Antimony-Based Flame Retardant Systems in Plasticized Polyvinyl Chloride Compounds

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A method of choosing the most effective way to meet specific flame retardant requirements in polyvinyl chloride compounds, which uses flammability tests based on oxygen indexes, shows that antimony-based and non-antimony retardants perform as well as commonly used antimony oxide retardants, and at a reduced cost.

INTRODUCTION

The flammability of flexible PVC compounds is an important property in many applications of this versatile plastic. In recent years, the cost of flame retardant additives and the number of additives available on the market have increased sharply. As a supplier of PVC compound to the wire and cable industry, we felt that it was important for us to understand the most effective way to provide materials with which our customers could make wire and cable products meeting various flammability requirements.

This study was planned to provide a base from which additional, more detailed work could be done. In order to provide a general data base, the flame retardant additives tested were broken down into the following categories: grades of antimony oxide, antimony oxide replacements, and antimony oxide synergists. The flammabillity data were converted into cost-effective data to provide a practical basis for comparison.

EXPERIMENTAL

The flame retardant additives were tested in a representative wire and cable compound formulation.

	phr
PVC resin	100.00
Plasticizer	50.0 and 60.0
Lead stabilizer	5.0
Lubricant	0.3
Calcium carbonate	20-y
Flame retardant	y

Since this study was directed towards wire and cable applications, DIDP was used as the plasticizer in the comparison of the flame retardant additives. The flame retardant additives were tested at 50-phr and 60-phr DIDP. DIDP was also compared against DOP, DTDP, and TOTM to determine the effect of plasticizer on flammability.

The type and parts level of flame retardant additive used was the most important variable in this study. The various types of flame retardants tested and their costs are listed in *Table 1*. The prices listed in *Table 1* are list prices based on truckload quantities as of October 1, 1980. These prices were the basis of the calculations that show the cost effectiveness of various additives.

The samples were milled on a two roll mill for five minutes at 320°F. Seventy-two mil thick plaques were pressed at 320°F and 40 tons of pressure. The test samples for oxygen index were cut from these plaques. The total calcium carbonate/flame retardant level was held constant at 20 phr. All samples were conditioned in accordance with ASTM D618.

Limiting oxygen index was chosen as the primary test criteria. The simplicity of the test and the high degree of reproducibility were considered important qualities in the testing of varied formulations. The limiting oxygen index was measured according to the procedure outlined in ASTM D2863 on an apparatus manufactured by General Electric. The oxygen index was measured to the nearest 0.5 percent. The U.L. 94 vertical burn test was also done. This test was done according to the procedure outlined in paragraphs 3.6 through 3.15. The sample thickness was 40 mil.

DISCUSSION

The mechanisms of flame retardancy have been studied (1). In halogenated polymers such as polyvinyl chloride (PVC), antimony oxide has been

Table 1.

Grades of Antimony Oxide	Cost/pound
Ultra fine (<1 micron particle size)	$1.96
Lowing tinting (2.5-3.5 micron particle size)	1.89
Antimony Oxide Substitutes	
Antimony-based inorganic complex (41.0% Sb)	1.39
Antimony-silicate complex (25.0% Sb_2O_3)	1.07
Antimony oxide/(25.0% Sb_2O_3) ammonium fluoroborate (50% Sb_2O_3)	1.80 2.05
Antimony Oxide Synergists	
Zinc borate	0.79
Magnesium oxide/zinc oxide	1.10

shown to be an effective flame retardant. It is believed that antimony oxide is activated by reaction with halogens, forming, antimony trihalides and antimony oxyhalides. These two compounds work primarily as flame-phase flame retarders.

The cost of antimony oxide has steadily increased over the last couple of years to nearly $2 per lb. In this study, we investigated the use of less expensive antimony-based flame retardant systems. Systems were studied that would completely replace the use of pure antimony oxide. Other systems were studied that would give a synergistic effect when added to antimony oxide, thus reducing the level of the more costly antimony oxide.

The study of flame retardance is complicated by the many variables in compound formulating and their effect on the flame retardant. Different formulations may yield different results. It is necessary to note that the results presented in this paper are based on limiting oxygen index values. The oxygen index value may not correlate to other types of flammability tests (2). However, it does provide an efficient means of accurately comparing various flame retardant additives on a small scale.

The results from limiting oxygen index testing were converted to a monetary value. This allows for a comparison of various flame retardant systems on a cost effectiveness basis. This paper assesses the cost of a 20-part flame retardant/calcium carbonate filler system per one hundred pounds of resin.

Table 2 is a list of results for two grades of antimony oxide and four antimony-based substitutes.

The results in *Table 2* show that the two grades of antimony oxide, the antimony-based inorganic complex, and the 1:1 antimony oxide/ammonium fluoroborate mixture had similar effects on oxygen index at 50-phr plasticizer level. These four flame retardant additives outperformed the silicate/antimony complex and the 1:3 antimony oxide/ammonium fluoroborate mixture.

Figure 1 shows the relative cost effectiveness of the antimony oxides and the antimony-based substitutes. It is apparent that there is a reduced cost effectiveness, with these additives, as higher limiting oxygen indexes are obtained. The decrease in cost effectiveness is a direct result of a leveling effect which occurs around 29.0 to 30.0 percent oxygen index. Much higher levels of flame retardant additive are required to achieve a given increase in oxygen index.

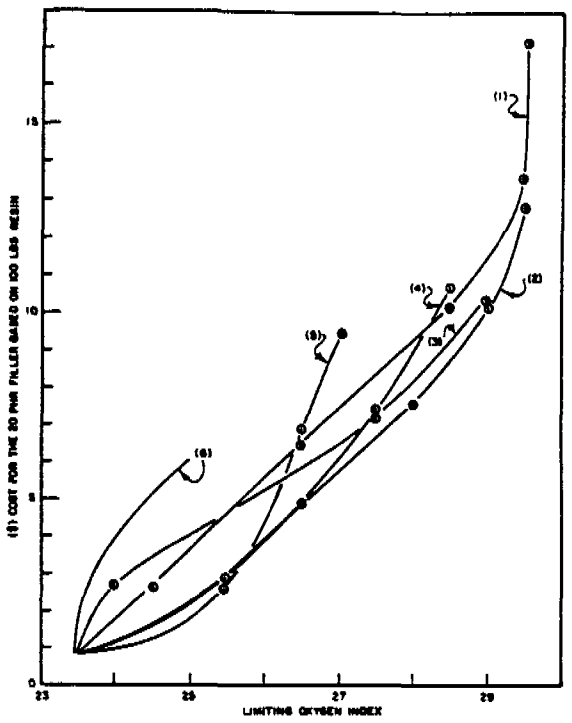

Fig. 1. Antimony oxide and antimony-based substitutes with 50 DIDP as plasticizer; (1) antimony oxide, (2) antimony-based inorganic complex, (3) ultrafine antimony oxide, (4) 1:1 antimony oxide/ammonium fluoroborate, (5) 1:3 antimony oxide/ammonium fluoroborate, (6) silicate-antimony complex.

It is important to notice that even though antimony oxide is widely used as a flame retardant, it may not be the most cost efficient. The antimony-based inorganic material can provide the same oxygen index as antimony oxide at a reduced cost. The 1:1 combination of antimony oxide and ammonium fluoroborate also appears to perform as well as pure antimony oxide at low and moderate oxygen indexes. The silicate-antimony complex seems to increase cost and lower oxygen index. The advantage of increasing the surface area of antimony oxide is more than offset by the reduced amount of antimony oxide obtained per dollar spent.

At 60-phr plasticizer, the flame retardant additives performed the same relative to one another as at 50-phr plasticizer. All testing showed lower oxygen indexes. However, at 60-phr plasticizer level, the antimony-based inorganic complex no longer performed as well as pure antimony oxide.

Table 2. Oxygen Index for Antimony Oxide and Antimony-Based Substitutes in 50-phr DIDP

phr of Flame retardant additive	Antimony oxide	Ultrafine antimony oxide	Antimony based inorganic	Silicate antimony complex	NH_4BF_4 1:1	NH_4BF_4 1:3
0	23.5	23.5	23.5	23.5	23.5	23.5
1	24.5	24.0	25.0	24.0	25.5	25.5
3	26.5	27.5	26.5	24.0	27.5	26.5
5	28.5	29.0	28.0	25.0	28.5	27.0
7	29.5	—	29.0	—	—	—
9	29.5	—	29.5	—	—	—

Table 3 is a list of results of two antimony synergists-zinc borate and a magnesium oxide/zinc oxide mixture mixed with 1- and 3-phr antimony oxide. At low levels, zinc borate appears to be more effective than the magnesium oxide/zinc oxide mixture. However, at higher part levels, there is a more pronounced leveling effect with zinc borate than with a magnesium oxide/zinc oxide mixture.

Figure 2 shows the relative cost effectiveness of the zinc borate and magnesium oxide/zinc oxide mixture. Zinc borate provides a better cost-efficient means of increasing oxygen index at low and moderate oxygen index values. For oxygen index values above 28 percent, the magnesium oxide/zinc oxide mixture becomes the best cost-efficient means.

At 60-phr plasticizer, the same pattern is seen as in *Fig. 2*, but all oxygen index values are lower.

When tested for rating in the U.L. 94 vertical burn test, all flame retardant mixtures received a V-0 rating. The standards containing no flame retardants were rated V-1.

The final part of this study investigated the effect different plasticizers have on flammability. *Table 4* is a list of oxygen index values when various levels of antimony oxide is added to 50-phr DOP, DIDP, DTDP, and TOTM. *Table 4* shows antimony oxide has the least effect on DIDP. The effectiveness of antimony oxide seems to begin to level off at 5 phr. When the part level was increased to 10 phr, there was only an increase of 0.5 percent in oxygen index for DOP and 1.0 percent for DIDP.

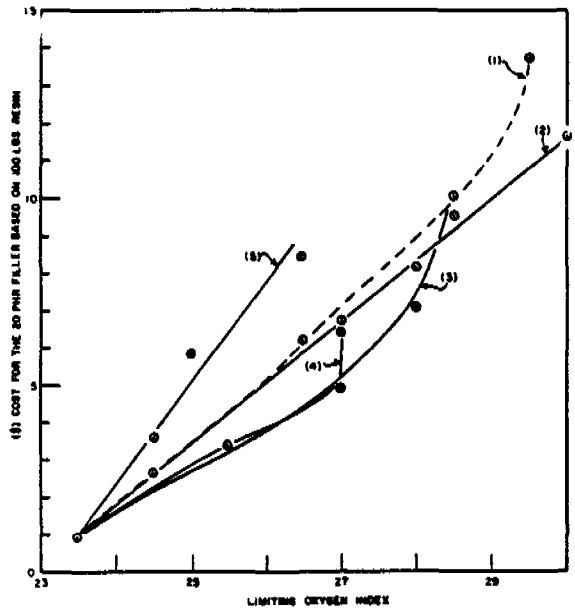

Fig. 2. Antimony oxide synergists with 50 phr DIDP as plasticizer; (1) antimony oxide, (2) 3 phr antimony oxide and magnesium oxide/zinc oxide, (3) 3 phr antimony oxide and zinc borate, (4) 1 phr antimony oxide and zinc borate, (5) 1 phr antimony oxide and magnesium oxide/zinc oxide.

Table 3. Oxygen Index for PVC Formulations Containing Antimony xide and a Synergist

Synergist, phr	Antimony oxide 1 phr	Antimony oxide 3 phr
Zinc borate		
0	24.5	26.5
1	25.5	28.0
3	27.0	28.0
5	27.0	28.5
Magnesium oxide/zinc oxide		
0	24.5	26.5
1	24.5	27.0
3	25.0	28.5
5	26.5	30.0

Table 4. The Oxygen Index of Plasticizers Containing Various Levels of Antimony Oxide (based on 50-phr plasticizer)

Antimony Oxide (phr)	DOP	DIDP	DTDP	TOTM
0	25.0	24.0	23.0	24.5
1	25.0	24.5	25.5	27.5
3	28.5	26.5	27.5	28.5
5	30.0	28.5	29.0	30.0
10	30.5	29.5	—	—

This study has attempted to provide a basis for choosing the most effective way to meet specific flame retardant requirements while keeping cost at a minimum. Specifically, it is important to consider antimony-based and non-antimony flame retardants for completely or partially replacing antimony oxide. Based on oxygen index values, many of these flame retardants will perform as well as pure antimony oxide at a reduced cost.

