

Flame-Retardant EPM Compositions for Cable Insulation, Containing Br-N-S Fire Retardants

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SYNOPSIS

The influence of ammonium salts of oligomeric Br-N-containing sulphonic acids and some inorganic fire retardants on the physico-mechanical properties, flammability characteristics, and thermooxidative degradation of EPM compositions for insulation of ship cables has been studied. The ternary system consisting of bromosulphaminic acid bromonitrosulphonic acid and antimony trioxide in 6.6 : 3.4 : 4–5 mass ratio has been found to exhibit an additive effect on the fire retardancy. A correlation between the flammability characteristics and some thermal properties of EPM compositions has also been established. The organic fire retardants of certain concentrations in EPM compositions have been found to exhibit a positive plasticizing performance. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

A trend toward substitution of halogen-containing materials for non-halogen-containing (NHC) materials based on polyolefins in order to prepare flame-retardant compositions has been observed in recent years. Poly(ethylene), poly(propylene), and the corresponding copolymers or elastomers, such as ethylene-propylene rubber (EPR), ethylene-vinyl-acetate copolymer (EVA), ternary copolymer of EPM (EPDM), etc. are known to be the basic NHC polymeric materials.¹ NHC materials are readily available and have excellent insulation properties, their burning being accompanied by an evolution of nontoxic products.

The preparation of EPM compositions with enhanced flame resistance requires a careful selection of fire retardant (FR) and fillers. However, if considerable quantities of these components are introduced into the composition, the mechanical properties may be deteriorated.

The flame resistance of the compositions of NHC polymers for cable insulation can be achieved by utilization of glass fibers preventing the dripping of material when burning or by introducing finely ground fillers such as $\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$, MgCO_3 as well as combinations of fillers and FR.

The introduction of FR, mainly bromine- and chlorine-containing organic compounds is known to be a basic method for decreasing the flammability of polyolefins.^{1,2} The synthetic hydrocarbon elastomers such as EPR burn with a smoke evolution in the absence of FR.³ X-cycloalkanes and antimony trioxide (AO),⁴ tribromo(methylidene)bisphenol oligomer, and AO,⁵ ethylene-bis-tetraphthalimide,⁶ brominated phosphate (a dinonil phenol phosphate ester),⁷ 4,4'-sulphonil bis-(2,6-dibromophenol), $\text{Mg}(\text{OH})_2$, threiallylcyanurate, substituted thio-diketones, etc.⁸ have been employed in order to reduce the flammability and smoke evolution.

The aim of the present study is to examine the influence of ammonium salts of some oligomeric Br-N-containing sulphaminic acids and inorganic FR on both the physicochemical properties and flammability of EPM compositions for insulation of ship cables.

EXPERIMENTAL

Materials and Methods

The following abbreviations will be used for FR studied:

1. Ammonium salt of Br-sulphaminic acid (Br-SA), utilized mostly with ammonium sulphate (AS) in 1 : 2 mass ratio;

2. Br-nitrosulphonic acid (Br-NSA);
3. Antimony trioxide (AO).

Ammonium salts of oligomeric Br-SA and Br-NSA were prepared by a three-stage synthetic procedure, described previously.⁹ Dichloroethane solution of butadiene-styrene rubber was subjected to nitration by a concentrated nitric acid in order to prepare nitrooligomer. The acid form of the latter reacted with bromine water at 0–15°C and a polybromonitro compound, containing 22% Br was then separated. The latter reacted with ammonium hydrogensulphite in 1,4-dioxane-water solution at 40°C, which resulted in preparation of the corresponding ammonium salts of Br-SA and Br-NSA.

The flame-retardant EPR composition for cable insulation contains the following parts by weight (phr):

1. EPM, CoO34, 90
2. PE, OB 20-108, 10
3. Martinal-OL104C, 200
4. Plasticizers, 8–20
5. Anti-aging agents, 1–3
6. Curing group, 5–8
7. FR, 8–15

The blends were prepared by means of laboratory rollers 350–500 mm in size, using a two-stage procedure. The first stage consisted of blending EPM with PE for 3–5 min at 100–120°C. In the second stage, the ingredients were introduced into the blend for 15–20 min at 50–60°C. The curing of the samples, 100 × 100 × 3 mm, was carried out by means of a laboratory press at 155°C for 30 min under a pressure of 22 MPa.

