Metal Smoke Retarders for Poly(vinyl Chloride)

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Synopsis

This article provides an overview of smoke-retarding rigid PVC using metal compounds. It shows that a large variety of metals from throughout the Periodic Table can form compounds which are smoke retarders for PVC. These metals act to change the thermal degradation pattern of the PVC and promote the formation of char. Most of the active metals are transition metals, although many of the post-transition metals and a few of the pretransition metals also are active. The activity of metal smoke retarders primarily is determined by the choice of metal and the environment surrounding the metal ion. Since most of the effective smoke retarders are transition metal compounds, the ability to undergo redox reactions may be important. The initial oxidation state, however, appears to be relatively unimportant. Particle and dispersion characteristics are secondary factors. Increasing the concentration of a smoke retarder can increase, decrease, or have no effect on its effectiveness. It is impossible to predict the influence of a tin stabilizer on a metal smoke retarder, but for many smoke retarders there is little effect. Transition metal compounds are the most effective metal smoke retarders. Smoke-reducing synergisms result when molybdenum trioxide is combined with certain compounds of copper, iron, and tin.

INTRODUCTION

Poly(vinyl chloride), PVC, is intrinsically fire retardant. When it is forced to burn, however, it behaves like most organic materials and evolves smoke. One obvious way to decrease the smoke generated from PVC is to add nonflammable fillers. If the filler is inert, possessing no smoke retardant activity, it lowers smoke by diluting the organic content of the compound with a nonflammable material. Another way to decrease the smoke evolved from burning PVC is to find a suitable smoke retarder which can be added to PVC compounds. Such additive smoke retarders will reduce the smoke generated during burning, relative to burning the same compound without the smoke retarder.

Since 1973, a large number of classes of chemical compounds have been reported to be smoke retarders for PVC in both the patent and the open literature. These classes include elements, alloys, inorganic compounds, coordination compounds, and organometallic compounds. But, essentially, all of the reported smoke retarders for PVC have one thing in common. They are either metals or metal compounds. And, the "active" metals do not have a narrow existence within the Periodic Table. Instead, they include examples of pretransition, transition, and post-transition elements. In spite of this, only one article in the chemical literature has presented a general discussion of smoke retarding PVC by means of a large variety of different metal compounds.[1]

The purpose of this article is to document a body of knowledge regarding smoke retarding rigid PVC with metal-based additives. It is hoped that it will draw together much of the literature data relating to smoke retarder additives for PVC, and will make it easier to use this information in the design of both commercial smoke retarders and smoke retardant PVC compounds.

This article reports the effectiveness of many of the reported smoke retarders and related compounds in a simple rigid PVC compound. It is based on:

(1) identifying a large number of classes of smoke retarders,

(2) contrasting performance within and between classes, and

(3) recognizing the important factors which govern the activity of smoke retarders.

The simple model PVC compound in this study is not suited for most commercial applications. In the same way, most of the effective smoke retarders discussed will not be useful in commercial PVC compounds, because of one or more of the following reasons:

(1) They are not commercially available.

(2) They are expensive.

(3) They are colored and impart color to PVC.

(4) They discolor PVC during processing.

(5) They create processing problems, especially in commercial compounds.

(6) They create thermal instability.

(7) They create UV instability.

(8) They impart poor physical properties.

EXPERIMENTAL

The model rigid PVC compound which is used throughout this article is 100 parts Geon 103EP resin, 2 parts Microthene 510 polyethylene, and 2 parts dibutylin bis(isooctylthioglycolate). The Geon resin is a homopolymer with an inherent viscosity of 0.98–1.04 and an ASTM classification of GP-5-1443. The Microthene 510 is a processing aid, while the tin thioglycolate is a stabilizer.

The PVC samples containing the candidate smoke retarders were prepared by milling at about 160°C on a rolling rubber mill. Sheets of appropriate thickness were molded under pressure at about 165°C.

Smoke evolution primarily was determined by means of the NBS smoke chamber test. The PVC samples measured $7.3 \times 7.3 \times 0.06$ cm and were burned in the flaming mode in accordance with ASTM-E-662-79 "Test for Specific Optical Density of Smoke Generated by Solid Materials." In this article, the NBS smoke number is expressed as D_m/g, which is the smoke generated per gram of sample.

In certain cases, smoke evolution was determined by both the NBS smoke chamber test and the Goodrich smoke–char test. The char-forming characteristics of certain of the polymer samples also were determined using the Goodrich smoke–char test.

This smoke–char test is a small scale laboratory test which is useful for quickly evaluating the smoke-forming and char-forming characteristics of polymer samples. Figures 1 and 2 provide a schematic outline of the smoke–char tester. Small (0.3–0.4 g) polymer samples measuring about $1.3 \times 0.95 \times 0.19$ cm are placed on the screen and forced to burn by being totally immersed in the flame from a propane torch (276 Pa) for 1 min. The smoke from the burning samples rises through the vertical chimney and passes through the beam of the photometer. The photometer is coupled with an intergrator which provides a measure of the total smoke evolved. The smoke number, S_{PVC}, is expressed as integrated area per gram of PVC in the polymer sample.
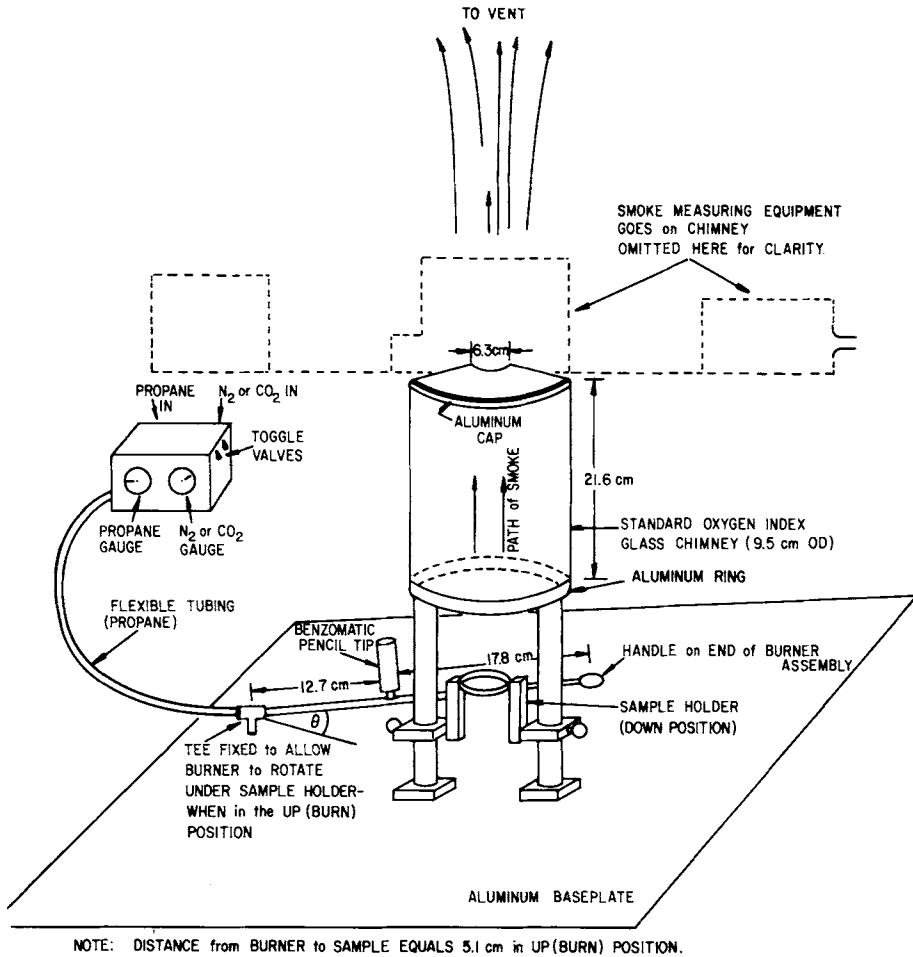
TO VENT

SMOKE MEASURING EQUIPMENT
GOES on CHIMNEY
OMITTED HERE for CLARITY.

