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Fire and Heat Shield Materials based on Sulfochlorinated Polyethylene

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Physico-chemical properties of efficient fire and heat shielding materials for use in flight information recording systems are reviewed. The focus is on newly developed fire shielding materials based on sulfochlorinated polyethylene.

KEY WORDS Fire heat shielding materials, sulfochlorinated polyethylenes, chlorinated polyethylenes, vulcanizing agents, inorganic additives, mechanical properties.

1. INTRODUCTION

The increase of aircraft safety depends on an objective, detailed study of accident causes. Therefore an analysis of the flight parameters and the crew working during start, flight and accident was performed.

Flight information recording systems (FIRS), which record the main parameters of a flight on tape, are objective witnesses of accident. The FIRS are usually placed in a metal container with a fire shield cover to block and decrease heat flow from the surroundings. A container with a fire shield cover should protect the recorded information from thermal degradation, mechanical destruction and humidity. This container or "black box," would provide the information regarding the cause of any accident that may occur.

Recently, similar information systems have been used in railway, water and underground transport systems.

This paper considers the physico-chemical properties of efficient fire and heat shielding materials (FHSM) for use in FIRS. The data on the development of FHSM based on sulfochlorinated polyethylene are shown. Great attention has been paid to the analysis of mechanism of fire protective action for the developed materials.

2. PHYSICO-CHEMICAL PROPERTIES OF EFFICIENT FHSM FOR USE IN FLIGHT INFORMATION RECORDING SYSTEMS

There are several types of FIRS, differing by construction and amount of the recorded information. The limit of acceptable temperature inside the container changes de-

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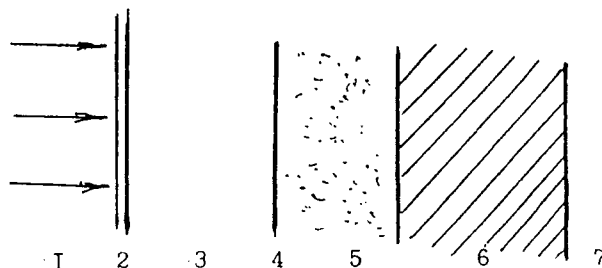


FIGURE 1 Scheme of layer disposition for fire and heat shield of fuel tanks: 1—flame; 2—thin steel cover; 3—vacuum or air; 4—reflecting surface; 5—thermal insulation; 6—tank wall; 7—fuel.

pending on the type of material used in making the tape (for example, 60°C for a polyester tape and 350°C—for a metal one). First, constructions of FIRS comprised an external fire and heat shielding cover and a metal blow resistant container, into which a heat isolation layer was placed. Glass reinforced plastics possess heat protective properties but their blow resistance is not high. If an aircraft should crash, such covers would break. Therefore it is necessary to create elastic, blow resistant covers, providing a safe heat shield for the device and to prevent it from breaking on aircraft crashing after it falls. Moreover, the task of decreasing the device's overall size and weight raised the question of the development of highly efficient FHSM, capable of protecting the information carrier without an internal thermal insulation layer.

The background for making the heat shield materials, including the elastic ones, was developed by rocket space technology research. However, the FHSMs for FIRS differ from heat shielding used in air-space vehicles. The temperature is lower (1100°–1600°C) while the heat exposure time is much longer (up to 30 min).

FHSM's performance consists of two stages, an active and a passive one. In case of FIRS the active stage is stipulated by the influence of flame on the surface of the cover for an extended period of time. After the end of the exposure to external heat, the passive stage starts. Here, the heat energy stored in the cover during active stage becomes the source of heat. For efficient work of FHSM it is important to dissipate a maximum amount of energy input for the transformation of material during the first stage. During the second stage, however, the objective of the cover material is to direct heat emission into the surroundings.

