

The Effects of a Synergistic Molybdenum–Copper Smoke Retarder Additive During the Pyrolysis and Combustion of Rigid Poly(vinyl chloride) Compounds

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Synopsis

The addition of an effective transition metal-based smoke retarder to rigid poly(vinyl chloride) (PVC) has three general effects during combustion and inert atmosphere pyrolysis: (1) smoke formation is reduced; (2) char formation is enhanced; and (3) volatile aromatic pyrolyzate formation is reduced while aliphatic pyrolyzate formation is enhanced. A very efficient molybdenum–copper smoke retarder additive has been developed for PVC. It consists of an equal weight mixture of melaminium beta-octamolybdate and copper(II) oxalate. This combination is synergistic in reducing smoke during the combustion of PVC, i.e., the mixture is more effective than either of the two ingredients used individually at the same concentration as the mixture. The molybdenum–copper system reduced smoke effectively in three rigid PVC compounds, two of which resemble commercial formulations. The combustibility and pyrolysis effects of this molybdenum–copper additive can be interpreted in terms of an “early cross-linking” mechanism of smoke retardation in PVC. In this mechanism the metal smoke retarder works primarily by catalytically promoting early crosslinking of decomposing PVC chains to yield char as a residue.

INTRODUCTION

It has been well established in the chemical literature that a large number of metal compounds, especially those of transition metals, can function as smoke retarders for poly(vinyl chloride) (PVC).¹ When added to PVC compounds, these materials reduce the amount of smoke generated when the compounds are forced to burn. Accompanying the reduction in smoke is an increase in the amount of char, carbonaceous residue, which remains after combustion.^{1,2} Although the inverse relationship between smoke and char has been established from the results of burning PVC compounds in small-scale laboratory tests such as the NBS Smoke Chamber test³ and the Goodrich Smoke-Char test,¹ it also has been observed in the conduct of larger-scale fire tests.⁴

Recently, a number of research groups have studied the mechanism by which metal smoke retarder compounds act to reduce smoke and form char in PVC.^{2,5–18} Several of these studies have used molybdenum trioxide (MoO_3) as a representative smoke retarder, although numerous other additives have been reported. In our most recent study, mixtures of MoO_3 and Cu_2O were investigated.¹⁸ The system consisting of an equal weight mixture of MoO_3 and Cu_2O was of particular interest, because it was previously reported to

give a smoke-reducing synergism in a simple model PVC compound.¹ However, a current detailed analysis of the $\text{MoO}_3\text{-Cu}_2\text{O}$ system showed that at the 5 phr (parts per hundred of PVC resin) level there was only a 71–77% probability of a statistically significant smoke reducing synergism.¹⁹ The same study, however, showed that the combination of melaminium beta-octamolybdate (K_c) and copper(II) oxalate (CuC_2O_4) gave a very strong smoke-reducing synergism in the same model PVC compound, in both the NBS Smoke Chamber test and the Goodrich Smoke-Char test. In fact, the probability that this synergism was statistically significant at 2.5, 5, and 10 phr concentration levels was >99.9%.¹⁹

This paper presents a study of the smoke-suppressant $\text{K}_c\text{-CuC}_2\text{O}_4$ system consisting of an equal weight mixture of both components. The smoke-reducing, char-forming, and aromatic pyrolyzate-reducing properties of this system have been investigated in three different PVC compounds. One of these compounds was the simple model PVC compound used in our earlier studies.^{1,2,17} The other two compounds were designed to simulate a commercial general purpose rigid PVC formulation and a commercial rigid PVC pipe formulation. The smoke and char studies were performed in the flaming mode of the NBS Smoke Chamber and in the Goodrich Smoke-Char test. Volatile pyrolyzate formation, during inert atmosphere micropyrolysis, was studied using pyrolysis–gas chromatography (Py-GC) and Py-GC-mass spectrometry techniques.

