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INVESTIGATIONS OF THERMAL BEHAVIOUR AND FLAMMABILITY OF ANTIPYRENE-CONTAINING POLYCHLOROPRENE COMPOSITIONS

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The effects of ammonium salt of sulphaminic acid (AS), introduced as antipyrene in polychloroprene compositions based on 'Byprene-210' in combination with antimony trioxide (AO) and chloroparaffin (ChP) are studied by means of a combined dynamic thermal analysis. After successive examination of the obtained thermal and flammability characteristics, it is assumed that AS and AO exhibit additive influence. The optimal range of concentrations of AS for which it is possible to substitute AO in the investigated polychloroprene compositions is established.

It is known that filled vulcanizates of chloroprene rubber belong to the group of the self-extinguishing compositions. Nevertheless, they should meet a number of additional requirements concerning smoke release, etc.

For reducing the flammability of chlorine-containing polymers releasing hydrogen chloride on heating, antimony trioxide (AO) is used as an antipyrene, because the hydrogen chloride/AO system exhibits a synergetic fire-retardation effect [1, 2].

The use of AO, however, has some disadvantages, such as raising the cost of the compositions, making worse the operational and ecological characteristics. These reasons necessitate the creation of fire-protected polychloroprene compositions (PChC) containing organic antipyrenes, which do not aggravate the operational characteristics and are easy to process and ecologically safe. Such a combination of properties can be found in some nitrogen-sulphur-containing organic compounds [3], having low toxicity both in the process of formation and in the process of exploitation of the polymer compositions.

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In one of our previous papers [4] we offered investigations on the influence of ammonium salt of sulphaminic acid (AS), obtained by us [5] in combination with AO and chloroparaffin, on the physicomechanical characteristics of PChC on the base of 'Byprene-2IO' produced for conveying belts. It was shown that in concentrations from 3 to 12 wt% AS does not change the basic strength characteristics of PChC beyond the practical standard, it is easy to dose and ensures good processability. AS was found to possess antipyrene qualities for the investigated compositions. The results obtained did not, however, make clear the mechanism of influence of AS on the processes taking place in the system on heating, i.e. what is the cause for its fire-retarding effect.

Valuable information on the total mechanisms of operation of antipyrenes can be obtained by studying the thermal behaviour of the polymer systems in a broad temperature interval. Such investigations are based on the correlations found between some characteristics of flammability, on one hand, and of thermal destruction of polymers, on the other, and they are of great help for marking the effect of the antipyrenes [6, 7].

The aim of the present work is to study the influence of organic ammonium salt of sulphaminic acid (AS) in combination with AO and chloroparaffin (ChP) on the thermal behaviour and flammability of PChC, produced for conveying belts.

Experimental

The organic antipyrene AS was obtained in a reactor having a capacity of 500 l by nitration of isoprene rubber SKI-3 with concentrated nitric acid at 60°C and a following sulphonation of the nitrooligomer with ammonium hydrogen sulphite at 60°–70°C and *pH* 6–7 in water solution. AS was obtained with reproducible characteristics: content of N = 16.3%, S = 23% and initial decomposition temperature –185°C.

An initial composition (IC), containing 7.4 wt.% AO and 5 wt.% ChP, was prepared and compared to three series of PChC with varying antipyrene additives: AS, AO, ChP (Table 1). PChC were prepared on a laboratory Banbury mixer with a capacity of 2.5 l, cured on an electrical press at a temperature of 160°C and steam pressure of 150 at at a curing optimum measured on a 'Monsanto' rheometer. The industrial PChC were prepared on a Banbury mixer with a capacity of 150 l.

The thermal characteristics of the three series of PChC and the IC were studied under the same conditions, the oxygen index (OI), the coefficients of

Table 1 Thermal characteristics of polychloroprene compositions (PChC), based on 'Bypren-210', containing ammonium salt of sulfaminic acid (AS), antimony oxide (AO) and chlorparaffin (ChP)

