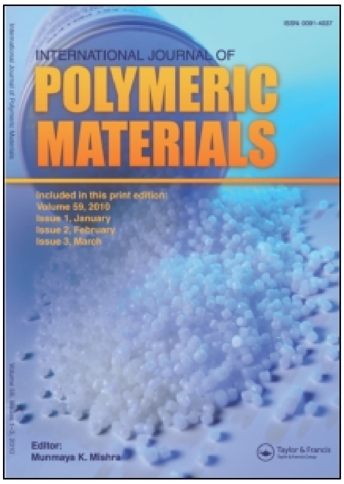

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Thermal Stability and Flammability of Sulphochlorinated Polyethylene Compositions

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Thermal Stability and Flammability of Sulphochlorinated Polyethylene Compositions

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The effect of some metal oxides used as nonactive fillers and fire retardant system components on thermal characteristics and flammability of sulphochlorinated polyethylene was studied. The flammability of compositions was estimated by the limiting LOJ method under standard conditions and also in the case of flame spreading in the horizontal direction and in the vertical one upwards. Temperature profiles in a burning wave were determined with the help of a thermocouple probe for optimum composition. Heat flows from the flame to the polymer surface were calculated. A materials fire-protective properties were estimated by the thermal shock method with single-side heating. The mechanism of a materials fire-protective effect was discussed.

KEY WORDS Thermal stability, flammability, sulphochlorinated polyethylene

INTRODUCTION

The selection of rational thermal protection for instruments or structural elements against exposure to high temperatures, observed in cases of crashes and fires, causing damage to the constructions and the loss of the information, is one of the most important problems in the design stage, when developing new aircraft and apparatus engineering.

Polymeric compositions with unique combinations of properties have found application as the most effective thermal protection materials. Their greatest advantages are the ability to withstand high temperature gradients, thermal shock resistance, low weight, technological efficiency in production, etc.

One of the applications for thermal protection materials is the external thermal protection of the flight information recorders (FIR), with which all aircraft are equipped in conformity with international agreements. Information retention is very important for revealing the causes of the crashes. In these situations exposure of the FIR surface to open flame with a temperature above 1100°C, and also instrument damage due to falling to the earth. In order to preserve the information carrier, it is placed in a container with a coating of impact resistant fire- and thermal protective material.

For this aim materials based on chlorosulfonated polyethylenes have been developed, the properties of which can be controlled in a wide range, by varying the coating formulation.

In order to understand the fire protection mechanism of the coating, the effect of individual components, formulation factors on the thermal and flammability characteristics of chlorosulfonated polyethylene compositions was studied. The effect of metal oxides used as the inert and reactive fillers has been studied, as well as the plasticizer-chloroparaffin-CP-470.

EXPERIMENTAL PART

The commercial polymer, produced by high-pressure polyethylene chlorosulfonation, containing 2.7% (by weight) of chlorine was used as the polymeric matrix.

The composition also includes the curing system, silicon and antimony oxides, and chlorinated paraffin CP-470, with 47% of chlorine.

The test specimens were prepared by mixing the components on rollers with subsequent moulding and curing at a temperature of 140°C and a pressure of 5 kgf/cm^2.

In order to determine the thermal characteristics of the composition, the derivatograph of an MOM-system (Hungary) was used.

Heating the specimen to 980°C in air was done at a rate of 7 deg/min. The weight of the specimens was 50 mg. The kinetic parameters of decomposition were calculated in accordance with the method proposed in Reference 1.

The composition's flammability was estimated by the limiting oxygen index method under standard conditions (GOST 12.1.044-84), and also under flame propagation in the horizontal and vertical upward directions.

The effect of the thermal insulating substrate on the burning limits and flame propagation was determined.

The temperature profiles in the burning wave were determined for the optimum composition with the use of Pt-Pt thermocouple.

The junction diameter was 0.1 mm. Oxygen content in the atmosphere (O_2 + N_2) was close to critical, comprising 46–50%. The data obtained were used for the evaluation of heat flows from the flame to the polymeric specimen's surface.

The fire-protective properties of the materials were estimated by the thermal shock method on a one-side action heater with a temperature of 1100°C (Figure 1). The method of one-side heating is a simplified model of the coating operation process and allows one to carry out the comparative selection of the most effective materials.

