Melaminium Molybdate Smoke and Fire Retarders for Poly(vinyl chloride)

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Synopsis

Melaminium molybdates are shown to be very effective smoke and fire retarder additives for PVC. In a simple tin stabilized rigid PVC compound the preferred melaminium β-octamolybdate outperformed MoO_3 and other common molybdenum smoke retarders. Combinations of melaminium molybdates with compounds of copper formed very efficient smoke-reducing and char-forming synergistic additive systems for PVC. For example, combining the octamolybdate with a series of different copper compounds consistently gave smoke reductions of about 85% in the flaming mode of the NBS Smoke Chamber at a total additive level of 5 parts per hundred parts of PVC. These large reductions in smoke were accompanied by large increases in the amount of char formed and retained as combustion residues.

INTRODUCTION

In an earlier paper many molybdenum compounds are shown to be effective smoke and fire retarder additives for poly(vinyl chloride), PVC.[1] Of these compounds, molybdenum trioxide, MoO_3, has been the most extensively studied. In fact, there exists a significant number of publications dealing with the development and use of MoO_3 and other molybdenum compounds as smoke and fire retarder additives for PVC (Ref. 1 and references cited therein). Because of the promotion of MoO_3 as a commercially feasible smoke and fire retarder, many studies have been made to understand exactly how it functions in PVC.[1-8] In a highly phenomonological sense, Ref. 1 discloses that MoO_3 acts to change the normal thermal degradation pattern of PVC and promotes the formation of a thermally stable char which acts as a physical barrier to oxidation and combustion.

The change in the thermal degradation pattern of PVC, which is promoted by MoO_3, concerns the formation of volatile aromatic hydrocarbons. In the absence of a condensed phase smoke retarder, such as MoO_3, the formation of benzene and other volatile aromatic hydrocarbons quickly follows the onset of dehydrochlorination, the first low temperature step in the thermal degradation process.[7,9,10] It is generally accepted that the combustion of these aromatic hydrocarbons gives rise to much of the smoke which is released during the flaming combustion of PVC.[3,5,7,8] In the presence of MoO_3, the generation of volatile aromatic hydrocarbons is greatly reduced. In the same way, the MoO_3 acts to greatly diminish the quantity of smoke generated when PVC is forced to undergo flaming combustion.[1,3-5,7]

Recently, two model compound studies have addressed the function of

MoO_3 as a smoke retarder for PVC on a molecular scale.[6-8] Both studies concluded that the primary role of the MoO_3 was to promote the early crosslinking of the thermally degrading PVC chains as earlier proposed.[1-3] But the conclusions of how this was accomplished showed some lack of agreement. One study concluded that the MoO_3 promoted early crosslinking almost exclusively by functioning as a Lewis acid catalytic crosslinking agent.[6] The other study concluded that while Lewis-acid-promoted cross-linking is certainly one of the dominant crosslinking mechanisms, other mechanisms also appear to be important.[8] One of these other mechanisms is crosslink formation by an oxidative addition-reductive coupling mecha-nism. Another mechanism has the MoO_3 acting as a very effective aroma-tization catalyst. In this regard, high molecular weight condensed ring ar-omatic hydrocarbons have been identified in the pyrolysis products. And these condensed aromatics are believed to be the precursors of the graphitic, thermally stable char formed both during combustion and during inert at-mosphere pyrolysis. Our attempts to successfully incorporate MoO_3 as a smoke retarder in commercial PVC compounds revealed some significant problems. First, as holds for most candidate metal smoke retarders for PVC, MoO_3 lowers the threshold temperature for dehydrochlorination. This can lead to serious problems during processing including decomposition of the PVC, inferior physical properties, and discoloration of the final product. Second, MoO_3, because of its sensitivity to photoreduction, is obtained as a light green to light blue powder. This color is imparted to the PVC containing it and must be overcome in developing a white or unpigmented base PVC compound.

Melaminium molybdate smoke retarders for PVC resulted from a program to develop molybdenum-based smoke retarders which outperform MoO_3 and are more readily incorporated into commercial PVC compounds. There are four distinctly different melaminium molybdates. Their synthesis and char-acterization has been the subject of other papers.[11,12] The two most important melaminium molybdates and the subject of this paper are melaminium heptamolybdate, $(HMel)_6Mo_7O_{24} \cdot nH_2O$, and melaminium β-octamolybdate, $(HMel)_4Mo_8O_{26}$, where Mel represents the melamine ring, $C_3H_6N_6$. Both of these molybdates are readily obtained as free-flowing, white pigment size particles. However, the octamolybdate is more suitable as a commercial smoke retarder for PVC, since it is anhydrous and thermally stable to 260°C,[11,12] well above the processing temperature of PVC. The useful ther-mal and chemical stabilities of $(HMel)_4Mo_8O_{26}$ are a direct consequence of the extensive hydrogen bonding which exists between the melaminium cat-ions and the octamolybdate anions and between the melaminium cations themselves.[12]

This paper was written as a companion paper to another paper,[13] which provides a detailed discussion of the smoke reducing, char forming, and aromatic pyrolyzate reducing properties of an important and representative melaminium molybdate–copper synergistic smoke reducing system, includ-ing the mechanism of smoke reduction. In contrast, this paper describes the synergistic smoke reducing and char forming performance of melaminium molybdates and their combinations with a wide variety of copper compounds.

