

The Effect of Sulfur- and Nitrogen-Containing Fire Retardants on Reducing the Flammability of a Polychloroprene Composition Used for Cables

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Synopsis

The influence of ammonium sulfamate (AS) independently or in a combination with antimony trioxide (AO) and chloroparaffin (ChP)-70% chlorine, on the oxygen index (OI) values as a flammability indicator, as well as on some physicommechanical and thermal characteristics of filled and unfilled compositions for cables based on chloroprene rubber (ChR), is studied here. It is found out that, at definite concentrations, AS and AO reveal an additive effect as fire retardants, decreasing the rate of heat release on heating. AS reveals a plasticizing effect as well.

INTRODUCTION

For their application range, fire retardants hold the third place among the additives in polymers, after fillers and plasticizers.¹ The main purpose of the research work and the elaborations of studies of fire retardants is to obtain highly effective products, reducing the flammability, with minimum aggravation of the physicommechanical properties of the polymers.

The research work on thermostable polymer materials when using halogen- and phosphorus-containing compounds are quite thorough in the literature. Nitrogen- and sulfur-containing organic compounds² and compounds containing both nitrogen and sulfur, are less studied for that purpose and are particularly prospective on account of their lower toxicity in the process of their formation as well as in the process of exploitation on the polymer composition.

Currently the following organic compounds, amines, amides, carbamates, ketimines, azocompounds, amino acids, and N-containing heterocycles,³ have found an application, being of nitrogen-containing fire retardants. Substituted aromatic sulfonic acids or their derivatives, halogen, amino, nitro, and other groups, are used as fire retardants in polyamides based on dicyandiamide and melamine,⁴ as well as sodium 2,5-dithiophene-3-sulfonate in a polyester composition.⁵

The following fire retardants are known: N,N' -(4-sulfophenyl)-pyromelalite diamides or their sulfonaphthyl derivatives,⁶ N -3(sodium salt of sulphopropyl)-lauramide, N -(3-potassium salt of sulfopropyl)-stearamide, etc.,⁷ used for polycarbonates. A 0.01–10 wt % sulfonat with formula RSO_3M or $(RSO_3)_2M'$ ⁸ in

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which M is an alkalimetal cation, M' an alkali-earth metal, R an aryl or substituted by a halogen or nitro group, which increases fire resistance of polyarylsulfones and polyarylsulfonates is used. 3,3'-Sulfonil bis-(6-hydroxybenzene sulphonic acid)⁹ is known as a fire retardant for polymers and other materials. Polychloroprene has long been known as an elastomer with superior flame-resistant characteristics.

McCormack¹⁰ has discussed profoundly the flame resistance of compositions of neoprene and Hypalon using the oxygen index method and investigating products of their pyrolysis and combustion. Johnson¹¹ has investigated the burning characteristics of polychloroprene composition and the correlation of oxygen index values with specific heat of combustion. Expandable composition¹² forming lightweight and fire-resistant foams comprises basic Al chloride, anionic surfactants, lauryl alkylsulfate esterammonium salt, chloroprene rubber latex crosslinking agents, and inorganic reinforcing fibers.

The aim of this work is to study the effect of the ammonium sulfamate as sulfur- and nitrogen-containing additives on reducing the flammability of an elastomeric composition for cables based on polychloroprene.

EXPERIMENTAL

The composition based on "Byprene C 210" chloroprene rubber, marked as ChR, contains the following parts by weight (wt %):

1. Polychloroprene—100
2. Fillers —90
3. Plasticizers —8
4. Curing group —5
5. Fire retardants —5–15

The blends were prepared by means of laboratory rollers sized 350–500 mm at temperatures of 50–60°C for a blending period of 45–50 min. The curing of the samples sized 100 × 100 × 3 mm was carried out at a temperature of 145°C and a pressure of 22 MPa for 40 min.

The physicomechanical properties were tested by means of a dynamometer type WPM-GDR. The oxygen index (OI) was determined by means of a DIG OXIMETER unit, according to the ASTM 2863-77 standard, with sample sizes 100 × 100 × 3 mm. The linear rate of combustion was determined by means of DIN 2278. The smoke evolution parameters were determined in a smoke camera with an optical cell. Heat aging of the samples was carried out in air at a temperature of 100°C for 168 h.