The surface of the specimen with a size of 80 × 80 mm and a thickness of 10 mm comes into contact with the heater. The evaluation criteria is the rate of temperature change on the protected surface.

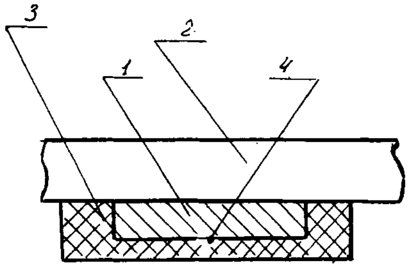

FIGURE 1 Unit scheme for testing of fire and heat protection properties: 1—Specimen; 2—heater; 3—thermal insulation; 4—thermocouple.

EXPERIMENTAL RESULTS AND DISCUSSION

Table I shows the results, illustrating the effect of metal oxides content on oxygen index and flame spread rate for specimens burning in different orientations. Attention should be paid to the fact, that the flame propagation direction, and the presence of the substrate greatly effect flammability parameters. When metal oxides are introduced, the oxygen index is increased and the flame spread rate is changed. At a filler content up to 30 mass parts antimony oxide is more effective than silicon oxide. Further increases of the filler content balances the effect of the filler nature on the oxygen index, if the flammability is determined under standard conditions. The flame propagation rate at the burning limit in this case is 2–4 times lower, compared to that of the initial composition, containing no silicon or antimony oxides (Table I).

The introduction of chlorparaffin produces little effect on the compositions flammability parameters, but improves their technological properties. The composition, containing both metals oxides and chlorparaffin has the highest values of oxygen index and the lowest flame propagation rate.

It was established, that the specimen thickness effects the flammability of the optimum formulation materials (Table II). At a thickness less than 3.5–4.0 mm the oxygen index is decreased. This is due to the change in the relative contribution of the heat losses from the flame.

Most significantly the oxygen index is changed with the transition from candle-type burning to upward flame spread.

Under these severe test conditions, the positive effect of antimony oxide is clearly manifested in the materials flammability decreasing at all filler levels. The unfilled cured elastomer can ignite and burn in the air atmosphere.

The compositions show the tendency to increase flame spread rate with an oxygen concentration increase.

The effect of oxygen content on the flame propagation rate is manifested most clearly in the case of a considerable deviation from the limiting oxygen concentration. The presence of the thermally insulating asbestos substrate promotes both an increase of 01 values and the flame propagation rate (Table I).

Flame spread rate in upward vertical direction is unstable, it increases with time.

Figure 2 shows the results of estimating the fire-protective properties of the control specimens (without the filler), containing 50 mass parts of metal oxides,

TABLE I

The effect of metal oxides on the flammability of sulphochlorinated polyethylene compositions (specimen thickness – 4–5 mm)

Flame spread direction	Parameters	SB_2O_3				SiO_2		
		0	30	50	70	30	50	70
	01V + 0.1%,	27.8	37.8	40	42.7	34.8	39.5	42.5
	10 mm/sec	2.01/28[a]	0.56/38	0.52/40	0.85/43	0.7/36	1.18/40	0.73/43
	01V_j + 0.1%,	26.8	38	40.5	43	33.8	36	40
	10 mm/sec	0.66/27	0.5/38	0.7/41	0.53/43	0.90/34	0.84/38	0.45/40
	01V_f ± 0.1%,	31	43.5	43.5	48	41	48.5	52.8
	10 mm/sec	1.64/31	—	1.82/46	0.68/48	1.75/41	2.5/49.0	1.35/53
With the asbestos substrate	01V_f ± 0.1%	20.5	34.5	35.8	37.8	27.5	29.5	30.5

[a] Denominator—oxygen content in the atmosphere.

