A Paradoxical Flame-Retardant Effect of Nitrates in ATH-Filled Ethylene–Vinyl Acetate Copolymer

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SYNOPSIS

In the course of a study of metal salts as flame retardants, it was surprisingly found that metal nitrates *reduced* the flammability of ATH-filled ethylene–vinyl acetate copolymer (EVA). The limiting oxygen index (LOI) of ATH-filled EVA was increased by the nitrates in the order of $Cu(NO_3)_2 \cdot 3H_2O > (NH_4)_2Ce(NO_3)_6 > Zn(NO_3)_2 \cdot 6H_2O > Fe(NO_3)_3 \cdot 9H_2O > Al(NO_3)_3 \cdot 9H_2O > NaNO_3$. The effects were not caused by the water of hydration. All metal nitrates except $NaNO_3$ reached a UL 94 V-2 rating at 3 phr. Based on TGA, DSC, FTIR, and gas detection, the proposed mechanism of the flame-retardant effect of nitrates is the oxidative degradation of the polymer to produce noncombustible products (CO_2 and nitrogen oxides) at a rate sufficient to interfere with the normal combustion process despite the exothermicity of the oxidative degradation. It is possible that surface carboxylic acid structures also contribute to the flame-retardant effect. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

We recently began exploratory research aimed at finding nonhalogen flame-retardant systems for polyolefins. The project was directed to newer and less conventional approaches in the hope of finding more efficient systems than those currently known. One of the approaches that we proposed[1] was to try to make use of oxidative dehydrogenation catalysis, or the stoichiometric equivalent, namely, a catalyzed reaction sequence of oxidation of C—H bonds followed by a catalyzed dehydration of the oxidized hydrocarbon to produce unsaturation and, by intermolecular addition, eventually a char layer. Such a process would result in lower heat of combustion (in the best case, hydrogen only oxidized) as well as formation of a carbonaceous barrier to heat and mass transport. Towards this objective, a number of transition metal oxidants were evaluated as hypothetical catalysts that might perform as flame retardants or synergists for other flame retardants.

Some support for the general idea was found in the literature. A combination of a Lewis acid and an oxidant was used by Brauman to promote char formation in the combustion of polystyrene.[2] The effective combinations included Fe_2O_3 with V_2O_5 or Fe_2O_3 with a chlorocarbon (Oxychem's Dechlorane Plus) and Cu_2Cl_2. The observed char formation was suggested via crosslinking of benzene rings. The oxidants served as catalysts for dehydrogenation. The increase of the char yield was observed in radiant pyrolysis experiments. In another example, which may have involved catalytic oxidation, the LOI of polypropylene was raised from 17.4 to 26.4 by a 1.5% level of chromium.[3] The active species in the system was a polymer-bound chromyl chloride structure prepared from the reaction of chromyl chloride and polypropylene. A mechanism of char formation was proposed to account for the LOI increase.

In our project, nitrates were only one group of salts and organometallics that we tried in a broad survey of metal salts for the indicated catalytic/flame-retardant synergist effect in ATH-filled ethylene–vinyl acetate copolymer (a polymer system of importance in nonhalogen flame-retardant wire and cable insulation formulations). We had included the nitrates mainly because a number of them are relatively low melting and relatively organic-soluble. It was our belief that the intended catalytic effect

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would be best seen if the metal compounds were, at least to some degree, in solution in the polymer either at the compounding temperature or perhaps at the fire-exposure temperature.

The attempted use of nitrates as flame retardants in polymers has rarely been reported, which is not surprising in view of the well-known oxidizing agent character of nitrates at elevated temperatures. Indeed, nitrates have been used in organic synthesis as oxidants at moderate reaction temperatures.[4-6] Nitrates can oxidize alcohols and hydrocarbons to corresponding ketones, acids, and other oxidation products. However, one patent issued to Standard Oil Co. did claim flame-retardant formulations containing polypropylene, halogen flame retardants, and alkali nitrates or ammonium nitrate.[7] The alkali nitrates and ammonium nitrate served as secondary flame retardants, which helped reduce the loading level of halogen flame retardants while the desired oxygen index of polypropylene formulations was maintained or improved. However, in this patent, the role of the nitrates in the flame-retardant action was unclear.