The thermal TG, DTG and DTA curves have been studied on a Q-derivatograph, supplied by MOM Company, Budapest, under the following conditions: heating rate, 10°C/min; initial weight of samples, 100 mg; medium, air (static). The ammonium sulfamate was synthesized according to our own methods.¹³

RESULT AND DISCUSSION

It is known that polychloroprenes belong to the group of self-extinguishing elastomers, i.e., their combustion discontinues at the removal of the combustion

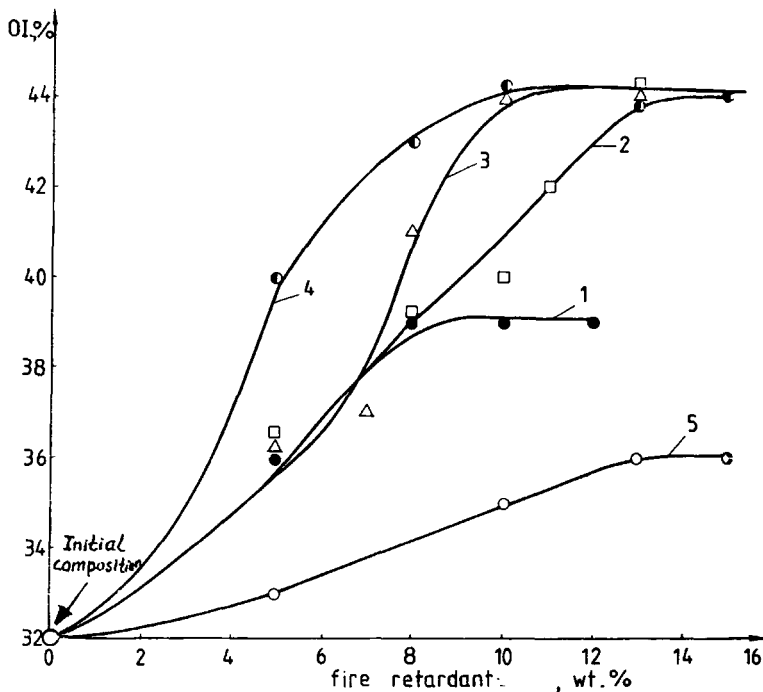


Fig. 1. Change of OI depending on the concentration of fire retardants in unfilled compositions of chloroprene rubber: (1) (●) AS; (2) (□) AS (8 wt %) by change of AO; (3) (△) AS (5 wt %) by change of AO; (4) (●) AO (5 wt %) by change of AS; (5) (○) ChP (5 wt %) by change of AS.

The second part of the experiments is directed to studying the effect of AS in a polychloroprene composition, containing fillers, plasticizers, and a curing group (Table II). In this case, the OI value increases from 32 to 38% (Fig. 2, curve 1), under the influence of AS (6–12 wt %) as well as it does in ChR compositions, containing only a curing group. It is ascertained that, at 12 wt % concentration, AS leads to a certain decrease in the physicomechanical indices (Table II, blend 8). At the introduction of AO (from 4 to 10 wt %) in filled compositions (blends 1, 3, and 4), OI rapidly increases from 32 to 42% (Fig. 2, curve 2).

After the additive effect of both fire retardants (AS and AO) is established, compositions with different AS and AO contents are prepared in order to increase the stability of combustion of ChR (Table II, blends 9–12). At 1 : 1 ratio, with fire retardants gradually increasing their quantity from 3 to 6 wt %, OI increases up to 45% (Fig. 2, curve 3) and the tensile strength decreases from 11.9 (for the initial composition) to 7.6 MPa, and the elongation changes from 800 to 720%. The relative worsening of physicomechanical properties can be explained with the additional plasticizing effect of AS on ChR. After removing the plasticizer (epoxyweichmacher-s), when AS content in the ChR composition is up to 10 wt % (blend N14), the tensile strength increases up to 13 MPa and this value is higher than that of the initial blend (12 MPa). These results show that AS is not only a fire retardant, but also exhibits a plasticizing effect, which would result in a considerable reduction of the price of the composition. It is