TABLE II

The effect of specimens thickness on flammability of sulphochlorinated polyethylene compositions (optimum formulation)

Flame spread direction	Parameters	Thickness, mm				
		1.3	3.2	3.5	7.3	8.5
	01 ± 0.1%	41.8	44	46.5	47	46.5
	$V_f \cdot 10$ mm/s	1.54/42[a]	0.84/44	1.43/47	0.5/47	1.05/47
	01 ± 0.1%	31.5	40.5	>0.42	—	>42
	01 ± 0.1%	43.0	58.0	57	—	52
	$V_f \cdot 10$ mm/s	1.9/43	4.5/58	3.0/57	—	4.7/57
	01 ± 0.1%	41.5	44.7	—	—	48
	$V_f \cdot 10$ mm/s	2.7/42	1.3/45	—	—	—

[a] Denominator—oxygen content in atmosphere.

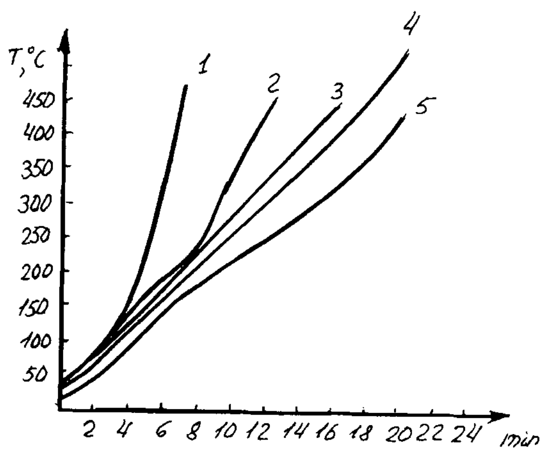

FIGURE 2 Fire and heat protection properties for compositions based on SCPE: 1—vulcanizated SCPE; 2—with Sb_2O_3 (50 pph); 3—with SiO_2 (50 pph); 4—with Sb_2O_3 (50 pph) and CP-470; 5—optimum formulation composition.

as well as for the optimum formulation composition. It is seen, that on exposure of more than 6–8 min silicon oxide allows a slowdown in the heating rate of the protected surface to a greater extent than antimony oxide. However, it should be noted that the increase in the temperature of the protected surface, in this case, takes place at practically a constant rate.

For the compositions containing antimony oxide during 6–8 min thermal exposure a certain slow-down of the rate of temperature increase is observed.

The fire-protective effect is increased, when using a combination of antimony and silicon oxides.

The peculiarities of the burning process of the specimens under the conditions of fire-protective coating properties testing should be taken into account.

Fast ignition of the specimen is observed. The flame envelopes the whole surface in contact with the heater. As a result the specimen "burning out" from the surface toward the inside takes place, accompanied by polymer carbonization. A layer of white powder mineral filler and then unchanged material were revealed under the carbonized layer. On achieving a temperature of 450°C at the protected surface the materials are carbonized over the whole thickness.

It was found with the help of X-ray analysis, that antimony is practically absent in the carbonized residue, while other metals are fully retained as oxides.

Is there any correlation of the fire-protective characteristics obtained with the 01 values? The standard method of 01 determination (candle-like burning) is the closest to the method of testing fire-protective properties as far as specimen orientation, ignition conditions, and flame propagation are concerned.

However, taking into account the use of thermal insulation and its possible effect on the material's flammability, it is rational to compare the data with the 01 values obtained on flame propagation along the surface of the specimens with the substrates. In this case the results lead to the same conclusion: silicon oxide exceeds antimony oxide in the efficiency of its actions (Figure 2 Table I).

The optimum formulation composition has the highest values of fire-protective properties and O.I. values in all burning directions (Table II).

The mechanism of the fire-protective coating's operation is a complex one. A simple increase in the content of the inert filler doesn't improve the protective properties. Only the combination of silicon and antimony oxides and the additional introduction of chlorparaffin ensures the necessary complex of fire-protective properties.

In order to understand the role of metal oxides in flame retardancy of sulphochlorinated rubber an analysis of the specimens derivatograms was conducted.

Thermooxidative decomposition of sulphochlorinated polyethylene, and compositions based on it, under dynamic conditions of heating to 900°C is a multistage process (Figure 3, Table III). The nature of metal oxide effects the temperature range and the rate of volatilization and also the yield of nonvolatile residue.

The transition to a high-elasticity state at a temperature exceeding 100°C is observed for the initial polymer.

The endopeak on the DTA curve with a maximum at 125°C corresponds to this transition. On heating to 260°C the polymer loses about 4% of its weight.