6.3cm

PROPANE   N₂ or CO₂ IN
IN

ALUMINUM
CAP

TOGGLE
VALVES

21.6 cm

PROPANE   N₂ or CO₂
GAUGE   GAUGE

PATH of SMOKE

STANDARD OXYGEN INDEX
GLASS CHIMNEY (9.5 cm OD)

FLEXIBLE TUBING
(PROPANE)

ALUMINUM RING

BENZOMATIC
PENCIL TIP

17.8 cm

HANDLE on END of BURNER
ASSEMBLY

12.7 cm

θ

SAMPLE HOLDER
(DOWN POSITION)

TEE FIXED to ALLOW
BURNER to ROTATE
UNDER SAMPLE HOLDER—
WHEN in the UP (BURN)
POSITION

ALUMINUM BASEPLATE

NOTE: DISTANCE from BURNER to SAMPLE EQUALS 5.1 cm in UP(BURN) POSITION.

Fig. 1. The BFGoodrich smoke–char tester.

The residue of "char" remaining after the smoke–char test is weighed and used to calculate the "percent of backbone char" (% *BC*).   Essentially, % *BC* represents the amount of the PVC hydrocarbon backbone which has been retained as a thermally stable char.   It is calculated as shown:

$$\% \, BC = \frac{\text{char wt.} - \text{nonburnable residue wt.}}{\text{sample wt.} - \text{non-PVC wt.} - \text{HCl wt.}} \times 100$$

For those unfamiliar with combustibility testing, the results of small scale laboratory tests will not necessarily reflect the performance of materials in either large scale tests or real fire situations.   The test results presented in this article are based on small scale tests that do not necessarily relate to the hazards encountered under real fire conditions.
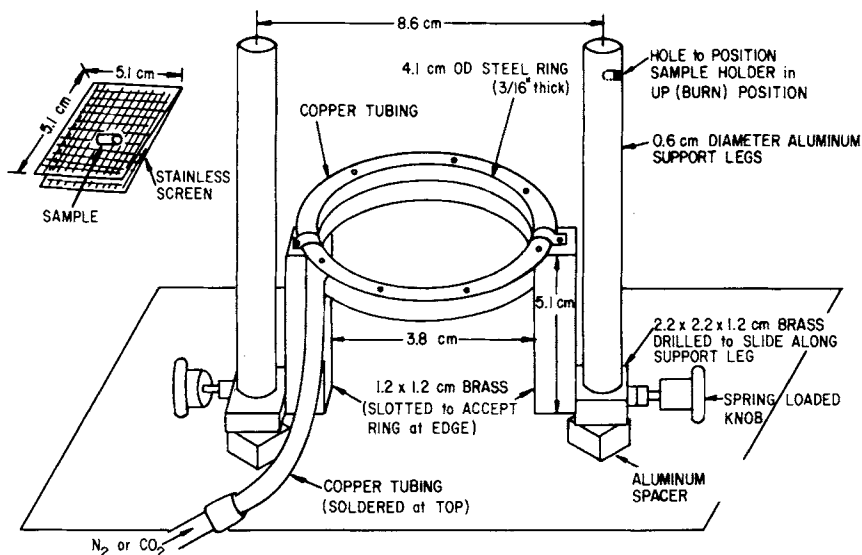
Fig. 2. The smoke–char holder.

RESULTS AND DISCUSSION

Model PVC Compound

Table I shows the performance of the model rigid PVC compound in the flaming mode of the NBS smoke chamber. Also included is the performance of the model compound without the tin stabilizer. σ represents the standard deviation while n is the number of independent measurements. It can be seen that the tin stabilizer has little effect on smoke formation. The same result was obtained when the model PVC compound was evaluated in the smoke–char test as shown in Table II. Table II also shows that the tin stabilizer has little effect on the char-forming properties of the model compound. In either case, the char yield is small.

TABLE I
Model Rigid PVC Compound: Smoke Formation in the NBS Smoke Chamber Test

Tin stabilizer	D_m/g	σ	n
no	57.6	4.2	6
yes	64.9	9.3	147

TABLE II
Model Rigid PVC Compound: Smoke and Char Formation in the Smoke–Char Test

Tin stabilizer	S_{PVC}	σ	n	$\% BC$	σ	n
no	103.0	16.9	9	11.0	6.6	9
yes	101.8	14.4	130	8.0	4.2	53

Potential Smoke Retarder Classes

A large number of metal compounds from throughout the Periodic Table were evaluated as smoke retarders for the model rigid PVC Compound. These evaluations were made in the flaming mode of the NBS smoke chamber test. The results are presented in Figures 4–16. The error bars represent the standard deviation. In every case, the loading level of the metal compound is 5 phr (parts per hundred parts of the PVC resin).

Of the pretransition metals only compounds of magnesium have been claimed to be useful smoke retarders for PVC.[1–10] The effects of alkali earth and alkaline earth compounds on smoke formation from the model PVC compound are summarized in Figures 3 and 4. Figure 3 suggests that alkali earth compounds are not effective smoke retarders for rigid PVC. In contrast, Figure 4 shows that
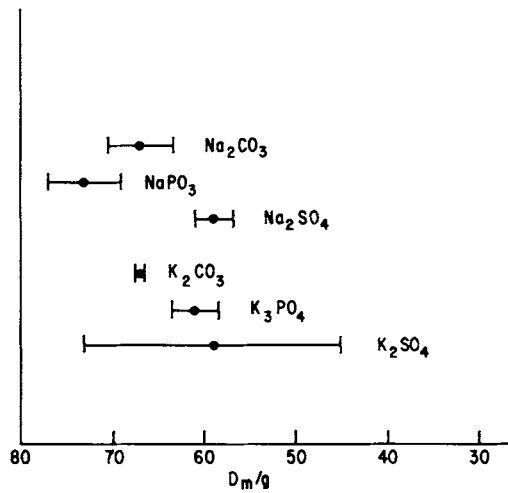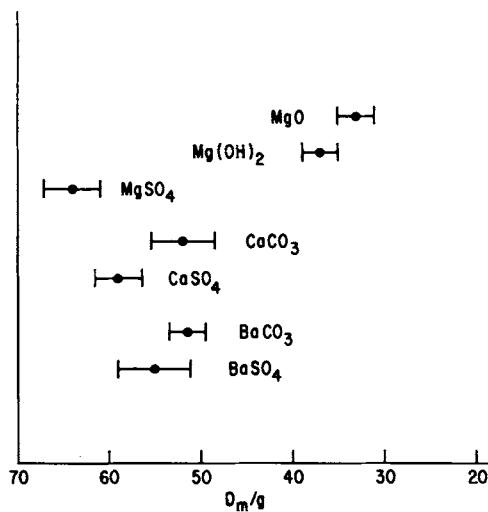
Fig. 3. Alkali metals.