The compositions containing FR alone, as well as both the binary Br-SA : Br-NSA and ternary Br-SA : Br-NSA : AO systems are shown in Table I.

Test Characterization

The physicomechanical properties were examined by means of a dynamometer type (WPM, Germany). The limited oxygen index (LOI) was determined by using a DIG-OXIMETER unit, according to the ASTM 2863-77 standard, with sample sizes 100 × 100 × 3 mm. The flame resistance was determined in accordance with UL-94 standard (vertical method) with sample sizes 100 × 100 × 3 mm. The smoke evolution parameters were determined in a smoke camera with an optical cell. The corresponding parameters for an evaluation were as follows: $D_{s_{max}}$, maximum optical density; t_{max} , time for reaching $D_{s_{max}}$, s; $D_{s_{90\%}}$, optical density for $t = 90$ s; $t_{90\%}$, time for reacting $D_{s_{90\%}}$, s; D_s at $t_{16} - D_s$, $t = 16$ s; the same concerned D_s for $t = 90$ s.

The thermal studies (TG, DTG and DTA examinations) were conducted by using an OD-102 derivatograph (MOM Company, Budapest, Hungary) under the following conditions: temperature range 20–550°C; heating rate, 6°C/min; initial weight of samples 100 ± 0.5 mg; in air (static). The samples were placed in a conical corundum crucible. The areas of the first exothermal effect recorded for the samples were determined graphically by a gravimetric method. These areas could be used as a unit of measurement for the quantity of released heat, bearing in mind that the samples were of an equal mass, having been heated under the same conditions.

RESULTS AND DISCUSSION

The selection of EPM in the present study can be explained by its excellent insulating properties, thus allowing the introduction of considerable amounts of mineral fillers into the composition without deteriorating the electrical characteristics.

LOI of EPM without FR introduced is known to

Table I Flame-Retardant EPR Compositions for Cable Insulation With Fire Retardants Containing Br-N-S

No.	FR (phr)	Blend No.															
		1 Initial	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16 ^a
1	Br-SA	—	10 ^b	10	—	—	2.5	5.0	7.5	6.65	5.00	3.35	6.65	6.65	6.65	6.65	6.65
2	Br-NSA	—	—	—	10	—	—	—	—	3.35	5.00	6.65	3.35	3.35	3.35	3.35	3.35
3	AO	—	—	—	—	8	—	—	—	—	—	—	2	3	4	5	4

^a Blend 16, 8 phr Sunpar 2280.

^b Blend 2, 10 phr AS.

be of low value, 17–22%, whereas for highly filled EVA compositions LOI reached 40–44%.¹⁰ An introduction of both the organic and inorganic FR-like synergistics or additives of AO as well as Al(OH)₃·3H₂O, MgCO₃, CaCO₃, etc. present in the composition is necessary for increasing the flame resistance of EPM.

The first task of the present study was to examine the independent influence of the organic products Br-SA and Br-NSA as well as AS and AO on both the physicomechanical parameters and flammability of EPM. The second task was associated with determining the optimum proportions between FR in order to prepare flame-retardant EPM with a diminished smoke evolution, as well as good physicomechanical and electrical parameters.

Influence of FR on the Physicomechanical Parameters of EPM Compositions

By introduction of the crystalline product Br-SA and the amorphous product (Br-NSA) into the corresponding compositions, a good processability of EPM can be ensured. As the concentration of these FR changed up to 10 mass parts, the elongation increased from 310 to 360% and scleroscope hardness was diminished from 82 to 65 Shore A. Such dependences were not observed for AS in the same amount (Table II, blends 3, 4).

The first series of compositions were associated with a study of the influence of Br-SA in concentrations from 2 to 10 phr. On increasing the amount of Br-SA the elongation increased as well, whereas the scleroscope hardness was diminished (Fig. 1, curve 1, 2). Similar dependences were observed with the binary system Br-SA : Br-NSA in 2 : 1, 1 : 1, and 1 : 2 mass ratios, respectively (Table II, blends 9–11). Together with the elongation increase, a trend toward a decrease of the tensile strength from 6.8 to 5.2 MPa was observed; however, the latter still remained within the permissible range up to 4.2 MPa (Fig. 1, curve 3).