EXPERIMENTAL

PVC Compounds and Metal Additives

Three different PVC compounds were used for the smoke, char, and volatile pyrolyzate studies. Each compound is based on a Geon[®] PVC homopolymer with an inherent viscosity of 0.98–1.04 and an ASTM classification of GP-5-1443. The compound recipes follow:

PVC Model Compound

- 100 parts Geon[®] 103EPF76 PVC Resin
- 2 parts Thermolite[®] 31 Dibutyltin-bis(isooctylthioglycolate)
- 2 parts Microthene[®] 510 Polyethylene

PVC Pipe Type Compound

- 100 parts Geon 103EPF76 Resin
- 2 parts Thermolite 31 Dibutyltin-bis(isooctylthioglycolate)
- 4 parts R&H K120N Acrylate Processing Aid
- 3 parts TiPure[®] R-100 TiO_2 Pigment
- 1 part Synpro[®] 24-46 Calcium Stearate
- 1 part Advawax[®] 280 Ethylene-bis-stearamide

PVC General Purpose Compound

- 100 parts Geon 103EPF76 Resin

- 2.5 parts Thermolite 31 Dibutyltin-bis(isooctylthioglycolate)
- 3.0 parts Hycar® 2301 × 36 Styrene-Acrylonitrile Copolymer
- 2.0 parts Synpro 24-46 Calcium Stearate
- 2.0 parts Advawax 280 Ethylene-bis-stearamide

The three PVC compounds were made up as 45.3 kg master batches by blending together the ingredients in a hot Henschel mixer.

Sample preparation consisted of milling ~750 g of each of the PVC compounds (with smoke retarder as specified) on a clean 15.2-cm rolling rubber mill. The mill temperature was about 160°C. After milling, the sheet stock was pressed into six 15.2 × 15.2 × 0.06-cm sheets, and about six ACS sheets (15.2 × 15.2 × 0.19 cm). The molding operation consisted of pressing the preheated sheets in the appropriate mold for about 4 min at about 165°C. The pressed samples were quickly cooled by removing the mold from the press.

The samples for pyrolysis were cut from the center of each of the 0.06-cm thick sheets. In practice, a 15.2-cm strip just under 1 mm thick was removed and subsequently cut into 4-mm strips. This gave samples for pyrolysis which weighed 3–4 mg. The samples for evaluation in the NBS Smoke Chamber test also were cut from the 0.06-cm thick sheets. They were 7.3 × 7.3 × 0.06 cm. One sample was cut from each 0.06-cm sheet. Smoke-Char test samples were made from 15.2 × 1.3-cm strips cut from the center of each of the 0.19-cm sheets. One piece, 1.3 × 1.0 × 0.19 cm, was cut from each strip.

The detailed description and structure of K_c melaminium beta-octamolybdate has been reported elsewhere.^{20,21} It was prepared in our laboratory according to published procedures and characterized by elemental analysis, infrared spectroscopy, and X-ray powder diffraction.²⁰ Copper oxalate was obtained from the Shepherd Chemical Co. (A-1326) and used as received. Both the K_c and the CuC₂O₄ had average particle sizes <5 μm and were readily dispersed and homogeneously incorporated into the three PVC compounds.

SMOKE AND CHAR ANALYSES

Two laboratory tests were used for determining the amounts of smoke formed when the PVC samples were forced to burn. One of these is the NBS Smoke Chamber test,³ which was always conducted in the flaming mode. The other is the Goodrich Smoke-Char test¹ which was also used to measure char formation during PVC combustion under a closely controlled set of experimental conditions. The exact description of burning the PVC samples in both tests, and the treatment of the experimental data are found elsewhere and will not be repeated here.¹ At least six individual combustion tests were made with each smoke-retarded PVC compound evaluated in either the NBS Smoke Chamber or Smoke-Char test. The average smoke and char values and their standard deviations were calculated and reported as the experimental results.

VOLATILE PYROLYZATES

Pyrolyses were carried out at 550°C in a dry helium atmosphere using a CDS 100 Pyroprobe. Identification of pyrolyzates was carried out (Py-GC-MS) with a Finnigan MAT 311A/Incos 2400 mass spectrometer system. Semiquantitative analysis of pyrolyzates was carried out by flame ionization gas chromatography (Py-FID-GC). The exact experimental details and procedures are described in earlier publications.^{2,17}

RESULTS AND DISCUSSION

Smoke Reduction

This section discusses the performance of the PVC compounds in both the NBS Smoke Chamber test and the Smoke-Char test. The smoke data are given in Table I (flaming mode of the NBS Smoke Chamber) and in Table II (Smoke-Char test). In both tests the performance of the K_c - CuC_2O_4 system was evaluated at three concentrations for each of the three different PVC compounds.