Fig. 4. Alkaline earth metals.

two of the alkaline earth compounds, magnesium oxide and magnesium hydroxide, have significant smoke retarding ability. Magnesium carbonate, which is not shown in Figure 4, also is effective like the oxide and the hydroxide. This is predictable, since the carbonate, like the oxide and the hydroxide, thermally decomposes into the oxide at temperatures less than 400°C. It is tempting to try to explain the activity of the effective magnesium compounds in terms of their basic character. However, the even more basic carbonates of calcium and barium are not effective. In contrast to calcium and barium, the oxide and hydroxide of magnesium, in the presence of HCl and water, are readily converted into a hydrated chloride which rapidly decomposes at elevated temperatures into a series of poorly characterized oxychlorides of variable composition. It should be possible for oxychlorides to form under the NBS smoke chamber conditions. Oxychloride formation may be the key to understanding why the basic magnesium compounds are effective smoke retardants. But it would require a careful study to either confirm or disprove this contention.

No rare earth smoke retarders are reported in the chemical literature. Certain compounds of lanthanum and cerium are considered in Figure 5. While lanthanum is certainly a pretransition element, cerium is an inner-transition metal. However, it is sensible to consider them together, since they are the first two members of a series known as the lanthanide elements. In keeping with its primary classification as a pretransition element, the compounds of lanthanum are ineffective. In contrast, one of the cerium compounds, ceric oxide, is moderately effective. Although CeO_2 contains Ce^{4+}, the very inactive oxalate contains Ce^{3+}. However, oxidation state differences will not adequately explain these results, since the relatively ineffective acetylacetonate also contains Ce^{4+}. Oxidation state effects will be discussed in a later section.

A large number of compounds of zinc have been disclosed as smoke retarders for PVC.[1,8,9,11-39] Only one compound of cadmium, CdO, however, has been disclosed.[30] The post-transition metal compounds exhibit varying degrees of effectiveness. This is illustrated in Figure 6 for four zinc compounds and cadmium oxide. Of the four zinc compounds, only the silicate and the phosphate are moderately effective. While anion effects may be important, concentration is a more important variable. The zinc compounds will be discussed in more detail in another section.
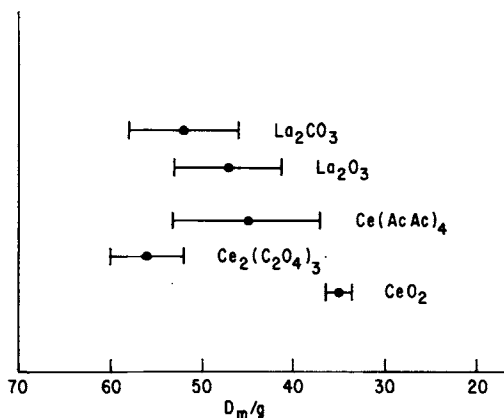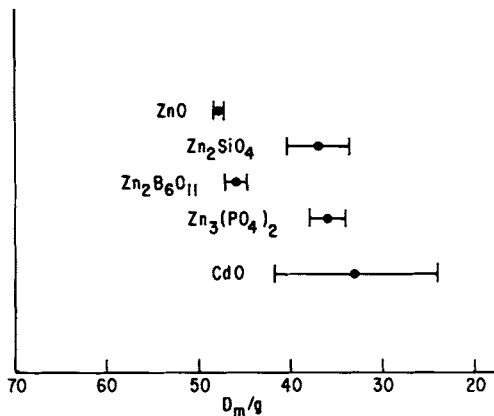

Fig. 5. Lanthanide metals.

Fig. 6. Group II-B post-transition metals.

Many compounds of aluminum are reported to be effective smoke retarders for PVC.[1,7,10,15,17,21,26,32,35,41–52]   Much of this work centers around the use of alumina trihydrate (aluminum hydroxide).   In contrast, only a limited number of boron compounds have been claimed as smoke retarders for PVC.[4,13,30,35,39,46,51,53]   All of them contain another metal which probably is the main contributor to the observed activity.   Compounds of the Group III-A metals, boron and aluminum, are covered in Figure 7.   Both the gamma-alumina and the alumina trihydrate are moderately effective.

Only a limited number of compounds of silicon[30,54] and tin[30,48,55,58] have been reported to be smoke retarders for PVC.   As a class, the tin compounds appear to be much more effective than the silicon compounds.   This is shown in Figure 8.   While all three of the tin compounds are moderately effective, only the Hi-Sil-233, which is a commercially available common silica filler, shows any significant activity.

Many bismuth compounds have been reported as smoke retarders for PVC.[10,30,50,58]   Antimony compounds also have been reported to be smoke retarder additives for PVC.[1,2,10,26,29,40,41,52,56,57]   In contrast to the bismuth based
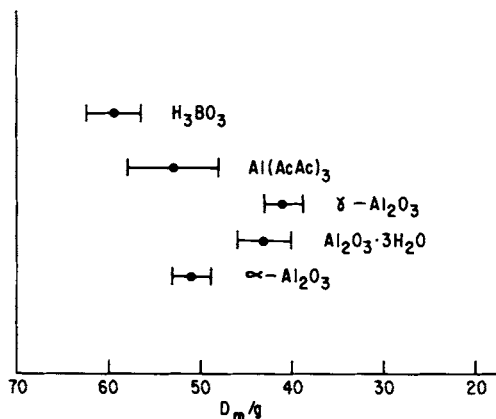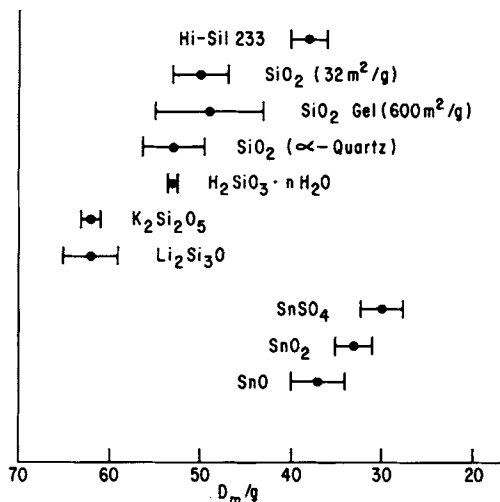

Fig. 7. Group III-A post-transition metals.

Fig. 8. Group IV-A post-transition metals.

smoke retarders,[10,30,50,58] the antimony compounds are less effective under most laboratory test conditions. In fact, many of the antimony compound smoke retarders are reported as part of smoke retarder systems which consist of one or more other metal compounds. It is likely that the other compounds, e.g., MoO_3,[40,41] are responsible for most of the observed smoke reduction.

A number of bismuth and antimony oxide compounds are shown in Figure 9. While neither of the antimony oxides are effective, all of the bismuth compounds effectively reduce smoke.