EXPERIMENTAL

The Model PVC Compound. All of the smoke retarder systems described in this report were evaluated in the model rigid PVC compound described as follows: 100 parts Geon 103EP PVC resin, 2 parts Microthene 510 polyethylene processing aid, 2 parts dibutyltinthioglycolate stabilizer. The PVC compounds containing the smoke retarder additives were prepared using conventional laboratory polymer processing procedures. First, the PVC resin, polyethylene processing aid, and tin stabilizer were blended on a hot (~160°C) rolling rubber mill. After addition of the smoke retarder(s), the milling was continued for about 5 min. Finally, the milled compound in sheet form was hot pressed at ~166°C into sheets 0.06 and 0.19 cm thick.

Combustibility Test Procedures. The combustibility characteristics of the smoke retarded PVC compounds were determined using small scale laboratory combustion tests. The performance of the PVC compounds in these tests does not necessarily correspond to their performance in either large scale tests or large scale real fires.
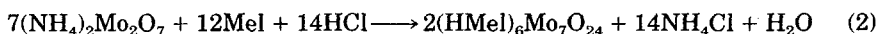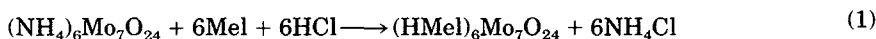
The NBS Smoke Chamber test was run in accordance with ASTM-E-662-79, Test for Specific Optical Density of Smoke Generated by Solid Materials." All tests were conducted under flaming conditions where PVC generates the most smoke. In this test, 7.3 × 7.3 × 0.06 cm samples are exposed to a radiant heat source of 2.5 W/cm² until the exposed part of the sample has stopped emitting smoke. A small pilot flame is located immediately in front of these samples in order to ignite flammable decomposition gases. Smoke evolved is measured photometrically by monitoring the optical density of the smoke which accumulates in the closed smoke chamber. The NBS smoke number reported in this paper, D_m/g, is the optical density smoke number normalized to the weight of the test specimen.

The Goodrich Smoke-Char test is a small scale laboratory test which was designed to measure both the formation of smoke and char. It has been described in detail in an earlier publication.[1] A small, approximately 0.3 gm, solid sample, approximately 0.19 cm thick, is exposed to a reproducible and well regulated (276 Pa), propane flame from a Benzomatic type burner for a period of 1 min. The generated smoke rises through a glass chimney and passes through the beam of a photocell coupled to an integrating circuit. The integrated area, when normalized to the weight of PVC in the sample, gives the smoke-char smoke number, S_{PVC}. As soon as the 1 min burn time has been reached, the flame is extinguished and the sample residue, char, is quenched in a rapid stream of nitrogen. The char yield is calculated from the weight loss observed during burning, expressed as % BC, the percent of the PVC backbone (that part of the hydrocarbon backbone left after complete dehydrochlorination) retained as a char residue. It is calculated as shown:
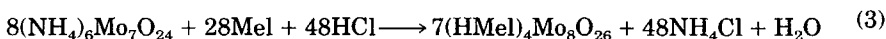
$$\% \text{ BC} = \frac{\text{char wt} - \text{nonburnable residue wt}}{\text{sample wt} - \text{non-PVC wt} - \text{HCl wt}} \times 100$$

Melaminium Isopolymolybdate Smoke Retarders. The $(HMel)_6Mo_7O_{24}\cdot8H_2O$ melaminium heptamolybdate, K_A, was prepared from

aqueous solution according to reactions (1) and (2), where Mel represents melamine, $C_3H_6N_6$:

$$(NH_4)_6Mo_7O_{24} + 6Mel + 6HCl \longrightarrow (HMel)_6Mo_7O_{24} + 6NH_4Cl \qquad (1)$$

$$7(NH_4)_2Mo_2O_7 + 12Mel + 14HCl \longrightarrow 2(HMel)_6Mo_7O_{24} + 14NH_4Cl + H_2O \qquad (2)$$

Similarly, the $(HMel)_4Mo_8O_{26}$ melaminium β-octamolybdate, K_C, was prepared from aqueous solution as shown in reactions (3) and (4):

$$8(NH_4)_6Mo_7O_{24} + 28Mel + 48HCl \longrightarrow 7(HMel)_4Mo_8O_{26} + 48NH_4Cl + H_2O \qquad (3)$$

$$4(NH_4)_2Mo_2O_7 + 4Mel + 8HCl \longrightarrow (HMel)_4Mo_8O_{26} + 8NH_4Cl + 2H_2O \qquad (4)$$

Reactions (1)–(4) were run at the temperature of reflux and the details are reported elsewhere.[11] Comparable products were obtained when H_2SO_4 or HNO_3 was substituted for HCl.