The ternary system, i.e., Br-SA : Br-NSA : AO was also studied on increasing the AO concentration up to 5 phr (Table I, blends 12–15). In this case the elongation increased to 370% whereas the scleroscope hardness decreased to 71 Shore A. The tensile strength decreased slightly to 5.5 MPa at 2 phr AO with a trend toward a further decrease on increasing AO concentration (Fig. 2).

The studies conducted proved the plasticizing effect of the organic FR introduced independently in a mixture or combined with AO. Methyl esters of the oligomeric sulphonic acids are known to act as plasticizers.¹¹

Table II Physicomechanical and Flammability Characteristics of Flame-Retardant EPR Compositions for Cable Insulation With Fire Retardants Containing Br-N-S

No.	Blend No.	Tensile Strength (MPa)	Elongation (%)	Residual Elongation (%)	Shore A	LOI (%)	Smoke Release							
							$D_{t_{max}}$ (s)	t_{max} (s)	D_s (90%)	$t_{90\%}$ (s)	$D_{s, t_{16}}$ (s)	$D_{s, t_{90}}$ (s)	UL-94 (s)	
1	1	6.8	310	28	82	29	125	22	110	15	5	0.0	V-O	16
2	2	4.8	310	24	78	31	152	32	136	23	7	0.0	V-O	20
3	3	5.2	338	32	70	33	170	33	153	26	9	1.0	V-O	No burn.
4	4	6.5	357	32	65	31	202	30	182	24	8	0.5	—	730 ^a
5	5	5.8	307	26	78	31	121	21	118	17	6	0.0	V-O	4
6	9	5.7	305	24	75	33	158	35	142	32	8	0.0	V-O	No burn.
7	10	5.0	343	32	74	32	189	30	171	24	6	0.5	V-O	No burn.
8	11	5.7	343	32	68	32	122	27	110	23	8	0.0	V-O	12
9	16	6.4	335	26	74	34	100	31	90	30	11	1.0	V-O	No burn.

^a No correspondence to class V = 0.

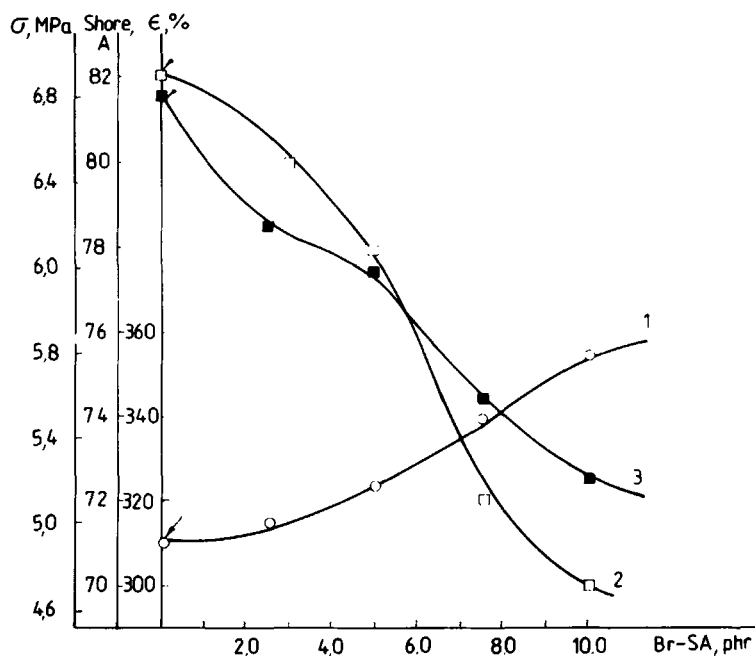


Figure 1 Influence of Br-SA on physicochemical parameters of EPM composition for cable insulation. (1) (O) elongation, %; (2) (X) scleroscope hardness, shore A; (3) (●) tensile strength, MPa.