In the FIRS construction, used in the former USSR during the 60 s, the external cover was made of rubber-fabric material with the binder based on silicon polymers. Another multilayer system used for this purpose consisted of an intumescent cellulose material, impregnated with products of amine condensation with aliphatic aldehydes. A thermoplastic with aluminum foil was used as external protective layer. The following materials were recommended for internal thermal insulation: mineral and glass wool, vermiculite or asbestos paper.¹

Efficient and good exploratory system has been suggested for the protection of fuel tanks.² The scheme of layer disposition in the construction is shown at Figure 1. FRG patent³ describes how to make fire and heat shielding container, in which polymeric foam is used as internal thermal insulation. The containers for the storage of magnet carriers and other materials susceptible to overheating are shown in the

works.^{4,5} Here, both an external layer for heat shield and an internal thermal insulation are used. USA patent⁶ proposes FSHM and a method for making it. The material consist of a few layers including an external ablative over. This layer swells up and decomposes at the heating, absorbing a large amount of heat energy. Thus, the influence of fire on lower layers of material is decreased.

Technology for making FSHM included the following procedure: a thin layer of material with porous or cellular structure was formed by pressing. Then the layer of thermoplastic with low decomposition temperature (93°–204°C) and the intumescent coating were prepared.

The above-described FSHM's represent complex systems with various mechanism for heat dissipation. A thorough understanding of global chemical and physical processes controlling mass and heat transfer in the systems is essential to develop new efficient FSHM's.

The heat transported from flame or other external source of thermal energy to the surface of polymeric material can increase its temperature that of decomposition. The resulting fuel vapor mixes and reacts with the oxidizer from the surroundings to initiate ignition and to provide flame spread. Therefore, the problem of efficient FSHM development is similar to that of flame retardancy of polymers.

Heat transfer is usually carried out from hot bodies to cold ones by thermal conduction or convection. Thermal conduction takes place in both gas and solid phase while convection is only through the gas phase. With a large fire the main mode for heat transfer from flame or incandescent body to FSHM surface is radiation. The external radiation flux transferred to any body surface may be divided in three components: reflected, absorbed and permeated ones.⁷⁻⁹ Radiation heat flux, passed through the cover, is brought to the surface of the protected object. Absorbed part of radiation energy is spent for the transformation of the cover material.^{10,11} The amount of the energy absorbed by polymer material depends on the level and spectral characteristics of the radiation flux, absorption and reflection abilities of the material. Reflection ability of the cover depends on such factors as the state of the surface, beam incidence and wave length of flux input, refraction indices of the mediums.

Radiation energy is dispersed when the wave length is much smaller than the size of irregularities on rough surface. The chemical composition of the material effect transmissivity and absorption coefficient of the cover. If absorption coefficient is small, radiative heat flux will penetrate the material thickness and its heating will be retarded. However, if absorption coefficient is large, radiative energy absorbed on the surface of the material will rapidly increase its temperature to critical value of the decomposition beginning. In this case the maximum temperature of the material is observed at its surface.

For efficient FSHM development it is important to increase reflecting power of the material. However, polymers and other organic compounds have low reflectivity.¹⁰ Reflecting power can be increased by a special modification of material surface or by the introduction in polymer of fillers which are capable of reflecting radiative energy. Oxides of different metals can be used as such fillers.

The thickness of the heated layer of the material and the time for its heating up to critical temperature depend on chemical nature of polymeric material, its thermophysical properties and power of incident heat flux.¹¹ The surface layer and heat-

ing time of this layer decrease with heat flux power or with the decrease of thermal inertia (*I_{rc}*). Cellular polymers with low value of thermal inertia have a higher thermal insulating properties. However, there are the danger for their faster ignition and flame spread over the material surface in comparison with monolithic counterparts.

Polymeric FHSM's are composite materials. They include many components for a different special purposes (fillers, plasticizers, flame retardants, etc.). The transformation processes of the components and the material on the whole at the action of heat energy are complicated. The effects of these processes on mass and heat transfer at the combustion of heat shielding cover are not well understood. However, it is quite evident that the endothermic processes, accompanied by heat absorption, and the processes of the energy dissipation into the surroundings are preferable.