An inspection of the smoke data in Table I shows that the pipe compound control (no smoke retarder) produced significantly less smoke than the other control compounds. This apparently reflects the 3 phr of TiO_2 which is present in the pipe compound recipe; we have shown that many pigment grades of TiO_2 are smoke retarders for PVC as determined in the NBS test.¹ The increased smoke observed for the general purpose rigid PVC compound control can be attributed to the presence of the styrene-acrylonitrile copolymer additive. This decomposes to yield styrene, acrylonitrile, and other

TABLE I
NBS Smoke Chamber Test Evaluations: Flaming Mode

PVC base compound	K_c (phr)	CuC_2O_4 (phr)	Smoke (D_m/g)	Smoke reduction (%)
Model	—	—	64.5 ± 8.7	—
	1.25	1.25	14.8 ± 1.7	77
	2.50	2.50	9.8 ± 1.5	85
	5.00	5.00	8.5 ± 0.5	87
	5.00	—	23.3 ± 1.1	64
	—	5.00	20.2 ± 1.9	69
Pipe type	—	—	55.4 ± 8.6	—
	1.25	1.25	18.5 ± 1.9	67
	2.50	2.50	14.5 ± 0.7	74
	5.00	5.00	13.2 ± 0.5	76
	5.00	—	29.5 ± 2.6	47
	—	5.00	29.9 ± 2.6	46
General purpose	—	—	80.5 ± 9.1	—
	1.25	1.25	36.7 ± 2.3	54
	2.50	2.50	23.8 ± 1.2	70
	5.00	5.00	22.0 ± 1.3	73
	5.00	—	38.5 ± 2.1	52
	—	5.00	39.2 ± 4.0	51

TABLE II
 Smoke-Char Test Evaluations

PVC base compound	K_c (phr)	CuC_2O_4 (phr)	Smoke (S_{PVC})	Smoke reduction (%)	Char (%BC)
Model	—	—	92 ± 6	—	7.7 ± 2.9
	1.25	1.25	51 ± 8	44	46.0 ± 1.9
	2.50	2.50	25 ± 2	73	55.4 ± 2.9
	5.00	5.00	8 ± 5	91	66.8 ± 2.6
	5.00	—	54 ± 4	42	49.3 ± 2.9
	—	5.00	83 ± 4	10	38.4 ± 5.7
Pipe type	—	—	135 ± 8	—	17.6 ± 2.8
	1.25	1.25	77 ± 11	43	43.5 ± 4.7
	2.50	2.50	25 ± 6	82	55.6 ± 3.8
	5.00	5.00	13 ± 3	90	74.0 ± 2.9
	5.00	—	60 ± 6	56	52.4 ± 0.8
	—	5.00	113 ± 5	16	34.4 ± 5.9
General purpose	—	—	157 ± 18	—	9.8 ± 4.2
	1.25	1.25	99 ± 6	37	40.0 ± 4.0
	2.50	2.50	41 ± 13	74	50.3 ± 4.6
	5.00	5.00	17 ± 5	89	72.6 ± 2.0
	5.00	—	41 ± 10	74	52.5 ± 4.7
	—	5.00	116 ± 12	26	31.1 ± 7.1

unsaturated pyrolyzates which generate copious quantities of smoke during combustion.

The general purpose rigid compound control generates more smoke than the other two control compounds in the Smoke-Char test (Table II), as expected. However, the model compound control is surprisingly less smoky than the pipe compound control. This apparently reflects the difference in the method of combustion and the presence of the ethylene-bis-stearamide. Although no detailed study has been made, our experience is that the addition of ethylene-bis-stearamide to a smoke-retarded PVC compound frequently interferes with the efficacy of the smoke retarder.

