.9	12.62
Zn	ZnO	0.58	0.072	1	1.25
Mo	MoO <sub>3</sub>	0.85	1.28	1.2	1.8
Total		14.39	24.152	22	39.25

## V. Discussion

In this work we have studied the effectiveness and influence on char formation of two commonly used smoke suppressants, ammonium octomolybdate and Kemgard 911C, a zinc molybdate based material. In several different flexible PVC systems, both AOM and Kemgard 911C proved to be equally effective in lowering the maximum smoke in the NBS smoke test ASTM E662. Similar results were also obtained in limited cone calorimeter studies.

Despite similar maximum smoke levels, in certain PVC compounds, AOM and Kemgard 911C show differences in their influence on the time course of smoke generation. This different performance has been observed principally in systems which include phosphate ester plasticizers, which are also reported to promote flame retardancy and low smoke by enhancing char formation. In systems containing both Kemgard 911C and phosphate ester, char formation appears to be more rapid and smoke levels are lower early in testing (compared to AOM).

Thermal analysis of blends of smoke suppressant and plasticizer indicate a chemical interaction between the zinc molybdate based Kemgard 911C and phosphate ester plasticizer. No similar interactions were observed with AOM and the phosphate ester or with either smoke suppressant with a brominated phthalate plasticizer. The mechanism (or even resulting products) of the zinc molybdate/phosphate ester interaction is not known. DSC data suggests that zinc molybdate may promote the decomposition of the phosphate ester, in which case the phosphate may contribute to char formation at a lower temperature.

XRD and chemical analyses indicate the presence of reduced molybdenum species in the char of PVC with AOM. The possible mechanisms of molybdenum based flame retardants have been discussed in detail by Innes and Cox. These mechanisms invoke the redox cycling between Mo(VI) and Mo(IV) and are consistent with our findings. The low levels of Sb and Al in PVC char indicates the formation of volatile oxychlorides. In the case of antimony, these are known to participate in flame retardancy. The char formed from PVC with Kemgard 911C is found to have higher levels of Al. In this system it appears that char formation inhibits the volatilization of aluminum species.

## VI. Conclusions

To achieve physical properties required for use as plenum jacket material and to pass the stringent requirements of UL 910, PVC compounds will contain a host of additives, including plasticizers, stabilizers, flame retardants, etc. All of these additives may contribute to smoke generation during combustion. A number of molybdate based materials, including AOM and Kemgard 911C are often employed to suppress smoke. Because of its patented coated-core structure, Kemgard 911C can provide effective smoke suppression at lower total Mo content than pure molybdate chemicals, resulting in significant economic benefit.

It is well established that molybdate smoke suppressants function in the condensed phase by enhancing char formation. However, our work suggests that beyond this common theme, molybdate smoke suppressants may differ mechanistically. Zinc molybdate smoke suppressants differ from AOM in their influence on the chemical composition of the char produced. The time course of char formation and smoke generation is also influenced by the choice of smoke suppressant. It also appears that molybdates can interact with other additives, influencing performance and producing apparent synergies. In particular the thermal behavior of phosphate ester plasticizers can be influenced by zinc molybdate. This in turn will influence char formation in PVC.

## VII. References

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