Additional work is planned to see if other flammability test methods lead to the same conclusions. Also, additional antimony oxide synergists and replacements will be examined.

ACKNOWLEDGMENTS

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Role of Poly(Vinylchloride) and Di-2-Ethyl Hexyl-Phthalate in the Smoke Formation from Plasticized Poly(Vinylchloride)

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The increase of the smoke level from PVC plasticized with di-2-ethyl hexyl phthalate with respect to the rigid PVC is caused mainly by interaction of the plasticizer with HCl evolved from the polymer when the temperature is higher than 200°C. This interaction causes the increase of the yield of phthalic anhydride probably through HCl as catalyst for DOP decomposition but phthalic anhydride formation parallels the formation of products enabled to increase the smoke level such as phthalic acid. In the presence of metallic compounds (iron, zinc, aluminium) it is possible to favor the formation of phthalic anhydride with respect to these products which are responsible for the smoke production. Then phthalic anhydride can be used as a tracer to estimate the efficiency of an additive or a combination of additives as smoke suppressant for DOP because its smoke level varies inversely with the yield of phthalic anhydride. The best combination to reduce the smoke level from plasticized PVC is obtained with the binary systems based upon copper compound, mainly efficient as smoke suppressant for PVC and either zinc or aluminium compounds, mainly efficient as smoke suppressant for DOP.

INTRODUCTION

The use of plastics in many applications is linked to their resistance to combustion and to smoke formation. In connection with the fire problem, the main advantage of the poly(vinylchloride) is a high self-ignition temperature which is above 500°C. Further, owing to its chemical structure it is a self-extinguishing polymer. Nevertheless PVC produces more smoke and toxic and corrosive gas than many other polymers upon combustion. Much of this is due to the presence of HCl. Furthermore PVC is used extensively in modern construction and most PVC uses require that the polymer be compounded with plasticizers. Plasticizer levels are usually specified in terms of parts by weight per hundred parts of PVC (phr). The common hardness and flexibility requirements are met in the range from about 30 to about 100 phr. The most important of these plasticizers are high boiling esters of dibasic aliphatic and aromatic acids which, of course, are flammable. The most extensively used plasticizer is the di-2-ethyl hexyl phthalate (DOP). Its flash point is 216°C and when PVC is compounded with DOP the result is a reduction in flame retardancy and an increase in the smoke level. Then the primary fuel is the plasticizer and not the polymer itself. Thus in compounded PVC fire retardant and smoke suppressant additives are often used. As a smoke suppressant an effective additive must reduce the smoke from plasticizer as well as from the resin. An improved knowledge of the mechanism of smoke formation from the polymer and from the plasticizer as well as from their mixture is important.

Studies on high temperature pyrolysis of PVC and plastisols either under nitrogen (1) or air (2) have shown that the nature of the main products of the decomposition of PVC, mainly HCl and benzene are unchanged. The three main products of the DOP decomposition (3) (4) (5) are phthalic anhydride, 2-ethyl-hexene and 2-ethyl-hexanol. The presence of HCl or PVC prevents the formation of this last product (3). This fact suggests that the PVC causes a change in the mechanism of DOP decomposition through HCl elimination, primarily between 200 and 300°C. Dickens (6) has shown that among the three previous products only phthalic anhydride and 2-ethyl-hexene have important smoke levels but they do not give the smoke level found for pure PVC. The purpose of this paper is to determine the exact origin of the smoke from the pyrolysis products of the individual components, both under smoldering and in flaming conditions and to understand the cause of the increase of the smoke level from plasticized PVC as compared with rigid PVC and pure DOP.

EXPERIMENTAL

Smoke Measurements

Measurements of the smoke density were carried out in dynamic conditions according to the AFNOR Test T 57073 already described (7, 8). The sample

placed into a quartz container is suddenly introduced into a quartz tube, itself inside a tubular oven previously heated at a fixed temperature. The experiments were carried out under air flow and sometimes nitrogen flow of 120 liters/h at temperatures ranging from 400-600°C. The smoke evolution was followed by optical measurement of the obscuration of a light beam across a measured path between a light source and a photo cell receiver. An additional air circulation prevents any redeposition on the windows of the light source and photocell receiver which would alter the light transmission. The attenuation of the light beam was measured by a device designed by us and which allows to record continuously the optical density variations (Log I_o/I) between 0 and 4 vs time. The smoke level (S) is calculated according to *Eq. 1*:

$$S = \frac{A}{uP} \qquad (1)$$

where A is the area of the surface under the obscuration curve, u is the area unit limited by the surface defined by the optical density equal to 1 and the time equal to 1 min. P is the weight of the sample in grams. Then S is expressed in decade · min · g^{-1}.

For the common use of the AFNOR test the smoke density chamber is connected to the furnace through a 2 liter flask to ensure good homogeneity of smoke. Nevertheless the suppression of this flask permits separation of the smokes produced from each component of the plasticized PVC as shown either in smoldering (*Fig. 1a*) or in flaming (*Fig. 1b*) conditions. However the amount of the DOP must not be higher than 50 phr. Above 50 phr the separation of the two waves is not great enough. At 600°C (flaming conditions) the response of the opacimeter shows only one peak and the contribution of the smoke produced from each component cannot be evaluated whatever the amount of plasticizer.

The DOP and PVC are mixed together as a powder at room temperature using an electric mill. Then the powder is pressed as rods under 1 ton/cm² using a mold of length 100 mm, width 6.5 mm and thickness 3 mm.

At 400°C and 500°C the weight of the samples is 40 mg for pure DOP and the weight of the plasticized PVC is such that the weight of the plasticizer is about 30-40 mg.

At 600°C the weight of pure DOP and the weight of plasticized PVC is 150 mg.

The influence of HCl on the smoke level from the DOP has been studied with a device designed by us. The polymer is put in the lower compartment of a parallelepipedic cell of quartz divided in two parts by means of a sintered glass disc. The plasticizer is placed in the upper side. The cell is joined to a cylindrical glass tube to introduce it inside the quartz tube itself inside the furnace. Gas flow (60 l/h) nitrogen or air forces HCl to diffuse across the sintered glass.

For experiments carried out at 400°C either under nitrogen or air the weight of DOP is 100 mg and the weight of PVC is 200 mg. For experiments carried out at 600°C under air a gas flow of pure HCl ($1.66.10^{-2}$ l/s) diffuses across the sintered glass.

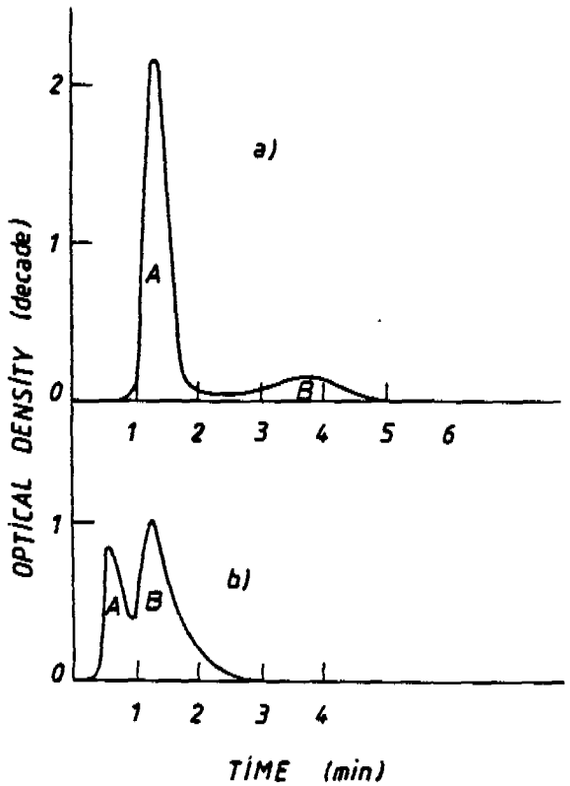


Fig. 1. Obscuration curves from PVC plasticized with di-2-ethyl-hexyl phthalate. a) Smoldering conditions (400°C)—DOP 16.6%; b) Flaming conditions (500°C)—DOP 33.3%; A—Response of the opacimeter for DOP; B—Response of the opacimeter for PVC.

Di-Ethyl-2-Hexyl Phthalate and Plasticized PVC Degradation

The DOP and the plasticized PVC degradation has been carried out either in the same furnace used for the smoke measurements or in a flash pyrolyser. In the first case a glass wool filter is put to the exit of the furnace to avoid flame propagation and to retain the soot. The products of decomposition are trapped after the filter in acetone cooled at −78°C. The furnace is connected to the trap through a heating jacket (300°C) to avoid the condensation of high molecular weight products such as phthalic anhydride.

Flash pyrolysis experiments were carried out using a Girdel pyrolyser connected to a gas chromatograph (Intersmat type IGC 15) equipped with a flame ionization detector. The DOP or plasticized PVC was dissolved in tetrahydrofuran at 3 percent by weight and 5 microliters of this solution was deposited on the filament. The pyrolysis time was selected as 50 s.

The separation and estimation of the products of degradation trapped in acetone or evolved during

flash pyrolysis was achieved through gas chromatography with temperature programming at heating rate of 10°C/min between 50 and 250°C. The column packing is SE-30 (silicone oil on chromosorb). Nitrogen was used as carrier gas at 2.2 kg/cm².

Carbon dioxide and carbon monoxide measurements have been carried out continuously with two infrared gas analyzers cosma apparatus type Rubis 3000) in line after the furnace and parallel to each other. The gas flow was 80 l/h. Then in smoldering and in flaming conditions it is always possible to separate the carbon dioxide resulting from each component (*Fig. 2*) but not carbon monoxide. As for smoke measurements, the samples are introduced in the furnace previously heated to the desired temperature. To avoid the saturation of the analyzers the amount of the samples (pure DOP or plasticized PVC) is 250 mg at 400°C, 50 mg at 500°C and 25 mg at 600°C for the experiments carried out under nitrogen. Under air the amount of the pure DOP and plasticized PVC is the same as previously at 400 and 500°C. At 600°C, it is 25 mg for pure DOP and 15 mg for plasticized PVC.

RESULTS AND DISCUSSION

In our experimental conditions the self-ignition temperatures is between 400 and 500°C according to the rate of the plasticizer because of its flash point at 216°C.

At 400 and 500°C under nitrogen most of the white smoke is produced from the sublimation of the phthalic anhydride evolved from the decomposition of the plasticizer. As shown in *Table 1* the percentage of char residue at 400 and 500°C does not change when the DOP fraction increases and from 500°C it is independent of the temperature and represents about 10 percent of the initial weight of the polymer. Furthermore the amount of benzene evolved in flash pyrolysis experiments is constant at 600°C, whatever is the DOP concentration but it becomes proportional to the plasticizer percentage from 700°C where the benzene is also a product of the DOP decomposition (*Fig. 3*).

In smoldering (400°C) or flaming (500°C) conditions the presence of DOP does not change the total amount of CO_2 evolved from the polymer and does not influence its smoke level.

All the previous results show that the degradation of the PVC is not influenced by the presence of the DOP and confirm the conclusions of O'Mara (1) and Boettner (2) who have shown that the pyrolysis of PVC and plastisols at high temperature under nitrogen or air does not modify the nature of the main products of the decomposition of the PVC.

In return PVC enhances strongly the smoke level from the DOP either under nitrogen or under air (*Table 2*). Under nitrogen or in smoldering conditions under air the response of the opacimeter is partly due to the sublimation of the phthalic anhydride coming from the DOP decomposition.

Under air, in smoldering conditions (400°C) the smoke level from pure DOP is about 12 times higher than the smoke level from PVC. When the two components are mixed, the smoke level from the plasticizer increases very much as well as the amount of phthalic anhydride and it increases when the molar ratio HCl/DOP increases. In flaming conditions (600°C) there is self-ignition of each mixture whatever may be the DOP content. The smoke level of each pure component is equivalent but when they are mixed the smoke level from plasticized PVC is higher by about 30 percent (*Table 3*).