The data from Tables I and II show that in all three of the PVC compounds, the addition of the K_c - CuC_2O_4 mixture effectively reduces smoke formation relative to the control compounds. Smoke formation is inversely proportional to the concentration of the metal additive. The NBS smoke-concentration dependencies are graphically illustrated in Figure 1. It can be seen that for the NBS test the smoke-concentration curves flatten out at a concentration of about 5 phr. That is, increasing the concentration of smoke retarder from 5 to 10 phr only affords a very small additional decrease in smoke. The same type of smoke/additive dependency is present in the Smoke-Char test results, except that higher concentrations of smoke retarder are required to show the "plateau" effect.

Table I also shows that at a smoke-retarder level of 5 phr there is a very strong smoke reducing synergism between K_c and CuC_2O_4 for each of the PVC compounds. These smoke-reducing synergisms are illustrated in Figure 2. In each case, the probability that the synergism is statistically significant is >99.9%. In another study¹⁹ (data not reported here), we found statistically significant synergisms at K_c - CuC_2O_4 loadings of 2.5 and 10 phr in the PVC model compound. In the Smoke-Char test (Table II), a smoke-reducing syn-

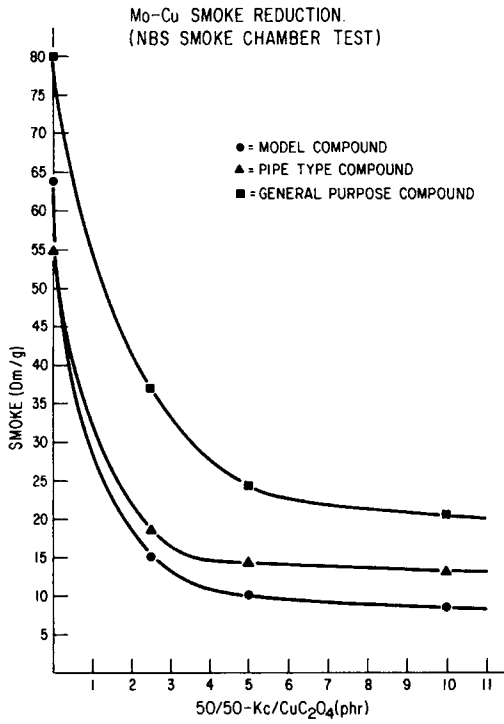


Fig. 1. Mo-Cu smoke reduction (NBS Smoke Chamber Test).

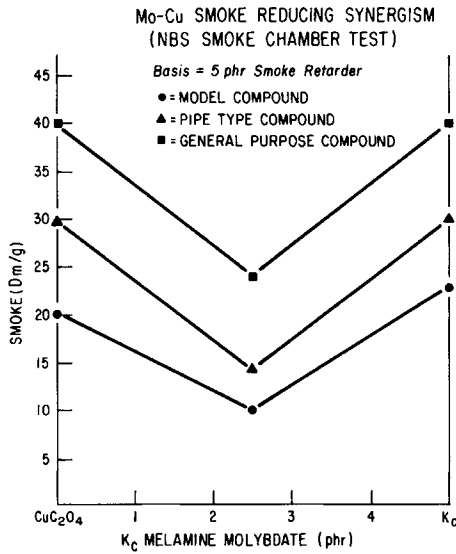


Fig. 2. Mo-Cu smoke-reducing synergism (NBS Smoke Chamber Test).

ergism was found only for the model compound and the pipe compound. Surprisingly, in the general purpose rigid PVC compound, 5 phr of K_c reduced smoke just as effectively as 5 phr of the K_c - CuC_2O_4 combination.

CHAR FORMATION

This section discusses the formation of char in the Smoke-Char test. As shown in Table II, all of the smoke-retarded compounds gave large char yields as compared to the controls. Consistent with earlier studies,¹⁹ the K_c molybdenum smoke retarder and the K_c - CuC_2O_4 combination were more effective promoters of char formation than CuC_2O_4 itself. For each of the three base PVC compounds the char yield was proportional to the concentration of smoke retarder used.

The data in Table II show that there are significant char-forming synergisms for the model PVC compound and for the PVC pipe compound. In the case of the general purpose PVC compound, however, no char-forming synergism is evident. It may be noted that this compound gave no smoke-reducing synergism, either.