PChC	AS % from total AP*	AS	AO	ChP	T_o	T_{10}	T_{50}	CR_{700}	T_1	T_2	T_3	S_{exo}	Change of S_{exo} /%
N°	content		wt %			°C		%		°C		cm^2	compared to IC
IC	0	0	7.4	5.0	210	300	510	28.0	320	500	590	71.5	–
1	30	3.5	3.5	5.0	215	300	560	32.0	310	495	610	55.0	– 23.0
	50	6.0	3.5	2.5	220	310	550	31.0	340	495	600	54.0	– 24.5
	75	9.0	1.25	1.75	210	310	560	33.0	340	490	600	51.0	– 28.5
	85	10.5	0.88	0.62	220	320	540	33.0	350	495	605	45.0	– 37.0
2	50	3.0	1.75	1.25	200	290	550	29.5	315	470	580	72.0	+ 0.5
	67	6.0	1.75	1.25	210	300	510	27.0	330	470	580	70.5	– 1.0
	75	9.0	1.75	1.25	200	300	540	29.0	330	490	590	60.0	– 15.0
	80	12.0	1.75	1.25	200	300	550	29.5	340	500	590	50.0	– 23.0
3	29	1.75	3.0	1.25	210	300	560	33.0	320	490	590	63.0	– 12.0
	19	1.75	6.0	1.25	220	300	550	34.5	320	480	590	64.0	– 10.5
	15	1.75	9.0	1.25	210	305	530	29.0	320	490	590	64.0	– 10.5
	12	1.75	12.0	1.25	210	280	490	26.5	310	480	570	58.0	– 19.0

* antipyrene

smoke release and rate of combustion and the flammability group were determined.

The thermal studies were carried out on an OD-102 derivatograph, MOM-Budapest in air medium (static) in the temperature range of 20 to 900°C at a heating rate of 10 deg/min and weight of samples 100±0.5 mg. The total areas of the DTA curves (S_{exo}) which may be used as relative characteristic for comparing the total heat release on heating samples with the same weight and studied under the same conditions, were measured by graphical integration. The coke remains (CR_{700}) were determined by the thermogravimetric curves (TG) at 700°C in wt.% of the initial sample.

The oxygen indices were determined according to the ASTM 2867–77 standard in % O_2, and the total optical density of smoke (D_w) – according to established methods [8]. The rate of combustion was determined according to the ISO 340:1982 standard, corresponding to the DIN 22103 standard. The flammability group was determined by means of a horizontal method of 'spreading the burned length', the sample size being 100×100×3 mm.

Results and discussion

Thermal characteristics

The DTA and TG curves of the organic antipyrene AS on Fig. 1 show that its thermal destruction proceeds in two stages in a broad temperature interval (from 200° to 500°C) with absorption of heat. The first endothermic effect with an extremum at 360°C and a corresponding weight loss is in connection mainly with the release of ammonia, and the second with a maximum at 460°C, with the release of sulphur dioxide. Judging from the character of the thermal destruction of AS, it is clear that in the above-mentioned temperature interval while decomposing AS absorbs a considerable amount of heat, which helps to cool down the system. At the same time AS releases incombustible gases which isolate the surface of PChC from the oxygen in the air.

The main thermal destruction of chloroprene rubbers in general and of the examined IC on the base of 'Byprene-210' (Fig. 1, curve 2), in particular, also takes place in the temperature interval of 200° to 500°C, but in contrast to AS on heating the IC sample releases a great amount of heat. These preliminary data on the behaviour of both the IC and AS on heating are in keeping with some experimentally established requirements for the effectiveness of the antipyrene in a polymer-antipyrene system [2]. Since this effectiveness is related chiefly to the influence of the antipyrene on the retardation of weight and/or heat release, the tendency to form coke remains after heating, etc., the thermal analysis in a dynamic regime gives the opportunity to establish these influences.