The effectiveness of post-transition metals in reducing smoke in PVC increases as each vertical group is descended. This is summarized in Table III. It is interesting to note that as each group is descended the covalent bond strength decreases and the lower oxidation states become more stable. But this observation certainly is not sufficient to explain the activity of aluminum, tin, and bismuth. And, it is especially insufficient to explain why bismuth is more ef-
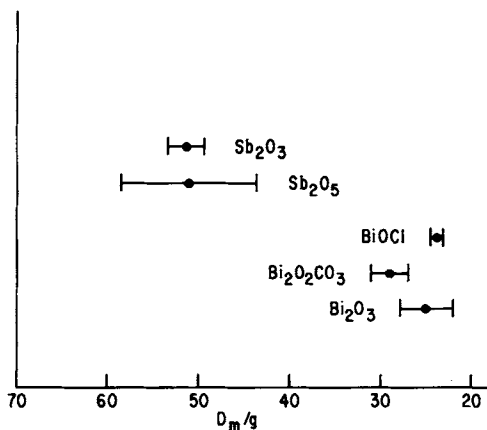

Fig. 9. Group V-A post-transition metals.

TABLE III
Post-Transition Elements: Smoke Retarding Activity and Atomic Number[a]

Group III-A	Group IV-A	Group V-A
5_B	6	7
13_{Al}	14_{Si}	15
31	32	33
49	50_{Sn}	51_{Sb}
81	82	83_{Bi}

[a] Arrows show increasing activity.

fective than tin, and why antimony, which lies just above bismuth, is relatively inactive. For bismuth it is tempting to suggest, in analogy to magnesium, that the ease with which teh oxychloride can be formed is the key factor. However, antimony also readily forms oxychlorides, although they may be so volatile that they migrate too rapidly into the vapor phase. This suggests that the bismuth compounds are active in the condensed phase.

The largest number of active smoke retarders is found in the general class of transition metal compounds. There are large variations in performance both between and within the periodic groups. Particular emphasis will be placed at comparing the activities of typical compounds of the first row transition metals, titanium through copper.

Only a few compounds of the Group IV-B metals titanium[10,23,30,48] and zirconium,[7,10,21,52] have been reported to be smoke retarders for PVC. Figure 10 illustrates the smoke retarding ability of a number of compounds of titanium and zirconium. One important point, the acetylacetonate and the titanium oxide compounds which were the most effective also dispersed readily in the PVC compound. The other compounds in Figure 10 did not. These results probably illustrate the importance of particle and dispersion characteristics on the performance of smoke retarder additives.

The TiO_2 in Figure 10 is actually a commercially available titanium oxide pigment, N.L. 2061 TiO_2. Because, of the wide spread use of TiO_2 as a pigment in plastics and rubber compounds, it is surprising that there is only one reference to its utility as a smoke retarder in PVC.[30] Not all pigment grades of TiO_2 are as effective as 2061 in reducing smoke, but many of them behave as smoke re-
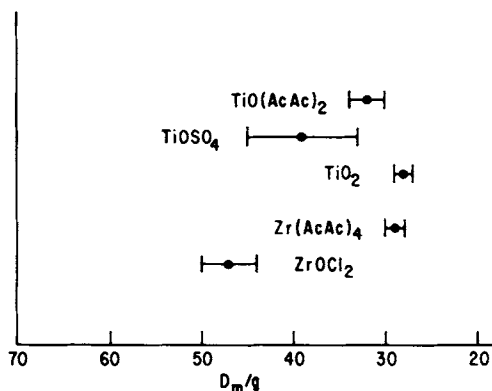

Fig. 10. Group IV-B transition metals.

tarders for PVC. Perhaps the differences relate to the proprietary surface coatings, usually alumino-silicates or related materials, which the TiO_2 pigment manufacturers use. However, it seems unlikely that the surface coatings are the key to the observed reductions in smoke, since certain untreated titanium oxides in both the rutile and anatase forms also are moderately effective smoke retarders, just like the active TiO_2 pigments.

Of the group V-B transition metals, only the compounds of vanadium have been widely publicized as smoke retarders for PVC,[1,59–63] although one compound of tantalum has been reported.[30] The Group V-B metals, as shown in Figure 11, show wide variations in performance. The vanadium pentoxide is more effective than the corresponding oxides of niobium and tantalum. Perhaps this is related to the fact that the vanadium oxide is more readily reduced. In addition, it can be seen that the vanadium (IV) acetylacetonate complex is as effective as the vanadium (V) oxide. This could mean that, at least in this case, the oxidation state of the metal is unimportant. Certainly the local environments around the vanadium atoms in these two complexes are very different, and yet they are equally effective.

The Group VI-B elements afford a number of strong contrasts. Few chromium compounds are reported to be smoke retarders for PVC.[1,10,48,64,65] However, many compounds of molybdenum are reported to be active.[10,14,30,35,40,41,48,49,52,54,55,57,65–85] Most of the published references are concerned with MoO_3. Analogous to chromium, only a few reports of tungsten compounds as smoke retarders for PVC are available.[10,23,30,77]

The effectiveness of Group VI-B compounds as smoke retarders for PVC is illustrated in Figure 12. The chromium (III) acetylacetonate complex is effective while the chromium (III) oxide is not, in spite of the chromium ions having the same oxidation state in each compound and the oxide dispersing much better than the acetylacetonate. The large difference in performance between the oxide and the acetylacetonate is even more impressive when you consider that the oxide contains over four times the concentration of chromium in the acetylacetonate. Apparently the Cr^{3+} ions in the oxide are too stable.

The compounds of molybdenum shown in Figure 12 all contain molybdenum in its highest state of oxidation, Mo^{6+}. Again, as with chromium, there is a wide
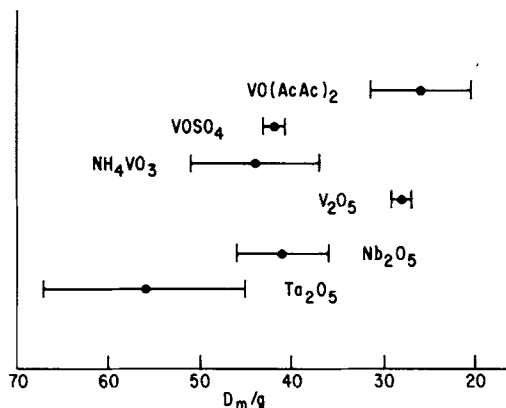

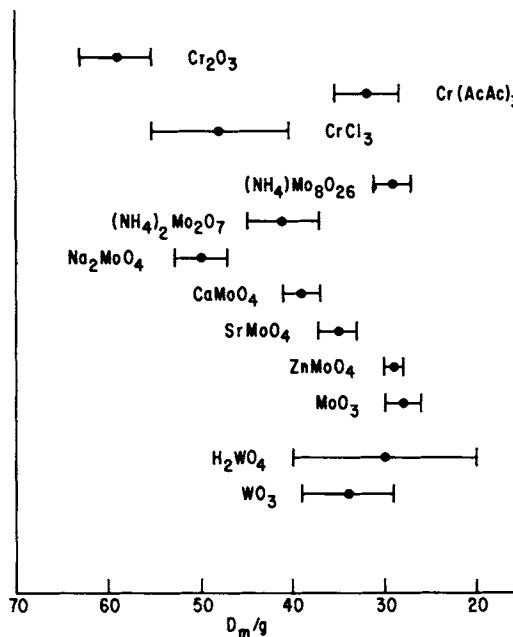Fig. 11. Group V-B transition metals.

