

Poly(vinyl chloride) Composition. II. Study of the Flammability and Smoke-Evolution of Unplasticized Poly(vinyl chloride) and Fire-Retardant Additives

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SYNOPSIS

The influence of natural, activated, and modified microzeolite with the general formula $\text{Me}_{2/m} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot p\text{H}_2\text{O}$ (where $\text{Me} = \text{Fe}^{3+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Zn}^{2+}, \text{K}^+, \text{Na}^+$) and an organic additive, such as ammonium sulfamate combined with ammonium sulfate on smoke formation and flammability of suspension poly(vinyl chloride) has been studied in the present work. Microzeolite in native (i.e., natural), activated, and modified forms has been found to possess both fire-retardant and smoke-suppressant effects in solid poly(vinyl chloride) compositions. Such effects have been best revealed by modified microzeolite containing 3.5–4% zinc. On the other hand, the ammonium sulfamate combined with ammonium sulfate is believed to act as a strong smoke-suppressant additive. Thermogravimetric examinations and limited oxygen index measurements show that microzeolite acts as a fire-resistant and smoke-suppressant additive predominantly in the condensed phase. The ammonium sulfamate in combination with ammonium sulfate gives evidence of the same effects, mostly in the gaseous phase.

INTRODUCTION

Poly(vinyl chloride), poly(vinylidene chloride), and poly(vinyl fluoride) are considered to be fire-resistant materials, which is due, mainly, to their high content of halogens.¹ A number of authors have determined the oxygen index (OI) of poly(vinyl chloride) without any additives as amounting to 42–47% O_2 (i.e., OI = 42,¹ 45,² 46,³ and 47%,⁴ respectively). The presence of chlorine within the polymer matrix is not the only factor affecting the fire-resistance. According to Grassie and Scott,⁴ the high OI values of poly(vinyl chloride) (PVC) are also due to a formation of a carbonized product as a result of a rapid evolution of hydrogen chloride. Such a carbonized product is believed to possess both conjugated and cross-linked structures that protect the polymer backbone during combustion. The amount of the

carbonized residue (coke) is found to be 15% at 500°C.¹

Although being hardly a flammable polymer, PVC is capable of significant smoke evolution. Therefore, highly effective additives have been searched in order to inhibit smoke evolution in the combustion process. A number of compositions containing PVC with both diminished flammability and smoke evolution has been invented.^{5–9} The influence of many fire-resistant and smoke-suppressant additives, such as CuCN or CuSCN ,⁵ ZnO and $\text{Al}(\text{OH})_3$,⁶ $\text{Sn}(\text{C}_2\text{O}_4)_2$ mixed with ZnO or MgO ,⁷ cuprium oxalate, ammonium molybdate, and active fillers, such as CaCO_3 , TiO_2 , and $\text{Al}(\text{OH})_3$,⁸ on the above-mentioned properties of PVC has been studied. According to Carette,⁹ the introduction of basic magnesium–aluminum silicate (i.e., vermiculate–clay with laminated structure) as the only additive or combined with CuSO_4 or Cu_2O and CuO increased the fire resistance of PVC significantly. Such a complex additive did not, however, decrease the maximum optical density of smoke. Little attention has been paid so far in the literature to the influence of high-

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melting dispersed additives on the flammability and smoke evolution of polymers.² The present work deals with some results obtained while studying powdered natural microzeolite with the general formula $\text{Me}_{2/m} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot p\text{H}_2\text{O}$ and an organic additive, such as ammonium sulfamate combined with ammonium sulfate, as fire-retardant and smoke-suppressant additives for unplasticized PVC.

EXPERIMENTAL

Materials

PVC suspension with a Ficentcher constant of 67.0 was used as a basic polymer. The ammonium sulfamate in combination with ammonium sulfate was obtained on the basis of polyisoprenic rubber.¹⁰

The natural microzeolite has the following composition: SiO_2 , 65.10%; Al_2O_3 , 10.74%; Fe_2O_3 , 0.98%; CaO , 0.88%; MgO , 0.88%; K_2O , 3.40%; Na_2O , 0.44%; H_2O , 6.45%. The average particle size of microzeolite (MZ) was 8 microns; the pH value of the aqueous extract, 8.36; and the active surface after BET, 108 m^2/g . The crystalline water content drops to 1% after thermal treatment (activation) at 360°C for 2 h. The natural MZ contains 3.5–4% zinc after treatment with an 0.3N zinc chloride solution at 75°C. The MZ so-modified was washed with distilled water until a negative reaction for chloride ions was observed, dried at 105°C for 2 h, and calcined at 360°C for another 2 h. It contained about 1% crystal water.