At 600°C it is not possible to differentiate experimentally the smoke levels from each compo-

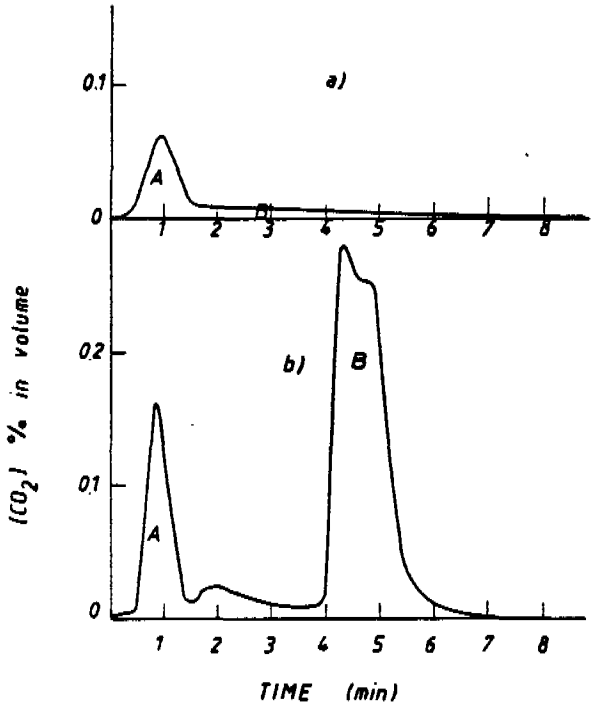


Fig. 2. Carbon dioxide evolution from plasticized PVC. a) Smoldering conditions (400°C)—DOP 33.3%; b) Flaming conditions (500°C)—DOP 33.3%; A—Response of the IR gas analyzer for DOP; B—Response of the IR gas analyzer for PVC.

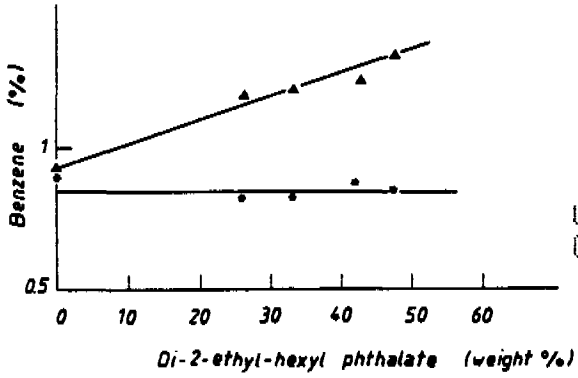


Fig. 3. Influence of the di-2-ethyl-hexyl phthalate on the benzene formation during flash pyrolysis of the plasticized PVC at 600°C (★) and at 700°C (▲).

Table 1. Influence of DOP on PVC Pyrolysis and Combustion

DOP X	PVC 1 − X	Temperature (°C)	Nitrogen: Char residue weight, %	Nitrogen: S_{PVC} decade · min · g^{-1}	Air: Char residue weight, %	Air: S_{PVC} decade · min · g^{-1}	Air: $CO_{2(PVC)}$ mole · g^{-1} · 10^{3}
0	1		29	0	25	3.5	2.64
0.166	0.834	400	26.5	0	26	4	2.70
0.333	0.667		29.5	0	24.5	traces	3.1
0.44	0.56		30.0	0	25.5	1.6	4.6
0	1		10	2.9	traces	16	8
0.166	0.834	500	9	2.2	traces	15.3	6.4
0.333	0.667		10	2.8	traces	10.7	10.4
0.44	0.56		10.5	4.5	traces	not defined	8.5

Table 2. Influence of PVC on DOP Pyrolysis and Combustion

T (°C)	DOP X	PVC 1 − X	Nitrogen: Degraded DOP mole %	Nitrogen: $S_{(DOP)}$ decade · min · g^{-1}	Nitrogen: $CO_{2(DOP)}$ mole · 10^{3}*	Nitrogen: Phthalic anhydride mole · 10^{3}*	Air: Degraded DOP mole %	Air: $S_{(DOP)}$ decade · min · g^{-1}	Air: $CO_{2(DOP)}$ mole · 10^{3}*	Air: Phthalic anhydride mole · 10^{3}*
400	0.166	0.834	95	56	5	1.7	91.5	94.2	0.144	7.4
	0.333	0.667	89	56.5	4.1	2	90	56.4	1.2	13.8
	0.44	0.56	89	39	3.1	2.6	82	82	0.39	9.8
	1	0	43	13	0	traces	78	43	1.8	4.4
500	0.166	0.834	100	19	46	6.8	100	15.2	0.5	4
	0.333	0.667	98	9	39	5.6	100	7	1.24	traces
	0.44	0.56	98	13.5	35	6.7	100	9	0.96	traces
	1	0	84	18	26	6.4	85	16.1	2.54	traces

* These values are given for one mole of degraded DOP.

Table 3. Smoke Level from Plasticized PVC (S_T) and from DOP Fraction (S_{DOP}) in Flaming Conditions (600°C)

DOP X	PVC 1 − X	S_T decade · min · g^{-1}	S^*_{DOP} decade · min · g^{-1}
0	1	9.8	9.8
0.166	0.834	12.1	24
0.333	0.667	12.0	16.5
0.444	0.556	11.0	12.8
1	0	8.3	8.3

* Calculated values according to *Eq 2*.

Table 4. Influence of HCl Evolved from PVC on the Smoke Level from Pure DOP

	Smoke level (decade · min · g^{-1})		
	Nitrogen	Air	
	400°C	400°C	600°C
DOP	7.2*	22*	9.4*
DOP + HCl	36.7	31	13

* These values cannot be comparable with the values for smoke level from DOP given in the *Table 2* because of the experimental conditions are different.

nent. Nevertheless as DOP does not influence the degradation of the PVC we can assume that it does not change the smoke level from the polymer (S_{PVC}) whatever may be the percentage of the plasticizer. Then with this assumption it is possible to calculate the smoke level from the plasticizer (S_{DOP}) (*Table 3*) with respect to its fraction (X) from the smoke level measurements of the plasticized PVC (S_T) according to *Eq 2*:

$$S_T = S_{DOP}(X) + S_{PVC}(1 - X) \qquad (2)$$

In flaming conditions PVC yet enhances the smoke level from the DOP fraction.

Besides phthalic anhydride and carbon dioxide undergo the influence of PVC from quantitative point of view (*Table 2*).

These results suggest that the increase of smoke level from plasticized PVC is due mainly to the interaction of the PVC with the mechanisms of DOP degradation through HCl which is the main product of PVC degradation evolved between 200 and 300°C. Furthermore HCl is an effective catalyst for the thermal degradation of DOP (*Fig. 4*) and causes an increase in its smoke level (*Table 4*).

The role of HCl as a catalyst for the degradation of the DOP appears in the following reactions:

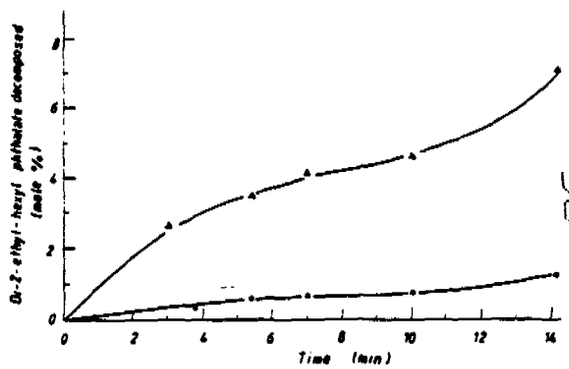
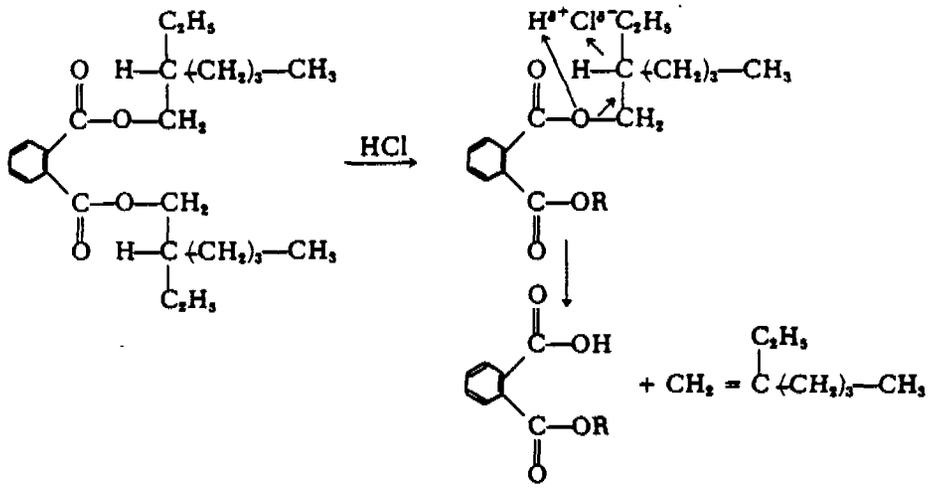


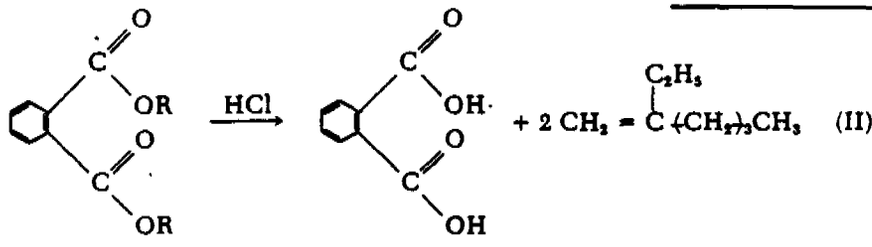
Fig. 4. DOP degradation at 244°C under nitrogen either in absence (★) or in the presence (▲) of HCl.



(I)

(A)

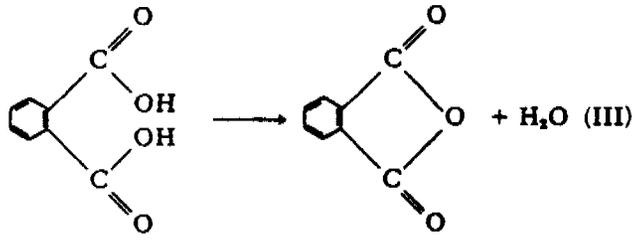
with an excess of HCl (low percentage of plasticizer) the two ester groups can be decomposed simultaneously into acid according to the *Reaction II*:



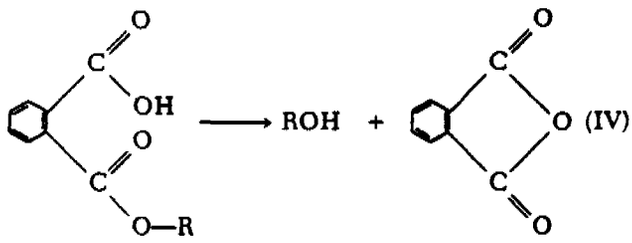
(II)

(B)

The phthalic anhydride can be formed either from the phthalic acid (B) according to the *Reaction III* or from the monoester (A) according to the *Reaction IV*:



(III)



(IV)

At moderate temperature (200°C) the *Reaction IV* is quantitative but at higher temperature the yield of phthalic anhydride can be reduced because of spontaneous decarboxylation of phthalic acid. Furthermore whatever may be the temperature the smoke level from phthalic acid either under nitrogen or under air is always higher than the smoke level from phthalic anhydride (*Table 5*). At temperature higher than 500°C the smoke level of these two compounds are in a ratio of about 2.

The previous observations suggest that any modification of the mechanisms of DOP decomposition favoring the formation of phthalic anhydride may contribute to decrease the smoke level from the plasticizer. This purpose can be achieved (*Table 6*) using metallic chlorides as Lewis acid or metallic oxides enabled to be transformed into chlorides as Lewis acid by reaction with HCl evolved from the polymer when the temperature is raised above 200°C.