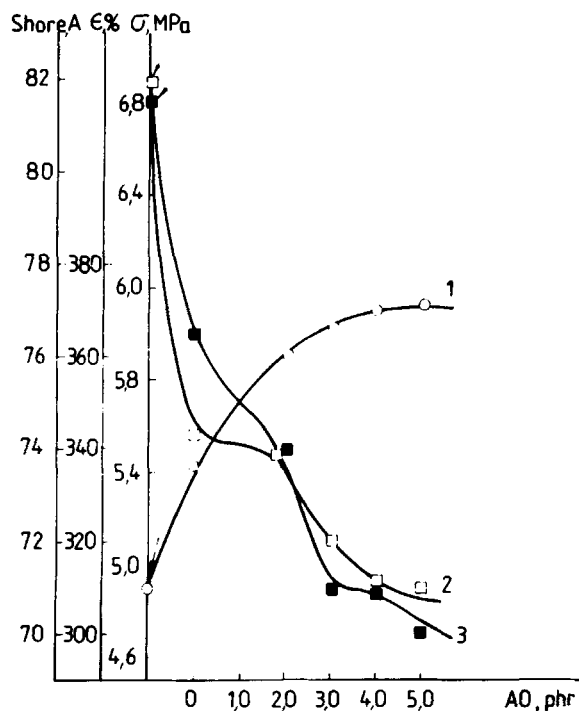


Figure 2 Influence of the ternary system Br-SA : Br-NSA : AO on the physicochemical parameters of EPM compositions for cable insulation. (1) (O) elongation, %; (2) (X) scleroscope hardness, shore A; (3) (●) tensile strength, MPa.

Taking into account the plasticizing effect of FR, the amount of plasticizer Sunpar 2280 was decreased from 10 to 8.6 phr in several EPM. As a result of the additive influence of both the plasticizer and FR, the tensile strength increased up to 6.0–6.4 MPa (Table II, blend 16), which approached the corresponding value of the basic composition.

The mechanical properties of the test compositions on aging (Table III) remained almost unchanged under the influence of FR. The values of the parameters corresponded to the specifications for ship cables.

The electrical characteristics of EPM test compositions were close to the basic composition, i.e., the specific volume resistance was $1.3 \times 10^{14} \Omega \text{ cm}^{-1}$ (Table III). Therefore, both the selected compositions and FR amounts are appropriate with respect to the corresponding standard requirements for specific volume resistance which was higher than $10^{13} \Omega \text{ cm}^{-1}$.

Influence of FR on the Flammability Characteristics and Thermal Degradation of EPM Compositions

Bromine-containing FR are used in the cases where the toxicological requirements for the presence of

hydrohalide in the gases evolved on burning are not high.

NHC polymers of polyolefin type are known to burn without coke formation. A considerable amount of volatile products are thus released; however, no hydrohalide is present, which favors extinguishing the flame.¹²

A thorough examination of the influence of FR on LOI, as well as flame resistance and the parameters of smoke evolution of EPM was also conducted in the present study.

Aluminum trihydrate up to 200 phr and zinc borate (10 phr) were used for increasing the flame resistance of the initial EPM, thus reaching LOI of 29%. LOI was found to increase from 29 to 33% with Br-SA or Br-NSA (10 phr) as well as with 2 : 1, 1 : 1, and 1 : 2 ratios at the same concentration (Table II). According to UL-94 standard all the compositions are of V-O class with the exception of composition 4 (Table II). No correlation between LOI (31%) and flame resistance was found with the latter composition.

On increasing the Br-SA concentration from 5 to 7.5 phr, LOI was found to increase from 29 to 33% (Fig. 3, curve 4). The ternary system Br-SA : Br-NSA : AO of a total concentration of 14 phr led to an LOI value of 34% (Fig. 4, curve 4). The additive performance of FR was observed with blends 14-16 (Table I). An interesting observation was also found with samples of some test compositions that did not burn when placed in the flame (Table II, blends 3, 9, 10, 16).