The weight losses are probably explained by the evaporation of low-molecular substances, contained in the polymer. The intensive decomposition is observed at temperatures higher than 230°C. In the 230–400°C temperature range the process is carried out in accordance with the first-order reaction having a constant rate $K = 4.3\ 10^8 \exp(-94700/RT)\ \text{min}^{-1}$.

For the cured elastomer the weight losses do not exceed 2% up to 182°C. The volatilization is accompanied by heat absorption. The first stage of the thermooxidative decomposition of the vulcanizate is almost thermally neutral, as the high-temperature stages are characterized by high exoeffects. It should be noted, that in spite of the reduction in the intensive polymer decomposition onset temperature after curing, the rate of this process at the first stage is slowed down. The activation energy is increased to 110 kg/mol and the reaction becomes second order. This is associated with the fact that curing results in conformational and steric changes in the polymer structure and a decrease in the macromolecules mobility.

The magnesium oxide contained in the curing system greatly effects such changes. The introduction of additional fillers (silicon or antimony oxides) results in an

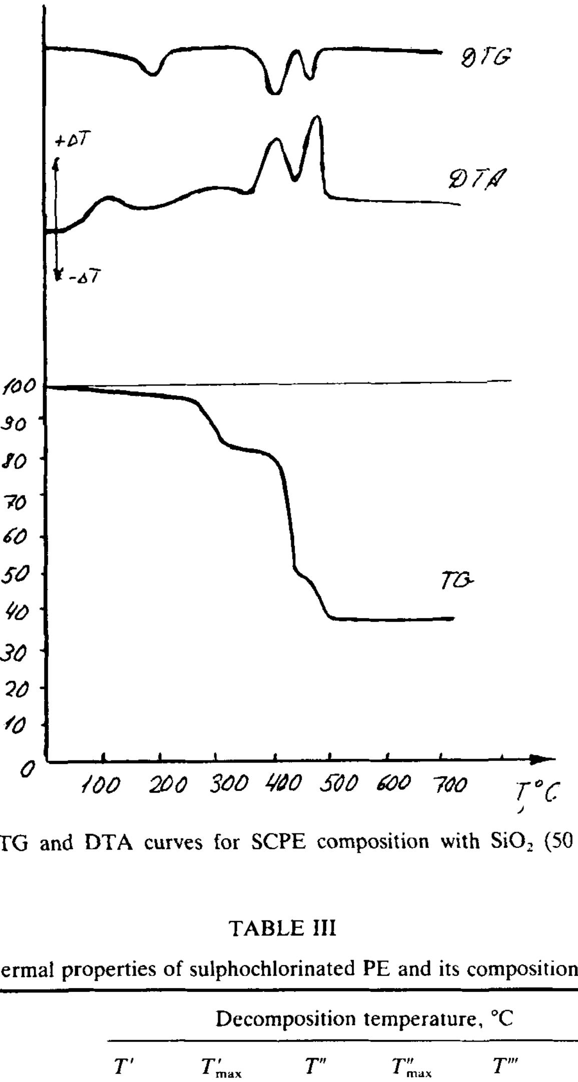

FIGURE 3 TG, DTG and DTA curves for SCPE composition with SiO_2 (50 pph) temperature distribution.

TABLE III

Thermal properties of sulphochlorinated PE and its compositions

Sample	Decomposition temperature, °C						Residue W, % (900°C)
	T'	T'_{max}	T''	T''_{max}	T'''	T'''_{max}	
SCPE	230	315	400	460	500	—	—
Vulcanizated SCPE (I)	182	258	362	460	492	538	14
I + SiO_2 (50 pph)	195	262	380	465	500	532	39
I + Sb_2O_3 (50 pph)	220	267	400	450	470	520	28
I + Sb_2O_3 + XII	220	258	385	455	477	517	20
I + Sb_2O_3 + SiO_2 + XII	220	265	393	460	480	530	37

increase in the cured polymer's stability. The opposite effect is observed for plasticizers. The value of the effect activation energy of polymer decomposition is particularly dependent on the process initiation energy. The observed changes in the E_{eff} values for sulfochlorinated polyethylene compositions with silicon or antimony oxides (Table IV) indicate the different character of the molecular inter-