Our finding that the nitrates were more flame retardant than various other salts of the same metals came as an unexpected discovery, and although we were skeptical of the practical utility of this finding, we decided to investigate it sufficiently to define its scope, to understand the phenomenon and, as we hoped, perhaps find clues to a relatively unexplored approach to flame retardancy.

EXPERIMENTAL SECTION

Materials

The ethylene–vinyl acetate copolymer (ELVAX 460, 17.5–18.5 wt % vinyl acetate content) was obtained from E.I. duPont de Nemours & Company and was used as received. Aluminum trihydrate (OL-104LE, Lonza), $Mg(OH)_2$ (Morton Thiokol), $Cu(NO_3)_2 \cdot 3H_2O$, $(NH_4)_2Ce(NO_3)_6$, $Zn(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $NaNO_3$, $Zn(NO_3)_2$ on silica gel [$Zn(NO_3)_2$ content: 20 wt %], $Cu(NO_3)_2$ on silica gel [$Cu(NO_3)_2$ content: 26 wt %], $Zn(SO_4)_2 \cdot 7H_2O$, H_3PO_4 (Aldrich), $Fe_2(SO_4)_3 \cdot 9H_2O$, and conc. HNO_3 (Fisher Scientific) were used as received. We did not dehydrate these salts before use, because the processing temperature was in many cases above the dehydration temperature of the hydrates or could be elevated to the dehydration range (see discussion below).

Nitric Acid Surface Treatment of ATH and $Mg(OH)_2$

In a rolling ball mill, conc. HNO_3 (70% aq. solution, 0.48 mL, 7.5 mmol) was added to aluminum trihydrate (ATH, 0.3 mol, 23.40 g) drop wise. The resulting powder was roll mixed for 5 h. The partially caked mixture was ground to a fine powder. The powder was roll mixed again overnight, and dried in an oven at 120°C until its weight became constant [calculated $Al(NO_3)_3$ content in the powder: 2.2 wt %]. The powder was dried at 120°C for 24 h again before being compounded with other ingredients.

$Mg(OH)_2$-HNO_3 was prepared by the same procedure as above except that 0.4 mol (23.33 g) of $Mg(OH)_2$ and 0.01 mol (0.64 mL of conc. solution) of HNO_3 were used [calculated $Mg(NO_3)_2$ content in the powder: 3.1 wt %]. The powder was dried at 120°C for 24 h again before being compounded with other ingredients.

Polymer Sample Preparation

Ethylene–vinyl acetate copolymer (EVA) and other ingredients were mixed in a Brabender Plasticorder (Brabender Co.) at 125°C for 10 min, followed by molding at 125–130°C in a Carver press for 5 min. The resulting sample plate was cut into test specimens of specific sizes required for ASTM D-2863 and UL 94 tests.

Testing

Limiting oxygen index (LOI) was determined by ASTM D-2863 using a Stanton Redcroft FTA Flammability Unit (Tarlin Scientific). In most of the experiments, in order to prevent melt dripping in measuring LOI, a glass fiber wick was melt-implanted into the test specimen. The UL 94 vertical burning test was done by the standard procedure developed by Underwriter Laboratories. The thickness of the sample for the UL 94 test was 1/16″ (1.6 mm).

The TGA measurements were done using a DuPont 951 thermogravimetric analyzer with a heating rate of 20°C/min and an air flow rate of 50 mL/min. The DSC experiments were completed on a DuPont DSC 910 differential scanning calorimeter with a heating rate of 20°C/min and an air flow rate of 30 mL/min. The FTIR spectra were run on a Bio-Rad Digilab FTS-60 equipped with a 3200 data station.

Measurement of Gases Released during the Thermal Decomposition of EVA and Filled EVA

A test tube of 20 mm (diameter) × 150 mm (length) in a vertical position was preheated to 300°C, and maintained at that temperature for 20 min. The granular sample (0.50 g) was added into the test tube, which was left open. After 2 min, a Dräger gas detector tube equipped with a tube bellows pump (both were purchased from SKC Inc.) was inserted into the test tube, and the bottom tip of the Dräger tube was 3 cm above the sample. To measure the gas evolved, the pump was stroked 5 to 10 times according to the instruction, and the resulting value on the Dräger tube was recorded.