The specific influence of FR on the smoke evolution of some EPM samples was also studied. As might be expected, the organic FR added independently or in combination increased the smoke evolution, related to the basic composition (Table II). Characteristic dependences were observed on burning the samples as a function of FR concentration. Br-SA did not affect the smoke evolution process in the beginning of burning and hence D_s value at t_{16} was found to be high (Fig. 3, curve 3). With the advance of the process, Br-SA inhibited the smoke evolution, i.e., smoke transparency was higher than that of the basic composition. This observation corresponded to the low values of $D_{s_{max}}$ and $D_{s_{90\%}}$ at Br-SA concentration within 2-7.5 phr (Fig. 3, curves 1, 2). At concentrations higher than 7.5 phr the optical density of the smoke increased. Therefore the permissible concentration of Br-SA was 7.5 phr, corresponding to LOI of 33%.

The additive performance of FR in the ternary system resulted in a considerable decrease of smoke evolution as AO concentration increased (Fig. 4,

Table III Physicomechanical and Electrical Properties of Fire-Retardant EPR Compositions for Cable Insulation With Fire Retardants Containing Br-N-S

Characteristics	Blend No.														
	1	2	3	4	5	6	7	8	9	10	11	13	14	15	
Heat aging after 168 h at 135°C															
$k_{e,t}$ (%)	5.8	26.3	24.5	20.5	8.8	6.1	10.4	16.4	24.5	27.3	29.2	24.5	22.0	25.8	
$k_{e,b}$ (%)	10.2	23.4	28.5	16.1	10.4	11.3	18.2	21.3	28.5	28.5	27.5	28.5	26.2	27.1	
Specific volume resistivity, Ω cm ⁻¹	1.3×10^{14}	9.4×10^{14}	1.0×10^{14}	9.5×10^{13}	1.1×10^{14}	1.0×10^{14}	9.8×10^{13}	9.5×10^{13}	9.5×10^{13}	9.8×10^{13}	1.0×10^{14}	8.7×10^{13}	8.8×10^{13}	9.5×10^{13}	

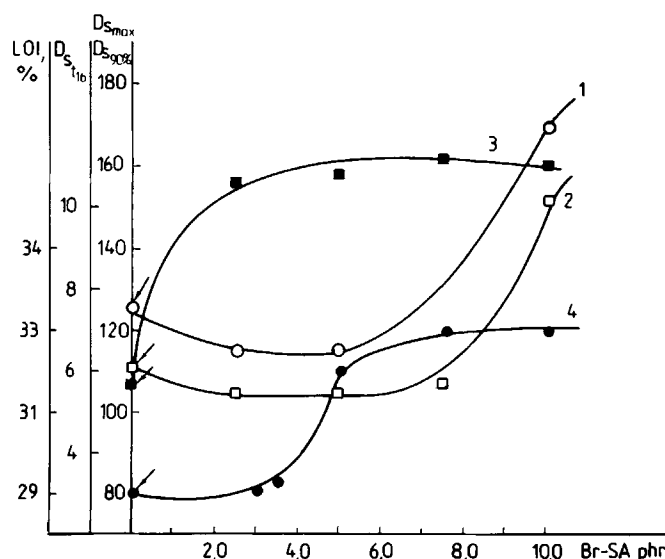


Figure 3 Change of the flammability characteristics of EPM compositions for cable insulation, depending on the concentration of fire retardant Br-SA. (1) (○) $D_{s,max}$; (2) (×) $D_{s,90\%}$; (3) (●) D_s at t_{16} ; (4) (◻) LOI, %.

curve 1, 2). Accordingly at 3–5 phr AO, $D_{s,max}$, and $D_{s,90\%}$ reached the corresponding values of the initial composition and LOI amounted to 34%. FR did not affect the smoke evolution at the beginning of burning in this case as well. Both Br-SA and the FR ternary system were found to exert a favorable influence on the times of reaching $D_{s,max}$ and $D_{s,90\%}$ (Fig. 5, curves 1–4).