From the previous results it appears as a general rule that the smoke level from DOP decreases when the phthalic anhydride yield increases. The

Table 5. Smoke Level from Phthalic Anhydride and Phthalic Acid

	Smoke level (decade · min · g⁻¹)			
	Nitrogen		Air	
T (°C)	Phthalic anhydride	Phthalic acid	Phthalic anhydride	Phthalic acid
400	2.92	16.4	3.6	14.3
515	4.38	14.25	4.23	10.35
600			5.75	8.76
645			5.32	8.00

Table 6. Influence of Metallic Additives on Phthalic Anhydride Formation and Smoke Level from D P and PVC in Smoldering Conditions (450°C) for PVC Plasticized with 16.6% of DOP (PVC 100 mg—DOP 20 mg—Additives 1.5 mg in Weight with Respect to the Polymer)

Additives	Phthalic anhydride mole/mole of degraded DOP	Smoke level from PVC decade · min · g⁻¹	Smoke level from DOP decade · min · g⁻¹
pure DOP			35
PVC-DOP	0.076	5.2	57.8
PVC-DOP-FeCl₃	0.36	—	—
PVC-DOP-Fe_2O_3	0.46	4.4	19.8
PVC-DOP-$ZnCl_2$	0.15	0.96	30.5
PVC-DOP-ZnO	0.29	4.8	31.8
PVC-DOP-$Al_2O_3,3H_2O$	0.17	1.1	46.8
PVC-DOP-$AlCl_3H_2O$	0.26	2.7	40.4

* In presence of FeCl₃ it is not possible to separate the response of the opacimeter for each component probably because of its strong efficiency as oxidative catalyst at temperatures higher than 300°C.
The amount of each metallic additive is 1.5 percent by weight with respect to the PVC.

most efficient additives are iron oxide and zinc compounds. These results suggest that phthalic anhydride can be used as a tracer to estimate the efficiency of any additive as smoke suppressant for the PVC plasticized with DOP. This statement is confirmed in *Fig.* 5 where it is shown that the smoke level from DOP is in reverse ratio with the amount of phthalic anhydride formed in smoldering conditions (400°C) in absence or in presence of ferrocene Fe55 supplied by ARAPAHOE chemical company. The ferrocene is well-known to reduce the smoke level from rigid PVC through its ability to lead to $FeCl_3$ and Fe_2O_3 which can act as an oxidative catalyst for the char residue after dehydrochlorination of the polymer. From the results (*Fig.* 5) the ferrocene also contributes to decrease the smoke level from DOP for plasticized PVC probably through the same previous by products because it has no influence on the nature and the yield of the products of pure DOP decomposition as on the smoke level from pure DOP in smoldering or in flaming conditions. Moreover ferrocene causes the increase of the char residue during pyrolysis under nitrogen whatever may be the percentage of the plasticizer and the temperature (*Fig.* 6) probably because of the influence of iron chlorides, well known as catalyst for PVC dehydrochlorination and crosslinking. Under air in smoldering conditions ferrocene reduces the char residue of about 75 percent because of the incandescence initiated by Fe_2O_3. Nevertheless the ferrocene efficiency as smoke suppressant for PVC fractions is not very great in smoldering or in flaming conditions because of a dilution effect which may favor its volatility and contribute to decrease its concentration in the char residue. These results suggest that it is necessary to combine at least two additives to obtain the best efficiency as smoke suppressant for plasticized PVC. One additive must be efficient as smoke suppressant for the polymer and the other as smoke suppressant for the plasticizer. For this purpose the combination of copper compound either with zinc oxide or hydrated alumina appears as the most efficient to reduce the smoke level from each component in smoldering conditions (*Table* 7).

From these results the efficiency of the copper compound as smoke suppressant for PVC is not modified in the presence of an efficient additive as smoke suppressant for DOP such as zinc oxide. Furthermore there is a synergistic effect between copper compound and zinc or aluminium compounds. The efficiency of these binary systems is

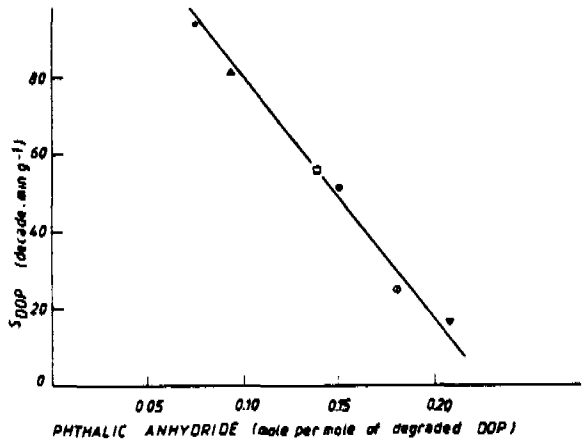


Fig. 5. Influence of the ferrocene Fe55 on the phthalic anhydride formation and the smoke level from DOP for plasticized PVC in smoldering conditions (400°C). (□) PVC—DOP (33.3%); (▫) PVC—DOP (33.3%) ferrocene 1.5%; (▲) PVC—DOP (44.4%); (●) PVC—DOP (44.4%) ferrocene 1.5%; (★) PVC—DOP (16.6%); (▼) PVC—DOP (16.6%) ferrocene 1.5%.

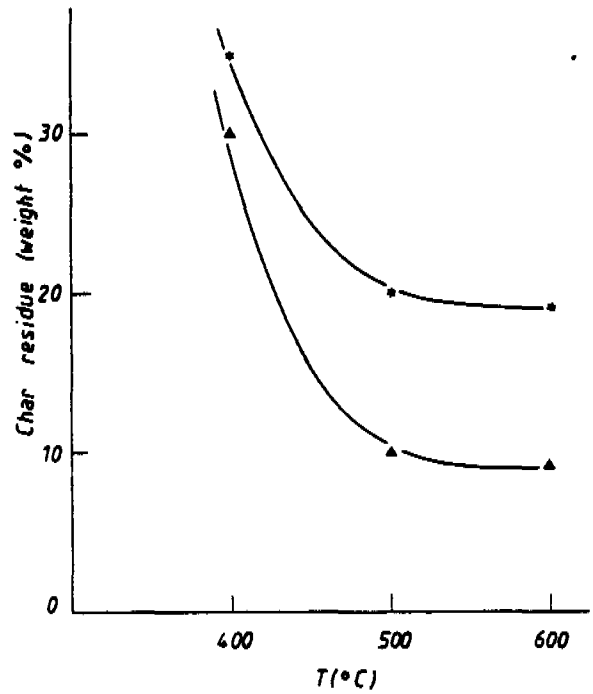


Fig. 6. Influence of the ferrocene Fe55 (★) (1.5%) on the char residue formed during the pyrolysis of plasticized PVC (DOP 33.3%) under nitrogen (▲).

Table 7. Influence of Metallic Compounds on the Smoke Level from DOP and PVC in Smoldering Conditions (450°C) for Plasticized PVC (DOP: 16.6%)

Additives	S_{DOP} decade · min · g^{-1}	S_{PVC} decade · min · g^{-1}
PVC-DOP	57.8	5.2
PVC-DOP-$CuSO_4$	40	0
PVC-DOP-ZnO	31.8	4.8
PVC-DOP-ZnO-$CuSO_4$	19.2	0.28
PVC-DOP-$ZnCl_2$	30.5	0.26
PVC-DOP-$ZnCl_2$-$CuSO_4$	25.2	0
PVC-DOP-$Al_2O_3H_2O$	46.8	1.1
PVC-DOP-$Al_2O_3H_2O$-$CuSO_4$	26.8	0

The amount of each metallic additive is 1.5% by weight with respect to the PVC.

conserved for higher concentration of DOP but also in flaming conditions (700°C), *Table 8*, where the most efficient combination is obtained with copper and aluminium compounds.

In conclusion this study suggests that the increase of the smoke level from PVC plasticized with di-2-ethyl-hexyl phthalate with respect to the rigid PVC is caused mainly by interaction of the plasticizer with HCl evolved from the polymer when the temperature is higher than 200°C. This interaction causes the increase of the yield of phthalic anhydride probably through HCl as catalyst for DOP decomposition but phthalic anhydride formation parallels the formation of products enabled to increase the smoke level such as phthalic acid. In the presence of metallic compounds (iron, zinc, aluminium) it is possible to favor the formation of phthalic anhydride with respect to these products which are responsible for the smoke production. Then phthalic anhydride can be used as a tracer to estimate the efficiency of an additive or a combination of additives as smoke suppressant for DOP because its smoke level varies inversely with the yield of phthalic anhydride.

Table 8. Smoke Level from Plasticized PVC (DOP 16.6%) in Flaming Conditions (700°C) in Presence of Metallic Compounds

Additives	S decade · min · g^{-1}
PVC-DOP	8.3
PVC-DOP-ZnO	4.6
PVC-DOP-$CuSO_4$	7.3
PVC-DOP-$Al_2O_3H_2O$	8.5
PVC-DOP-$Al_2O_3H_2O$-$CuSO_4$	5.2

The amount of each metallic additive is 1.5% by weight with respect to the PVC.

The best combination to reduce the smoke level from plasticized PVC is obtained with the binary systems based upon copper compound, mainly efficient as smoke suppressant for PVC and either zinc or aluminium compounds, mainly efficient as smoke suppressant for DOP.

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Basic Studies of Smoke Reduction in Rigid Poly(Vinylchloride)

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A review of recent results in the literature and from our laboratory lead to drive a general picture of the combustion or rigid PVC as well as to the mechanism by which the most powerful additive can reduce the production of smoke. It is shown that, in smoldering condition the black smoke comes chiefly from direct volatilization of heavy tar molecules from the decomposing residue. The additives change the degradation process of the PVC by catalysis of the intermolecular crosslinking reactions, which compete with the intramolecular reactions leading to formation of benzene. Whatever their initial nature, they are at least partly transformed into chlorides and then into oxides during the combustion process. The oxide of Cu, Fe and also Zn are catalysts of the oxidation of the char residue, which may be partially inhibited by phosphorous compounds. The catalytic effects seem less pronounced in flaming conditions, which cause the productions of soots from the initial tars.

INTRODUCTION

Because of its self-extinguishing character, PVC has became popular in many parts of the building and housing industry. However, it suffers for two major drawbacks in case of fire: first the evolution of a large amount of HCl which is produced at rather low temperatures, and second the production of large amount of black smoke as well in smoldering as in flaming conditions. The evolution of HCl can be partly overcome by the addition of large amounts of finely divided magnesium or calcium oxide or carbonate; however HCl is easily condensed with water so that its concentration decreases very rapidly at increasing distance from the fire location. Its more dangerous carrier is the black smoke, soot or tar particles, where it may be condensed as well. So, if we forget the corrosion problem caused by droplets of HCl water solutions, the more serious problem is the one raised by the production of smoke.

A large variety of compounds have been patented as smoke suppressors for rigid than for plasticized PVC. They include ferrocene (1), iron oxides (2-3), alumina trihydrate (4, 5), molybdenum oxide (6, 7), vanadium oxide and acetylacetonate (8), copper cyanide and thiocyanate (9), mixture of iron powder and copper oxide (10), zinc and alkaline metal ferrocyanide (11) various alkaline, alkalin-earth or magnesium oxide (12) and even nickolcene (13) and many other compounds or mixtures.

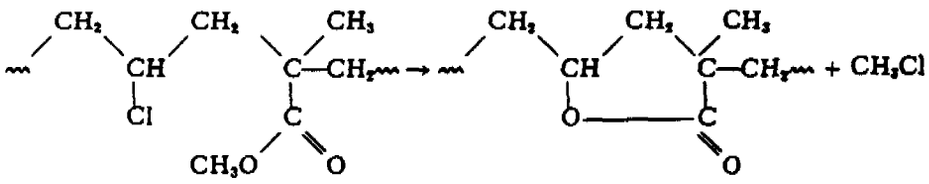
The various mechanisms by which these various additives may be efficient are not clearly established and remain the object of controversy in recent discussions (14, 15). It is the purpose of this paper to try to clarify some points by critically reviewing the work carried out in our laboratory (16-18) as well as other works recently published (14, 15, 19, 20, 21). We will limit our discussions here to rigid PVC, without any other additives than the smoke suppressors or a very simplified stabilization recipe. Another paper has dealt with PVC plasticized with dioctyl phthalate (22).