Ammonium sulfamate in combination with ammonium sulfate (AS-1A), the natural MZ with 6.5% water (MZ-6.5% H_2O), the activated MZ with 1% water (MZ-1% H_2O), and the modified MZ containing 3.5–4% zinc (Zn-MZ) was added to PVC in the amounts 3, 5, 8, 10, and 15 wt %. The following system of stabilizers was employed, i.e., calcium stearate, 1.0 wt %; dibutyltin maleinate, 4.0 wt %; and Irganox 1010, 0.25 wt %.

The ingredients were mixed by plastication on rolls in the interval of 170–180°C for 7 min. After that, sheets were pressed at 180°C and 3.0 MPa.

Measurements

The strength–deformation indices (i.e., yield stress, σ_Y ; stress-at-break, σ_B ; elongation at break, ϵ) were measured according to CMEA[†] standard 1199-78 at a stretching rate of 50 mm/min. The notched Sharpy impact strength (σ_{IM}) was measured according to CMEA[†] standard 1491-79. The melt index (I_m) was

determined on a capillary plastometer IIRT (USSR) at 200°C and a load of 21.6 kg. The limited oxygen index (LOI) was determined in accordance with ASTM-D-2863 on a modulus FTA apparatus made by Stanton-Redcroft, England.

The mass optical density of smoke (D_m) was determined according to a method described by Apostolov et al.¹¹ The sample for analysis was preliminarily cut into small pieces (by pounding, cutting, etc.) so that the particle size did not exceed 3 mm. Then, 1 ± 0.1 g was weighed accurately on an analytical balance. The sample was, subsequently, placed into a pannikin made of thermally resistant steel and was then introduced into a crucible electric furnace provided with a light source and photodiode. The volume of the furnace chamber was 0.486 m^3 and a constant temperature of $800 \pm 10^\circ\text{C}$ was maintained. Under these conditions, self-ignition of the sample occurred, followed by its burning. As a result of the burning in air, a smoke medium was formed within the chamber volume. The optical density of the medium increased, whereas the corresponding voltage (U) decreased, since the light intensity onto the photodiode was, accordingly, diminished. The change of voltage was followed continuously by using a millivoltmeter and its minimum value (U_{\min}) established within 5–10 s after the end of burning was recorded. The mass optical density of the smoke was calculated, as follows:

$$D_m = \frac{V}{\Delta ml} \cdot 2.3 \log \frac{U_0}{U_{\min}} [m^2/\text{kg}]$$

where V is the volume of the furnace chamber, $V = 0.486 \text{ m}^3$; l is the distance between the light source and the photodiode, $l = 0.6 \text{ m}$; Δm is the mass loss, $\Delta m = m_0 - m$; m_0 is the initial mass of the sample (kg), m is mass of the solid residue after burning (kg); U_0 is the initial voltage of the photodiode metering circuit, $U_0 = 100 \text{ mV}$; and U_{\min} is a minimum voltage of the metering circuit measured after the complete burning of sample (mV).

The value of the mass optical density was determined as an average from at least three measurements for each sample. The thermal TG, DTG, and DTA curves were studied on a Q-derivatograph supplied by MOM Company, Hungary, under the following conditions: heating rate, 5°C/min; initial weight of samples, 100 mg; medium, air (static). The differential curves of pore-size distribution were recorded by using a Hg-porosimeter type 1500 Carlo Erba with dilatometer of 3 mm internal diameter. The heat resistance was determined by a Vicat apparatus type FWV, Germany.

[†] Council for Mutual Economic Assistance.

RESULTS AND DISCUSSION

The decrease of flammability and smoke evolution of polymers can be achieved by using additives diminishing the decomposition rate in a condensed phase. Another way to this purpose is the application of additives whose decomposition products inhibit the gas-phase combustion. These processes are difficult to be distinguished in most cases; however, it may be assumed that the additive acts, preferably, in either the condensed or gaseous phase. A complex inhibition of the different PVC combustion stages cannot be achieved by a single additive only. It is a common practice to use a mixture of different compounds, everyone of them being effective at a certain stage of polymer decomposition.²

The additives studied are different by their chemical nature. MZ is a highly dispersed inorganic additive. Ammonium sulfamate is an organic additive combined with ammonium sulfate in a 2 : 1 mass ratio (AS-1A). The thermal DTA and TG curves of natural and modified MZ as well as AS-

1A are shown in Figure 1, curves 1, 2, and 3, respectively. A negligible endothermal effect within 80–100°C is observed on curves 1 and 2, which is associated with the initial evaporation of crystallization water. Two endothermal effects at 350 and 460°C are considered to be typical for the thermal decomposition of AS-1A. These effects are associated with the corresponding two-stage weight loss.