Physical endothermic processes are a phase transitions of the substances: the melting of crystal ones, the evaporation or the sublimation, the transition from solid state to viscous liquid one.

Chemical reactions with the dissociation of molecular bonds are also accompanied by heat absorption. However, total thermal effect of the substance decomposition depends on energetics of following elementary reactions.

The thermal decomposition of polymers in dependence on their chemical nature can be carried out by different paths.

Two large groups of polymers are usually distinguished: the polymers, which degradate at high temperatures practically completely with the formation of low molecular volatiles, and the polymers, which form a carbonized product or non-volatile residue.

In spite of the differences in the decomposition mechanism (for example, reverse depolymerization or random scission of the main macromolecular chain with the formation of smaller fragments), decomposition of polymers of the first group is characterized by endothermic effect. Polymers of the second group show the tendency to exothermic reactions of the decomposition. Such reactions, as elimination of side substituents in main chains with the formation of conjugated double bonds, cyclization, intermolecular cross-linking, recombination are exothermic. They can cause carbonization of nonvolatile residue. The bond scission and volatilization of low molecular products also take place at the decomposition of the polymers. Therefore, total heat effect for low temperature step of the decomposition is often endothermal or close to neutral due to the compensation by the heat of exothermic reactions. More high temperature steps of the decomposition for char-forming polymers are carried out with heat release, as well as the reactions with oxygen participation.

Carbonizable thermoplastics at the first steps of the process can expand and swell up, promoting the formation of foamed char. Morphological structure of the char layer affect polymer flammability and heat shielding properties of the material. On one hand, surface char layer due to high absorptive ability accumulates a large amount of heat energy. At the rise of temperature on the surface of the char layer, the heat quantity emitted in the surroundings as well as transferred to lower material layers increases.⁷ On the other hand, foamed char has a lower density and thermal conductivity than initial polymeric material. As the result, the thermal insulating ability of the foamed char layer begins to play a dominant role in the protective action of FHSM. The char strength is important for effective heat shield. The change

of cover volume at constant sizes of protected surface, thermal contractions and volatilization of the decomposition products are the cause for the appearance of strains in FHSM and partial destruction of the cover.

Chars with large-cell structure are usually friable and ineffective as thermal insulation. To understand physical and chemical processes participating in the formation of firm foamed char on cover surface, it is necessary to develop the new efficient FHSMs.

Theoretical models for intumescent char formation are discussed in papers.^{12,13} Mathematical models for pyrolysis of carbonizing polymers at unidimensional heating are represented by researchers.^{14,15} Paper¹⁵ considers one-stage and double-stage char formation at pyrolysis of polymers. The influence of surface heterogeneous chemical reaction and the formation of porous structure of char due to the appearance and the motion of bubbles of volatile decomposition products was analyzed.

The suggested models are based on some simplifying assumptions. In particular, complex kinetics of pyrolysis is described by only one global temperature dependence with Arrhenius law. It is supposed that substance transformation into char begins after the reaching some threshold temperature, which is specific for the polymer.

Heterogeneous reaction of char oxidation leads to the generation and the accumulation of heat inside the cover. Therefore, polymers decomposed to nonsmouldering residue and unflammable gases are preferable for FHSM development.

Flame retardancy of polymer materials can be carried out by physical and chemical methods.¹⁶

Physical methods must help to decrease the heat input, to increase the dissipation of heat into the surroundings and to make worse mass transfer of fuel to the zone of the combustion reaction.

The change of polymer structure, the composition and component ratio of material may be considered as chemical measures for the regulation of the combustion of polymeric material. For the development of flame retardant polymeric materials the following ways are important: the synthesis of noncombustible or hardly combustible polymers; the surface and voluminal chemical modification of materials; the application of efficient flame retardants; the aimed blending of polymers; applying fire shield coatings; the combination of the above mentioned ways. As a result the resistance of material to ignition should increase. The rate of flame spread over the polymer surface and heat release should be decreased.