Fig. 12. Group VI-B transition metals.

variation in performance. These variations again appear to be mainly related to changes in the environment around the molybdenum ion. Some comments about particle size and dispersion characteristics, however, are in order. Although molybdenum trioxide is the most effective compound, it and ammonium dimolybdate have the poorest dispersion characteristics. Grinding the ammonium dimolybdate to reduce its average particle size improved its performance, so it behaved much like the ammonium octamolybdate. In contrast, while grinding improved the dispersion characteristics of the molybdenum trioxide, it did not improve its performance. In addition, commercially available samples of molybdenum trioxide, designed to have higher surface areas and smaller particle sizes, gave the same level of performance.

The literature contains only a few references to manganese compounds as smoke retarders for PVC.[1,7,10,30,32,53]   Manganese is a first row transition element from Group VII-B. It can exist in a large number of relatively stable oxidation states. Figure 13 shows that compounds of both manganese (II) and managanese (III) can be moderately effective smoke retarders for PVC. The manganese (II) oxide may not be as bad as it looks. For example, the effective $MnCO_3$ thermally decomposes into manganese (II) oxide. In addition, the manganese (II) oxide was of a large particle size, tending to agglomerate, and dispersing poorly, relative to the carbonate and manganese (III) oxide.

The Group VIII metal compounds of iron, cobalt, and nickel are mentioned extensively as smoke retarders for PVC. The iron literature is especially extensive.[1,5,7,10,18,19,34,41,48,58,65,68,70,78,86-93]   Although the cobalt literature is much smaller, there are still a reasonable number of cobalt compounds claimed to be smoke retarders for PVC.[1,10,32,51,74,94]   As in the case of iron, there is an extensive literature which discloses a very large variety of nickel compounds as smoke retarders for PVC.[1,10,24,26,41,49,56,58,59,61,63,65,76,85,88,94]
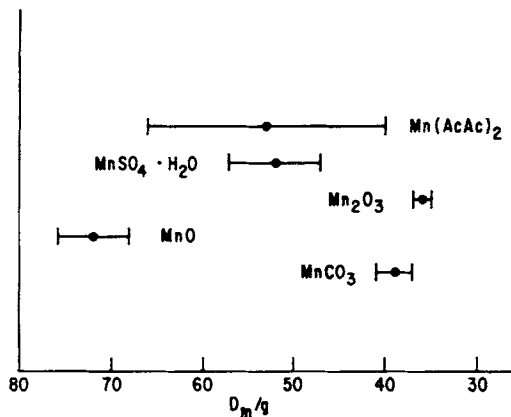
Fig. 13. Group VII-B transition metals.

The Group VIII metals shown in Figure 14 are limited to those of the first row transition metal series. Essentially all of the iron compounds are effective. This is not the case with cobalt and nickel. The nickel compounds vary from relatively ineffective to moderately effective. Cobalt exhibits a wider variation in performance and appears to be active in both the II and III oxidation states.

Copper is a first row transition metal from Group I-B. Many researchers have reported compounds of copper which are smoke retarders for PVC.[10,20,22,41,48,62,67-70,73-75,85,93,95-97] As a class, the compounds of copper are very effective smoke retarders for PVC. This is shown in Figure 15. The small
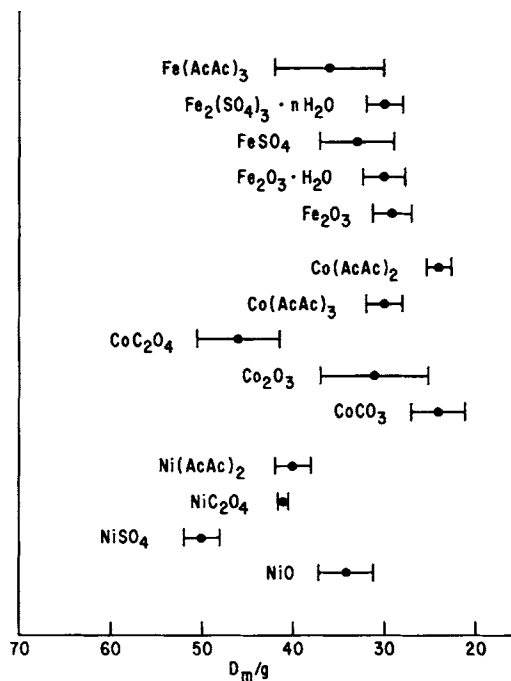

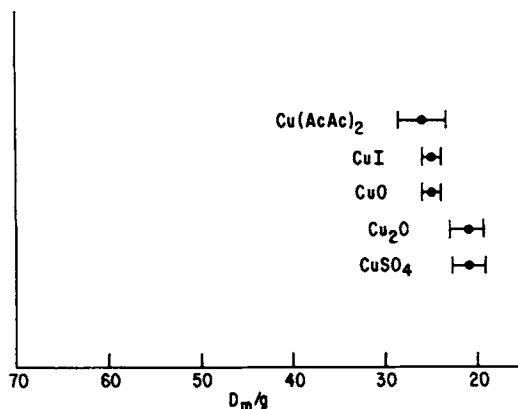Fig. 14. Group VIII transition metals.

Fig. 15. Group I-B transition metals.

variations in activity of the five illustrated copper compounds appear to be independent of copper content, oxidation state, particle size effects, and dispersion characteristics.

Initially, it was expected that the oxidation state of the metal might be one of the most sensitive parameters in determining the smoke retarding activity of metal-based smoke retarders in PVC. This expectation was not substantiated based on experiments with first row transition metal compounds (Fig. 10–15). Five of the first row metals were examined in two different oxidation states. Within the accuracy of the data, the results are essentially independent of oxidation state. Earlier, the same result was reported for tin (II) and tin (IV) (Fig. 9). Only cerium, an inner transition metal, appeared to show an oxidation state preference; cerium (IV) being more active than cerium (III) (Fig. 6). However, one can certainly speculate, based on the large number of transition metal compounds which are active, that multiple oxidation states and the ability to undergo redox reactions may be an important criterion in determining the activity of smoke retarders for PVC.

It is difficult to discern any general periodic trends in the transition groups which form active smoke retarders. For example, in Group V-B the most active metal, vanadium, is from the first row. In contrast, molybdenum and tungsten, the most active metals from Group VI-B are from the second and third rows.

It is useful to study the first row transition metal compounds in more detail. Figure 16 is a plot of the NBS smoke number against the atomic number for both the oxides and the acetylacetonates of the first row metals. With the exception of chromium, where there is the large discrepancy between the activity of the oxide and the acetylacetonate, the trends across the first row are almost identical. Essentially, the same trend results when the performance of all the different compounds of each metal are averaged and plotted against their atomic number. This also is shown in Figure 16. It can be seen that titanium and vanadium are active, chromium appears to be active under specific conditions, manganese is relatively inactive, iron and cobalt are active, nickel is relatively inactive, and copper is very active. The variation in activity going across the first row of transition elements appears to correlate with the acid–base properties of the metal oxides. For example, all of the active metals form acidic oxides. In
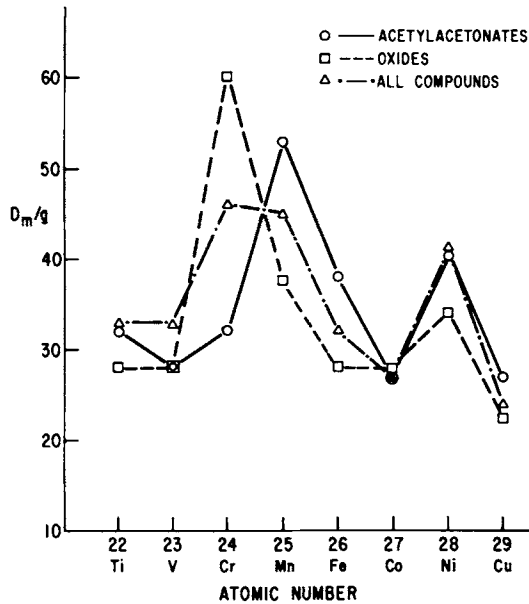
Fig. 16. Smoke-retarding activity of first run transition metals. (○—○) Acetylacetonates; - (□---□) oxides; (△—△) all compounds.