TABLE II
Effect of the Following Fire Retardants: AS in Combinations with AO and ChP on the Physicomechanical Indices of CHR Compositions

No.	Fire retardants (wt %), 100 wt % elastomer	Blend no.															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	AS	—	—	—	—	6	8	10	12	3	4	5	6	—	10	6	6
2	AO	8	—	4	10	—	—	—	—	3	4	5	6	—	—	—	4
3	"Perechlorine",—72% Cl (ChP)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	4	4
4	Plasticizer (wt %)	5	5	5	5	5	5	5	5	5	5	5	5	—	—	5	5
5	Tensile strength (MPa)	12.0	11.9	12.6	12.1	11.6	12.0	11.0	9.6	8.2	7.4	6.4	7.6	13.2	13.0	6.6	6.5
6	Elongation (%)	800	820	800	805	732	730	716	645	785	760	730	720	676	667	775	780
7	Retention of tensile strength after aging (%) ^a	96.2	96.8	97.2	96.5	96.3	97	96.7	96.3	97.2	96.9	97.5	96.6	97.8	97.3	96.6	96.3
8	Retention of elongation after aging (%) ^a	84.7	85.6	85	84.2	83.8	84.5	84.9	85	85.8	84.9	85.2	84.4	86.5	86.3	84.8	84.2

^a Aging at 100°C, for 168 h.

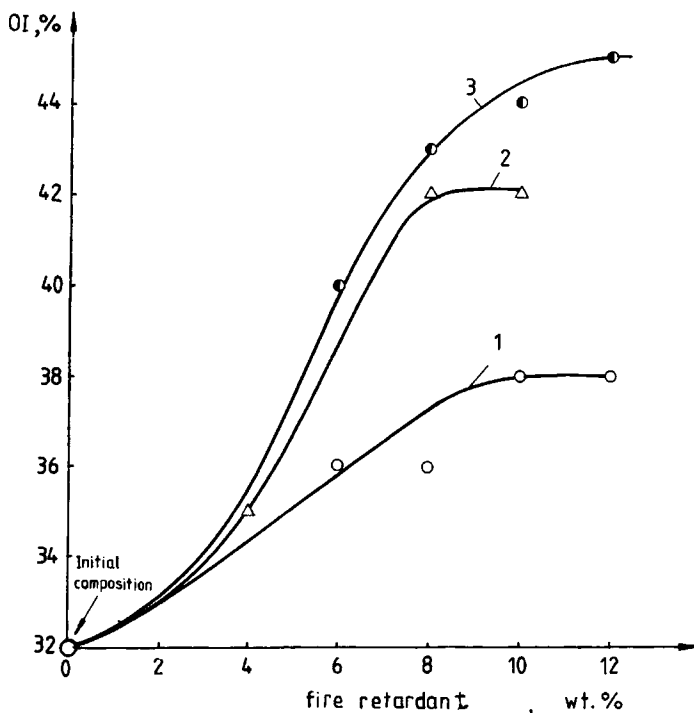


Fig. 2. Change of OI depending on the concentration of fire retardants in filled compositions of chloroprene rubber: (1)(○) AS; (2)(△) AO; (3)(●) AS : AO = 1 : 1 (wt %).

known from the literature that methylesters of oligomer sulfonic acids¹⁴ are used as plasticizers in poly(vinyl chloride) resins.

After finding the optimal AS : AO ratios in filled compositions (blends 11 and 12), ChP (4 wt %) is added to a blend containing only 6 wt % AS and to a blend containing AS and AO in a 6 : 4 wt % ratio (Table II, blends 15 and 16). Furthermore, OI decreases in comparison with optimal compositions.

The heat aging of ChR that is carried out at 100°C, for 168 h, in the presence of AS or in a combination of both AS and AO, does not result in worsening of the stability of the cured samples. After aging, the tensile strength and elongation values remain at 96.3–97.8% and 83.8–86.5% of the initial values, respectively, so that they do not differ essentially from those of the initial blend (Table II).