Molybdenum Trioxide Smoke Retarder. Molybdenum trioxide, MoO_3, as described in the introduction section, is the most widely studied molybdenum based smoke and fire retarder additive for PVC. Therefore, it was used in these studies as a control for the experimental melaminium isopolymolybdates. The MoO_3 used was from Fisher and designated as A-674 reagent grade molybdic anhydride. It was used as received. Grinding the reagent grade MoO_3 to reduce its average particle size slightly improved its dispersion characteristics in PVC, but without improvement in its ability to perform as a smoke and fire retarder. In the same way, an experimental MoO_3 product of small particle size and relatively low bulk density, which was supplied by the Climax Molybdenum Co., did not outperform the A-674 MoO_3 as a smoke and fire retarder additive for PVC.

Copper Synergists for Melaminium Isopolymolybdate Smoke Retarders. A number of different copper compounds were investigated as smoke reducing synergists for K_A and K_C molybdates and for MoO_3. The specific copper compounds and their sources are listed below:

Copper(I) iodide	CuI	Shepherd 070-701
Copper(II) oxalate	CuC_2O_4	Shepherd A1326
Copper(I) oxide	Cu_2O	Fisher C-477
Copper(II) oxide	CuO	Fisher C-472
Copper(II) sulfate	$CuSO_4$	Fisher C-495
Copper(I) thiocyanate	CuSCN	ROC/RIC CU76
Bis-(2,4-petanedionato)-copper(II)	$Cu(AcAc)_2$	J. T. Baker S975

where $AcAc = C_5H_7O_2{}^-$. All of the compounds were used as received. Because the commercial Cu_2O (red) contained a surface coating of a pine oil as an antioxidant, a finer particle size Cu_2O (yellow) free from pine oil was prepared by reducing an aqueous Cu(II) solution with hydrazine. The red and yellow copper(I) oxides gave comparable results.

Smoke-Reducing Synergisms. A binary smoke retarder system consisting of K_A or K_C and a copper compound was classified as synergistic when a given concentration gave a statistically significant lower smoke rating compared to either component at the same concentration. We used a statistical procedure to decide whether any selected binary system exhibited a smoke reducing or char forming synergism. This procedure is based on using the T-test to determine the probability that the lower smoke rating for the binary system is different from the smoke rating obtained for each of the components. The calculation of the T-test statistic for the equality of the means of two independent samples using pooled variance, and the probability significance of the T-test statistic was based on the statistical algorithms in the SPSS-X statistical software program.[14] In the context of this paper, synergism is only claimed for a binary mixture when its mean value for the property being measured is different from the mean values of its components at or above the 95% confidence level.

RESULTS AND DISCUSSION

Melaminium Molybdate Smoke Retarders vs. Molybdenum Trioxide. Comparative smoke and char data for MoO_3, K_A melaminium heptamolybdate and K_C melaminium β-octamolybdate are shown in Table I. The data show that while K_A and MoO_3 give comparable smoke and char reductions, K_C significantly outperforms them at all loading levels. In the flaming mode of the NBS smoke chamber test, all three compounds effectively lowered smoke at low concentration levels (2–2.5 phr). However, K_C was the most effective, giving a reduction of 54% compared to 27% and 37% for K_A and MoO_3. The performance of all three compounds as a function of

TABLE I
Comparison of Molybdenum Smoke Retarders

Retarder	Level (phr)	Smoke (D_m/g)[a]	% Decrease	Smoke (S_{PVC})[b]	% Decrease	Char (% BC)[b]	% Increase
None	—	64.2 ± 9.5	—	100.9 ± 13.3	—	7.8 ± 4.1	—
MoO_3	2	40.3 ± 2.7	37.2	48.0 ± 8.5	52.4	28.4 ± 0.5	264
MoO_3	5	27.3 ± 2.0	57.5	54.6 ± 15.1	45.9	33.4 ± 3.3	328
MoO_3	10	27.2 ± 2.1	57.6	35.9 ± 9.9	64.4	37.8 ± 3.0	385
K_A[c]	2.5	46.7 ± 8.3	27.3	—	—	—	—
K_A	5	32.8 ± 3.0	48.9	46.9 ± 6.5	53.5	34.1 ± 1.6	337
K_A	10	29.2 ±3.9	54.5	28.7 ± 0.1	71.6	42.0 ± 0.5	438
K_C[d]	2	29.8 ± 2.1	53.6	—	—	—	—
K_C	2.5	29.5 ± 2.9	54.1	—	—	—	—
K_C	5	24.3 ± 2.3	62.2	49.6 ± 8.1	50.8	45.2 ± 6.7	479
K_C	10	24.0 ± 0.8	62.6	23.3 ± 0.3	76.9	50.8 ± 1.4	551

[a] NBS Smoke Chamber flaming mode.
[b] Smoke-Char test.
[c] Melamimium heptamolybdate.
[d] Melaminium β-octamolybdate.

concentration is very similar. The maximum smoke reduction is obtained near a concentration of about 5 phr. Increasing the concentration to 10 phr and above provides no significant additional reduction in smoke. In fact, beyond 10 phr any additional reductions in smoke would result from diluting a burnable organic composition with a nonburnable inorganic additive. At a loading of 5 phr, K_C again produces the greatest reduction of smoke, 62% compared to 49% and 58% for K_A and MoO_3.