The results from both the limited oxygen index (LOI) and mass optical density (D_m) as a function of MZ and AS-1A content in PVC compositions are shown in Figures 2 and 3, respectively. It is obvious that the increase of the single additive concentrations leads to a corresponding fire-resistance increase [Fig. 2(a)]. The LOI change is the sharpest within 3–8 wt % of additive content in the polymer composition. The modified MZ (Zn-MZ) has the best-expressed fire-retardant action, as shown in Figure 2(a), curve 4. A composition of PVC, stabilizers, and 5 wt % Zn-MZ shows an LOI of 64.2%, whereas the same composition without Zn-MZ has an LOI of 46.4% only. MZ containing 1% and 6.5%

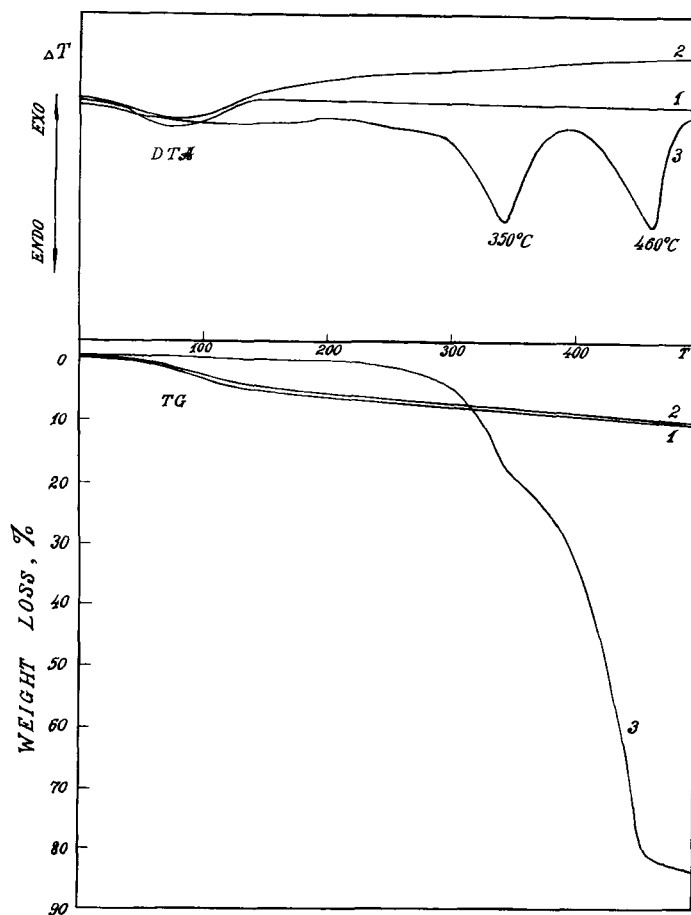


Figure 1 DTA and TG curves of (1) MZ-6.5% H₂O, (2) Zn-MZ, and (3) AS-1A.

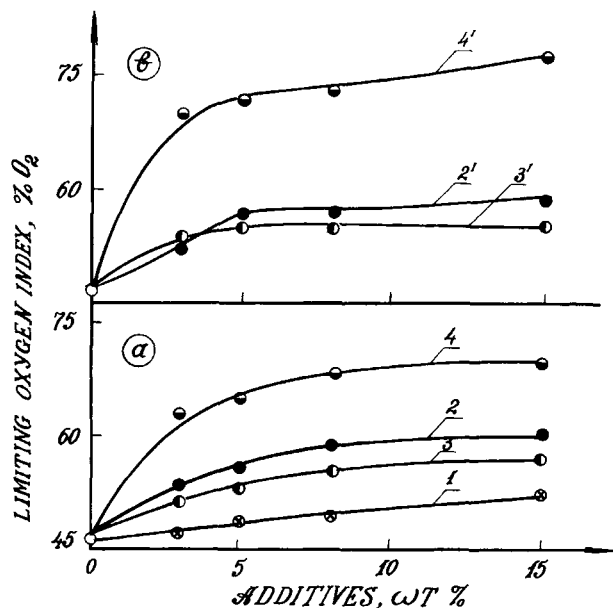


Figure 2 Dependence of the limited oxygen index on (a) PVC from content of (1-⊗) AS-1A, (2-●) MZ-6.5% H₂O, (3-○) MZ-1% H₂O, and (4-⊖) Zn-MZ and (b) blends of PVC + 5% AS-1A from content of (2'-●) MZ-6.5% H₂O, (3'-○) MZ-1% H₂O, and (4'-⊖) Zn-MZ.