Besides these important indices, fire safety of polymeric materials is characterized by toxicity of combustion products and the level of smoke formation.

Stable flame combustion of polymers includes the totality of mutually adjusted gas and solid-phase processes. This adjustment is stipulated by level and rate of heat flux incident from flame to polymer surface. It can be expressed by concept of Spoulding mass transfer number, B , taking into account radiative component and heat losses or combustion efficiency.¹⁷

Mass transfer number, B , is connected directly with rate of gasification, \dot{m}'' , by the following expression:

$$\dot{m}'' = h \ln(1 + B)/c_p,$$

where h = convective coefficient of heat transfer; c_p = heat capacity of the polymeric material.

Mass transfer number, B , can be represented as follows;

$$B = \{ [Y_{\text{ox}}\Delta H_c(1 - X_R)X_A/r] - c_p(T_s - T_0) \} / \{ L(1 - E) \}$$

Here Y_{ox} is mass content of oxygen in the surroundings; ΔH_c is the heat of full combustion; X_A = combustion degree; X_R = radiation energy part; T_s, T_0 = temperature of the surface and the surroundings; L = the gasification heat of polymeric material; E = the combustion efficiency.

E , taking into account radiative heat losses from the material surface, can be expressed as follows:

$$E = (\dot{q}_e'' + \dot{q}_{fr}'' - \dot{q}_{rr}'') / \dot{m}''L,$$

where \dot{q}_e'' is external heat flux; \dot{q}_{fr}'' = reverse radiative heat flux from flame; \dot{q}_{rr}'' = radiative heat losses from the material surface. Other modes of heat losses at material combustion can be taken into consideration.

Polymers with low combustion heat and high gasification heat values are relatively lower combustible materials. Therefore, inorganic polymers with silicon, nitrogen, fluorine and other non-carbon elements in the main chains of macromolecules are a special interest.

Thermal stable polymers with aromatic or heterocyclic structure are also important.¹⁶ However, such polymers are expensive. Moreover, their processing is often difficult. Hydrolytic stability of the polymers is not enough in some cases.

Other above mentioned ways to develop flame retardancy of polymeric materials are more accessible.

The thermal stability of polymer can affect its flammability characteristics. For example, it was found that anomalous structural units in main chains of PMMA decreases thermal stability of the polymer. The gasification rate increases by 25% and flame spread over the surface of material increases by 4 times, comparing with more stable sample.¹⁷

The definite scaling relationships between thermal parameters and the fire response of idealized polymeric materials were found by R. E. Lyon.^{18a} However, the similar interconnection between thermal stability and flammability indices for flame retardant polymer is not universal. Besides the gasification rate, the content of combustible degradation products is very important. Flame retardant polymeric materials are often characterized by more lower decomposition temperature than initial polymers.

The application of flame retardants with aimed functions (fillers, plasticizers, foaming agents, etc.) is the most wide-spread approach to fire protective materials development.

Flame retardants represent the substances, containing such chemical elements as B, P, halogens, nitrogen, different metals. Mechanism of flame retardant action depends on the nature of an element, chemical composition of the substance and polymer and the conditions of heat influence on the system. A number of the studies is devoted to this question.^{18,19}

Flame retardants are distinguished according to the zone in which their action predominantly takes place. Some substances act primarily in gas phase, while the others act in the condensed phase. Halogen-containing compounds represent typical flame retardants of gas phase action. Volatile products of their decomposition act as inert dilutors of flame medium or inhibitors of gas phase chain reactions.