It is generally accepted that in the combustion of polymers, the development of heat due to the fire causes the pyrolysis of the polymer which leads to the formation of volatile fuel which burns to give the combustion gas as well as the tar or soot particles. So much attention has been paid to the composition of the volatile compounds upon pyrolysis. In the case of PVC, for instance, in addition to the non-combustible hydrochloric acid which is the major product, the main volatile product is benzene, and Wooley (24) was the first to point out that the origin of the smoke is to be found in the production of aromatic compounds during the pyrolysis. We will begin by a discussion of the pyrolysis experiment and will discuss the combustion experiments later.

PYROLYSIS OF PVC

Coupling thermogravimetric analysis (t.g.a.) and gas chromatography (g.c.) allows to show that the pyrolysis of pure PVC takes place in two steps (16, 17, 24). The first one corresponds to dehydrochlorination which is practically complete at 300°C, and is highly endothermic. The elimination of HCl is accompanied by a significant loss of benzene, which may account for up to 3 percent of the weight loss and a very small amount of volatiles such as ethylene and propane. The second step begin at

350°C and gives a very complex set of volatile compounds including H_2, light aliphatics such as methane, ethylene, propylene, butene ... alkylaromatics as toluene and many others. The combination of pyrolysis, g.c., and mass spectrometry give a complete analysis of all these products (23, 25-28). Because of the suspected influence of the benzene and other aromatic compounds on the production of smoke, the mechanism of benzene formation has been studied in detail. Using mixtures of PVC and perdeuterated PVC, O'Mara (29) has shown that benzene is produced through an intramolecular mechanism. Such conclusion was confirmed recently and extended to pure conjugated products (benzene, styrene, naphthalene, biphenyl, anthracene) by Lattimer and Kroenke (20). These authors showed further that mixed aromatic-aliphatic compounds are formed at least partially via intermolecular mechanisms which may be crosslinking or hydrogen transfer. In our laboratory (30), another indirect proof of the intramolecular mechanism of benzene formation came from the study of the pyrolysis of vinyl-chloride (VC)/methyl methacrylate (MMA) copolymers. In these products the more striking reaction is a lactonization between adjacent co-monomer units which leads to the formation of methyl chloride, according to the reaction scheme:



Between these adjacents diads, the degradation of the inner sequence of either VC or MMA takes place as in pure homopolymer: it has been shown that the amount of benzene produced is exactly proportional to the amount of VC units in sequences larger than 5 units. Taking into account the two extreme units engaged in the lactonization reaction, it is clear that the benzene results from sequences of conjugated dienes with at least 3 units.

The precise mechanism of benzene formation has been discussed in detail by Starnes (14) who concluded that it results from the intramolecular cyclization of conjugated polyene segments into 1,3-cyclohexadiene moieties, followed by the removal of polymeric ring substituents through sequential C-C homolysis. It is interesting to notice here that this mechanism involves the scission of the main chain and thus may lead to the formation of higher volatile compounds. It must be pointed out also that the mechanism involves the cis conformation around at least two successive unsaturated units; for that reason the formation of benzene is inhibited by a trans-trans conformation of the main-chain as in syndiotactic units and so the amount of benzene produced upon pyrolysis is dependant on the polymerization temperature which governs the extent of syndiotacticity (31).

Although the major part of the benzene is produced during the first step of the pyrolysis, its amount is dependent on kinetic factors. So in time resolved g.c. the total amount is dependent on the heating rate and tends to increase when the heating rate decreases (*Table 1*). In flash pyrolysis experiments (16) the amount of benzene is lower (less than 1.5 percent), and further, the relative amount of benzene in the whole production of volatiles decreases from 70 to 37 percent when the nominal pyrolysis temperature increases from 500 to 700°C (27). It means that there may be competition between the process of benzene formation with other processes like isomerization from cis to trans conformer in the polyene sequence, or crosslinking through intermolecular processes. Obviously the competition is in favor of the intramolecular "benzene" process when the temperature is moderate. At high temperatures, the other processes are favored and during the second step of the pyrolysis a very small amount of benzene is produced.

Most of the additives tried, and chiefly those which show a positive action in the reduction of smoke, exert some influence on the pyrolysis process (16, 17). Generally speaking, they do accelerate the dehydrochlorination reaction and they reduce the benzene formation. A rather extensive study of the effect of 33 metal oxides and 23 metal chlorides has been recently published by Iida and Goto (39). They have shown that the more acidic metal compounds, and specially $FeCl_2$ and $FeCl_3$ drastically increase the amount of aliphatic volatiles and also mixed aromatics as well as chlorinated aromatics, and decrease in the same way the amount of pure aromatics. The reverse effect was observed for the basic metal compounds. These catalytic effects were interpreted in term of the

Table 1. Reduction of Benzene (Percent from Pure PVC) by Selected Additives (1.5% Weight) in PVC Pyrolysis

Additive	Heating rate 2°C/min	Heating rate 1°C/min
CuO	10.8	26.2
Fe_2O_3	11.2	18.3
$FeCl_2$	3.2	—
Ferrocene	10.8	—
$ZnCl_2$	44	—
Sb_2O_3	100	—
MoO_3	—	41.6
none	2.5*	3*

* Percent of the initial weight transformed in benzene.

capacity of the chlorides (eventually formed from reaction of HCl with the oxides) to promote the addition of HCl and Cl_2 onto the polyene chain. The behavior of copper and some other compounds of Sn, Bi and Ga, was interpreted in term of the ability of their chloride to dissociate to give Cl_2. Iida and Goto stated that the mixed aromatics and the chlorinated aromatics come from partially saturated or chlorinated polyene chains formed after readdition of HCl or Cl_2. We do not agree with that view, at least for the formation of mixed aromatics, which has been shown by Kroenke and Lattimer (20) to result from intermolecular process. We do consider that the effect of the acidic chloride and of $CuCl_2$ is more likely to be catalysts for these intermolecular processes through Friedel-Craft reaction, for instance, owing to their Lewis acid character. Nevertheless, the possibility of some readdition process must be considered which can be also catalyzed by a charge transfer complex between the polyene and the metal chlorides.

Some typical results from our laboratory concerning the reduction of benzene are reported in *Table 1*. Again, the influence of the kinetics are to be noted: the slower the heating rate, the smaller the benzene reduction is. However it seems difficult to find a direct correlation between the benzene reduction ability of an additive with its catalytic effect of one of the several reaction during pyrolysis. Dehydrochlorination (DHC) itself seems to be out of consideration if one compares the action of iron compounds which strongly accelerate the DHC process, and that of the copper compounds which do not vary much, both lead to about the same activity in benzene reduction. The zinc derivative, especially $ZnCl_2$, which is known as a very powerful catalyst for both DHC and crosslinking, shows a rather moderate activity in benzene reduction. However it must be pointed out that it might be dangerous to make too much comparison between various additives because their mixing with PVC powder may be very dependent on its initial physical state (morphology, grain size . . . .).

Special attention has been paid recently to MoO_3. It has been reported to reduce the benzene formation (14) and also to accelerate the DHC and improve the crosslinking during pyrolysis (15). The most recent results of Kroenke and Lattimer (15) show that it enhances the rate of formation of mixed aromatics formed upon intermolecular mechanism. For that reason, the authors suggest that a reductive-coupling mechanism is operative. This mechanism, well documented in the literature for copper compounds, involves first the formation of an organometallic compound upon reaction of an organic radical R°, followed by the reaction with a reactive organic chloride R'Cl. The resulting moiety RR'MeCl where Me is the metal atom (which may have other ligands) undergoes a reductive coupling which leads to the formation of a reduced MeCl moiety and a coupling of R and R' to give a R-R' molecule. This mechanism is believed to explain both crosslinkinig and dehydrochlorination as well as the reverse chlorination of polyenes. It is believed also to explain the synergistic effects between Mo and Cu compounds. As proof of its reality, the authors state that Cu^{II} may be reduced to Cu^{I} and CuO in the presence of PVC, and also that reduction of MoO_3 has occurred, owing to the presence of MoO_2 and MoC in the residue. Using a laser-microprobe analysis, Lum (19) was able to show that the products of reduction of MoO_3 by the carbon residue are able to chemisorb benzene and other aromatics and then concluded that Mo compounds may act through the formation of π-arene complexes, but Kroenke and Lattimer pointed that such a mechanism cannot explain the catalysis of intermolecular reaction by MoO_3. On the other hand, Starnes and Edelson (14) concluded that the ability of MoO_3 to reduce the yield of benzene is likely to be connected with their ability to function as Lewis acid. By that way it can accelerate the heterolysis of a C-Cl bond by coordination the intermediate Cl^- ion in an ionic DHC mechanism, to give a more stable anion, thus enhancing the ionization of the system. Lewis acid may also catalyze the isomerization of diene from cis to trans so that the cyclization mechanism leading to benzene is less favorable. Finally they can catalyze intermolecular Diels-Alder cyclization as well as Fried l-Crafts alkylations.

In our opinion, it seems dangerous to extrapolate at high temperature, various mechanisms which have been well established at moderate temperatures. It is dangerous also to try to explain everything with only one kind of mechanism. The only point which is clear is that all the additives which are good smoke suppressors do reduce the benzene formation most probably by catalyzing the various competitive processes which may take place during the first step of the pyrolysis of PVC.

COMBUSTION OF RIGID PVC

The first studies which dealt with the problem of smoke pointed out two major ideas: the first one was the correlation between the production of benzene during pyrolysis and the production of smoke during combustion. After the initial suggestion of Wooley (23), it comes from the work by Liebman, *et al.* (32) comparing the behavior of PVC with chlorinated PVC and polyethylene in the production of benzene, chlorobenzene and smoke. We have found actually a fine correlation between the amount of benzene produced upon time resolved g.c. pyrolysis experiments and the combustion at 600°C (flaming) with PVC plus various amount of ferrocene as smoke suppressor (16). The second idea, issued from the work of Kracklauer and Sparkes (1), was a correlation between the reduction of smoke and the increased char residue. Again we have found a very good correlation (*Fig. 1*) by comparing both results for pure PVC in smoldering

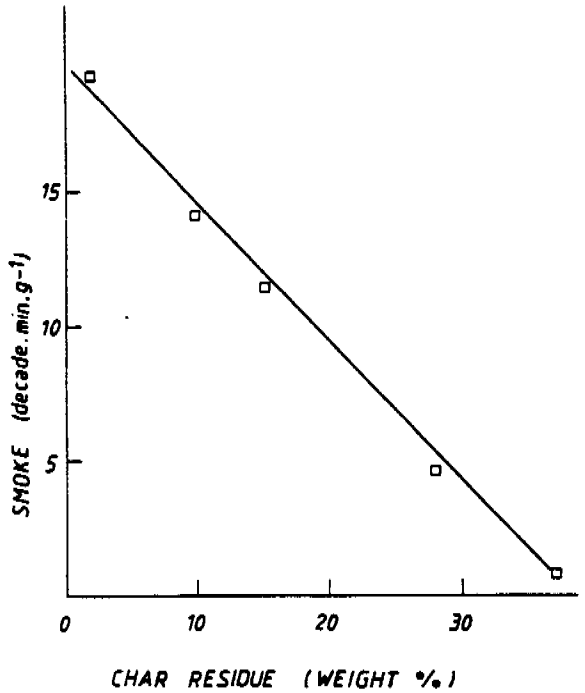


Fig. 1. Smoke level from pure PVC (250 mg) vs char residue after the end of smoke wave in smoldering conditions at various temperatures between 300 and 550°C.

conditions at various temperatures. These two ideas have remained popular, as, for instance, Starnes and Edelson (14) stated that "benzene combustion is the major source of smoke during the burning of the polymer"; on the other hand, Kroenke (21) states that "a large variety of metals can form compounds which are smoke-retarder and act to change the thermal degradation pattern of the PVC and promote the formation of char".

Other experiments seem to lead to inverse conclusions. So, in one of our experiments in smoldering conditions (400°C) introduction of benzene in the air stream did not increase the amount of smoke; clearly, higher temperatures are necessary to cause benzene dehydrogenation and condensation into soot particles as present in black smoke. On the other hand, we have observed (16) that ferrocene causes a decrease of the char residue in combustion experiments carried out at 400°C and higher temperatures, and the best smoke-suppressor additives which were oxidation catalysts or precursors of oxidation catalysts cause the char residue to be totally consumed (17).