Smoke reduction in the Smoke-Char test gave a different concentration dependence compared to the NBS test. K_C, K_A, and MoO_3 were found to be significantly more effective at 10 phr than at 5 phr. Again, K_C was found to be the most effective smoke retarder with a reduction of 77% compared to 72% and 64% for K_A and MoO_3. Interestingly, at a loading of 5 phr all three compounds were equally effective in reducing smoke generation by about 50%.

As reported earlier,[1] one of the important characteristics of condensed phase smoke retarders for PVC is their ability to change the normal thermal degradation pattern of PVC in such a way as to promote the formation of a char residue which forms an effective thermal barrier to protect unburned material and minimize flame spread. Char forming data for the three Mo smoke retarders are included in Table I. In each case, smoke reduction is accompanied by a significant increase in char formation. As shown, and consistent with its exceptional smoke reducing ability, K_C is a more effective promoter of char formation compared to either K_A or MoO_3. At 10 phr K_C, over 50% of the PVC backbone from the model compound was retained as a structurally intact thermally stable char residue.

Although the data in Table I have been compared on an equal weight basis of added smoke retarder, differences in molybdenum concentration were neglected. The actual Mo concentrations in K_A, K_C, and MoO_3 are 34.22, 45.36, and 66.65%, respectively. However, if the data in Table I are normalized to the concentration of Mo, K_C remains the most effective additive for reducing smoke from the model PVC compound in the NBS Smoke chamber test. At both levels, K_A and K_C are much more effective than MoO_3. When the char data in Table I are normalized to Mo, K_C is a much more effective char former than K_A which is much more effective than MoO_3.

The fact that on a Mo normalized basis the relative performances of K_C and K_A reversed in going from the NBS Smoke Chamber test to the Smoke-Char test probably reflects the differences in the test conditions. For example, in the NBS test the samples are exposed to a radiant heat source in a stagnant air atmosphere. In contrast, the samples are completely immersed in the flame of a propane burner under dynamic air conditions in the Smoke-Char test. As described in Ref. 1, the Smoke-Char test was developed in part as a rapid screening test for smoke evolution. The smoke results from the Smoke-Char test for a wide range of different samples statistically correlate to the smoke results obtained from the NBS test for the same series of samples. However, for any one sample run in both tests the % reduction in smoke may show considerable variation. Nevertheless, as shown by the smoke data included in this paper, smoke reductions in the NBS test are reflected in smoke reductions in the Smoke-Char test.

TABLE II
Comparison of Copper Smoke Retarders

Retarder	Level (phr)	Smoke $(D_m/g)^a$	% Decrease	Smoke $(S_{PVC})^b$	% Decrease	Char (% BC)^b	% Increase
None	—	64.2 ± 9.5	—	100.9 ± 13.3	—	7.8 ± 4.1	—
CuI	5	25.3 ± 0.6	60.6	71.0 ± 1.1	29.6	—	—
CuC_2O_4	2.5	24.2 ± 1.7	62.3	—	—	—	—
CuC_2O_4	5	18.9 ± 2.4	70.6	57.8 ± 0.8	42.7	30.8 ± 0.3	295
CuC_2O_4	10	15.5 ± 1.4	75.9	36.7 ± 6.5	63.6	40.2 ± 1.4	415
Cu_2O	5	23.0 ± 3.3	64.2	49.1 ± 13.4	51.3	38.8 ± 2.0	397
CuO	5	24.7 ± 0.6	61.5	64.2 ± 2.0	36.4	—	—
$CuSO_4$	5	21.0 ± 2.1	67.3	55.8 ± 7.2	44.7	32.1 ± 0.2	312
CuSCN	5	23.8 ± 2.6	62.9	70.1 ± 6.3	30.5	34.9 ± 1.6	347
$Cu(AcAc)_2$	5	26.5 ± 3.0	58.7	77.8 ± 4.5	22.9	—	—

[a] NBS Smoke Chamber flaming mode.
[b] Smoke-Char test.

Copper Compounds as Smoke and Fire Retarders for PVC. As reported earlier[1] compounds of copper form the most effective class of single metal smoke retarders for PVC. Table II presents smoke and char data for seven different compounds of copper. At a concentration of 5 phr in the model PVC compound, they are about as effective as K_C melaminium β-octamolybdate in reducing smoke formation in the flaming mode of the NBS Smoke Chamber test (see Table I). In contrast, it can be seen that the copper compounds are not as effective as K_C in reducing smoke formation in the
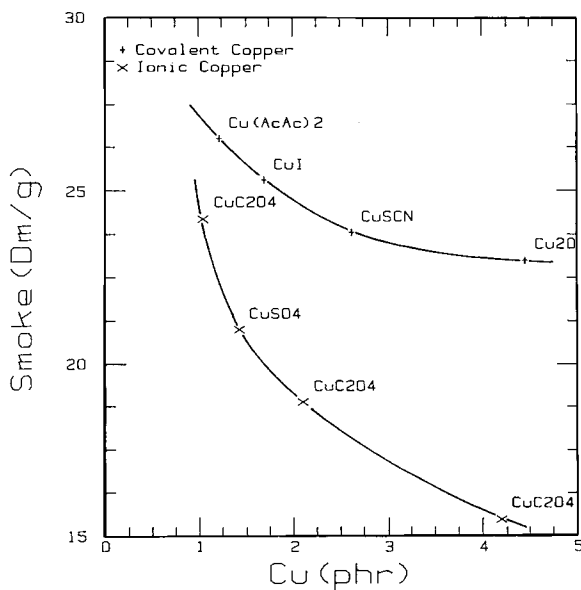

Fig. 1. Smoke vs. Cu level in NBS Smoke Chamber test: (+) covalent copper; (×) ionic copper.