RESULTS AND DISCUSSION

The Effect of Various Nitrates on Flammability

Results in Table I showed that all of the nitrates tested increased the LOI values of ATH-filled EVA, with the order of $Cu(NO_3)_2 \cdot 3H_2O$ > $(NH_4)_2Ce(NO_3)_6$ > $Zn(NO_3)_2 \cdot 6H_2O$ > $Fe(NO_3)_3 \cdot 9H_2O$ > $Al(NO_3)_3 \cdot 9H_2O$ > $NaNO_3$. By comparison, silica-gel-bound Cu and Zn nitrates had almost the same effect on the flame retardancy as their hydrate analogs. Except for $NaNO_3$, all of the nitrates caused ATH-filled EVA to reach a UL 94 V-2 rating.

To explain the role of these nitrates in elevating LOI, we first postulated that either enhanced melt flow and/or the water of hydration might be responsible. The melt flow was minimized or eliminated by the incorporation of a wick into the specimen. The presence of a wick had been earlier shown to affect the LOI values of ATH-nitrate-EVA for-

mulations (Table II). As we indicated previously, all samples tested contained a glass fiber wick, and in fact, the wick did seem to largely prevent melt dripping. To further check this hypothesis, we prepared several crosslinked formulations of ATH-nitrate-EVA. These crosslinked formulations did not exhibit melt dripping during the LOI measurement even without a wick, because the crosslinking virtually stopped the melt flow (Table III). The crosslinked formulations containing nitrates also showed an increase in LOI. Thus, the hypothesis that the action of the nitrates was due to enhanced melt flow was substantially negated by the results shown in Tables II and III. We then turned to the possible effect of any water of hydration that had survived the processing.

Several methodologies were employed to study the water effect. First, postdehydrated nitric acid treated ATH and $Mg(OH)_2$ were evaluated in the filled EVA. These nitric acid treated ATH and $Mg(OH)_2$ did not contain water because they were continuously dried at 120°C to constant weight. As shown in Table IV, the formulations of nitric acid treated ATH and $Mg(OH)_2$ had higher LOI values than those containing untreated ATH.

The second method involved the removal of water from hydrated nitrates at elevated temperature, and retesting of the flame-retardant effect. Samples containing $Fe(NO_3)_3 \cdot 9H_2O$ were processed at 140°C and molded at 100°C or 180°C, respectively. The subsequent measurements in LOI indicated little effect of the processing temperature on LOI (Table V). A sample with $Cu(NO_3)_2 \cdot 3H_2O$ also reached the same outcome after the high temperature treatment. A further evaluation of the water effect was completed as follows: a sample of EVA (100 phr)-ATH

Table I   Flammability of ATH-Nitrate-EVA

Sample[a]	Hydrated or Silica Gel Bound Nitrate (phr[b])	Metal Nitrate (phr)	LOI	UL 94 Rating and Burning Time (s)
1	—	—	23.0	Burning
2	$NaNO_3$ (3)	$NaNO_3$ (3)	25.8	Burning
3	$Al(NO_3)_3 \cdot 9H_2O$ (5.3)	$Al(NO_3)_3$ (3)	27.4	V-2 (2)
4	$Fe(NO_3)_3 \cdot 9H_2O$ (5)	$Fe(NO_3)_3$ (3)	28.2	V-2 (3)
5	$Zn(NO_3)_2 \cdot 6H_2O$ (4.7)	$Zn(NO_3)_2$ (3)	28.4	V-2 (8)
6	$(NH_4)_2Ce(NO_3)_6$ (3)	$(NH_4)_2Ce(NO_3)_6$ (3)	29.6	V-2 (4)
7	$Cu(NO_3)_2 \cdot 3H_2O$ (3.9)	$Cu(NO_3)_2$ (3)	30.0	V-2 (3)
8	$Cu(NO_3)_2$ on silica gel (11.5)	$Cu(NO_3)_2$ (3)	30.2	V-2 (3)
9	$Zn(NO_3)_2$ on silica gel (15)	$Zn(NO_3)_2$ (3)	27.8	V-2 (5)

[a] All samples contain 100 phr of EVA (ELVAX 460) and 50 phr of ATH.
[b] phr = parts per hundred resin.