H₂O (curves 2 and 3) possesses lower fire-retardant action and the lowest is observed with AS-1A (curve 1). Activation of the natural MZ did not lead to an increase of LOI (Fig. 2, curve 3). Therefore, it is considered economically advisable to use a natural nonactivated MZ. Compositions containing 5% AS-1A and various microzeolite content indicate a high fire-resistant effect, provided Zn-MZ has been introduced previously [Fig. 2(b), curve 4']. The LOI of a composition containing 5% AS-1A and 5% Zn-MZ is 72.2% O₂.

Both the additives studied have influence on the smoke formation of PVC, which is found to decrease as their concentration increases (Fig. 3). MZ containing 1% and 6.5% H₂O have approximately the same smoke-suppressant action (curves 2 and 3, respectively) as Zn-MZ and AS-1A (curves 1 and 4). Introduction of 5% Zn-MZ or 5% AS-1A into the PVC composition is found to lead to an optical density decrease from 385.1 m²/kg to 207.4 m²/kg and 196.3 m²/kg, respectively. A more significant decrease of smoke evolution with PVC combustion is found to take place as 5% AS-1A and 5% MZ are combined (Fig. 3, curves 2'-4'). A composition containing 5% AS-1A and 5% Zn-MZ has a mass optical density of 130.4 m²/kg, i.e., smoke evolution amounts to 34% with respect to the same characteristic of PVC.

Taking into account the studies of a number of authors,^{3,6-8,12-16} a decrease of both the flammability and smoke evolution of PVC can be achieved by a catalysis of reactions resulting in higher yield of coke. Quite effective catalysts to this purpose are ferrocene, as well as zinc, molybdenum, magnesium, cupreous, stannic, and aluminum compounds; additives containing sulfur, phosphorus, and nitrogen have also been considered to be convenient.¹² Some cations such as Zn²⁺, Fe³⁺, and Mo⁶⁺ have been found to be significantly more effective than Sn⁴⁺, Ni²⁺, and Ba²⁺. The capability of the metal-containing additives to promote coke formation has been associated with the Lewis acidity of the corresponding cations as well as the volatility of their salts (halides).³

The MZ studied contains some metal oxides widely recommended as smoke-suppressant additives, such as Al₂O₃, Fe₂O₃, CaO, and MgO. Modification of MZ leads also to an introduction of Zn²⁺, and since the whole composition acts as a weak base (pH 8.4), it is believed to meet the corresponding requirements for a smoke-suppressant additive. Both the activation and chemical modification result in some changes of the secondary porous structure of MZ. These changes are shown in Figure 4 by the differential curves of pore-size distribution. Several groups of peaks have been observed. The first one

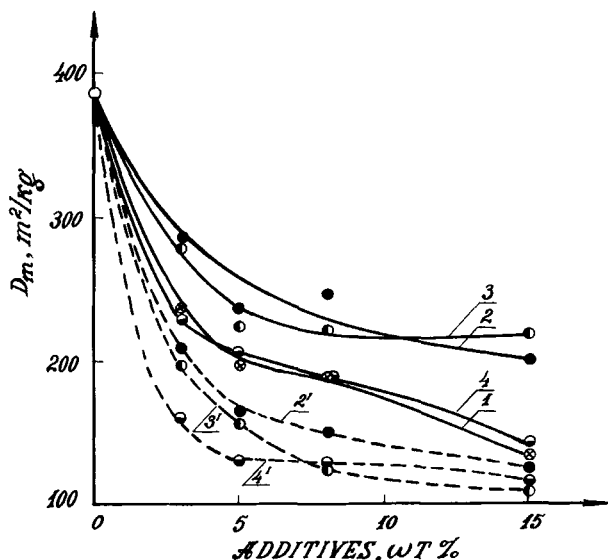


Figure 3 Dependence of the mass optical density (D_m) of PVC smoke on the content of (1-⊗) AS-1A, (2-●) MZ-6.5% H₂O, (3-○) MZ-1% H₂O, and (4-⊖) Zn-MZ. Mass optical density of PVC + 5% AS-1A as a function of the content of (2'-●) MZ-6.5% H₂O, (3'-○) MZ-1% H₂O, and (4'-⊖) Zn-MZ.