The Smoke-Char relationships derived from the data in Table II are plotted in Figure 3. For each of the base PVC compounds, smoke formation decreased as char production increased. The relationship is not linear, however. It is interesting to note that all three of the Smoke-Char curves appear to pass through an inflection point at an S_{PVC} smoke number of about 40

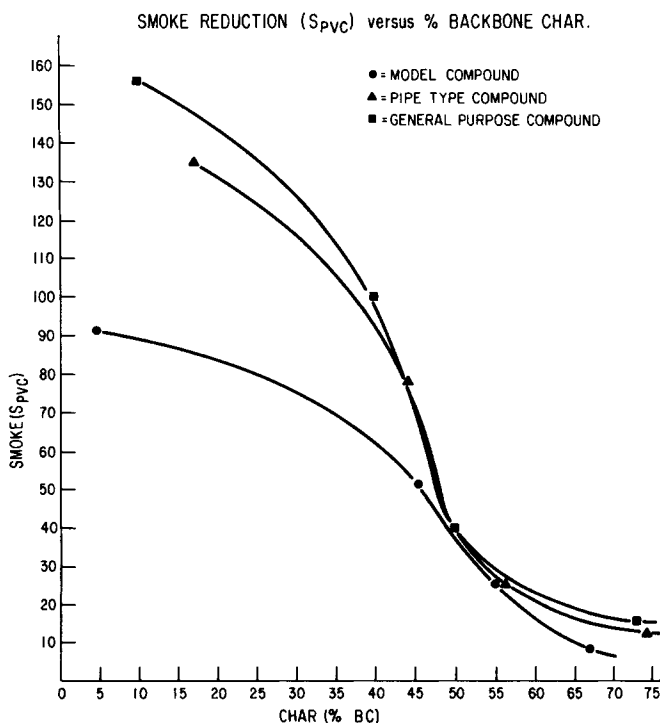


Fig. 3. Smoke reduction (S_{PVC}) versus % backbone char.

and a backbone char yield of about 50%. This phenomenon has not been studied in detail, but it may be related to the efficacy of the char-forming (and smoke-reducing) process and the rate at which the char can be oxidized. The observed relationships between the K_c - CuC_2O_4 level and both smoke reduction and char formation suggest the following explanation.

At the low, 2.5 phr smoke-retarder level, smoke is generated throughout most of the Smoke-Char 1-min burn cycle. Apparently, at this smoke-retarder level, the conversion of the decomposing polymer into char is relatively inefficient. Furthermore, this char will have a relatively high hydrogen concentration and thus be subject to weight loss by oxidation, especially during the latter stages of the burn experiment. In contrast, at 5 or 10 phr, smoke generation is complete in the first one-third of the burn cycle, with the formation of a relatively low hydrogen-content char which is thermally stable and relatively resistant to oxidation. The shape of the Smoke-Char curves in Figure 3 and the presence of an inflection point about 5 phr smoke retarder are consistent with this explanation.

VOLATILE PYROLYZATE FORMATION

The pertinent semiquantitative Py-FID-GC results for the smoke-retarded compounds are given in Table III. The format is the same as that used previously,¹⁷ with relative peak areas of several key pyrolyzates or groups of pyrolyzates listed separately. All of the metal additives that were tested reduced the production of volatile aromatic compounds. The "pure" conjugated aromatics (principally benzene and naphthalene) were reduced considerably more than the nonconjugated "mixed" aromatics containing aliphatic side groups (such as toluene and the C_2 -benzenes). This is consistent with our earlier studies and conclusions.^{2,17,18}

A comparison of Tables I and III shows that there is a general (but non-linear) correlation between smoke and aromatic pyrolyzate reduction. This correlation is not surprising since the combustion of benzene and other aromatics is a major source of smoke from burning PVC.⁵ There also appears to be a synergism in aromatic pyrolyzate reduction for the K_c - CuC_2O_4 combination in each of the three PVC base compounds.