Table II   Effect of the Presence of a Wick on LOI

Formulation	Specimen Type	LOI
ATH-EVA[a]	Bar specimen without a wick	24.5
ATH-EVA[a]	Bar specimen with a wick	23.0
ATH-Fe(NO₃)₃-EVA[b]	Bar specimen without a wick	30.3
ATH-Fe(NO₃)₃-EVA[b]	Bar specimen with a wick	28.2

[a] The formulation contains 100 phr of EVA and 50 phr of ATH.
[b] The formulation contains 100 phr of EVA, 50 phr of ATH, and 3 phr of Fe(NO₃)₃.

(50 phr)-$Al(NO_3)_3 \cdot 9H_2O$ [$Al(NO_3)_3$ (3 phr)] was dried at 100°C for 3 days in an oven to remove as much water as possible (constant weight was reached after 2 days of drying). The sample was immediately placed in a dry box under dry N_2 and cut into test bars in which a wick was melt-implanted. This treated sample had an LOI of 27.2, compared with 27.4 for the nondehydrated sample.

Finally, in two control experiments, $Zn(SO_4)_2 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ were evaluated in place of the nitrates. These sulfates are comparable in level of hydration to the flame-retardant nitrates. The two sulfate-containing samples were prepared by mixing the ingredients at 100°C for 10 min and molding at 100°C for 5 min to prevent them from losing water. Under the condition of the same water content, $Zn(SO_4)_2 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ had a very small effect in elevation of LOI, while,

Table III   Influence of Crosslinking on Flammability

Formulation[a]	LOI without Wick	LOI with Wick
ATH (50 phr)-EVA (100 phr)	22.2	22.2
ATH (50 phr)-(NH₄)₂Ce(NO₃)₆ (3 phr)-EVA (100 phr)	25.9	25.8
ATH (50 phr)-Fe(NO₃)₃·9H₂O (5 phr)-EVA (100 phr)	26.5	26.0
ATH (50 phr)-Cu(NO₃)₂·3H₂O (3.9 phr)-EVA (100 phr)	27.0	27.0

[a] The crosslinking was completed using dicumyl peroxide (2 phr) at 180°C for 30 min.

Table IV   LOI vs. Treated and Untreated ATH and Mg(OH)₂[a]

Metal Hydroxide or Treated Metal Hydroxide (phr)	Metal Nitrate Nitrate Type (phr)	LOI
ATH (50 phr)	—	23.0
ATH-HNO₃ (51)	Al(NO₃)₃ (1.1)	25.7
Mg(OH)₂ (50 phr)	—	23.9
Mg(OH)₂-HNO₃ (52)	Mg(NO₃)₂ (1.6)	26.3

[a] All formulations contain 100 phr of EVA.

by comparison, $Fe(NO_3)_3 \cdot 9H_2O$ showed a substantial effect in elevating LOI (Table VI).

A study by Gadally and Yu indicated that $Fe(NO_3)_3 \cdot 9H_2O$ undergoes thermal dehydration at 130–160°C to form $Fe(NO_3)_3 \cdot 2H_2O$.[8] Then, further decomposition led to Fe_2O_3. Our samples 2 and 3 in Table V was processed at 140°C for 15 min and sample 3 was molded at even higher temperature (180°C). Therefore, these two samples should contain very little water of hydration after processing. If water in the nitrate plays the main role in elevating LOI, such heavy loss of water should greatly affect the LOI value. In fact, samples 2 and 3 in Table V had almost the same LOI as that of sample 1.

A situation was observed with the sample containing $Al(NO_3)_3 \cdot 9H_2O$. $Al(NO_3)_3 \cdot 9H_2O$ loses 7.5 mol of water at 100°C after 36 h to $Al(NO_3)_3 \cdot 1.5H_2O$.[9] As indicated above, the treated sample showed very little change in LOI after the removal of most of water.

The data in Table IV indicates that the dry form of nitrates had a substantial influence in raising LOI. Table VI further confirms the key role of the nitrate instead of the hydrate in LOI elevation, because both highly hydrated $Zn(SO_4)_2 \cdot 7H_2O$ and $Fe_2(SO_4)_2 \cdot 9H_2O$ were nearly ineffective in raising LOI.