Bromine-containing flame retardants are more efficient than those containing chlorine. However, temperature affects the efficiency of halogen-containing flame retardants. In a large fire, when the temperature exceeds 1200–1300°C, bromine shows oxidative properties and catalyzes chain gas phase reactions. Thus bromine can perform unwanted influence on the combustion process as a whole.²⁰

The action of most phosphorus-containing flame retardants is mainly in the condensed phase. Phosphorus-containing substances can decompose at the combustion of polymeric materials to oxides or acid derivatives of phosphorus. Dense surface layer of polyacid compounds of phosphorus creates physical barrier for oxygen and for the diffusion of the combustible products of pyrolysis into the zone of flame reaction. Phosphorus-containing compounds promote an increase of carbonized residue. Besides, they change the direction of oxidative reactions for char residue, decreasing their exothermicity and suppressing the material smouldering. Nitrogen-containing substances increase the effect of phosphorus flame retardants.

Borates, silicates, different salts of alkali metals can also form glass protective layers.²¹

It should be noted that the flame retardancy of polymeric materials is often carried out by mixed, condensed and gas phase mechanism.

A great number of the substances were suggested as flame retardants and smoke smoke suppressants.²² Besides simple substances with high content of flame retardant element (red phosphorus, as example), some natural mineral and inorganic synthetic compounds were suggested: asbestos, talcum,²³ bismuth and molybdenum, by themselves or in mixtures,²⁴ oxide and hydroxide of aluminum,²⁵ ammonium salts,²⁶ carbides of metals.²⁷

Fillers for flame retardant polymeric material are often separated as inert and active. However, this separation is relative. It is necessary to take into account concrete temperature conditions in the material use. Asbestos fiber at temperature below 900°C is usual inert dilutor with low thermal conductivity. At temperatures of 900°–1400°C, asbestos releases crystal water. Above 1400°C endothermic process of reforming chemical structure of asbestos is carried out. The chemical interaction between asbestos components and polymer decomposition products is possible.

The flame retardant effect of inorganic fillers is usually considered as result of the decrease of fuel part of the material or the change in thermophysical properties. However, it could be as a surprising coincidence that some inorganic flame retardants are catalysts for the reactions of polymerization and polycondensation in polymer synthesis. Therefore, it should be supposed that they can accelerate the reactions of cross-linking and char-forming at polymer combustion. TiO₂, Co₂O₃, Al₂O₃, aluminum phosphates are catalysts for the reactions of dehydrocyclization and aromatization of hydrocarbons.²⁹ The action mechanism for high effective flame retardants of the intumescent type is connected with catalysis of char forming reactions in polymeric system.²⁹

There are a great number of known flame retardants. However, specific demands limit choice for the particular material development. The main demands for flame retardants of polymers are: compatibility with the polymer; stability at temperature of material processing; nontoxicity and corrosion inactivity; absence of the negative effects on technological properties; mechanical and other characteristics of the material.

The following factors were taken into account to select the polymer for FHSM development: accessibility of raw basis; developed industrial production; relatively low price; inherent decreased combustibility. Elastomers are preferable for impact-resistant FHSM development.

Halogen-containing polymers are very appropriate for this purpose. Native industry produces different chlorine-containing polymers: homopolymers and copolymers of vinylchloride or vinyliden chloride; chlorinated butylrubber, polyisoprene and polyvinylchloride; chlorinated and sulfochlorinated polyethylene, etc. Additional halogenation of polymers enlarges the application spheres of the products.^{30,31}

Polymer chlorination can be carried out in medium of organic solvents, in water suspension and in solid phase by gas or liquid chlorine action. Sulfonation can be performed simultaneously with chlorination. The process is initiated by visible, UV, ionizing radiation or radical initiators (organic peroxides, hydroperoxides, diazo compounds and metalorganic ones).³⁰ The properties of chlorinated polymers depend on the nature of initial polymer, chlorination degree, the way and the conditions of making.³⁰

Chlorinated and sulfochlorinated polyolefines are widely used for the different purposes.