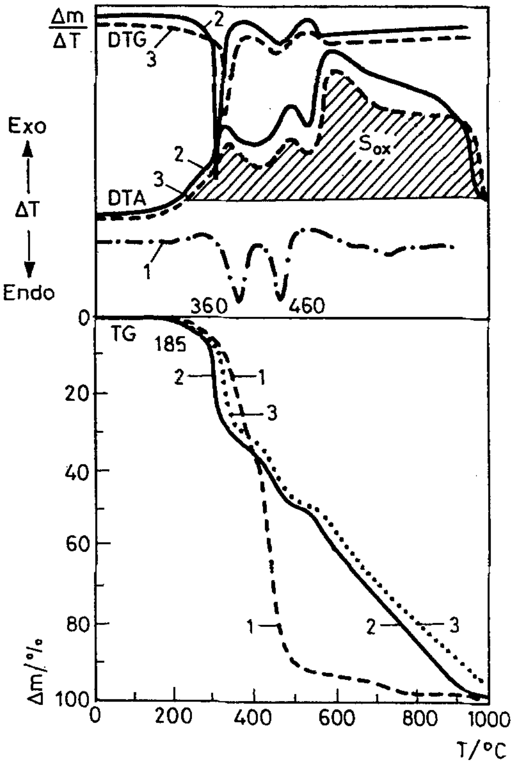

Fig. 1 DTA, TG and DTG curves of: 1. —— AS; 2.—— IC; 3. ···· polychloroprene composition (PChC), containing 6 wt% AS, 3.5 wt % AO and 2.5 wt % ChP(PChC I)

Comparing the thermal curves of the IC with those of the other PChC with different antipyrene contents, some changes in the thermal characteristics related to the typical effects of antipyrenes can be observed. From the thermal curves (Fig. 1) of the IC and PChC, in which 50% AO is substituted by AS, it can be established that there is a retardation of weight release (TG curves 2 and 3) and a considerable decrease of heat release shown by the total area of exothermal effects – S_{exo} (DTA curves 2 and 3). To some extent there is an increase in the tendency to form CR. Such changes are observed in each of the investigated compositions, though to a different degree (Table 1).

The influence of different concentrations of AS in combination with AO and ChP on the progress of the thermodestructive reactions in the whole studied temperature range can be evaluated using the thermal characteristics of the three compositions and the IC shown in Table 1. The temperatures of the initial weight loss (T_o) and the temperatures of 10% decomposition (T_{10}) in most cases do not change or shift slightly towards higher temperatures, while the temperatures of 50% decomposition (T_{50}) increase to a larger extent compared to those of the IC. This fact shows that there is a slight retardation of the decomposition reactions in the solid phase, which reflects of the quantity of solid residue after heating under these conditions (Table 1). In most of the compositions CR_{700} has a larger percentage than that of the IC, this tendency being expressed at its best for compositions 1.

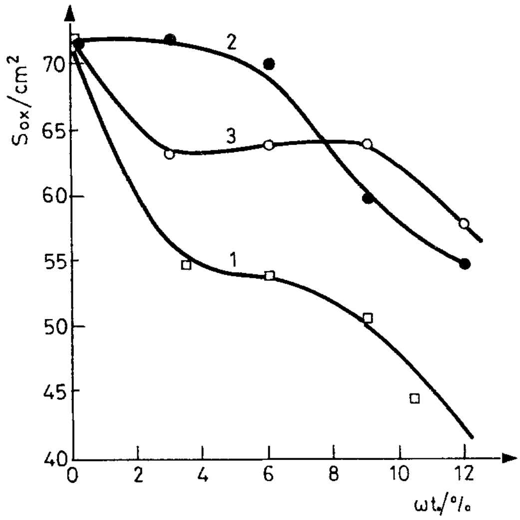

Fig. 2 Change of S_{exo}(cm^2) of polychloroprene composition (PChC), depending on AS content (PChC 1 and 2) and AO (PChC 3): 1. -□; 2. – O; 3. – O

The antipyrene content (Table 1) influences more considerably the temperature of the first exothermic effect (T_1), which is in connection with the flammability tendency of polymers [9–15]. For most of the studied PChC, T_1 shifts towards higher temperatures, especially for compositions 1 and 2 which have a higher AS content, while for compositions 3 T_1 does not change its position on the temperature scale. AS has a considerable influence on the decrease of the total heat release on heating (Fig. 2) for the compositions studied. This effect is the largest for composition 1, probably because of the increase of AS concentration compared to AO and ChP, where S_{exo} decreases to 45 cm^2 (Fig. 2, curve 1).

For composition 2, because of the low AS content (up to 3 wt.%) and the low AO and ChP contents, the heat release of the system does not change considerably. In this composition the influence of AS is displayed only after 70% substitution with it at a total antipyrene content of 12 wt.%. Curve 3 (Fig. 2) shows that unlike AS AO cannot cause considerable changes in the total heat release, even when its relative content is increased over 80% of the total antipyrene content.