comparison, the oxides of the relatively inactive metals, manganese and nickel, are basic. This certainly is consistent with the suggestion that certain metal smoke retarders function, because they either are, or are converted into Lewis acids.[83,84,86,91]

Concentration Effects

Concentration effects must be considered in using additive smoke retarders to design low smoke PVC compounds. There are three possibilities. One of these is performance which is independent of concentration, at least over some restricted range of concentration. Another is an inverse relationship between concentration and smoke, so that as the additive concentration increases, the smoke decreases. Yet another possibility, and an undesirable one, is to have the smoke increase as the additive concentration increases. Examples of all three types of behavior were found. They are illustrated in Figures 17–19.

Figure 17 shows performance data as a function of concentration for four very different smoke retarders. In each case, their performance exhibits essentially no dependence on concentration.

Figure 18 illustrates a contrasting behavior pattern for molybdenum trioxide. Increasing the loading from 2 to 10 phr continually reduces smoke formation. It must be mentioned again that such relationships only hold over a limited range of concentration. For example, in the case of molybdenum trioxide, the concentration-loading curve normally plateaus out around 10 phr. So additional molybdenum trioxide above this level will provide relatively small improvements in performance.
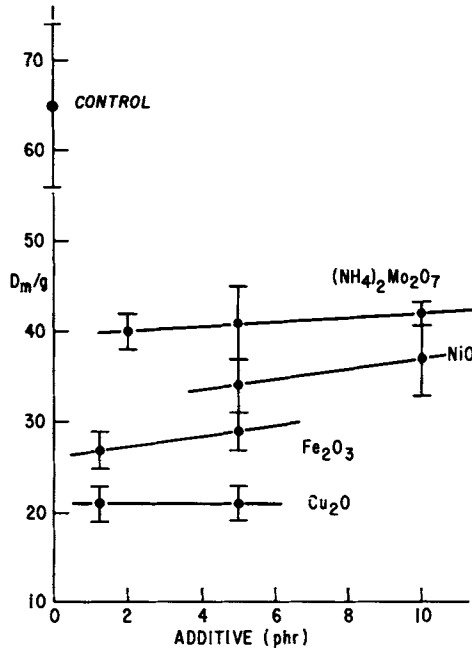
Fig. 17. Concentration and smoke formation.

Zinc oxide is an example of a smoke retarder which exhibits significant decreases in performance as its loading level is increased above 1 phr. This is shown in Figure 19. Data for zinc silicate is included in Figure 19 to illustrate the point
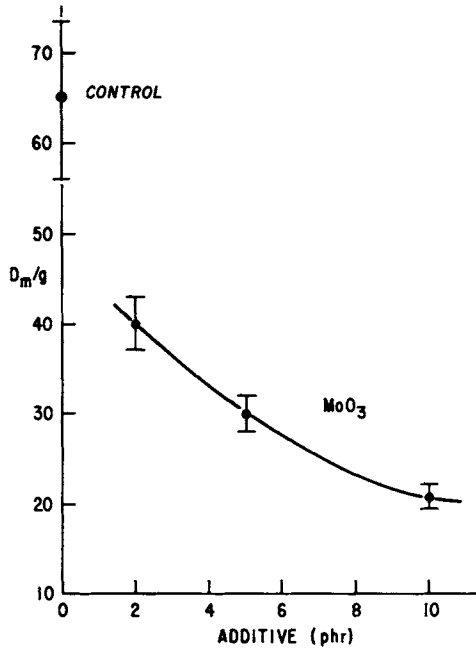

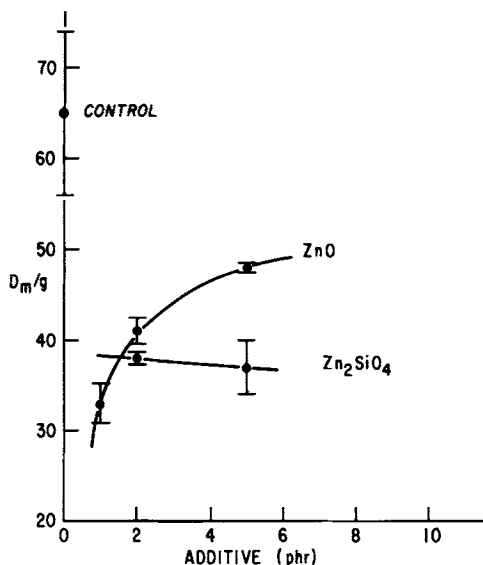Fig. 18. Concentration and smoke formation.

Fig. 19. Concentration and smoke formation.

that not all the compounds of a given metal will exhibit the same concentration-dependency pattern.

Although zinc oxide does not vaporize below 1000°C, the presence of reducing gases (pyrolysis and combustion products) could provide a lower temperature volatilization route. In this route, free zinc metal would be an intermediate phase, and zinc oxide aerosols or particles would be counted by the photometer as smoke. Since zinc silicate is harder to reduce than zinc oxide, zinc silicate probably will not contribute zinc oxide particles to the vapor phase in an NBS smoke chamber flaming mode experiment.

The same type of argument could be made for the volatilization of zinc chloride. It could be formed directly from zinc oxide (or a zinc metal intermediate state) and hydrogen chloride from the thermally degrading PVC. The boiling point of zinc chloride is only 732°C at 1 atm.

The Role of the Tin Stabilizer

Tables I and II showed that the tin stabilizer has little effect on the smoke generated from burning the model rigid PVC compound in either the NBS smoke chamber test or in the Goodrich smoke–char test. But what is the effect of the tin stabilizer when typical smoke retarders are added to the model compound? The observed effects are shown in Tables IV–VI for a number of representative smoke retarders. Most of the smoke retarders behaved like the model compound and were independent of the tin stabilizer. This is shown in Table IV for two copper compounds, two iron compounds, and bismuth trioxide. Not all smoke retarders, however, behave this way.

Table V shows that both stannic oxide and zinc oxide (at the 1 phr level) are more effective in the presence of the tin stabilizer. In direct contrast, ferrous sulfate and molybdenum trioxide are more effective in the absence of the tin stabilizer. This is shown in Table VI.