A more careful examination of the literature shows that the reasons for these apparent discrepancies are to be found in the different protocol of the experimentation. Most of the smoke measurements have been carried out in the NBS smoke chamber where the smoke is accumulated in a limited volume. The thermal stress, or the flame, may be applied for different times. In the Goodrich Smoke-Char Test of Kroenke (21) quenching in nitrogen atmosphere and at room temperature after one minute is done: such conditions are well designed to keep the amount of char residue high. It was shown to be the case for MoO_3 and other additives, but different conclusions were reported in a real fire test (33). In our laboratory we have chosen to work with a tubular reactor kept at a preselected temperature, under an air stream (in the range 200-300 l/h). The sample, pelleted powder, between 15 and 500 mg, is introduced rapidly at a given time. Various devices may be placed following the tube: optical cell for smoke obscuration, infrared analyzer for CO or CO_2, heated glass-wool filter to retain the soot particles, cold glass-wool filter to condense the tars. A thermocouple placed near the sample allows detection of any endo or exothermic event. Finally the experiment may be quenched after a given time by switching the air stream to a nitrogen stream and opening the furnace around the tubular reactor. Experiments have been carried out at various temperatures between 300 and 900°C, with different amounts of PVC (25 to 500 mg) or PVC plus 1.5 percent of different additives. A set of remarks must be made:

(1) The quantitative as well as the qualitative results are very dependent upon the weight of the sample: the self-ignition temperature of pure PVC decreases from about 750°C to about 500°C when the weight increases from a few milligrams to 500 mg (18). The maximum amount of smoke is observed to shift from 490 to 550°C when the weight decreases from 250 to 175 mg. Moreover, the amount of smoke is not proportional to the weight of the sample in the whole range of weight. As shown in *Fig. 2* there are at least two ranges.

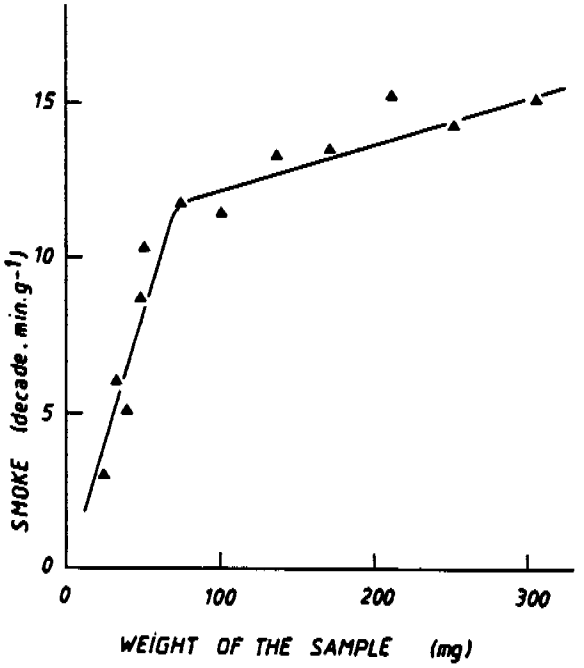


Fig. 2. Smoke level from pure PVC vs the weight of the sample.

These observations may be tentatively explained as follows. A bigger sample gives more volatile fuel so that the ratio O_2/fuel is more favorable for ignition at lower temperature. Concerning the second observation one may speculate that the temperature inside the sample increases more rapidly to nominal temperature in a smaller sample so that the competition between the various processes during pyrolysis is in favor of those occurring at higher temperatures, such as the ratio of aliphatic to aromatic compounds.

This first remark may give a first explanation of the fact that it is quite impossible to extrapolate to a real fire on large scale fire experiment the results obtained at a laboratory scale.

(2) The dynamic nature of the test chosen allows us to separate a set of successive events, at least if the temperature is low enough, i.e., in smoldering conditions. A convenient temperature is 450°C.

The first event is the endothermic dehydrochlorination which causes a delay of about 30 s for the nominal temperature to be reached. A first wave of smoke is evolved during and after that event. The major part of the smoke is produced after, in a second wave with a maximum. The two waves are the more separated when the amount of sample is the smaller. Typical results are shown in *Fig. 3*. Tentatively it may be suggested to associate each of the smoke waves to each step of the pyrolysis process quoted above. Under 400°C the amount of smoke is quite negligible. When the temperature increases the two waves become less and less separated. Above 500°C only one wave is observed. In smoldering conditions, CO and CO_2 are not detected before 450°C. At that temperature, the production of CO and CO_2 begins before the second smoke wave, but is observed for a very long time after the end of the smoke production. Both gases are produced in approximately equal molar amount, not dependent on the temperature up to 700°C. They both account for between 60 and 70 percent of the carbon. It seems that the major source of these gases is the slow combustion of the char residue. A part may come from the combustion of volatile hydrocarbons but we have not checked if that combustion is completed or not. Pyrolysis in air does not change the weight loss significantly after the first step of pyrolysis; the same is true for the benzene production; however the production of aliphatic volatile compounds is significantly decreased by about 60 percent (16). Recently Lattimer and Kroenke (20) have shown that pyrolysis of PVC in air does not change the nature and the distribution of the primary pyrolysis products which are only partly oxidized to a great degree. Most probably the same situation is valid for the smoldering conditions and changes only if the temperature is high enough for the self-ignition to take place.

(3) The char residue which remains after the end of evolution of smoke (10-12 min), accounts for the major part of the carbon in the PVC at 300°C or lower, and decreases at higher temperature to disappear totally above 550°C (18). Obviously this is because enough time has been given for a slow combustion of the residue in smoldering conditions. If the experiment is stopped at shorter times, the char residue is more important. So, at 450°C, quenching after the first smoke wave (4 min) leaves a char residue which accounts for 35 percent of the initial weight of 100 mg. After the second wave (10 min) the value drop to 28 percent. At the same time the production of CO and CO_2 accounts for 3 and 14 percent of the weight of carbon, respectiv ly. For the same conditions, when full time is given (100 min) the residue disappears totally and CO + CO_2 account for more than 80 percent of the carbon.

As shown in *Fig. 1*, there in a good correlation between the amount of char residue left by 250 mg of PVC when the smoke emission ceased and the total amount of smoke produced in a range of temperature between 300 and 550°C. It does not mean that the amount of material evolved as smoke does correspond to the weight of char missing. The maximum amount of material obtained by both hot and cold filters, observed at 670°C in flaming conditions (*Fig. 4*) accounts for 10.7 percent of the initial weight (18). In smoldering conditions, this amount does correspond to about 7 percent between 450 and 550°C and the smoke is made exclusively of tars condensed at room temperature. Soot appears only in flaming conditions and tends also to level at 7 percent around 700°C. Some tars remain at the lower temperatures and disappear at about 700°C.

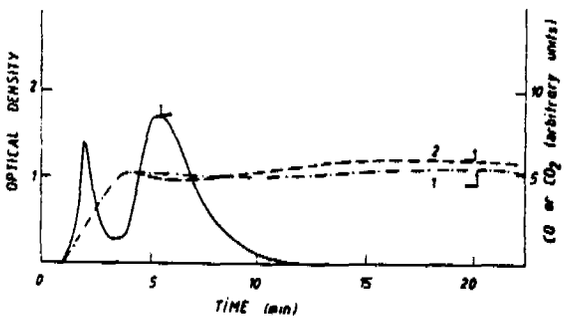


Fig. 3. Obscuration curve (———) CO_2 (1) and CO (2) evolved vs time at 450°C (smoldering conditions) for PVC (100 mg).

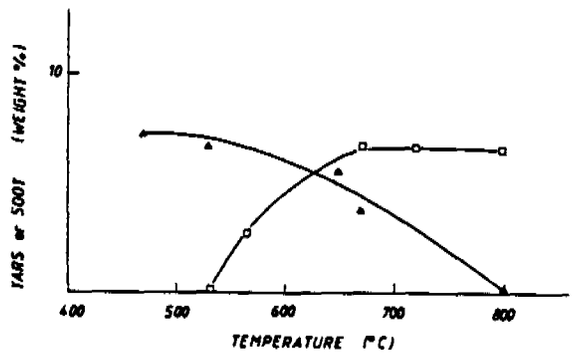


Fig. 4. Weight of material retained by the filter as soot (□) or tars (▲) for PVC (500 mg) at various temperatures.

It may be concluded that the tars lead to the soots upon flaming. The exact nature of the tars is not known; they are soluble in many solvents, and from GPC experiments in tetrahydrofuran, their molecular weight is of the order of magnitude of 1000-2000. The pyrolysis process involves not only crosslinking reactions, but also chain scission reactions so that it may be suggested that the tars may be formed, at least partly, through a direct volatilization of the residue after dehydrochlorination. In fact, some heavy products, accounting for about 3.5 percent of the initial polymer weight can be condensed by a cold ring system at the exit of the oven in pyrolysis experiments (16). Of course direct polycondensation of aromatic volatile compounds may be another process, more generally accepted, but its contribution is probably important mostly at high temperatures. It is known that the combustion of aromatics to produce soot needs temperature of the order of 1000°C (34). Further, it may be noted that the amount of tars condensed on the cold filter represents about the double of all of the hydrocarbons identified. So, at least a large part of the tars comes from larger volatile molecules.

INFLUENCE OF THE SMOKE REDUCERS ON THE COMBUSTION OF PVC

In most of the work already published, the influence of the smoke suppressor additives has been discussed in terms of their action on the char residue. The various mechanisms by which they are able to modify the amount and the distribution of hydrocarbon pyrolysis products has been discussed too, as shown earlier in the present paper. The reason for that was the belief that the smoke comes exclusively from the combustion products of the pyrolyzate. We have just shown that this belief is not correct to describe the smoldering conditions and is only partly correct in flaming conditions. On the other hand, after observation of some incandescence within the char residue, exothermicity and also increased amount of CO_2 produced, we have suggested that the major way of action of the best smoke-suppressors additives was through an oxidation catalysis (17). It has been shown that a list of compounds, or combination of compounds known as catalysts for total oxidation (35), were efficient smoke suppressors at 400°C (i.e. smoldering conditions). Most of them also cause a decrease of char residue to a level sometimes lower than the amount of additive introduced (1.5 percent). However, it might be argued that in our experiments enough time is given to allow a slow combustion of the char residue to take place so that the oxidation catalysis effect is mostly a post effect not really connected with the mechanism of smoke reduction. So, further experiments have been carried out with a more limited number of additives in order to clarify a number of points.

The first observation does concern the observation of ignition: the additive seems not to change significantly the ignition temperature, so with a sample of 50 mg the same temperature, 680°C is observed for pure PVC as well as for PVC plus 2.5 percent of $FeCl_2$, $FeCl_3$, CuO although it is 705°C with Fe_2O_3 and 720°C with ferrocene; on the other hand, Cr_2O_3, although it is neither very efficient for the reduction of benzene during pyrolysis nor for the reduction of smoke in smoldering or in flaming conditions, tends to cause the self-ignition at a lower temperature (see *Table 2*).

Most of the additives cause the char residue to disappear at rather low temperatures: for instance, with 500 mg of product with 1.5 percent of additives, the residue which was 26 percent in the case of pure PVC is quasi null at 400°C for all the additives except for Cr_2O_3 where it is 20 percent and for ZnO (5 percent). For all the others, CuO, Fe_2O_3, ferrocene, MoO_3, V_2O_5 . . . it is less than the amount of additive so that a part of the additive has been evolved as aerosol. This was clearly visible in the case of CuO where incandescence can be observed on the filter so that the soots are very much reduced (18).