Smoke-Char test. And in keeping with the established relationship between smoke reduction and char formation,[1] they are less effective than K_C in promoting char formation. Nevertheless, as shown in Table II, the five copper compounds, which were evaluated at the 5 phr level in the Smoke-Char test, effectively promoted the formation of a relatively large char residue.

The two most effective copper compounds for reducing smoke in the NBS test at the 5 phr level were CuC_2O_4 and $CuSO_4$. However, only CuC_2O_4 was significantly superior to 5 phr of K_C using the 95% probability of being different criterion, as described in the Introduction section. Because CuC_2O_4 was a very effective smoke retarder, relatively light in color, thermally stable under processing conditions, and relatively processable in rigid PVC compounds, it was studied in more detail. The NBS smoke data in Table II show that as the concentration of CuC_2O_4 increased from 2 to 10 phr, smoke formation continuously decreased, but with a curvelinear rather than a linear relationship.

As in the case of the molybdenum smoke retarders, each of the copper compounds in Table II has a different copper concentration. Therefore, the data in Table II were normalized to copper by plotting the D_m/g smoke no. as a function of copper concentration. The result is Figure 1, which unexpectedly shows that the data fall into two separate curves. The upper curve fits the data for the relatively covalently bonded copper compounds while the lower curve fits the data from $CuSO_4$ and CuC_2O_4 compounds, in which the interaction between the Cu(II) ions and the sulfate and oxalate anions is largely ionic. Since the ionic copper curve always lies below the covalent copper curve, a reasonable interpretation appears to be that under conditions of thermal stress the Cu(II) ions from the ionic copper compounds are more readily accessible to the thermally degrading PVC chains.

MoO_3–Copper Smoke-Retarder Systems. It was reported earlier that MoO_3 and Cu_2O combinations appeared to give a weak smoke reducing synergism in the flaming mode of the NBS Smoke Chamber test.[1] Therefore, the MoO_3–Cu_2O smoke retarder system for PVC was studied in greater detail. This study was extended to include smoke reduction in the Smoke-Char test. The results, which are summarized in Table III, suggest the possibility of a weak smoke reducing synergism between MoO_3 and Cu_2O

TABLE III
MoO_3–Cu_2O Smoke Retarder System

MoO_3 (phr)	Cu_2O (phr)	Smoke (D_m/g)[a]	Smoke (S_{PVC})[b]	Char (% BC)[b]
5.00	—	27.3 ± 2.0	54.6 ± 15.1	33.4 ± 3.3
4.45	0.55	20.4 ± 2.6	67.8 ± 7.9	36.3 ± 1.3
3.90	1.10	19.4 ± 1.8	76.5 ± 0.6	35.9 ± 0.7
3.34	1.66	18.8 ± 1.7	67.4 ± 12.2	37.2 ± 1.4
3.00	2.00	18.6 ± 0.7	62.6 ± 12.8	37.4 ± 2.0
2.50	2.50	21.4 ± 3.5	67.4 ± 9.9	37.2 ± 1.1
2.25	2.75	20.0 ± 2.0	69.8 ± 9.4	36.2 ± 0.5
—	5.00	23.0 ± 3.3	48.1 ± 13.4	38.8 ± 2.0

[a] NBS Smoke Chamber flaming mode.
[b] Smoke-Char test.

in the NBS test. However, the highest probability of synergism, 92% (for the Mo/Cu = 3.00/2.00 composition) was well below the target 95% probability level. As shown in Table III, the MoO_3–Cu_2O combinations were not very effective in reducing smoke formation in the Smoke-Char test. In fact, none of these compositions at the 5 phr level were more effective than either 5 phr of Cu_2O or 5 phr of MoO_3.

The MoO_3–CuC_2O_4 binary system also was investigated for synergistic smoke reducing compositions in the flaming mode of the NBS Smoke Chamber test. None were found. For example, 5 phr of an equal weight mixture of MoO_3 and CuC_2O_4 gave a smoke number of 19.1 ± 2.3, essentially identical to the smoke number from 5 phr of CuC_2O_4, 18.9 ± 2.4.

K_A Melaminium Heptamolybdate–Copper Smoke Reducing Synergisms. Two K_A–copper systems were investigated for smoke reducing synergisms in the NBS Smoke Chamber test. One system was K_A–CuSCN at a concentration level of 6 phr; the other was K_A–CuC_2O_4 at a concentration level of 5 phr. The smoke data for both systems are listed in Table IV. For both systems, every binary combination was synergistic at the 95% confidence level. These smoke reducing synergisms are graphically illustrated in Figure 2. As shown, the K_A–CuC_2O_4 system at a 5 phr level outperformed the K_A–CuSCN system at a 6 phr level.