TABLE IV

Kinetic parameters of thermooxidative decomposition for SCPE compositions

Sample	Temperature range, °C	$E_{eff} \pm 2$, kJ/mol	z, min^{-1}	n
SCPE	230–400	94.7	4.3 10^8	1
Vulcanizated SCPE (I)	182–362	110.0	1.6 10^{11}	2
I + SiO_2	195–380	130.0	1.2 10^{13}	2
I + Sb_2O_3	220–400	167.2	8.1 10^{17}	2
I + Sb_2O_3 + XII	110–385	145.0	7.2 10^{14}	1.6
I + Sb_2O_3 + SiO_2 + XII	120–400	149.0	2.8 10^{13}	2

action of the polymer matrix with the filler surface. As a result, of the specific interaction of sulphochlorinated polyethylene macromolecules with the atoms or atom boundaries of the metal oxide surface inactivation of mobile centers is likely to take place, initiating dehydrochlorination of the network polymer. It's not by chance that the plasticizer reduces the E_{eff} value of highly filled sulphochlorinated polyethylene decomposition. The characteristic feature of the process of the thermooxidative decomposition is the presence of secondary reactions, resulting in the formation of carbonized product and its oxidation at temperatures exceeding 500°C.

Transformation to the carbonized structure is observed after the dehydrochlorination and the formation of products with the system of π-conjugated double carbon bonds.

The interaction of antimony oxide with hydrogen chloride results in the formation of oxychlorides and volatile antimony chloride. That is why the total weight losses of the compositions, containing antimony oxides exceed the weight losses in similar compositions with silicon oxide. However, taking into account the removal of the antimony oxide from the system in the form of the volatile derivatives, the conclusion can be made that compared to the initial polymer or is vulcanizate the yield of coke residue is increased in the presence of antimony oxide.

Magnesium and silicon oxide have practically no effect on coke yield. The results obtained make it possible to assume that the silicon oxide effect is not associated with the supposed variations in the chemistry of pyrolitic processes during burning.

The decrease of the material's flammability is due to physical factors, i.e., the effect of the filler on the material's thermophysical characteristics and heat transfer from the flame.

The mechanism of reactive filler action is more complicated than that of silicon oxide. Not only physical factors, but also chemical reactions in the condensed phase in the presence of antimony oxide, play an important role in the decrease in flammability.

Figure 4 shows some temperature profiles obtained in the process of candle-type burning of sulphochlorinated polyethylene compositions with 30 parts by weight of antimony oxide under the conditions close to the flame self-extinguishing limit (oxygen content in the atmosphere is 46%). When processing the experimental results the following thermophysical characteristics of the composition were used: temperature conductivity coefficient, $a = 1.6\ 10^{-7}$ m^2/sec; thermal conductivity coefficient, $\lambda = 0.33$ W/m deg, specific heat capacity, $C_p = 1.3$ kj/kg deg.