Thus, based on the above results obtained from these three methods, we can conclude that neither melt flow nor an effect of the water of hydration are responsible for the effect of the nitrates in the ATH-EVA formulations.

Synergism of Nitrates with ATH

Experiments were performed to determine the interaction between ATH and nitrates. Two formulations of nitrate-EVA were also prepared by the same procedure for comparison. Results in Table VII showed that the $Cu(NO_3)_2 \cdot 3H_2O$-ATH system

Table V   Flammability of Samples Prepared at Different Temperatures

Sample[a]	Nitrate (phr)	Preparation Method	LOI
1	$Fe(NO_3)_3 \cdot 9H_2O$ (5)	Mixing at 125°C for 10 min, molding at 125°C for 5 min.	30.3
2	$Fe(NO_3)_3 \cdot 9H_2O$ (5)	Mixing at 140°C for 15 min, molding at 100°C for 5 min.	30.1
3	$Fe(NO_3)_3 \cdot 9H_2O$ (5)	Mixing at 140°C for 15 min, molding at 180°C for 30 min.	30.1
4	$Cu(NO_3)_2 \cdot 3H_2O$ (3.9)	Mixing at 125°C for 10 min, molding at 125°C for 5 min.	30.0
5	$Cu(NO_3)_2 \cdot 3H_2O$ (3.9)	Mixing at 125°C for 10 min, molding at 160°C for 10 min.	29.9

[a] The samples contains 100 phr of EVA and 50 phr of ATH.

was more effective in raising LOI than the $Fe(NO_3)_3 \cdot 9H_2O$-ATH system.

The synergism here is defined as an effect substantially greater than the linear addition of the effects of the separate flame retardants. Therefore, the $Cu(NO_3)_2 \cdot 3H_2O$-ATH system was found to show synergism in LOI, because the measured increase of LOI was much greater than the calculated one. The $Fe(NO_3)_3 \cdot 9H_2O$-ATH system did not show this same synergism, because the LOI values from experiment and calculation were close. The results suggest the possible interaction between ATH and certain metal ions of nitrates in elevating LOI. We also speculate that the transition metal ions in the nitrates might be involved in catalytic oxidation or catalytic oxidative dehydrogenation of the polymer, giving better flame retardancy (such as higher LOI) for the polymer. This speculated action by transition metals is consistent with our original proposal of the catalytic approach.

Thermal Analyses of Nitrate-EVA and ATH-Nitrate-EVA Formulations

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are useful tools to evaluate the thermal behavior and possible mechanism of the flame retardants in polymers. In the present study, TGA experiments were carried out under air with nitrate and ATH-filled EVA (Table VIII). The

Table VI   Comparative Effect of Various Hydrated Salts on LOI[a]

Additive (phr)	Water Content, phr	LOI
—	—	24.5
$Zn(SO_4)_2 \cdot 7H_2O$ (4.6)	2	24.8
$Fe_2(SO_4)_2 \cdot 9H_2O$ (7.1)	2	25.0
$Fe(NO_3)_3 \cdot 9H_2O$ (5)	2	30.3

[a] All samples contain 100 phr of EVA and 50 phr of ATH.

phenomena that were observed in TGA were the following:

1. EVA and nitrate-filled EVA decomposed via two major steps, corresponding to two decompositions: first, elimination of acetic acid from vinyl acetate units and then further decomposition probably involving ethylene units. The latter decomposition caused the maximum weight loss. The decomposition occurred earlier when the nitrate was present, because the temperature for the initial (1% weight loss) decomposition was lower with the nitrate than that without the nitrate. The temperature for the maximum weight loss (or maximum decomposition) was increased by the presence of the nitrate (see first three examples in Table VIII).

2. ATH-filled EVA and ATH-nitrate–filled EVA decomposed via three major steps, the decompositions of ATH (dehydration), plus two decompositions mentioned above, and the maximum weight loss occurred in the third step.

3. Contrary to the results of non-ATH EVA, the temperature for the initial 1% decomposition of ATH-filled EVA seemed to be higher in the presence of nitrates than that without nitrates.

4. No appreciable char was formed either from nitrate-EVA, ATH-EVA, and ATH-nitrate-EVA. No increase in the final residue was observed with ATH-nitrate-EVA other than that expected from the inorganic content.