The K_A–CuC_2O_4 synergism study was extended to include evaluation in the Smoke-Char test. Table V presents the results of that evaluation. Clearly, the smoke reducing synergism holds in both the NBS Smoke Chamber and Smoke-Char tests. Table V also shows that the synergistic interaction between K_A and CuC_2O_4 holds for the formation of char. Compared to the two end member components, 5 phr K_A and 5 phr CuC_2O_4, the 2.5/2.5 K_A/CuC_2O_4 combination gave about a 50% increase in char formation.

K_C Melaminium β-Octamolybdate–Copper Smoke Reducing Synergisms. K_C, which was found to be the most effective molybdenum smoke retarder for the model PVC compound (see Table I), has a high thermal stability and processes well, without discoloration, in the model compound. Therefore, the smoke retarding properties of binary combinations of K_C and the copper compounds listed in Table II were investigated. This study was

TABLE IV
K_A Melaminium Heptamolybdate Smoke Retarder Systems with Cu_2O and CuSCN

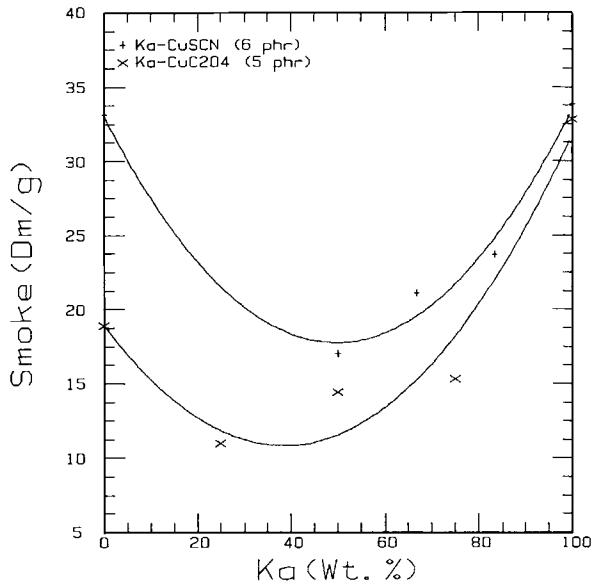| K_A (phr)	Cu_2O (phr)	CuSCN (phr)	Smoke (D_m/g)[a]
5.00	—	—	32.8 ± 3.0
3.75	1.25	—	15.3 ± 0.3
2.50	2.50	—	14.4 ± 2.2
1.25	3.75	—	11.0 ± 2.2
—	5.00	—	18.9 ± 2.4
6.00	—	—	33.8 ± 3.2
5.00	—	1.00	23.7 ± 2.7
4.00	—	2.00	21.1 ± 1.7
3.00	—	3.00	17.0 ± 0.7
—	—	6.00	33.1 ± 1.9

[a] NBS Smoke Chamber flaming mode.

Fig. 2. Ka–Cu smoke retarders in NBS Smoke Chamber test: (+) Ka–CuSCN (6 phr); (×) Ka–CuC$_2$O$_4$ (5 phr).

made at a smoke retarder level of 5 phr in the model PVC compound. In each case the performance of an equal weight mixture of K_C and copper compound was compared to the same weight of each of the components. Smoke generation was measured in both the flaming mode of the NBS Smoke Chamber test and the Smoke-Char test. The results are tabulated in Table VI. As shown, K_C gave a very strong smoke reducing synergism with every copper compound tested in both the NBS test and the Smoke-Char test. In fact, with only one exception, the probability of synergism for each of the K_C–copper binary systems was greater than 99.9%.

In order to better understand the character of the impressive smoke reducing interaction between K_C and copper compounds, the K_C–CuC$_2$O$_4$ system was studied in greater detail. CuC$_2$O$_4$ was chosen as the representative

TABLE V
Smoke-Char Data for the K_A Melaminium Heptamolybdate-CuC$_2$O$_4$ Smoke Retarder System

K_A (phr)	CuC$_2$O$_4$ (phr)	Smoke (D_m/g)[a]	Smoke (S_{PVC})[b]	Char (% BC)[b]
5.00	—	32.8 ± 3.0	46.9 ± 6.5	34.1 ± 1.6
2.50	2.50	14.4 ± 2.2	21.0 ± 0.4	48.4 ± 0.7
—	5.00	18.9 ± 2.4	57.8 ± 0.8	30.8 ± 0.3

[a] NBS Smoke Chamber flaming mode.
[b] Smoke-Char test.