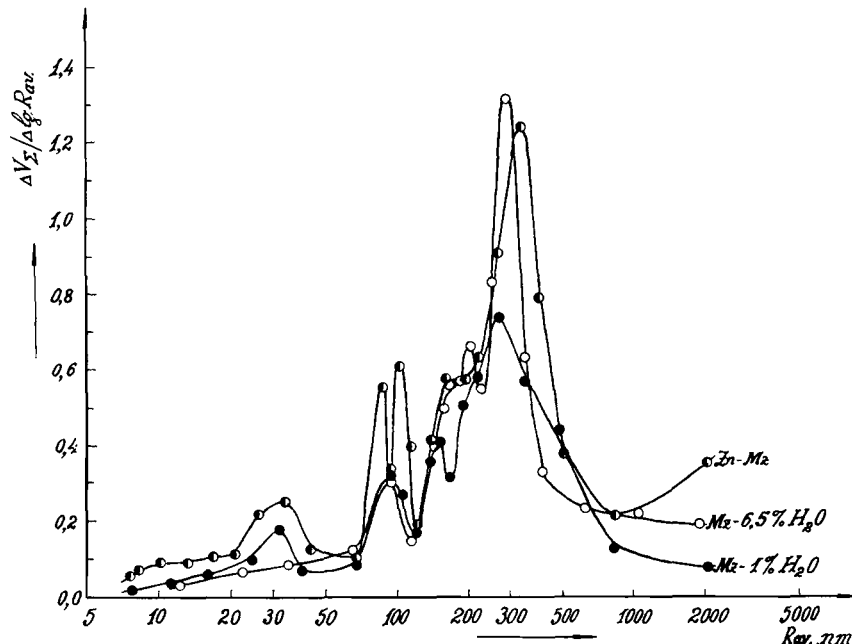


Figure 4 Differential curves of pore-size distribution of MZ-6.5% H₂O, MZ-1% H₂O, and Zn-MZ.

is associated with macropores of an average radius of about 30 nm, and it is characteristic for MZ-1% H₂O and Zn-MZ. A second group of peaks corresponds to macropores of an average radius of 70–110 nm, Zn-MZ indicating the doublet peak, while MZ-6.5% H₂O, the singlet one. The third maximum with pores of an average radius of 150–200 nm is best indicated by MZ-1% H₂O ($R_{av} = 150$ nm) and MZ-6.5% H₂O ($R_{av} = 190$ nm). Macropores with an average radius within 200–500 nm correspond to a fourth maximum of the differential curve, which is best indicated by MZ-6.5% H₂O and Zn-MZ. The relative volume of pores corresponding to $R_{av} = 297$ nm is 11.6% for MZ-6.5% H₂O, whereas Zn-MZ with $R_{av} = 333$ nm corresponds to 9.9%, respectively. The surface of macropores measured by Hg porosimetry increases about 2–2.5 times for activated (MZ-1% H₂O) and modified (Zn-MZ) MZ as compared with natural MZ, the corresponding values being 15.5, 19.7, and 8.8 m²/g, respectively.

The results obtained by the thermogravimetric studies of some PVC compositions are presented in Figures 5 and 6 and Table I. Nonmodified MZ containing both 1% and 6.5% H₂O shows properties not only of fire-retardant and smoke-suppressant additives (Figs. 2 and 3), but also acts as a thermal stabilizer (Fig. 5, curves 3 and 4). MZ-6.5% H₂O indicates better properties as a thermal stabilizer, which is confirmed by both the temperature of 1%

PVC weight loss (240°C) and the temperature of maximum rate of decomposition (290°C).

Several factors are believed to determine the complex action of MZ as a fire-retardant, smoke-suppressant additive and thermal stabilizer. First of all, water evaporation might result in dilution of burning gases and a corresponding decrease of temperature due to the endothermal process. Second, the nonvolatile Al₂O₃ and SiO₂ sol on the burning polymeric surface protects the deeper layers of the polymer from both the flame and oxygen. According to Grassie and Scott⁴ Al₂O₃ · 3H₂O acts as a smoke-suppressant additive and the corresponding mechanism of action has not been established yet. It might be assumed that Al₂O₃ in combination with Fe₂O₃ and MgO promote formation of coke. The mechanism of action for Al₂O₃ might be similar to that of MoO₃ suggested by Starns and Edelson.¹⁷ Such an assumption may be confirmed by the increased content of coke residue at 500°C for a composition containing 5 wt % MZ-1% H₂O and MZ-6.5% H₂O, which is found to be 23.8% and 24.2%, respectively (Table I). Lastly, the MZ is a porous sorbent with a rigid skeleton structure and high active surface after BET, thus enabling it to absorb HCl evolved followed by chemical reaction due to the basic metal oxides. Both micro- and mesopores of zeolite are considered to play an important role in this process, the action of macropores having been