All of the smoke retarders tested increased the production of volatile aliphatic pyrolyzates. The increase was typically by a factor of two or three. This effect has been noted previously.^{2,17} Chlorine-containing aliphatic pyrolyzates were present in appreciable amounts only in the pipe-type compound. Independent pyrolysis experiments showed that aliphatic chlorides (mostly methyl chloride and ethyl chloride) are produced mainly by degradation of the poly(methyl methacrylate) (PMMA) processing aid in the presence of PVC. The thermal degradation of PVC/PMMA blends has been reported previously,²² and mechanisms have been proposed for methyl chloride formation in this system.²³

CONCLUSIONS

The performance of a synergistic molybdenum/copper-based smoke-retarder system for rigid PVC compounds has been described. This system be-

TABLE III
Relative Abundance of Selected Pyrolyzates at 550°C^a

PVC base compound ^b	K _c (phr)	Cu ₂ O ₄ (phr)	C ₁ -C ₃ aliphatics	C ₄ -C ₆ aliphatics	Benzene	Toluene	Dimethyl- & ethyl benzenes	Naphthalene	Methyl- naphthalene	Biphenyl	Total aliphatics ^c	Total aromatics ^d	Total chloro ^e
Model	1.25	1.25	2.6	2.9	.12	.39	.89	.12	.57	.26	2.6	.42	/
	2.50	2.50	2.6	2.9	.08	.35	.81	.05	.40	.07	2.6	.30	/
	5.00	5.00	3.5	3.4	.03	.22	.51	.04	.24	.04	3.4	.25	/
	5.00	—	2.5	2.6	.10	.47	.91	.09	.54	.14	2.5	.40	/
	—	5.00	1.7	2.7	.08	.34	.55	.05	.44	.07	2.0	.32	/
Pipe Type	1.25	1.25	2.0	1.8	.21	.62	1.2	.3	~1.	/	1.9	.36	~1.
	2.50	2.50	1.8	1.7	.18	.62	1.2	.2	~1.	/	1.8	.35	~1.
	5.00	5.00	2.1	2.1	.10	.50	1.5	.2	~1.	/	2.1	.26	~1.
	5.00	—	2.0	2.1	.15	.75	1.2	.7	~1.	/	2.0	.43	~1.
	—	5.00	2.1	2.1	.21	.62	.7	.3	.5	/	2.1	.57	~1.
Gen. Purpose	1.25	1.25	2.6	1.2	.22	.66	.81	.20	.56	.26	1.8	.53	/
	2.50	2.50	3.1	1.4	.11	.45	.67	.10	.38	.08	2.2	.38	/
	5.00	5.00	4.1	1.5	.06	.40	.54	.06	.34	.06	2.7	.30	/
	5.00	—	3.2	1.4	.12	.60	.67	.15	.61	.20	2.3	.47	/
	—	5.00	3.1	1.4	.17	.50	.81	.12	.50	.14	2.2	.47	/

^a Ratio of Py-FID-GC peak area of smoke-retarded compound to the control compound (average of multiple runs).

^b The PVC base compound (without metal smoke retarder) was the control compound in each case.

^c Sum of C₁-C₆ aliphatic hydrocarbons.

^d Sum of all aromatic compounds detected.

^e Mostly methyl chloride and ethyl chloride.

/ Only a trace was detected.

haves in a similar manner to other transition-metal systems that have been reported previously.^{1,2,17} Namely, it (1) reduces smoke formation, (2) increases char production, and (3) decreases aromatic pyrolyzate formation. The K_c - CuC_2O_4 system is noteworthy in that it promotes these effects more efficiently than other metal additives that have been studied. Also, the processing characteristics of this additive are such that it can be used effectively in commercial formulations.

Metal-based smoke retarders work primarily by promoting crosslinking of decomposing PVC chains very early in the thermal degradation process. This process yields carbonaceous char as a stable residue.^{2,17,18} The K_c - CuC_2O_4 combination is strongly synergistic in terms of smoke retardation in PVC. This synergism is due at least in part to the fact that molybdenum and copper can promote *different types* of cross-linking reactions, so that the overall effect of the combination is synergistic.¹⁸ Model compound experiments have shown that copper compounds primarily promote dehydrochlorination and Lewis acid oligomerization during pyrolysis. Molybdenum, on the other hand, promotes a number of other reactions as well, including chain scission, aromatization, coupling, and chain-segment saturation.¹⁸ It also has been speculated that molybdenum and copper might *interact* as a redox couple, but this has not been verified experimentally.^{2,18}

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