TABLE VI
Smoke Reducing Synergisms Between K_C Melaminium β-Octamolybdate and Copper
Compounds

K_C (phr)	Copper Compound	Level (phr)	Smoke $(D_m/g)^a$	Smoke $(S_{PVC})^b$
5.0	—	—	24.3 ± 2.3	49.6 ± 8.1
2.5	CuI	2.5	8.0 ± 1.5	11.2 ± 1.9
—	CuI	5.0	25.3 ± 0.6	71.0 ± 1.1
2.5	CuC_2O_4	2.5	10.5 ± 1.9	25.4 ± 1.6
—	CuC_2O_4	5.0	18.9 ± 2.4	57.2 ± 1.7
2.5	Cu_2O	2.5	8.7 ± 1.0	19.7 ± 4.3
—	Cu_2O	5.0	23.0 ± 3.3	49.1 ± 13.4
2.5	CuO	2.5	11.1 ± 2.1	19.9 ± 3.7
—	CuO	5.0	24.7 ± 0.6	64.2 ± 2.0
2.5	$CuSO_4$	2.5	14.0 ± 1.7	18.8 ± 2.8
—	$CuSO_4$	5.0	21.0 ± 2.1	55.8 ± 7.2
2.5	CuSCN	2.5	8.4 ± 0.9	17.8 ± 1.8
—	CuSCN	5.0	23.8 ± 2.6	70.1 ± 6.3
2.5	$Cu(AcAc)_2^c$	2.5	8.1 ± 0.7	16.0 ± 0.1
—	$Cu(AcAc)_2$	5.0	26.5 ± 3.0	77.8 ± 4.5

[a] NBS Smoke Chamber flaming mode.
[b] Smoke-Char test.
[c] AcAc = $C_5H_7O_2^-$.

copper compound because the K_A–CuC_2O_4 system had been studied earlier
(Tables IV and V), and because CuC_2O_4 is relatively easy to incorporate
into the model PVC compound. Table VII shows the effectiveness of different
ratios of K_C and CuC_2O_4 for reducing smoke in the flaming mode of the
NBS Smoke Chamber test at an overall smoke retarder level of 5 phr. The
probability of a smoke reducing synergism for all three of the K_C–CuC_2O_4
combinations in Table VII is greater than 99.5%. The data in Table VII are
graphically presented in Figure 3 to illustrate the broad extent of the smoke
reducing synergism between K_C and CuC_2O_4.

The smoke reducing interaction between equal weight mixtures of K_C and
CuC_2O_4 also was studied at three different overall smoke retarder concen-
tration levels (2.5, 5.0, and 10 phr). The results are shown in Table VIII.
At each loading level the equal weight K_C–CuC_2O_4 mixture exhibited a

TABLE VII
The K_C^a–CuC_2O_4 Smoke Reducing Synergism

K_C (phr)	CuC_2O_4 (phr)	Smoke $(D_m/g)^b$	% Decrease
—	—	64.2 ± 9.5	—
5.00	—	24.3 ± 2.3	62.1
3.75	1.25	13.6 ± 1.5	78.8
2.50	2.50	10.5 ± 1.9	83.6
1.25	3.75	10.4 ± 1.6	83.8
—	5.00	18.9 ± 2.4	70.6

[a] Melaminium β-octamolybdate.
[b] NBS Smoke Chamber flaming mode.

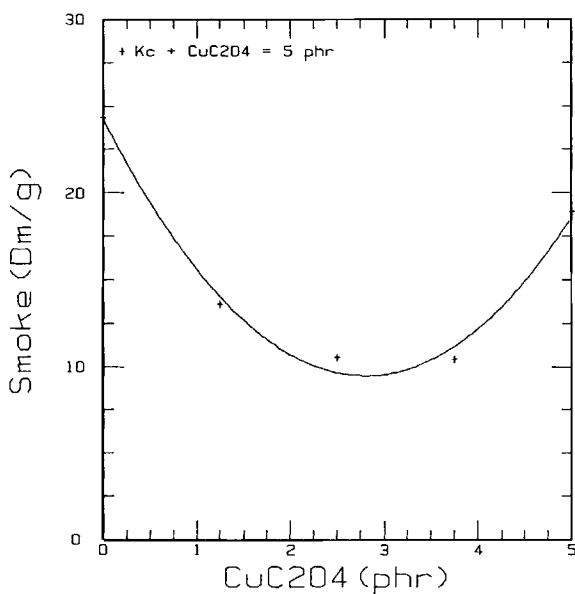Fig. 3. Kc–CuC$_2$O$_4$ synergism in NBS Smoke Chamber test: (+) Kc + CuC$_2$O$_4$ = 5 phr.

strong smoke reducing synergism (>99.9% probability) in the NBS Smoke Chamber test. At the 5 and 10 phr levels the equal weight K$_C$–CuC$_2$O$_4$ mixture exhibited an equally strong smoke reducing synergism (>99.2% probability) in the Smoke-Char test.

Table VIII also presents the char forming characteristics of the equal weight K$_C$–CuC$_2$O$_4$ system at the 5 and 10 phr loading levels. The important conclusion is that K$_C$–CuC$_2$O$_4$ is a very effective promoter of char formation

TABLE VIII
Equal Weight Mixtures of the K$_C$[a]–CuC$_2$O$_4$ Synergistic Smoke Retarder System