TABLE IV
Tin Stabilizer–Smoke Retarder Interaction: None

Additive (5phr)	Stabilizer	D_m/g	σ	S_{PVC}	σ	$\% BC$	σ
$Fe_2(SO_4)_3 \cdot nH_2O$	yes	30.0	2.1	46	3	36.6	0.1
$Fe_2(SO_4)_3 \cdot nH_2O$	no	30.6	2.9	52	2	35.1	0.9
Fe_2O_3	yes	29.2	2.3	68	21	37.6	0.9
Fe_2O_3	no	23.3	3.1	68	1	33.1	3.4
Cu_2O	yes	20.9	2.2	54	16	36.8	3.8
Cu_2O	no	22.5	5.2	57	2	30.0	1.2
$CuSO_4$	yes	21.0	2.1	56	7	32.1	0.2
$CuSO_4$	no	22.1	1.2	51	2	35.6	0.1
Bi_2O_3	yes	25.2	3.0	53	10	27.9	2.3
Bi_2O_3	no	27.7	3.3	50	3	36.6	2.6

Smoke Reduction and Char Formation

The smoke and char data presented in Tables IV–VI shows that smoke reduction and char formation are related.   Essentially all of the effective metal-based smoke retarders studied appear to work in the solid state, not in the vapor state.   While the possibility that some of the retarders provide a vapor phase activity cannot be ruled out, their main function appears to be that of interfering with the normal thermal degradation pattern of the PVC.   Recent publications have substantiated this premise for ferrocene, Fe_2O_3, and MoO_3.[82,86,91]   The most visible manifestation of this solid-state activity is the formation of char.   All of the effective smoke retarders reported here promoted the formation of char.   Char yields of 30–50 expressed as $\% BC$ are typical.   This compares to $\% BC$ of about 10 for the rigid control compound (Table II).   However, in a series of closely

TABLE V
Tin Stabilizer–Smoke Retarder Interaction: Smoke Enhancement

	With stabilizer	Without stabilizer
SnO_2 (5phr)		
D_m/g	33.0 ± 2.1	40.3 ± 7.6
S_{PVC}	58 ± 18	93 ± 6
$\% BC$	32.9 ± 0.9	30.7 ± 1.5
ZnO (1phr)		
D_m/g	33.1 ± 2.4	40.4 ± 4.2
S_{PVC}	72 ± 8	83 ± 7
$\% BC$	28.6 ± 1.2	32.2 ± 0.7

TABLE VI
Tin Stabilizer–Smoke Retarder Interaction: Smoke Reduction

	With stabilizer	Without stabilizer
$FeSO_4$ (5phr)		
D_m/g	37.2 ± 4.4	27.2 ± 1.1
S_{PVC}	44 ± 4	34 ± 1
$\% BC$	36.4 ± 1.3	41.4 ± 0.7
MoO_3 (5phr)		
D_m/g	27.6 ± 2.2	29.6 ± 3.9
S_{PVC}	52 ± 15	30 ± 8
$\% BC$	33.9 ± 3.3	46.0 ± 3.3

related smoke retarders or retarders used at different loading levels, there may be a nonregular relationship between smoke reduction and char formation. For example, in such a series, the compound giving the lowest smoke may not always form the most char. But using the Goodrich smoke–char test and the flaming mode of the NBS smoke chamber, even in these cases, smoke reduction is accompanied by char formation.

Until this article, no convincing correlation between smoke reduction and char formation has appeared in the open literature. This can be attributed to the test conditions used and the ability of the char to be oxidized to CO and CO_2. A detailed discussion of the smoke–char phenomenon and the failure of other researchers to fir.d convincing smoke–char relationships is contained in a companion article co-authored by R. P. Lattimer and myself.[98] It will not be repeated here. However, in order to appreciate the smoke and char data in this article, it is necessary to realize that the smoke–char test was specifically designed to search for meaningful smoke—char relationships, which also could be generally correlated with the results of NBS smoke chamber experiments. The smoke–char test was designed to measure char formation during the early combustion period when essentially all of the smoke is evolved. In addition, the test was designed to eliminate sample mass effects, and to eliminate or minimize oxidation (incandescence) of the char residue which forms during the primary thermal degradation and combustion period.

The smoke and char data for molybdenum trioxide in Figure 6 are especially interesting. The tin stabilizer has little effect on the smoke generated in the NBS smoke chamber. However, in the absence of the tin stabilizer, molybdenum trioxide is significantly more effective in reducing smoke in the Goodrich smoke–char test. And this decrease in smoke is accompanied by a large increase in char. The lesson is very clear. It becomes very difficult, if not impossible, to completely characterize the smoke forming properties of a polymer compound based on only one type of test or one set of test conditions.

Smoke Retarder Mechanisms

The article in which Lattimer and I give a detailed discussion of the smoke–char relationship, provides a detailed discussion of the role of molybdenum trioxide and other transition metal smoke retarders in rigid PVC.[98] We show that there is a direct relationship between smoke reduction, char formation, and the ability of smoke retarders to greatly reduce the yield of aromatic hydrocarbons during pyrolysis in either an inert atmosphere or air. We conclude from the results of our studies using normal, perdeuterated, and syndiotactic PVC that the dominant role of molybdenum trioxide and other metal smoke retarders is to promote the crosslinking of PVC chain segments early in the thermal degradation process. In the same article,[98] we propose a "reductive coupling" mechanism to explain how the metal smoke retarders function to promote crosslinking of the thermally degrading PVC chain segments. It is consistent with our experimental results and the experimental results reported in the literature.

Complex Smoke Retarders

The patent literature reports a large number of smoke retarder systems which consist of a combination of two or more chemical compounds. Some of these mixtures are claimed to be useful, while others are reported to be synergistic. Useful systems include compounds of molybdenum and copper,[67] iron and copper oxides,[68] iron, molybdenum trioxide, and copper oxides,[67] ferric oxide, copper oxides, and molybdenum compounds,[70] and ferric oxide and basic magnesium carbonate.[5] Synergistic combinations include cuprous oxide and molybdenum trioxide,[68] zinc borate and alumina trihydrate,[15] zinc oxide and alumina trihydrate,[17] nickel compounds with a large variety of other metal compounds,[24,26,49,56,58,59,61,63,65,85] and amine molybdates with a large number of other metal compounds.[30,73,76,78]

This section shows the smoke formation properties of a number of combinations of molybdenum trioxide with different smoke retarders. Smoke was determined in the flaming mode of the NBS smoke chamber as already described. The data points represent the smoke from the model compound containing 5 phr of either of the smoke retarder components or their mixtures. This article uses a classical definition of synergism determined on a weight basis. For a binary mixture to be synergistic, its performance must exceed the performance of either component at the *same* concentration level. Even synergistic systems can be misleading as indicators of goodness. For example, Figure 19 shows how 1 phr of zinc oxide is significantly more effective in reducing smoke than 5 phr. Therefore, a synergistic mixture of zinc oxide and another compound at the 5 phr level will be of significance only if it performs better than 1 phr of zinc oxide.

The stannic oxide–molybdenum trioxide system is presented in Figure 20. It can be seen that there is a weak, but real synergism for mixtures which lie close to molybdenum trioxide.

A similar pattern appears to hold for the ferric oxide–molybdenum trioxide system. This is shown in Figure 21. Although there is more scatter in the data, the point closest to molybdenum trioxide does indeed represent a synergistic mixture.

Although most copper compounds create serious processing and stability problems in PVC, combinations of copper compounds and molybdenum trioxide have been claimed in the patent literature.[67–69] The molybdenum trioxide-cupric sulfate system is shown in Figure 22. Although there is a large uncertainty in the data, synergistic mixtures do appear to exist near molybdenum trioxide.