These TGA observations suggest that the hypothetical char forming mechanism (by dehydrogenation or oxidative dehydrogenation catalysis) can be ruled out as an explanation for the mode of action of nitrates because no char increase was found. Although the presence of nitrates led to slightly higher

Table VII Comparison of Nitrate-EVA and ATH-Nitrate-EVA[a]

ATH, phr	Nitrate (phr)	Measured LOI	Calculated LOI by Addition Method
0	—	18.4	—
50	—	23.0	—
0	$Fe(NO_3)_3$ (3)	23.1	—
50	$Fe(NO_3)_3$ (3)	28.2	18.4 + 4.6 + 4.7 = 27.7
0	$Cu(NO_3)_2$ (3)	19.9	—
50	$Cu(NO_3)_2$ (3)	30.0	18.4 + 4.6 + 1.5 = 24.5

[a] All samples contain 100 phr of EVA.

thermal stability by raising the temperature for 1 wt % decomposition, this small difference can probably be related to dehydration of the salts.

The early decomposition of EVA caused by the nitrates suggested the oxidation of the polymer by the nitrates. To confirm the possible oxidation, we carried out DSC experiments on formulations of EVA alone, $Fe(NO_3)_3$-EVA, ATH-EVA, and $Fe(NO_3)_3$-ATH-EVA. EVA showed a broad, exothermic decomposition in the region of 215 to 350°C (curve A in Fig. 1), while $Fe(NO_3)_3$-EVA gave a more intense and broad exothermic decomposition starting at 195°C (curve B in Fig. 1). These exothermic decompositions were suppressed by the presence of ATH. A large endothermic peak at 339°C with a heat absorption of 245 J/g was observed on the ATH-EVA formulation upon heating, while 338°C and 195 J/g were observed for $Fe(NO_3)_3$-ATH-EVA. The smaller heat absorption for the latter formulation may be due to the presence of $Fe(NO_3)_3$,

because the nitrate oxidation would result in an exothermic process, which would counteract some of the endothermic heat flux.

Both TGA and DSC results are consistent with the postulate that the nitrate oxidizes the EVA copolymer, accelerating the decomposition of EVA, and giving a broad, intense exotherm in the early stage of the EVA decomposition.

Identification of Possible Oxidation Products by FTIR on the Surface of the Burning Residue

Fourier transform infrared spectroscopy (FTIR) was employed to study the composition of EVA, ATH-EVA, and $ATH-Fe(NO_3)_3 \cdot 9H_2O$-EVA systems, and to identify the possible oxidation products on the surface of the self-extinguished specimen. Thin films were used throughout the FTIR study. The film for the burning residue was prepared by carefully scraping off the black, waxy residue from the surface

Table VIII TGA Results of EVA and Filled EVA[a]

Formulation	Temperature at 1 wt % Decomposition, °C	Temperature at Max DTG peak, °C	Residue, %
EVA	305	420	1.6
$Fe(NO_3)_3$-EVA[b]	268	450	2.9
$Cu(NO_3)_2$-EVA[b]	280	460	3.9
ATH-EVA[c]	240	467	24.3
ATH-$NaNO_3$-EVA[d]	260	442	24.4
ATH-$Al(NO_3)_3$-EVA[d]	257	470	23.9
ATH-$Fe(NO_3)_3$-EVA[d]	272	473	22.9
ATH-$Zn(NO_3)_2$-EVA[d]	250	460	24.0
ATH-$(NH_4)_2Ce(NO_3)_6$-EVA[d]	248	460	24.5
ATH-$Cu(NO_3)_2$-EVA[d]	262	471	25.6