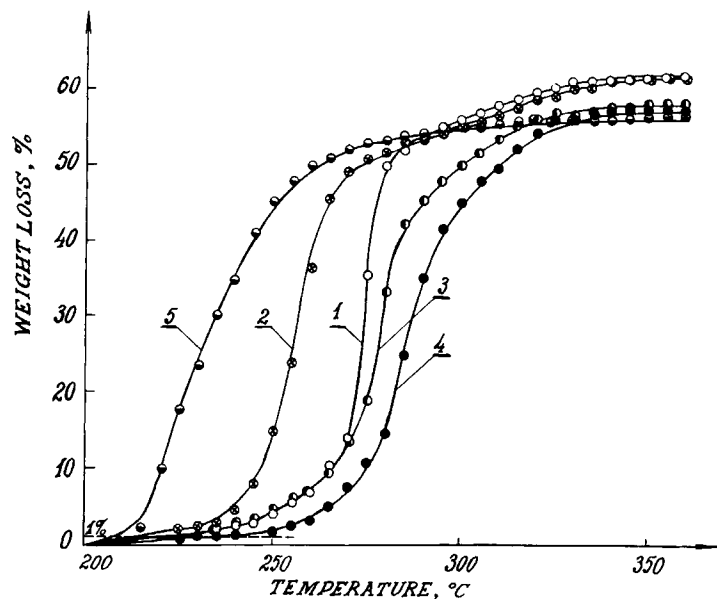


Figure 5 Weight loss curves of (1-○) PVC and (2-◻) PVC blends with 5% AS-1A, (3-△) 5% MZ-1% H₂O, (4-●) 5% MZ-6.5% H₂O, and (5-◼) 5% Zn-MZ.

estimated as negligible. This assumption is confirmed by the fact that an increase of the macropore surface after MZ activation (up to 15.5 m²/g) does not improve its sorption capacity (Fig. 5, curve 3).

The modified MZ (Zn-MZ) shows both the high fire-protecting and smoke-suppressant actions (Figs. 2 and 3); however, it accelerates dehydrochlorination of PVC (Fig. 5, curve 5). Thus, PVC containing

several stabilizers, such as calcium stearate, dibutyltin maleinate, and Irganox 1010 has 1% weight loss at 223°C as compared with 210°C for PVC containing the same stabilizers combined with 5 wt % Zn-MZ (Table I). Zinc-containing organic compounds are very good smoke-suppressant additives for both the burning and smoulder processes^{3,7,8,13-15}; however, some of them decrease

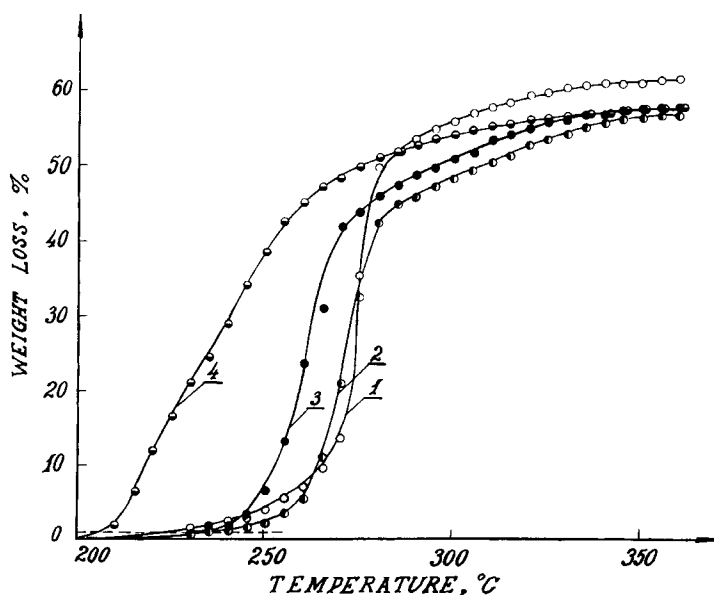


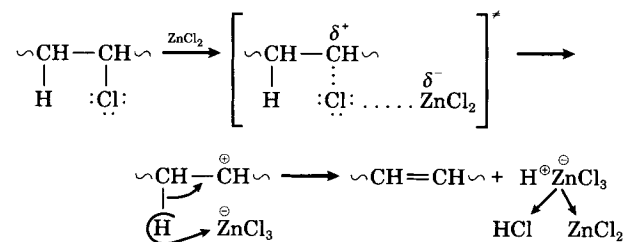
Figure 6 Weight loss curves of (1-○) PVC, (2-◻) PVC + 5% AS-1A + 5% MZ-1% H₂O, (3-△) PVC + 5% AS-1A + 5% MZ-6.5% H₂O, and (4-●) PVC + 5% AS-1A + 5% Zn-MZ.