The cuprous oxide–molybdenum trioxide system which is shown in Figure 23 affords some interesting contrasts. A small amount of cuprous oxide added to molybdenum trioxide does improve its performance, but without forming a synergistic mixture. Because of the uncertainty in the experimental data, it is hard to be certain whether there is an authentic synergism between cuprous oxide and molybdenum trioxide. Additional studies have confirmed that cuprous oxide does interact with molybdenum trioxide to give weakly synergistic mixtures containing about equal parts by weight of each component.
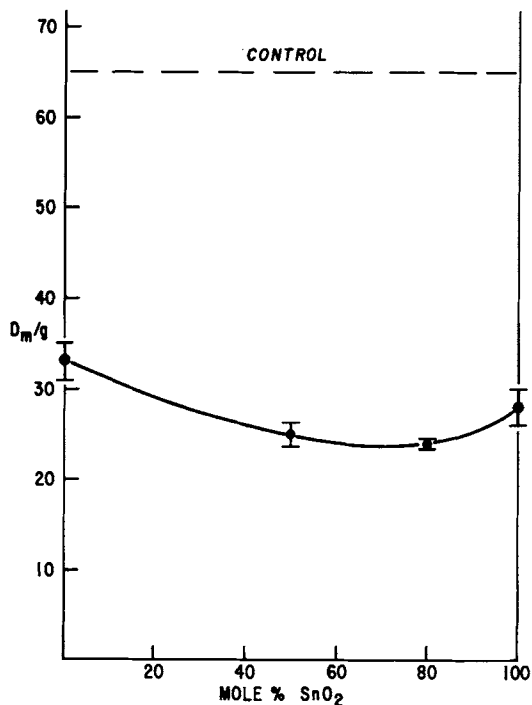
Fig. 20. SnO$_2$–MoO$_3$ system.

CONCLUSIONS

Compounds of a wide variety of metals can be active smoke retarders for PVC. The activity primarily is determined by the metal ion and its environment. Since the majority of the known smoke retarders for PVC are compounds of the transition metals, the ability to participate in redox reactions may be important. The initial state of oxidation of the metal, however, appears to be relatively unimportant. Secondary factors are particle and dispersion characteristics, but large particles and poor dispersion can decrease the activity of a smoke retarder in PVC. Concentration is an important parameter which can effect the performance of smoke retarders. Increasing the concentration can reduce, decrease, or have no effect on the formation of smoke. Certain binary mixtures of smoke retarders can be more effective than either of the components used at the same concentration. The exact role of smoke retarders in rigid PVC remains to be determined, but the smoke retarders manifest themselves by changing the normal degradation pattern of the PVC and promoting the formation of char.

In a simple rigid PVC compound, the tin stabilizer can act to either enhance or decrease the effectiveness of the smoke retarders. The activity of many metal compound smoke retarders, however, is independent of the presence or absence of a tin stabilizer.

Copper compounds are very effective smoke retarders for rigid PVC. Compared to the other first row transition metals, the compounds of manganese and nickel are relatively ineffective smoke retarders. The variation in smoke retarding activity of the first row transition metal compounds appears to correspond to changes in acidity of their dominant oxides. The compounds of metals
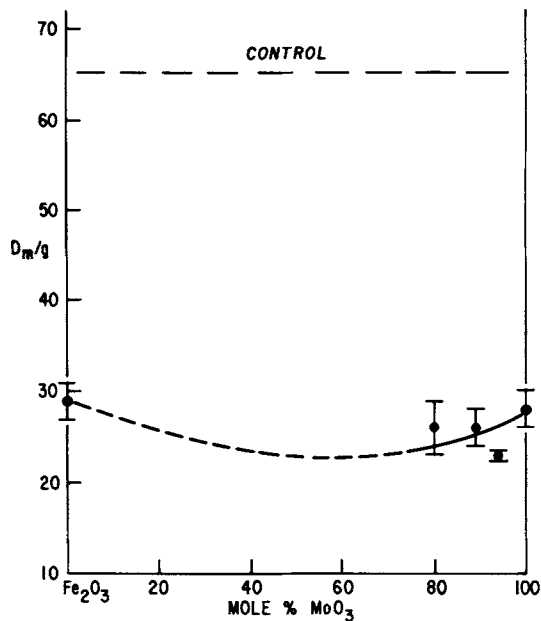
Fig. 21. Fe_2O_3–MoO_3 system.

which form the most basic normal oxides are relatively inactive.   Molybdenum trioxide when combined with some compounds of copper, iron, and tin can form synergistic binary systems for reducing smoke from rigid PVC.   The nature of the synergism is unknown.
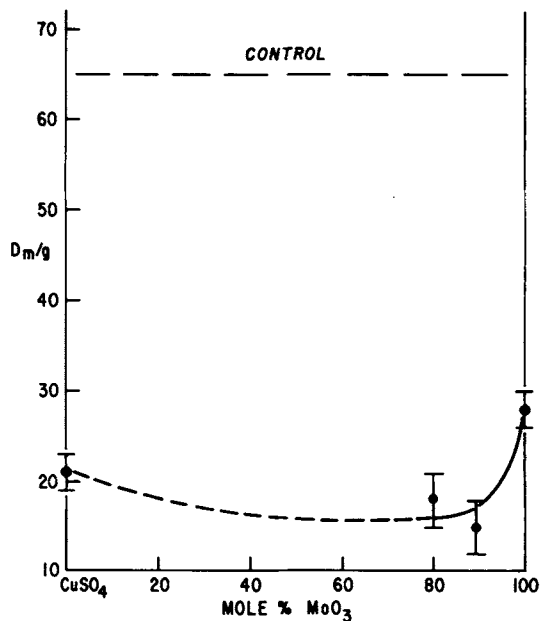
Fig. 22. $CuSO_4$–MoO_3 system.
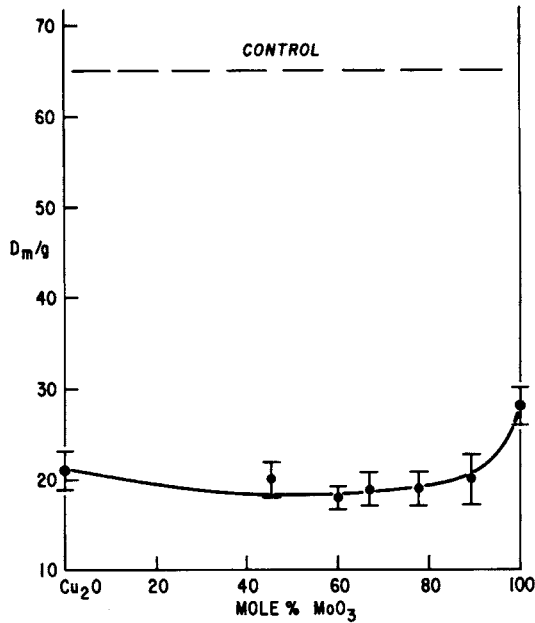
Fig. 23. Cu_2O–MoO_3 system.

Of the pretransition metal compounds tested, only the oxide, hydroxide, and carbonate of magnesium showed any significant smoke retarding ability in PVC. The activity of the basic magnesium compounds may be related to the ease with which they can react with HCl and H_2O at low temperatures to form oxychlorides.

Certain compounds of the post-transition metals, bismuth, tin, and aluminum, are effective smoke retarders for rigid PVC. Excluding compounds of zinc and cadmium, the activity of the effective post-transition metal smoke retarders increases with increasing atomic number.

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