Besides the OI as a characteristic of the burning of ChR compositions, the linear velocity of burning (Table III), the heat of burning and the smoke release parameters (Table IV) have also been studied as such. Table IV shows that AS and AO increase the flammability group of ChR from third to fourth. The influence of AS is more favorable for the decrease of the burnt length and the influence of AO for the decrease of the extinction time in filled and unfilled compositions.

The additive effect of both fillers is observed in all compositions especially in composition 11, in which the extinction time falls from 67 s (in the initial composition) to 56 s and the burnt length decreases from 15 to 10 mm. The

TABLE III
Influence of the Fire Retardants, Ammonium Sulfamate (AS) and Antimony Trioxide (AO),
on the Linear Velocity of Burning of ChR Compositions

No.	Blend no. ^a	Fire retardants (wt %), 100 wt % elastomer		Extinction time (S)	Length burnt (mm)	Flammability group	Peculiarities of burning
		AO	SA				
0 ^b	0	—	—	67	15	III	Solitary drop release
1	2	5	—	62	12	III	They burn with a smoky flame with no drop release
2	3	—	5	64	11	III	
3	9	2	5	60	12	IV	
4	11	3	5	55	10	IV	
5	14	5	5	55	9	IV	
6	15	5	8	57	8	IV	
7	0	—	—	61	12	III	Slightly smoky flame with no drop release
8	7	—	10	60	11	IV	
9	8'	5	—	60	15	IV	
10	11	5	5	56	10	IV	

^a Out of five parallel samples.

^b 0-6 unfilled compositions; 7-10 filled compositions.

influence of the fillers in the filled compositions 7-10 is not clearly expressed. It is known that OI depends considerably on the tendency of the polymeric materials to form drops on heating. Our investigations on ChR have shown that the latter can be characterized by OI values, since they do not melt by means of dripping (excluding the initial blend). These conclusions of ours correspond to McCormack's investigations.¹⁰

TABLE IV
Influence of the Fire Retardants, Ammonium Sulfamate (AS) and Antimony Trioxide (AO), on the Oxygen Index (OI), the Heat of Burning, and the Smoke Release of ChR Compositions

Blend no.	Fire retardants (wt %), 100 wt % elastomer		OI (%)	Heat of burning (kcal/mol)	Smoke release ^a			
	AO	SA			$D_{S_{max}}$	R	CST	T_{16} (s)
0	—	—	32	4230	195	180	473	60
1	8	—	42	3670	125	96	341	92
7	—	10	38	3600	86	77	290	105
11'	8	5	44	3420	88	75	295	115

^a $D_{S_{max}}$ = maximum optical density; R = velocity of the smoke's distribution (%/min); CST = coefficient of smoke's transparency; T_{16} = time to reach $D_s = 16$ min.

TABLE V
Thermal Characteristics and OI Values of Unfilled ChR Compositions,
Containing Fire Retardants and a Curing Group

Blend no. from Table I	Sample composition (wt %)	$T_{10\%}$ (°C)	T_{\max} (°C)	$T_{50\%}$ (°C)	S_{exo} (cm ²)	ΔS_{exo} (%) of the initial composition	RB _{700°} (%)	OI (%)
1	ChR (100)	305	340	410	29.1	—	0	32
2	ChR + AO (5)	285	350	410	29.8	+2.0	4	40
5	ChR + AS (10)	310	350	420	26.0	-11.0	5	39
17	ChR + AS (10) + AO (5)	305	350	410	21.9	-25.0	1	44
18	ChR + AS (10) + AO (5) + ChP (5)	270	340	405	17.2	-41.0	3	43

Table V shows that the introduction of AS and AO leads to an increase of the OI and a decrease in the heat of burning. AO raises the OI more than AS does, but, as far as the heat of burning is concerned, their influence is equal. The use of both fire retardants makes better the smoke release characteristics of the ChR compositions. The comparison between the effects of AS and AO shows that AS has a more favorable effect on $D_{S_{\max}}$, R , CST, and T_{16} . The additive effect of both fillers not only on the increase of the OI, but also on the decrease of the heat of burning can be observed in composition 11' too. Composition 7 containing AS is equal to composition 11' concerning the smoke release characteristics $D_{S_{\max}}$, R , CST, and T_{16} .