The thermal analyses data unequivocally show that the antipyrene AS in suitable combinations with AO and ChP influences the thermal behaviour of PChC towards retardation of the heat and weight release processes, which may be related to the behaviour of PChC under the conditions of burning.

Flammability and characteristics

The dependences of the total optical density of smoke (D_w) on the AS (compositions 1 and 2) and AO (composition 3) concentration display a reduction of smoke release for all PChC compared to the IC (Fig. 3). This is a good characteristic feature of the investigated PChC, because in a number of cases the introduction of antipyrenes causes an increase of the total

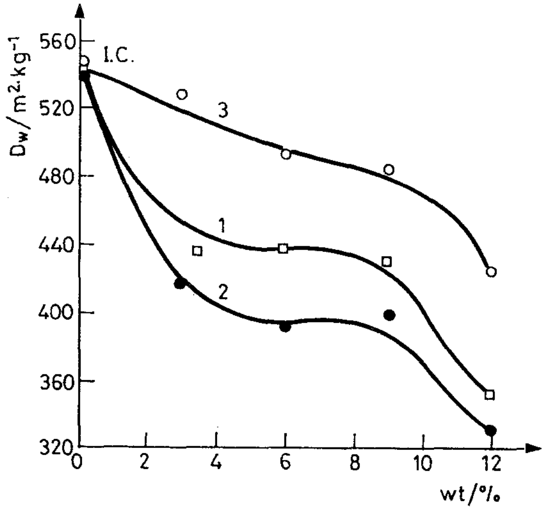

Fig. 3 Change of smoke release coefficient of polychloroprene composition(PChC), depending on the AS content: 1. - □ ; 2. - O; 3. - O

Table 2 Flammability characteristics of polychloroprene compositions (PChC), based on 'Byprene – 210', containing ammonium salt of sulphaminic acid (AS), antimony oxide (AO) and chlorparaffin (ChP)

PChC N°	AS, % from total AP content	AS	AO	ChP	Extinction time/	Lenght burnt/	Rate of combustion/	OI/
			wt.%		s	mm	s	% O2
IC	0	0	7.4	5	60	9	9	39.5
1	30	3.5	3.5	5	60	7	9	38.5
	50	6.0	3.5	2.5	60	5	9.5	37.5
	75	9.0	1.25	1.75	60	10	15.0	35.0
	85	10.5	0.88	0.62	60	11	17.5	34.5
2	50	3.0	1.75	1.25	59	9	21.0	32.5
	67	6.0	1.75	1.25	57	7	15.0	33.0
	75	9.0	1.75	1.25	56	7	12.0	33.0
	80	12.0	1.75	1.25	54	6	9.0	34.0
3	29	1.75	3.0	1.25	62	11	14.0	32.0
	19	1.75	6.0	1.25	61	11	14.0	33.0
	15	1.75	9.0	1.25	59	9	15.0	34.0
	12	1.75	12.0	1.25	59	8	14.0	34.5

smoke release in the polymer systems [2], despite the fact that the other incombustibility indices are good.

It was established that with the increase of the AS content (compositions 1 and 2), the reduction of smoke release is more considerable (D_w decreases from 540 m^2/kg to 330–350 m^2/kg) than with the increase of the relative content of AO (composition 3).

The total antipyrene content in the compositions also exhorts some influence. For example, for composition 2 (Fig. 3, curve 2) the smoke release is the lowest, probably because together with the higher AS content, the amount of the other antipyrenes is lower.

Table 2 offers the following indices: flammability group, determined by the length burnt, in mm and extinction time, sec. The influence of AS on these indices is positive for concentrations of 3.5 and 6.0 wt.% when the length burnt is 7 and 5 mm.

The solitary influence of AS is particularly obvious for composition 2, where with the increase of AS concentration from 3 to 12 wt.%, the length burnt, as well as the extinction time, gradually decrease. AO (composition 3) exhorts weaker positive influence on the investigated indices in comparison with SA.

All samples from compositions 1, 2 and 3 burn without drop release, which together with the values for the extinction time and length burnt, corresponds to flammability group IV.

With the change of OI and the rate of combustion an analogy can be established (Table 2). With the increase of AS concentration from 3.5 to 9 wt.%, they do not change significantly compared to the IC. These results show that a substitution of up to 70% AO with SA (composition 1) would be successful.