An attempt was also made to study the total

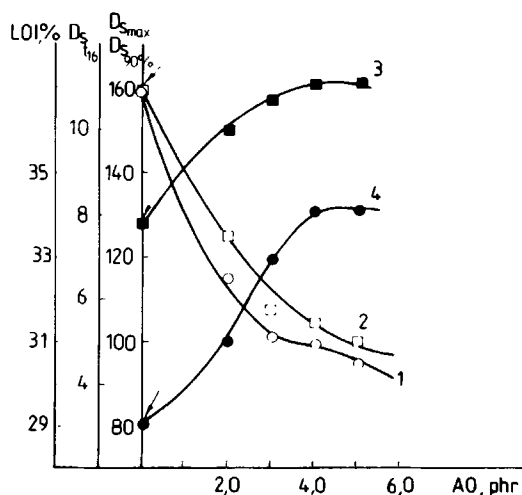


Figure 4 Change of the flammability characteristics of EPM compositions for cables insulation depending on the concentration of AO in ternary system Br-SA : Br-NSA : AO. (1) (○) $D_{s,max}$; (2) (×) $D_{s,90\%}$; (3) (●) D_s at t_{16} ; (4) (◻) LOI, %.

mechanism of fire retardancy in accordance with the characteristics of flammability described above. This purpose was achieved by examining the influence of FR on the thermal degradation, the latter being an initial and crucial stage of polymer combustion.

The thermal curves of organic FR (Br-NSA and Br-SA) showed that the corresponding intervals of gas evolution covered those of EPM (Fig. 6, curves 2, 4) and the maximum gas evolution preceded that of EPM particularly for Br-NSA. Keeping in mind the composition of FR studied that contains mainly $-\text{SO}_3\text{NH}_4$ and $-\text{NHSO}_3\text{NH}_4$ functional groups, it becomes clear that prior to EPM degradation the gas phase is saturated with nonflammable gases, such as NH_3 , SO_2 , HBr etc. Moreover Br-NSA and particularly Br-SA are known to absorb a significant amount of heat on their thermal degradation. Thus the corresponding endothermic effects observed indicated peaks at 340 and 470°C for Br-SA, which promoted the cooling of the system and its insulation from the air. An exothermic peak was observed on DTA curve of Br-NSA at 220°C, which was due to decomposition of nitrogroups and dehydrobromation. At the same time some foaming of Br-NSA was observed, which under the conditions of heating at properly selected FR quantitative ratios did promote the insulation of the system from air. These specific properties of FR promote the fire retardancy of EPM, taking into account that the initial EPM decomposes exothermally within the whole temperature range (Fig. 6, curve 1).

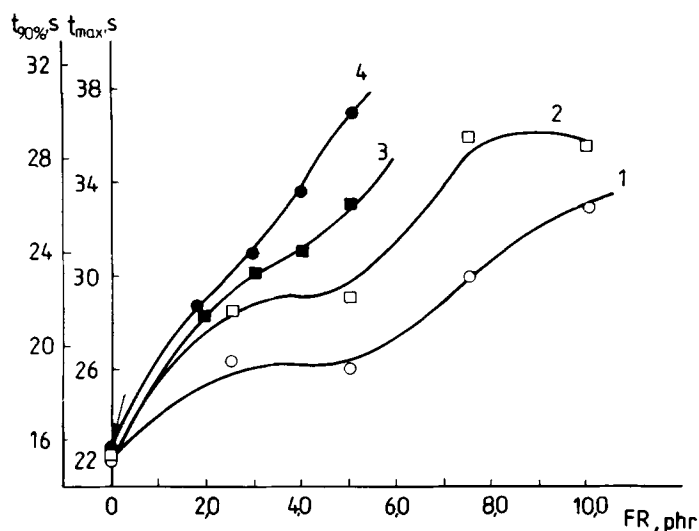


Figure 5 Change of the flammability characteristics of EPM compositions for cable insulation depending on the fire-retardant concentration. (1) (○) t_{\max} , Br-SA; (2) (×) $t_{90\%}$, Br-SA; (3) (●) t_{\max} , AO in ternary system; (4) (○) $t_{90\%}$, AO in ternary system FR.