The effect of AS on ChR is studied by means of the combined dynamic thermal analysis of some unfilled compositions, containing only AS or AO, or a combination of them with ChP (Table I, blends 1, 2, 5, 17, and 18). An attempt is made to enrich the concept of effect of the fire retardants, studied here on ChR, by comparison of thermal analyses data with OI values (Table V, Figs. 3 and 4). The TG, DTG, and DTA thermal curves of the initial materials are recorded first.

Under the chosen conditions of thermal treatment, the decomposition of the initial polychloroprene continues until total combustion in the temperature interval 290–650°C (Fig. 3). The summary thermal effects, at that, are highly exothermal, accompanied by a weight loss and a maximum gas release velocity at 340°C.

The two-phase decomposition of the additive AS in the temperature interval 260–450°C can be observed from its thermal curves (Fig. 3), registered under the same conditions. This is the temperature interval in which the greater part of ChR decomposes. The AS decomposition, however, is accompanied by quite intensive heat consumption, which would promote the cooling of the system under the combustion conditions.

Some thermal characteristics of chosen ChR compositions, containing the fire retardants studied, are presented in Table V. As it can be seen in the table, the additive AS in the composition does not worsen the initial thermostability (at 10% decomposition) of the composition, but it even raises it, while, in the presence of both AO and ChP, the thermostability may decrease essentially. The temperatures of 50% destruction and maximum decomposition velocity change insignificantly, but in the same direction. AS exerts some positive effect on the formation of coke remains (RC) on heating up to 700°C. The relatively

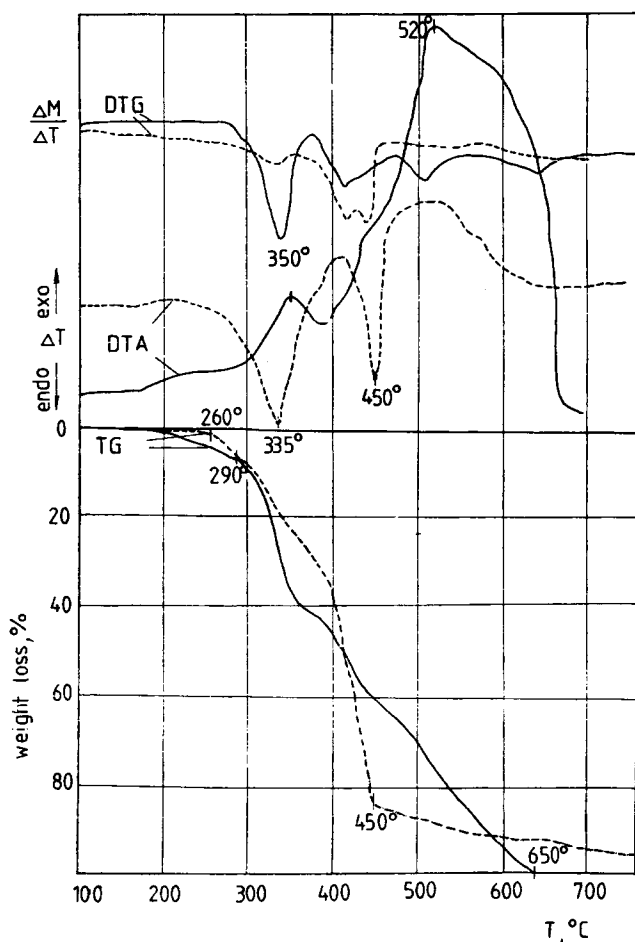


Fig. 3. DTA, TG, and DTG plots of chloroprene rubber (—) and AS (---); rate of heating 10°C/min.

low percentage of RC in the compositions is probably due to both the aliphatic character of the main elastomer and the additives used.