Some results concerning the distribution of the aerosols between tars and soot are reported in *Table 2*. In these experiments with a rather large sample weight, two glass wool filters have been placed after the reactor. It is clear that CuO does reduce the amount of tars by about 50 percent whatever the temperature in smoldering conditions and causes the soot to practically disappear probably because of its catalytic oxidation power: incandescence is observed on the soot filt r in the presence of CuO. On the other hand, Fe_2O_3 and Cr_2O_3 do not reduce the amount of tars in smolder-

Table 2. Influence of the Additive (1.5%) on the Distribution of Tars and Soot at Different Temperatures—Sample Weight: 500 mg—Air Stream: 214 l/h

T(°C)	Additive	Flame	Char residue, (%)	Tars, weight %	Soot, weight %
470	none	no	26	7.2	0
	CuO	no	1.2	4.4	0.5
	Fe_2O_3	no		7.2	0.4
	Cr_2O_3	no		5.8	0
530	none	no	traces	6.8	0
	CuO	no	1.2	4.2	0
	Fe_2O_3	no		6.6	0
	Cr_2O_3	yes		4.7	1.6
565	none	yes	traces	4.2	2.9
	CuO	yes	1.1	3.0	1.1
	Fe_2O_3	no		6.1	0
	Cr_2O_3	yes		4.4	1.5
670	no	yes	traces	3.9	6.8
	CuO	yes	1.1	1.4	0.8
	Fe_2O_3	yes		2.0	2.2
720	none	yes	traces	0.1	6.6
	CuO	yes	0.8	0	oxid.
	Fe_2O_3	yes		1.2	4.2
800	none	yes	traces	0.1	6.6
	CuO	yes	0.8	0	oxid.
	Fe_2O_3	yes		—	—

ing conditions and Fe_2O_3 only is active in flaming conditions. Finally it is confirmed that the presence of soot is to be associated with the presence of flame. Corresponding smoke data are reported in *Table 3*. A filter for soot has been placed between the reactor and the optical device for measuring the obscuration so that the contribution of the smoke from tars might be estimated. Surprisingly here, although there is no flame, a part of the smoke seems to have been stopped by the heated filter. Possibly a few larger particles of tar have been retained on the filter. The weight of these particles may be negligible but their contribution to the obscuration measurements should have been rather large, thus explaining the apparent reduction of smoke. Nevertheless, all the additive cause a rather large reduction in smoke, and again, CuO is the most active. Some other results are given in *Table 4* to compare the effect of CuO with MoO_3 and Fe_2O_3. Again, CuO is the most active and it may be concluded that the efficiency of MoO_3 is comparable to that of Fe_2O_3.

The last series of experiments with 50 mg of PVC was carried out to compare the effect of ferrocene, Fe_2O_3, $FeCl_2$, $FeCl_3$ and CuO at various temperatures between 300 and 710°C (*Table 5*). Surprisingly, although they reduce the amount of smoke above 550°C as compared with PVC, $FeCl_2$ and moreover $FeCl_3$ cause a significant amount of smoke to be observed at 300°C. These additives and also CuO and even Fe_2O_3 cause the production of significant amount of CO and CO_2 at such low temperatures, with a ratio of CO_2/CO always larger than 1. (Table 6)

Table 3. Smoke Production at 570°C (Non-Flaming) from 50 mg of PVC with 1.5% of Various Additives

	Additive					
	None	CuO	Fe_2O_3	V_2O_5	ZnO	Cr_2O_3
Smoke total	18	4.75	9.5	13.6	17.8	20.5
Smoke from tars	13.4	4.9	6.8	9	5.2	6.7

Table 4. Smoke Reduction (% of Smoke from Pure PVC) by CuO, MoO_3 and Fe_2O_3 (1.5%) at Different Temperatures

	Temperature, °C						
	450	471	508	553	593	640	680
MoO_3	68	78	59.6	87	87	65.5	85
Fe_2O_3	57	100.2	64.5	75	84	69.4	40
CuO	12.4	44.7	48.2	58	52.6	49.3	53.6

Table 6. Influence of Various Additives on the Whole Production of CO and CO_2, as Compared with Pure PVC

Additive	520°C, 175 mg		720°C, 50 mg	
	CO + CO_2*	CO_2/C	CO + CO_2*	CO_2/CO
none	1	0.84	1.54	1.02
Fe_2O_3	1.52	1.50	1.69	1.19
Ferrocene	1.47	0	0	0
CuO	1.54	2.49	1.36	1.69
V_2O_5	1.25	2.68	0	0
Cr_2O_3	1.71	1.20	1.64	1.02
ZnO	1.61	0.90	1.62	1.28

* Relative values on the basis of the total amount of CO + CO_2 produced with pure PVC at 520°C (175 mg).

Table 7. Molar Ratio CO_2/CO for Selected Additives at Various Temperatures (Smoldering Conditions)

Temperature (°C)	Weight (mg)	CuO	Fe_2O_3	MoO_3	PVC
450	150	1.93	1.78	1.87	0.78
471	75	2.63	2.11	1.78	0
508	75	2.34	1.73	1.78	0
553	50	1.97	1.62	1.47	0
593	25	1.83	1.17	1.25	0
640	25	1.15	0.85	1.28	0
680	25	0.94	0.79	1.22	0

Other results are reported in *Table* 7 f r CuO, Fe_2O_3 and MoO_3 at various temperatures. The quality of the combustion, as measured by the ratio CO_2/CO, is the best for CuO but is optimum at moderate temperature. Surprisingly it decreases significantly by increasing the temperature. Th variation is less important for MoO_3 which is better, in this respect, at the highest temperatures. However, the results may be influenced by the weight of sample which is varied in order to avoid at any time the saturation of the apparatus. Another possible explanation lies in the fact that a part of the additive may be swept out as aerosol and do not work completely at the highest temperatures.

The kinetic aspects of the process have been studied for the smoke (obscuration) and also for the production of CO or CO_2. With pure PVC, two waves of smoke have been observed at 450°C with a small sample (*Fig. 3*). Some results concerning the effect of a few additives are shown in (*Figs. 5* and *6*). *Figure 5* shows that CuO does reduce drastically both waves, while ZnO totally suppress the first one and reduce significantly the second one. With iron compounds (*Fig. 6*), the two waves are not separated and $FeCl_3$ is the most efficient additive. A difference can be observed between Fe_2O_3 and

Table 5. Amount of Smoke (Decade · Min · g^{-1}) Produced upon Combustion of PVC (50 mg) at Various Temperatures (°C) with 1.5% of Additives

Additive	Smoldering							Flaming	
	300°C	414°C	470°C	530°C	574°C	607°C	628°C	671°C	710°C
none	0	0	0	6.9	18.8	18	22	12	8.6
$FeCl_2$	0	6.75	8.4	10	11.1	11.1	12.2	0	4.16
$FeCl_3$	3.6	4.95	6.25	6.85	7.01	7.62	7.31	1.52	1
Ferrocene	0	0	2.9	5.6	5.48	8.32	7.92	4.56	3.96
Fe_2O_3	0	0	0	7.8	9.35	9.35	12.2	5.7	4.98
CuO	0	0	traces	2	2.7	7.2	8.2	2.84	4.56

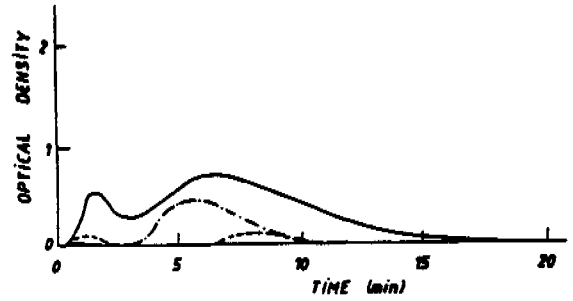


Fig. 5. Obscuration curves at 450°C for pure PVC (200 mg) (———) or in presence of 1.5 wt percent of either CuO (——) or ZnO (-.-.-.-).

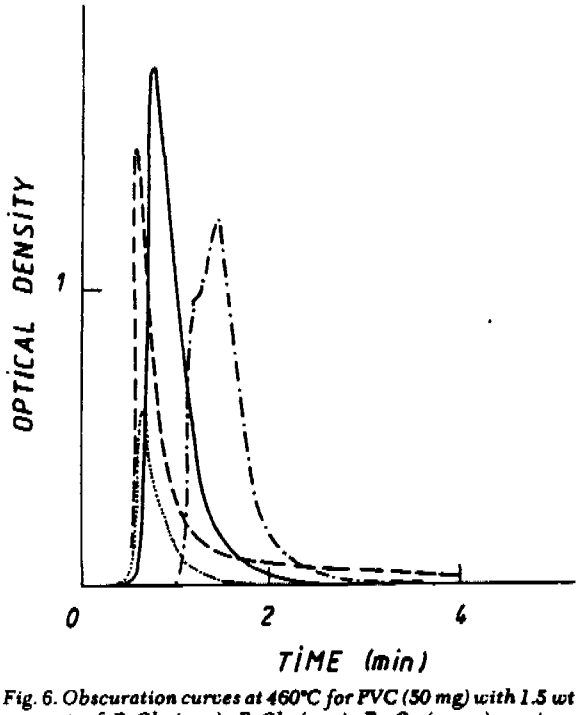


Fig. 6. Obscuration curves at 460°C for PVC (50 mg) with 1.5 wt percent of $FeCl_2$ (——), $FeCl_3$ (.....), Fe_2O_3 (-.-.-.-), or iron acetylacetonate (———).

either $FeCl_2$, $FeCl_3$, or the acetlyacetonate; an induction period is observed with the former compound. The effect of the additive on the production of CO and CO_2 is even more important. Although the total amount of carbon evolved as CO + CO_2 was increased by a rather small proportion (actually it may approach 100% of the initial carbon contents), the rate at which it is produced is much more increased. Typical results are shown in *Figs. 7* and *8*. Most of the gas is produced in a big wave which began at about the same time that the obscuration curve and the process came to the end by about 20 to 30 min at 450°C instead of 100 to 150 min for pure PVC. This wave is obviously caused by the catalyzed combustion of the char residue. A part of it, as well as some secondary waves which modulate the major one, may be due to the combustion of volatiles or of some tars including a part of oxidation catalyst.

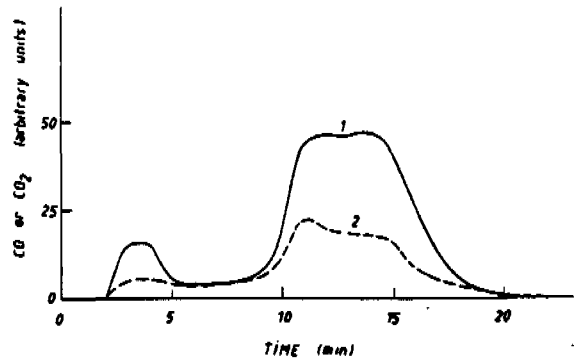


Fig. 7. CO_2 (1) and CO (2) evolved from PVC (100 mg) at 450°C with 1.5 wt percent of CuO.

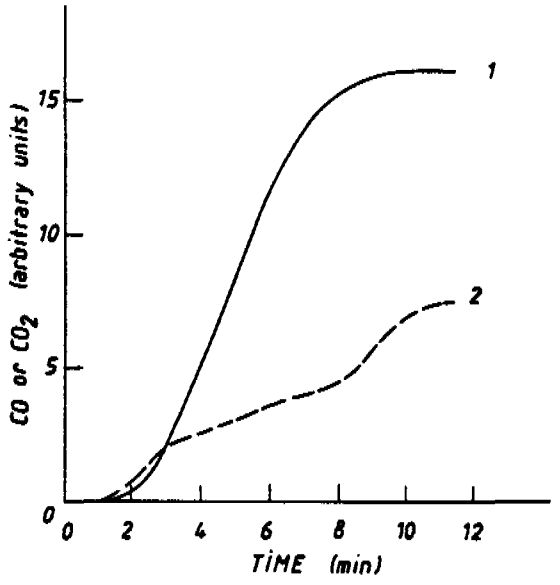


Fig. 8. CO_2 (1) and CO (2) evolved from PVC (100 mg) at 450°C with 1.5 wt percent of ZnO.

Additional results obtained at 500°C with 100 mg of PVC show that the catalytic action of CuO may be partially inhibited by phosphorous compounds which are often used in fire-retardancy of many polymers, including plasticized PVC. The results concerning CO_2 are shown in *Fig. 9*. Here, P_2O_5 has been used to represent the phosphor compounds, of which it is the more oxidized and dehydrated form. It does not inhibit totally the catalytic character of CuO, for the kinetics of the CO_2 production, and also because the CO_2/CO ratio which is then 0.95 for pure PVC, reaches 2.33 with CuO and is reduced to 1.36 if P_2O_5 is added to CuO.