Table I Thermal Characteristics of PVC-Containing MZs and Ammonium Sulfamate Combined with Ammonium Sulfate

No.	Composition	$T_{1\%}$ (°C)	T_{\max} (°C)	T_{end} (°C)	$-\Delta M_{T_{\text{end}}}$ (%)	Coke _{500°} (%)
1	PVC + stabilizers	223	275	330	60.7	21.5
2	PVC + 5% AS-1A	215	255	345	61.0	20.0
3	PVC + 5% MZ-1% H ₂ O	223	280	340	57.8	23.8
4	PVC + 5% MZ-6.5% H ₂ O	240	290	340	57.0	24.2
5	PVC + 5% Zn-MZ	210	218/240	310	55.5	29.5
6	PVC + 5% AS-1A + 5% MZ-1% H ₂ O	238	275	345	56.3	25.3
7	PVC + 5% AS-1A + 5% MZ-6.5% H ₂ O	238	265	345	57.5	24.3
8	PVC + 5% AS-1A + 5% Zn-MZ	208	216/245	330	56.8	25.7

$T_{1\%}$, temperature of 1% sample weight loss; T_{\max} , temperature of maximum decomposition; T_{end} , temperature of the end of decomposition; Coke_{500°}, coke residue at 500°C.

the thermal stability of chlorine-containing polymers.^{4,18} This is supposed to be due to a formation of ZnCl₂ accompanying the thermal decomposition of the polymer. Consequently, ZnCl₂ acts as an effective catalyst for the ionic dehydrochlorination of polymer because of its strong Lewis acidity. The following mechanism might be proposed:



Dehydrochlorination in the presence of Zn-MZ under the influence of the ZnCl₂ formed occurs, probably, with a formation of *trans*-polyene structures followed by intermolecular cyclization. As a result, a carbonized residue is formed. Such an action of Zn-MZ in a condensed phase has been proved by the increased content of coke residue (29.5% at 500°C) for a composition containing 5 wt % Zn-MZ (Table I). Regardless of the fact that Zn-MZ catalyzes dehydrochlorination of PVC, it also accelerates the coke formation, thus decreasing smoke evolution. At the same time, part of HCl evolved as well as ZnCl₂ formed enter into the gaseous phase and act as inhibitors of chain-combusting reactions by trapping radicals, such as HO·, H·, and ·CH₂.

The MZ action as a highly dispersed active filler and fire-retardant additive takes place predominantly in a condensed phase. However, ammonium sulfamate combined with ammonium sulfate acts mainly in a gaseous phase. Evidence for this as-

sumption is believed to be the slight increase of LOI observed (Fig. 2, curve 1) as well as the absence of any positive effect during the coke formation (Table I). According to the results of thermal analysis (Fig. 1), AS-1A undergoes a two-stage endothermic decomposition. The first stage is associated with an evolution of ammonia at 350°C. Since at 350°C the main decomposition of PVC associated with dehydrochlorination has already been finished (Table I), ammonia evolved acts predominantly as a diluent for the pyrolysis gases. Besides, taking into account the decrease of smoke evolution caused by AS-1A without promoting any coke formation (Fig. 3, curve 1), it may be assumed that ammonia inhibits some of the radical processes in the gaseous phase. The second stage of AS-1A decomposition is associated with sulfur dioxide evolution. Sulfur dioxide acts as a retardant of the combustion process in the gaseous phase by trapping active radicals and facilitating the cooling of the whole system. On the other hand, interaction of sulfur dioxide with the basic and amphoteric oxides present in the MZ (Al₂O₃, Fe₂O₃, MgO, CaO, K₂O, Na₂O) might be considered as a source of formation of the corresponding basic or normal salts (sulfates). These high-melting compounds probably create a protecting layer onto the polymeric surface, thus limiting the flame spreading.