K$_C$ (phr)	CuC$_2$O$_4$ (phr)	Smoke (D_m/g)[b]	Smoke (S_{PVC})[c]	Char (% BC)[c]
2.50	—	29.5 ± 2.9	—	—
1.25	1.25	14.8 ± 1.7	51.1 ± 7.5	46.0 ± 1.9
—	2.50	24.2 ± 1.7	—	—
5.00	—	24.3 ± 2.3	49.6 ± 8.1	45.2 ± 6.7
2.50	2.50	10.5 ± 1.9	25.4 ± 1.6	55.4 ± 2.9
—	5.00	18.9 ± 2.4	57.2 ± 1.7	30.8 ± 0.3
10.00	—	24.0 ± 0.8	23.3 ± 0.2	50.8 ± 1.0
5.00	5.00	8.5 ± 0.5	7.8 ± 4.7	66.8 ± 2.6
—	10.00	15.5 ± 1.4	36.7 ± 6.5	40.2 ± 1.4

[a] Melaminium β-octamolybdate.
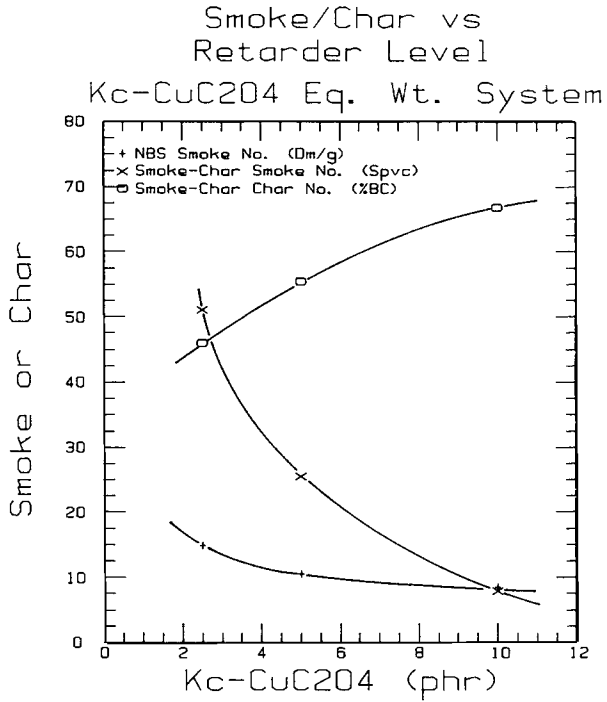[b] NBS Smoke Chamber flaming mode.
[c] Smoke-Char test.

Fig. 4. Smoke/char vs. retarder level: Kc–CuC$_2$0$_4$ eq. wt. system: (+) NBS smoke no. (D_m/g); (×) Smoke–Char smoke no. (S_{PVC}); (O) Smoke–Char char no. (% BC).
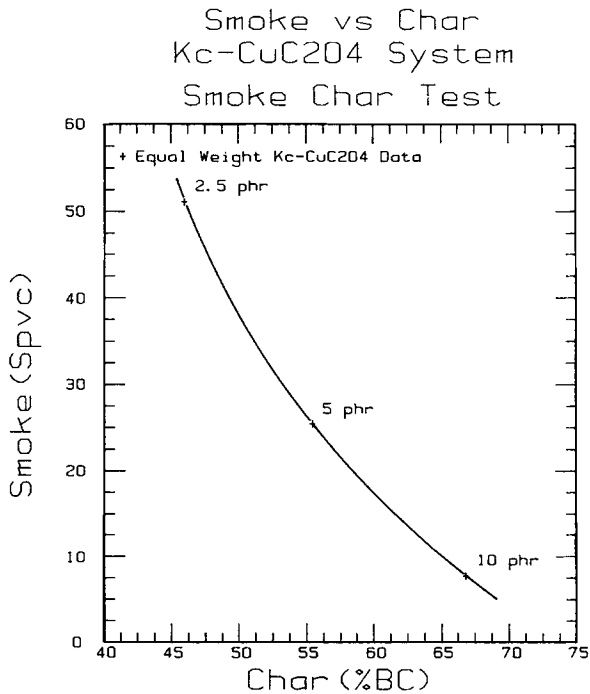
Fig. 5. Smoke vs. char for Kc–CuC$_2$0$_4$ system in Smoke Char test: (+) equal weight Kc–CuC$_2$0$_4$ data.

in the Smoke-Char test. In fact, at both loading levels the equal weight mixture gave a strong char forming synergism (>97.7% probability for 5 phr and >99.8% probability for 10 phr).

The data in Table VIII illustrate the effect of concentration on the equal weight synergistic smoke reducing and char forming K_C–CuC_2O_4 combinations. These effects are graphically illustrated in Figure 4. In both the NBS test and the Smoke-Char test there is a continual decrease in smoke formation as the concentration of the K_C–CuC_2O_4 smoke retarder increases. But, as shown in Figure 4, the response of the NBS smoke no. (D_m/g) to concentration changes is relatively small.

The char forming data in Table VIII reveal that as the concentration of the K_C–CuC_2O_4 retarder system is increased from 2.5 to 10 phr the char yield continually increases from 46 to 67% of the theoretical yield of backbone char. This char–concentration relationship is also shown in Figure 4. As discussed in the Introduction section, during the combustion of PVC, char formation always accompanies smoke reduction promoted by smoke retarder additives which function in the condensed phase to change the normal PVC thermal degradation pattern. This relation of causality between the smoke reduction and char formation is illustrated in Figure 5 for the Smoke-Char data listed in Table VIII and plotted in Figure 4.

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