In *Table 8* a set of results dealt with the data obtained after the first wave (4 min) and the s cond wave (10 min) are reported. In the absence of any volatilization except for complete dehydrochlorination, the residue should have been 41.6 percent for pure PVC or 43.1 percent for PVC plus additive (44.6 percent in the case of CuO + P_2O_5). During the first wave, with pure PVC a rather large amount of material has been volatilized and a small part of it

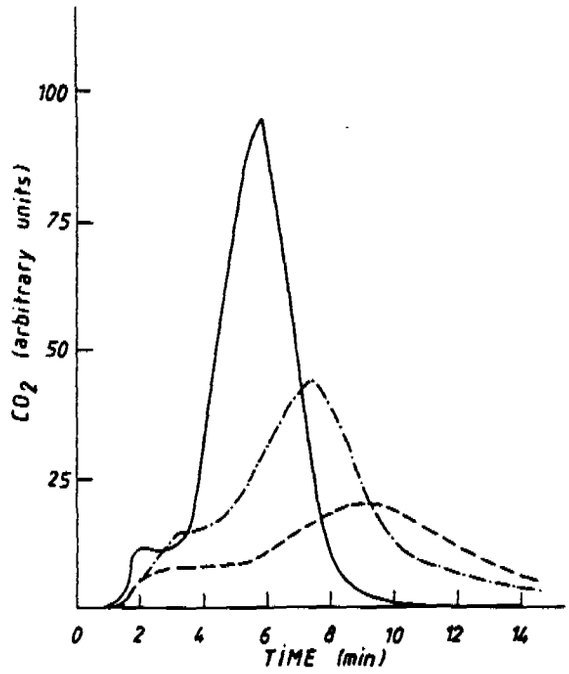


Fig. 9. CO_2 evolved from PVC (100 mg) at 500°C without (——) or in presence of either 1.5 percent CuO (———) or 1.5 percent CuO plus 1.5 percent P_2O_5 (-.-.-.-).

is fully oxidized. The amount of volatilization is not increased by CuO but the volatile material is rather fully oxidized so that the reduction of smoke is very large. P_2O_5 causes the volatilization to be quite suppressed, but the amount which reamins is enough to give a comparatively high level of obscuration. Ferric oxide causes a high level of volatilization, but moderates oxidation so that the obscuration is not reduced that much. Zinc oxide causes a strong reduction of volatilization and then a strong reduction of obscuration. About the same reduction is observed with zinc chloride, although it causes much more volatilization and moderates oxidation. Finally, alumina causes only a small change in both volatilization and obscuration.

The results are rather different for the second wave. The amount of volatilization is higher and is reduced chiefly by P_2O_5 and also Al_2O_3, but enhanced by Fe_2O_3. Although it causes a very high oxidation, the latter does not reduce the smoke. High levels of oxidation are always observed, taking into account the amount of volatilization. Copper and zinc compounds lead both to strong reduction of the smoke, without big difference for oxidation activity. Alumina again shows a moderate activity just reducing the volatilization and the obscuration to the same extent.

It is interesting also to try to follow the additive themselves. We have already noted that a part of it may be evolved as an aerosol or even might give a volatile product: that is the case of ferrocene for which only about 20 percent of the iron remain in the solid residue. This compound has been shown to give a monochloro-monocyclopentadienyl volatile compound (36) and may further react with HCl to give $FeCl_3$ at about 200°C. We have already reported that, in the presence of air, it leads finally to Fe_2O_3 which causes incandescence and is a good oxidation catalyst (16). We have carried out a more recent study, the details of which will be published elsewhere (37), to compare the effect of various iron compounds at different times. In that study, larger amount of additive, up to 6%, have been used, and the experiments have been quenched at various times, such as indicated by letters in *Fig. 10*. The char residues have been studied through Mossbauer spectroscopy. In addition they have been extracted with hot water (80°C) for a long time and the chloride ions titrated by coulometry. Whatever is the initial iron additive, $FeCl_2$, $FeCl_3$, Fe_2O_3 or acetylacetonate (FeAcAc), the whole iron is finally transformed into Fe_2O_3, which is already

Table 8. Char Residue Volatilization, Carbon Transformation into CO_2 and CO and Smoke Level Variation during Heating Time at 450°C (Smoldering Conditions) for 100 mg of PVC

Time	Additive	Residue wt %	Total ΔR wt %[a]	Partial ΔR wt %[b]	C_{CO_2}/C_{CO}	C(CO + CO_2) wt % Total	C(CO + CO_2) wt % Partial[c]	±ΔS % decade · min · g^{-1}[d]
	none	35	−13.4		0.45	2.9		0
	CuO	36.4	−12.5		1.38	13.3		−84
4 min	CuO + P_2O_5	42.9	+3.1		0.30	1.4		−45
(at the end	Fe_2O_3	31.5	−24.3		5.95	9.4		−30
of the	ZnO	41.1	−1.2		0.80	3.1		−73
first wave	$ZnCl_2$	36.1	−13.2		9.85	6.7		−67
of smokes)	Al_2O_3	37.1	−10.8		0.38	5.1		−14
	none	28.2	−32.2	18.8	0.71	14	11.1	0
10 min	CuO	23.6	−43.2	30.7	1.44	47.7	34.4	−96
(at the end	CuO + P_2O_5	37.5	−9.8	12.9	0.19	19.5	18.1	−63
of the	Fe_2O_3	10	−76	51.7	1.45	89.9	80.5	+9
second wave	ZnO	23.7	−43.7	42.5	3.18	48.9	45.8	−71
of smokes)	$ZnCl_2$	23.2	−44.2	31.0	1.27	44.7	38.0	−92
	Al_2O_3	32	−23.1	12.3	0.71	19.5	14.4	−37

[a] ΔR is calculated from the theoretical char residue after total dehydrochlorination (41.6%).
[b] Partial ΔR represents the difference between the total char residue after the second wave (10 min) and the first wave of smoke (4 min).
[c] The partial carbon transformed into CO_2 and CO corresponds to the difference between the carbon transformed into CO_2 and CO after the second wave (10 min) and the first wave (4 min).
[d] ΔS % represents the percentage of the variation of the total smoke level after the first wave (4 min) and after the second wave (10 min).

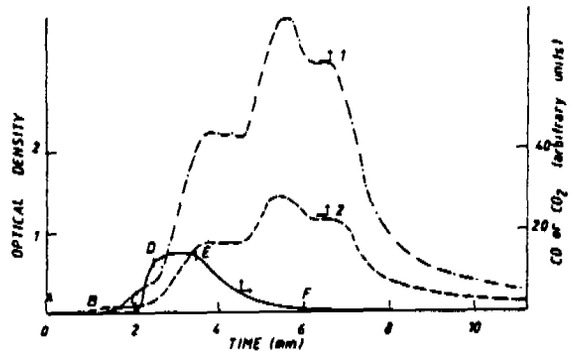


Fig. 10. Obscuration curve (———), CO_2 (1) and CO (2) evolved from PVC (750 mg) at 450°C in the presence of 6 wt percent of Fe_2O_3. Quenching of the experiments have been carried out at time indicated by the letters A, B, C, D, E, F for Mossbauer analysis.

detected through its characteristic six peaks spectrum as shown in *Fig. 11*, after about 60 s in the case of FeAcAc for instance. Intermediate production of a chloride is proved also by the Mossbauer spectrum, and specific coloration test, such as with phenol, potassium thiocyanate, or potassium ferrocyanide, show the presence of Fe^{3+}. Except for $FeCl_3$ which may be easily oxidized to a mixture of $FeCl_3$ and Fe_2O_3, the amount of $FeCl_3$, as titrated by coulometry, is limited; with FeAcAc the maximum is observed as 32 percent of Fe after about 60 s, and with Fe_2O_3 it remains less than 20 percent of Fe reacted to give $FeCl_3$. Of these additives, Fe_2O_3 is the less efficient to reduce the smoke although it is the only one initially in the state of an oxidation catalyst; it may be noted a long delay before the evolution of smoke as well as for the production of CO and CO_2. Such a delay is not observed with the other compounds which lead to $FeCl_3$ sooner and in a larger amount. The delay is not observed also in the case of CuO but it is known (38) that CuO reacts readily with HCl to give $CuCl_2$. So it is suggested that these chlorides of transition metals play an important part in the reduction of smoke. According to the recent work of Iida and Goto (39), $FeCl_2$, $FeCl_3$ and $CuCl_2$ are among the strongest catalyst for the degradation of PVC. They cause a rather large increase of the production of aliphatic products during the pyrolysis. On the other hand it is

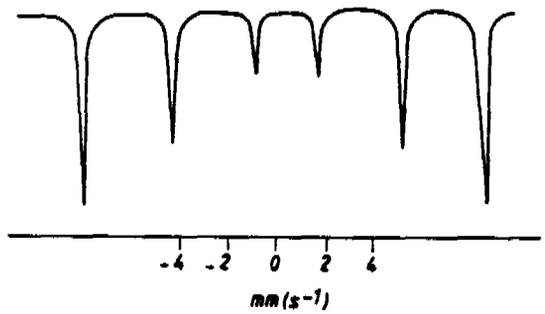


Fig. 11. Mossbauer spectrum taken from the residue of the experiment quenched at the point F of Fig. 10.

clear that the production of smoke level drops off as soon as Fe_2O_3 does appear in the residue in the case of (FeAcAc) or of the chlorides. So both mechanisms of catalytic modification of the degradation process, and catalytic oxidation of the residue are operative in the reduction of smoke; the former mechanism causes enhancement of the production of aliphatic volatiles (instead of aromatic compounds) which are oxidized to give CO and CO_2. If this mechanism is less efficient, as in the case of Fe_2O_3, a larger amount of material is evolved without total oxidation and thus gives the tars which produce obscuration.

The oxidation catalysis does operate in the solid phase where it causes a direct oxidation of the char to CO_2 and CO. The oxidation also involves the volatile compounds at the very time of their formation. It is interesting to note that the initial sample of Fe_2O_3 is not very active as an oxidation catalyst, possibly because of the presence of a part of Fe_3O_4; it becomes more active later and also, as shown by the Mossbauer analysis, it gives a better crystalline organization.

CONCLUSION

A general picture of the combustion process of rigid PVC might be as follows: the thermal degradation of PVC causes the production of volatile material in two successive steps more or less separated according to the temperature and amount of material. The first step does correspond to the endothermic dehydrochlorination (DHC) and is accompanied with the production of most of the benzene and also some aliphatic light material. The DHC process may be accelerated by various additives, mostly chlorides, which are able to catalyze the formation of aliphatic volatiles and also the crosslinking process, so that the amount of benzene is reduced drastically. The second step of the degradation gives more aliphatic volatiles and also produces heavier mixed aromatic compounds which are condensed as tars. Some additives are again able to enhance the production of aliphatic volatiles and reduce the production of tars during that second step. In the presence of air, the aliphatic volatiles are easily oxidized to CO and CO_2 but the main pyrolysis process is not affected otherwise. In smoldering conditions, the black smok is mainly formed from these tars coming from the decomposition of the residue left after dehydrochlorination with, possibly, a small contribution of the combustion products of the volatiles. After the production of smoke has ceased, a char residu remains which is slowly oxidized to give CO and CO_2. Most of the smoke suppressor additives are oxidation catalysts which accelerate this combustion process of the residue which is some cases may be as rapid as the production of smoke. They also increase the ratio CO_2 and CO. If the temperature and and amount of material are high enough, self ignition takes place. Then the total amount of

smoke is reduced, the tars disappear, but soot is formed and more CO and CO_2 is produced; the additives do not change the conditions of self-ignition. They again accelerate all the processes but their effect is not so dramatic as in smoldering conditions.

Whatever their initial nature, the additives react with the HCl formed upon DHC to give chlorides which are strong Lewis acid catalysts and are able to modify the degradation process. They favor the decomposition of the residue into light volatile easily oxidizable compounds, instead of the heavy tars which do constitute the actual smoke, either as such in smoldering conditions or after transformation into soot in flaming conditions.

Further they are oxidized to oxides which are the oxidation catalyst. Depending on the nature of the metal, these processes are more or less complete and rapid. For such reason the additive may show the optimum of their activity at different temperature. So copper is specially active at low temperature and also zinc and some iron compounds as $FeCl_3$. But other compounds of iron (Fe_2O_3) and mostly molybdenum and vanadium seem to be useful only at higher temperature. Moreover, some compounds or iron may cause the smoke to appear a lower temperature than for pure PVC and then lead to an increase of the smoke up to rather high temperature. They become actually smoke suppressors only near the ignition temperature or in flaming conditions.

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