The change of selected thermal characteristics of EPM, which might correlate with the corresponding combustion properties (e.g., LOI, smoke evolution, etc.) was also examined. For example Br-NSA independently present results in an increase of both the first exothermal effect (Fig. 7, curve 4) and gas evolution. On the other hand a decrease of the solid residue at $550^{\circ}\text{C}/R_{550^{\circ}}$ was observed. LOI was found to be lower than that obtained after addition of Br-SA. The first exothermal effect (S_{10X0}) in the presence of Br-SA was only three times weaker than that with Br-NSA and LOI increased accordingly (Fig. 7, curve 3, Table IV). The slight increase of the first effect with respect to the initial EPM is likely the result of the catalytic action of HBr on the primary oxidation reactions of EPM.¹³

All the characteristics of combustion in the presence of FR indicate an optimum on the corresponding curves. The first exothermal effect showed a minimum intensity and was shifted toward the higher temperatures, whereas the second one was totally absorbed in the endothermal decomposition of FR (Fig. 7, curve 5). $R_{550^{\circ}}$ in this case was found to be slightly higher than the rest of EPM containing FR; however, it still remained lower with respect to the initial EPM. This phenomenon might be expected since $(\text{NH}_4)_2\text{SO}_4$ does not promote a formation of solid residue.¹³

Therefore, the probable mechanisms of the fire-retardant action of the FR studied are associated with both the process occurring in the gas phase and heat transfer. These processes take place stepwise

within the whole temperature range of thermal degradation. The effect of fire retardancy is also believed to be associated with an additive performance of the ternary FR system. Accordingly the following mechanism might be suggested: C-Br chemical bonds break at 200°C and thus nonflammable HBr is eliminated. Simultaneously Br-NSA decomposition results in foaming, which preserves the polymer bulk from fast heating. Both bromide and sulphur-containing gases evolved as a result of the decomposition form together with AO nonflammable antimony-bromine and antimony-sulphur compounds.¹⁴ On the other hand the evolution of nonflammable NH_3 and SO_2 from Br-SA, Br-NSA, and $(\text{NH}_4)_2\text{SO}_4$ is accompanied by an absorption of heat for the system within a wide temperature range up to 450°C . Regardless of the great amount of gases evolved in the initial stage of thermal degradation (up to 350°) the effect of fire retardancy as a final result is apparent.

The recent studies on EPM compounds are associated with preparation of non-halogen-containing flame retardant compositions based on Dutral CTX 053 by an introduction of combination of mineral fillers,¹⁵ thus achieving good results.

The studies conducted are believed to favor an application of the new Br-N-S-containing FR as additives to AO in concentrations up to 10–14 phr. These additives ensure a good processability of EPM and act as plasticizers (ϵ , 370%, scleroscope hardness 70–71 Shore A). EPM have good electrical and thermal characteristics, LOI values are close to 33–