The dependence of weight loss on the temperature of PVC compositions containing both 5 wt % AS-1A and 5 wt % MZs is presented in Figure 6. PVC composition containing 5% AS-1A and 5% Zn-MZ is associated with the lowest starting temperature of dehydrochlorination—208°C; the rate of the main destruction, however, is lower than the one observed with the rest of compositions studied. The corresponding coke residue formed at 500°C is 25.7%.

The following observations have been made dur-

Table II Characterization of Blends of PVC and Fire Retardants, AS-1A, MZ-6.5% H₂O, MZ-1% H₂O, Zn-MZ, in Combination with Sb₂O₃

No.	Composition	σ_Y (MPa)	σ_B (MPa)	ϵ (%)	σ_{IM} (kJ/m ²)	I_m (g/10 min)	D_m (m ² /kg)	LOI (% O ₂)	Heat Resistance (°C)
	PVC + stabilizers	64.3	51.2	39	3.0	1.95	385.1	46.4	83.3
1	5% AS-1A + 3% Sb ₂ O ₃	59.7		24	3.1	1.51	341.2	57.0	—
2	5% AS-1A + 5% Sb ₂ O ₃	57.2		26	3.3	1.76	348.4	57.3	82.2
3	5% AS-1A + 8% Sb ₂ O ₃	57.8		24	3.4	1.82	369.2	56.6	—
4	5% MZ-6.5% H ₂ O + 3% Sb ₂ O ₃	69.7	51.3	37	3.4	2.30	237.1	58.1	—
5	5% MZ-6.5% H ₂ O + 5% Sb ₂ O ₃	66.0	52.8	48	3.6	2.31	181.7	59.4	83.1
6	5% MZ-6.5% H ₂ O + 8% Sb ₂ O ₃	67.0	64.9	40	3.4	2.47	143.1	58.4	—
7	5% MZ-1% H ₂ O + 3% Sb ₂ O ₃	68.0	51.2	43	3.5	2.09	303.8	59.8	—
8	5% MZ-1% H ₂ O + 5% Sb ₂ O ₃	66.3	52.2	48	3.6	1.78	179.7	61.0	83.7
9	5% MZ-1% H ₂ O + 8% Sb ₂ O ₃	65.8	59.0	35	3.5	1.89	161.2	57.5	—
10	5% Zn-MZ + 3% Sb ₂ O ₃	66.1	51.9	41	3.4	1.72	328.3	70.3	—
11	5% Zn-MZ + 5% Sb ₂ O ₃	65.6	54.0	53	3.4	1.71	303.6	69.5	83.4
12	5% Zn-MZ + 8% Sb ₂ O ₃	64.8	57.9	34	3.4	1.71	279.7	64.1	—
13	5% AS-1A + 5% Zn-MZ + 3% Sb ₂ O ₃	61.1		24	3.4	1.55	211.9	67.6	—
14	5% AS-1A + 5% Zn-MZ + 5% Sb ₂ O ₃	59.2		25	3.4	1.22	223.5	70.6	83.6
15	5% AS-1A + 5% Zn-MZ + 8% Sb ₂ O ₃	60.5		24	2.9	1.23	279.7	67.9	—

ing the study of some combinations of MZs and AS-1A with Sb_2O_3 (Table II):

- (i) Compositions containing AS-1A and Sb_2O_3 possess a good fire-resistance; however, their smoke evolution resembles the one of the starting material (PVC).
- (ii) Compositions containing MZs with 1% and 6.5% H_2O and various Sb_2O_3 content have both high tensile strength and flowability, a good fire-resistance, and a diminished smoke formation. The latter is commensurable with the smoke formation of compositions containing AS-1A and MZs.
- (iii) Compositions containing Zn-MZ and Sb_2O_3 as well as those containing AS-1A, Zn-MZ, and Sb_2O_3 have a high fire-resistance; however, the smoke formation is also considered to be high.

Therefore, introduction of Sb_2O_3 (5–8 wt %) as a second component into the compositions of both the native (MZ–6.5% H_2O) and activated (MZ–1% H_2O) MZ leads to a significant decrease of smoke evolution. However, the introduction of Sb_2O_3 together with Zn-MZ or as a third component into compositions, such as PVC + AS-1A + Zn-MZ, is considered to be inefficient, in this case because of the high smoke formation of PVC.

CONCLUSION

The MZs studied as well as their combination with ammonium sulfamate containing ammonium sulfate are considered to be efficient fire-retardant and smoke-suppressant additives for unplasticized PVC. The results obtained from both the thermogravimetric studies and oxygen index determination lead to an assumption that MZs act in a condensed phase, whereas ammonium sulfamate combined with ammonium sulfate acts in a gaseous phase predominantly.

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