[a] Air flow rate of 50 mL/min and heating rate of 20°C/min were used in TGA.
[b] The formulations contain 100 phr of EVA and 3 phr of nitrate.
[c] The formulations contain 100 phr of EVA and 50 phr of ATH.
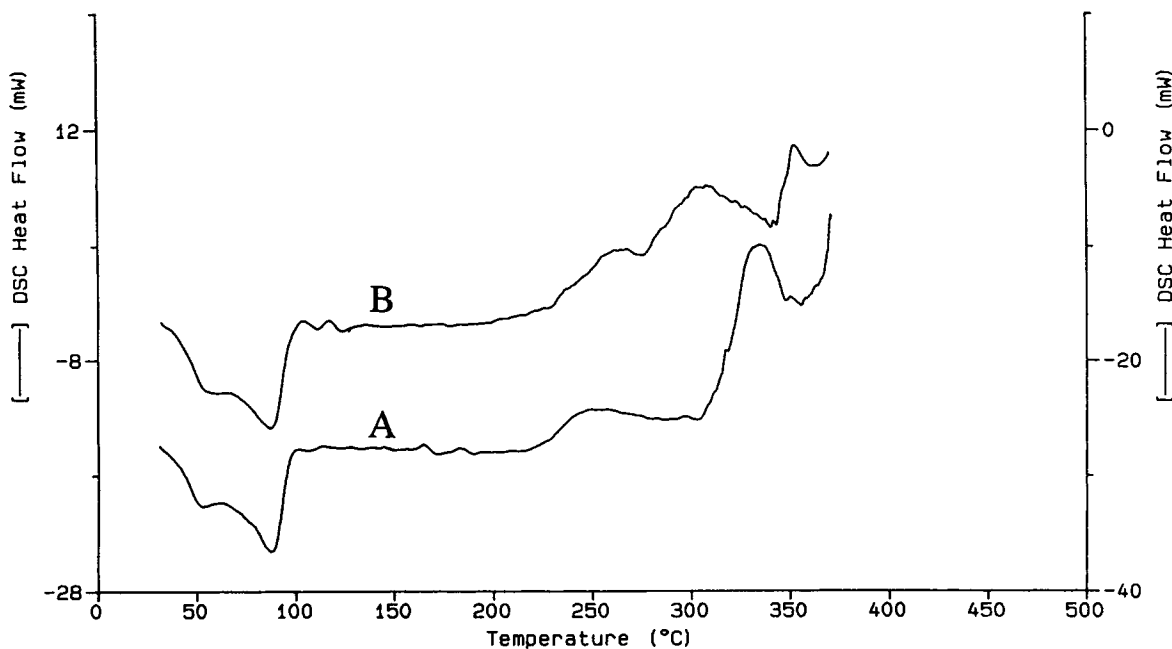[d] The formulations contain 100 phr of EVA, 50 phr of ATH, and 3 phr of nitrate.

Figure 1 DSC curves of (A) EVA and (B) $Fe(NO_3)_3(3\ phr)$-EVA(100 phr).

of the sample after burning of the sample in air and allowing it to self-extinguish.

The data from the FTIR study is listed in Table IX. The pure EVA showed two major peaks at 2900–2800 and 1740 cm^{-1}, respectively. Introduction of ATH resulted in two additional strong peaks at 3600 and 3450 cm^{-1}, which are assignable to absorptions of OH groups in ATH. The most important observation was that the burning residue of ATH-$Fe(NO_3)_3 \cdot 9H_2O$-EVA showed a number of new peaks that were not seen in the unburned compositions, which may indicate the presence of carboxylic acid groups and carboxylate salt. A broad peak at 3400–2600 cm^{-1} was a characteristic absorption of carboxylic acid. Peaks at 1717 and 1418 cm^{-1} were also attributed to the presence of carboxylic acid. A broad absorption at 1650–1520 cm^{-1} might be due the presence of carboxylate salt.[10] Furthermore, in

order to identify whether the carboxylic acid was free acetic acid generated from the acetoxy group of EVA and merely absorbed on the surface of the residue, we dried the films to be studied at 90°C for 48 h under vacuo (with a mechanical pump), which should have removed any acetic acid, and ran the FTIR again. The FTIR spectra still showed the same absorption peaks of the carboxylic acid.