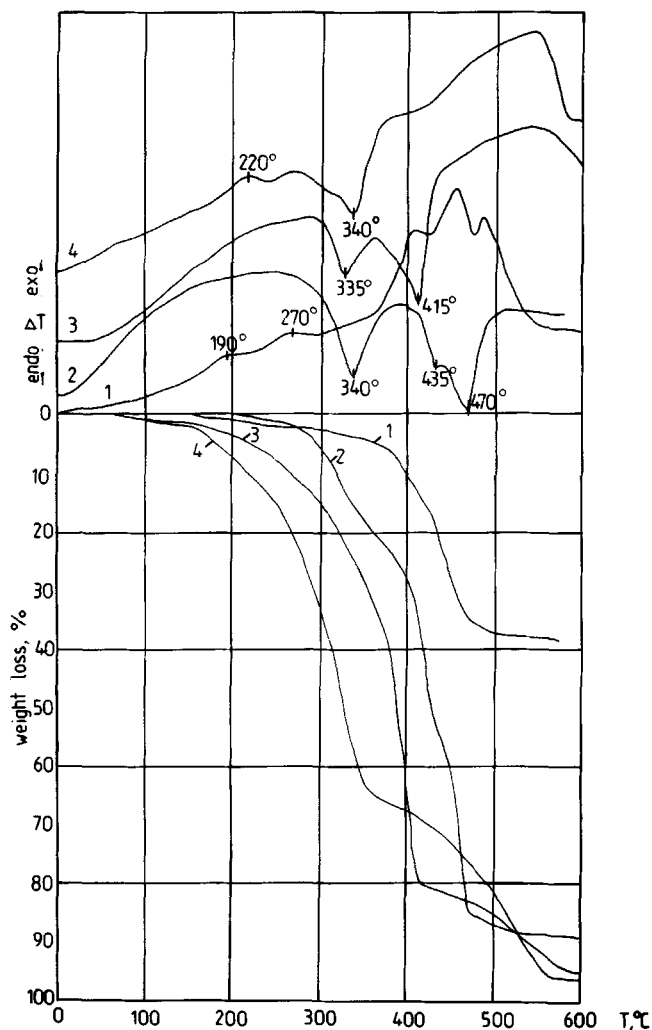


Figure 6 DTA and TG-curves of the initial EPM composition and FR used. (1) initial EPM composition; (2) Br-SA; (3) Br-SA : Br-NSA, 2 : 1; (4) Br-NSA.

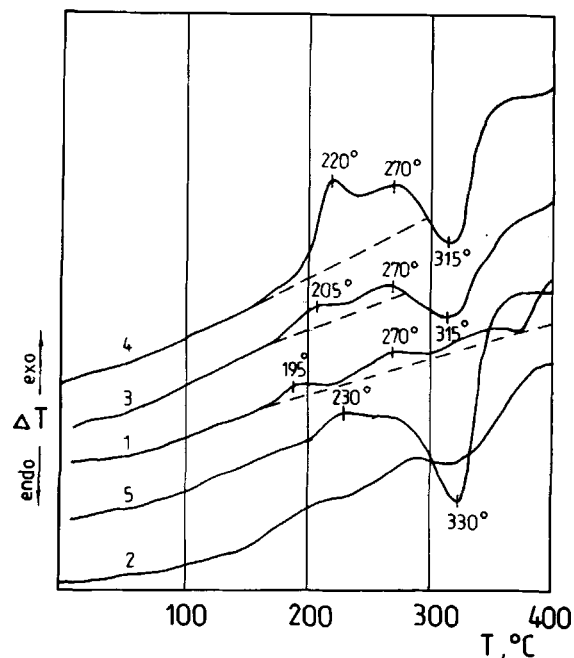


Figure 7 DTA and TG-curves of EPM compositions for cables insulation, containing fire retardants. (1) initial EPM composition; (2) AS, 10 phr; (3) Br-SA, 10 phr; (4) Br-NSA, 10 phr; (5) Br-SA : Br-NSA : AO, 6.6 : 3.4 : 4.0.

34% and $D_{s,max} = 100$, whereas the main part of some compositions studied previously¹⁵ has LOI at 30–32%.

CONCLUSIONS

1. Flame-retardant EPM compositions for ship cables insulation have been prepared by the introduction of a ternary system of fire re-

Table IV Thermal Characteristics and LOI of Flame-Retardant EPR Compositions for Cable Insulation With Fire Retardants Containing Br-N-S

Blend No.	FR	phr	LOI (%)	$T_{3\%destr.}$ (°C)	T_i^a (°C)	S_{Iexo} (mg)	ΔM_{350° (%)	R_{550° (%)
1	Initial composition		29	310	375	1.2	4.5	62.0
2	AS	10	31	260	280	1.3	19.0	48.0
3	Br-SA	10	33	250	275	2.2	20.0	45.0
5	Br-NSA	10	31	260	275	6.0	18.0	44.0
9	Br-SA	6.65						
	Br-NSA	3.35	32	265	275	2.8	19.0	46.0
14	Br-SA	6.65						
	Br-NSA	3.35	34	260	280	2.4	20.0	47.0
	AO	4.0						

^a T_i , beginning of an intensive destruction.

tardants with additive properties. This system consists of ammonium salt of bromo-sulphaminic acid, bromo-nitrosulphonic acid and antimony trioxide in a mass ratio of 6.6 : 3.4 : 4-5, respectively and it shows a diminished smoke evolution, LOI up to 34% etc., corresponding to V-O class.

2. Br-SA and Br-NSA in concentrations within 2-10 phr have a plasticizing effect on EPM compositions and do not change essentially the physicochemical parameters and specific volume resistance.

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