On the basis of these investigations it may be concluded that the antipyrene AS introduced in the PChC together with AO and ChP exhorts a definitely retarding effect chiefly by cooling the system as a result of its endothermic decomposition. What is more, with the increase of AS content, a decrease in the smoke release in the PChC is observed, probably as a result of the reaction of hydrogen chloride and the ammonia, generated by AS. On the other hand, it is known [2] that ammonia as a non-burning gas has a fire-resistant effect of its own. The results obtained show that the fire retarding effect of AS is best manifested in combination with AO, which suggests an additive action of the two antipyrenes. Probably antimonylsulphur compounds are formed from the two antipyrenes, and then easily decompose forming a molt of antimony oxides on the surface of the burning material [2].

The effect of ChP in this case is not so strong and is seen mainly in the processing of PChC.

Conclusions

It was established that ammonium salt of sulphaminic acid (AS) introduced as an antipyrene in polychloroprene compositions based on 'Byprene-210' in combination with antimony trioxide (AO) and chloroparaffin (ChP) effects the thermal behaviour and flammability characteristics of the system as follows:

The total heat release on heating is reduced; the first exothermic effect is shifted towards higher temperatures during decomposition; the total smoke release is reduced, the oxygen index and the rate of combustion increase; optimal influence in the compositions is observes for AS content from 3.5 to 9.0 wt.%; AS can partially substitute antimony trioxide (AO) from 50 to 70% in the studied polychloroprene compositions, in which case not only the flammability characteristics are preserved, but also the heat and smoke release are reduced. Such compositions are more easily processed, ecologically safe and available; it is assumed that in the investigated compositions AS and AO probably exhibit an additive effect.

References

1 I. W. Lyons, The chemistry and uses of fire retardants, Wiley Interscience, New York 1970.
2 V. I. Kodolov, Flame Retardants of Polymeric materials, Chem., Moscow 1980, p. 266.
3 L. P. Gustova and G. R. Masina, Poluthenie ognestojkich isdelij is Latexa, CNIITE neftechim Moscow, No. 1, 1975.
4 M. Karaivanova, D. Bajdarov, I. Patov and I. Bajdarova, Wissenschaftliche Zeitschrift T. H. Leuna, Merseburg (in press).
5 Bg. Pat. 39549 (1985).
6 D. W. Van Krevelen, Advances in the chemistry of Therm. Stable Polym., 1977, pp. 119, 2659.
7 P. R. Jounson, J. Appl. Polym. Sci., 18 (1974) 491.
8 A. Apostolov, V. Raitman, V. Gerganov and B. Ivanov, Njakoj problemi na pasarnata prophilactika v stroitelstvovo, Sofia 1982, p. 58.
9 S. H. Zeronian, M. S. Ellison and K. Alger, J. Appl. Polym. Sci., 25 (1980) 1311.
10 O. Egyed and J. Simon, J. Thermal Anal., 16 (1979) 307.
11 M. A. Bingham and B. J. Hill, J. Thermal Anal., 7 (1975) 347.
12 C. S. Leamonth, A. Nesbitt and D. G. Thwaito, Brit. Polym. J., 1 (1969) 149.
13 K. Gjurova, Chr. Bechev, K. Troev and G. Borisov, J. Thermal Anal., 27 (1983) 367.
14 K. Gjurova, Chr. Bechev, K. Troev and G. Borisov, J. Thermal Anal., 31 (1986) 853.
15 K. Gjurova, K. Troev, Chr. Bechev and G. Borisov, J. Thermal Anal., 32 (1987) 97.

Zusammenfassung — Mittels eines kombinierten DTA-Verfahrens wurde der Einfluß von als Antipyren in einer Polychloroprenkomposition auf 'Byprene-210'-Basis eingeführten Ammoniumsulphaminaten (AS) in Verbindung mit Antimontrioxid (AO) und Chlorparaffin (ChP) untersucht. Nach erfolgreicher Untersuchung der beobachteten thermischen und Brennbarkeitseigenschaften wird angenommen, daß AS und AO einem additiven Einfluß aufweisen. Es wird ein optimaler Bereich für die AS-Konzentration gefunden, in dem es möglich ist, AO in den untersuchten Polychloroprenkompositionen zu substituieren.