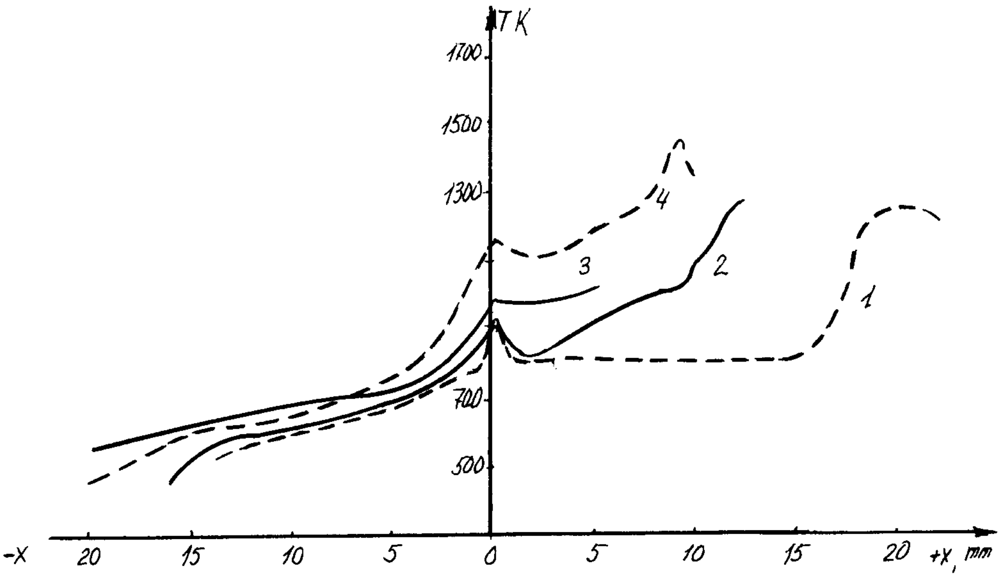

FIGURE 4 At downward flame spread along the surface of SCPE vulcanizate with Sb_2O_3 (30 pph). Thermocouple junction distance from the surface *m*: 1—0; 2—1; 3—2; 4—3.

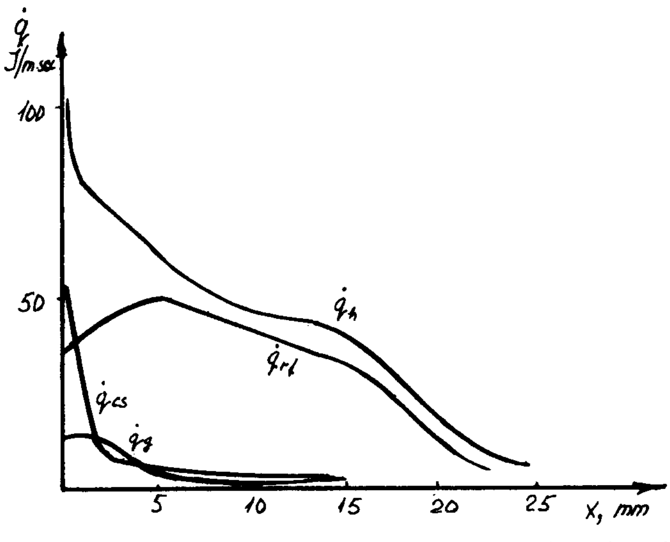

FIGURE 5 Distribution of heat fluxes at downward flame spread along the surface of SCPE vulcanizate with Sb_2O_3 (30 pph).

In the flame edge at a distance of 3 mm from the surface the temperature reaches more than 1100 K. The minimum temperature outside the edge is almost 1500 K. On the material surface, as a result of the coke formation and its burnout, the maximum temperature far from the flame edge is also rather high (1230 K). The flame edge is determined by the position of the maximum temperature gradient and maximum temperature.

The thermal balance on the surface inside the burning wave should take into account the heat flows, coming to the surface from the flame by heat conductivity $\dot{q}_{cs}$ through the gas ($\dot{q}_g$) and condensed phases, and also by radiation ($\dot{q}_{rf}$).

Heat losses are possible due to radiation ($\dot{q}_{rs}$) and reflection ($\dot{q}_{rr}$) of the thermal energy: $\dot{q}_s = \dot{q}_g + \dot{q}_{cs} + \dot{q}_{rf} - (\dot{q}_{rs} + \dot{q}_r)$.

Figure 5 shows the thermal flows on the specimen surface.

In front of the pyrolysis the heat is consumed for changing the enthalpy of the surface layer. It is interesting to note, that a major part of the heat is transferred from the flame to the ignited surface by radiation and through the condensed phase in the zone close to the edge.

The character of the heat flow change by radiation from the flame, $\dot{q}_{rf}$, before the edge at a distance of 5 mm indicates that in this area the contribution of heat losses is noticeable by radiation and reflection from the material surface. Under the flame edge the heat is transferred to the surface of the sulphochlorinated polyethylene composite with antimonium oxide 41.7%—by conductivity through the condensed phase, and by 9.5%—through the gas phase. The contribution of the heat flow by radiation is 49.1%. It compensates the heat losses from the surface as a result of radiation and reflection. The great contribution of heat transfer by radiation for the small-size specimens is probably due, to the considerable carbon black formation on burning. Thus, the mechanism of the fire protective action of the high-filled materials, based on sulphochlorinated polyethylene and metal oxides includes chemical and physical factors, effecting the heat and mass transfer on burning.

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