The calculations of the total thermal balance of the system, on the basis of thermal effects from DTA curves (Fig. 4), ascertain that, in the presence of AS, the heat release during thermooxidizing destruction of the system elastomer–fire retardant decreases, which is combined with heightened thermostability in compositions 2 and 3 and with maximum increase of OI, in composition 3. This composition is most probably close to the optimal one. It can also be seen from Table V that AO is not able to influence by itself either the increase of thermostability or the decrease of heat release of ChR. The adding of ChP leads to a considerable decrease of heat release at the expense of a decrease of thermostability. It can be said that the mechanism of action of both fire retardants (AS and AO) is complicated and depends on their nature and the ChR composition.

It is known that in air medium the thermochemical decomposition of ChR involves dehydrochlorination reactions. During the decomposition of AS, con-

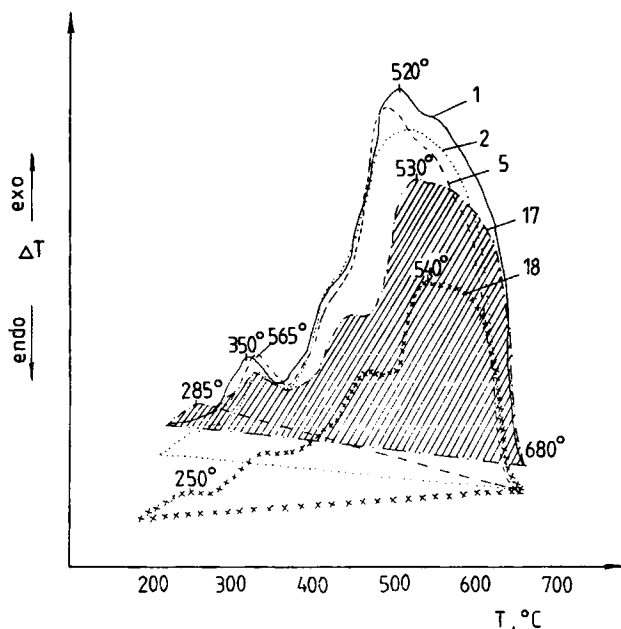


Fig. 4. DTA: plots of unfilled compositions with blend nos. 1, 2, 5, 17, and 18 (Table V).

taining sulfo and sulfamic groups (as ammonium salts), ammonia is generated, and it interacts with the hydrogen chloride. Ammonia exhibits also a self-dependent flame-resisting action, as well as halogens, sulfur dioxide, carbon dioxide, and nitrogen.² On the other hand, during thermal decomposition of AS in the presence of AO, sulfur-containing compounds of antimony are probably formed and they are easily decomposed, forming a melt of antimony oxides on the surface of the burning material. Similar reactions are observed in polycarbonate compositions, stabilized with polymer sulphone.²

These assumptions may, to a certain degree, account for the additive effect of the flame-retarding action of AS and AO in ChR. AS is a source of gases, ammonia, sulfur dioxide, etc., and the gas release at 320–370°C (Fig. 3) is connected with heat consumption; therefore, AS is an effective additive in ChR.

The initiation of ChP into both fire retardants in ChR does not result in a beneficial effect, according to OI values. In the presence of ChP, however, a decrease of heat release during ChR combustion is achieved. It is probably due to the synthesizing of antimony trichloride and antimony oxychloride and the generating of AO from them in the combustion process.

CONCLUSIONS

1. It is found that, in the presence of 8–10 wt % ammonium sulfamate, in combination with 3–5 wt % diantimony trioxide, in unfilled cable compositions based on chloroprene rubber, the oxygen index increases from 32 to 44%, and this increase is combined with an increase of thermostability and a decrease of heat release on heating. In filled compositions,

prepared on the same basis the effective concentrations of the fire retardants mentioned above should be decreased in order to reach the same oxygen index values.

2. The total mechanism of the flame-retarding effect of sulfur- and nitrogen-containing additives in chloroprene compositions is mainly brought to the suppression of heat release of the system on heating.
3. The sulfur- and nitrogen-containing fire retardants under study exhibit a plasticizing effect, which can supersede the epoxyweichmacher-s plasticizer, retaining the strength properties of the compositions.
4. In the presence of chloroparaffin (70% chlorine) in the polychloroprene compositions with sulfur- and nitrogen-containing additives and antimony trioxide, the heat release decreases but the oxygen index does not increase.

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