This fact suggests the oxidation of C—H bonds and ester groups in the EVA polymer by nitrates. Metal nitrates are strong oxidizing agents. Clay- and silica gel-supported nitrates have been reported to oxidize secondary alcohols to the corresponding ketones along with other byproducts.[2,3] Barton's group reported the oxidation of saturated C—H bonds to alcohols and further oxidation products.[6] $Fe(NO_3)_3 \cdot 9H_2O$ was involved in this type of oxidation. In our ATH-nitrate-EVA system, it is rea-

Table IX   FTIR Results

Sample	IR Peak (cm^{-1}) and Assignment
EVA	2900–2800, C—H; 1740, —COOR
ATH-EVA	3600, 3450, OH from ATH; 2900–2800, C—H; 1740, —COOR
ATH-$Fe(NO_3)_3 \cdot 9H_2O$-EVA	3600, 3450, OH from ATH; 2900–2800, C—H; 1740, —COOR
Surface residue of burnt ATH-$Fe(NO_3)_3 \cdot 9H_2O$-EVA	3600 (small peak), OH from ATH; 3400–2600, broad, OH from COOH; 2900–2800, C—H; 1738, COOR; 1717, COOH; 1650–1520, broad, COO^-, 1552, NO_3^-, 1418, COOH

sonable that the nitrates should be able to oxidize the EVA polymer. Chemically deep-seated, albeit superficial, oxidation of the polymer surface also can produce carboxylic end groups, which might undergo further oxidations to CO_2 and H_2O. Low volatility carboxylic acids have been shown to be flame retarding by Nasybullin et al.[11] Moreover, Suzuki and Wilkie reported that the grafting of carboxylic acid containing monomers such as methacrylic acid onto ABS terpolymers enhanced the flame retardancy of these terpolymers.[12]

Identification and Estimation of Gases Released in the Thermal Decomposition of EVA and Filled EVA

Because the nitrates were hypothesized to oxidize the EVA polymer to produce carboxylic acids and possibly CO_2, we predict that more CO_2 should be generated from the formulations containing nitrates than those without nitrates, while the nitrates will be reduced to NO_2 or NO. To test this prediction, a number of measurements were conducted to determine the amount of CO_2 and nitrogen oxides (as NO_2 + NO) during the thermal decomposition of EVA, ATH-filled EVA, nitrate-filled EVA, and ATH-nitrate-filled EVA at 300°C.

Data in Table X clearly showed that upon thermodecomposition, nitrate-containing formulations, either $Fe(NO_3)_3$-EVA or ATH-$Fe(NO_3)_3$-EVA, generated higher amount of CO_2 than non-nitrate-containing formulations, EVA itself or ATH-EVA. The nitrate-containing formulations also produced the nitrogen oxides (NO_2 + NO). The presence of ATH seemed to help generate more CO_2 than the absence of ATH. The measurement was reproducible, as indicated in the table. These results confirmed our prediction.

Based on the results from TGA, DSC, FTIR study, and the gas detection, we, therefore, conclude that the mode of action in nitrate-EVA and ATH-nitrate-EVA may be the oxidative degradation of EVA by the nitrate, producing carboxylic acid structures, H_2O, CO_2, and probably other oxidation products, which are noncombustible and are able to reduce the flammability of EVA through the dilution of fuel, the effect of the outgoing inert gas in reducing the retention time of fuel in the combustion zone, and possibly reduction of oxygen concentration in the vapor phase adjacent to the heated surface. The nonflammable gases evolved from the surface may be able to retard the further thermooxidative decomposition of the EVA polymer, as we observed

Table X   Detection of Gases Released in Thermal Decomposition of EVA and Filled EVA

Formulation[a]	CO_2 (%)	NO_2 + NO (ppm)
EVA	0.22[b]	—
$Fe(NO_3)_3$-EVA	0.40[c]	90
ATH-EVA	0.29	—
$Fe(NO_3)_3$-ATH-EVA	0.52	100

[a] For information on the composition of the formulations, see footnotes in Table VIII.
[b] This value is an average of 0.21 and 0.22.
[c] This value is an average of 0.40 and 0.39.

the nitrates actually raised the temperature for the maximum weight loss (first three examples in Table VIII). The carboxylic acid and carboxylate salt structures observed by FTIR may represent the intermediates in the oxidation process, and these structures may also contribute to the flame-retardant effect. This oxidation process does not produce char as confirmed by TGA experiments.

These results represented the flame-retardant effect of noncombustible gases generated through an *exothermic* process in contrast to the more common situation (with ATH, melamine, etc.) where *endothermic* gas release is involved. They also led us to exploring other means for producing noncombustible gases at or near the polymer ignition temperature.[13]

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