Let us consider the peculiarities of the making and the properties of the products.

3. THE PROPERTIES OF CHLORINATED AND SULFOCHLORINATED POLYETHYLENES

Halogenation of polyolefines shows some features, stipulated by chemical passivity of initial polymers and also the presence of amorphous and crystalline parts in their structure. The reactions of halogenation can be accompanied by the degradation and crosslinking of the main chains of macromolecules.^{32,33} The process is mainly carried out in solvent medium or in water suspension. At room temperature, polyethylene is not soluble in common solvents. In the dependence on the crystallinity degree, PE begins to dissolve in chlorinated aliphatic and aromatic hydrocarbons at temperatures above 53°C. PEHD is dissolved fully in CCl₄ at the temperature closed to boiling one. PELD solubility is observed at higher temperatures (80–100°C).³⁰ The solubility of chlorinated PE depends on chlorine content in the polymer. The solubility of chlorinated PE increases with chlorine content up to 30% mass, then it decreases. The polymer becomes insoluble at 50–60% mass of chlorine content.³⁰

USA patent describes PE chlorination in CCl₄ solution with radical initiators.³⁴ Using chlorobenzene with higher solving ability allows to increase the reaction rate.³⁵ The different radical initiators^{36,37} and their mixtures,³⁸ as example, dinitril of isobutyric acid with benzoyl or laurylperoxides, chloral dihydroxyperoxide together

with acetylcyclohexylsulfonyl peroxide, were suggested. ICI Company (Great Britain) developed technology for PEHD chlorination in CCl_4 suspension or acetic acid by using metal chlorides.³⁰ Liquid chlorine was suggested as chlorinating agent.³⁹ However, gaseous reagent is mostly applied. The product with chlorine content of 40–44% mass was obtained by suspensional way using gaseous chlorine.⁴⁰ The different surface-active substances were used for water suspensional chlorination of low density PE.⁴¹ Chlorinated PEs with chlorine content of 25–50% represent amorphous or low-crystal polymers having the tensile strength from 8 to 17 MPa and elongation at break of 350–800%. At larger levels of chlorination (from 14 to 70%) the various products ranging from thermoplastics to friable solids are obtained.⁴² The modification changes the polymer structure. Polymer crystallinity is destroyed more by chlorination in solution stronger than by chlorination in suspension. In the latter case, polymer crystallinity is partially retained at chlorine contents of up to 55 mass %.³² It was found that $-\text{CCl}_2-$ groups are absent in the macromolecule chains of chlorinated PE. The $-\text{CHCl}-\text{CHCl}-$ groups are absent when chlorine content is lower than 55%.³² At first, amorphous areas of polymer take part in chlorination reaction, then more ordered ones are attacked. The reaction of hydrogen substitution by chlorine proceeds statistically, resulting in a random distribution of chlorine in polymer chain.

The submolecular structure of polymer changes from spiral for PE to spherulitic (monocrystal) at chlorine content of 8 mass %. The increase in chlorine content up to 14–18% is accompanied by the appearance of short fibrils. At chlorine content of 22–30 mass % packs and globules are observed.³² Completely amorphous structure of polymer is observed at chlorine contents above 55%. Physical state of PE changes with chlorination degree in the following way⁴¹:

Polymer state	Chlorine content, % mass.
Semielastical thermoplastics	10
Thermoplastical elastomer	20
Thermoplastical, viscous elastomer	30
Thermoplastical elastomer	40
Semielastical thermoplastic	50
Rigid thermoplastic	60
Friable polymer	75

Glass transition temperature for the polymers with chlorine content of 25–35% lies in the limits from -20° to $+30^\circ\text{C}$. The value increases up to 100 – 180°C when the chlorine content is of 38–73% mass. Softening temperature change is of parabolic character with the minimum for 35–40% mass chlorine content.³⁰ Chlorinated PE is resistant to acids, weak alkali and salt solutions. It shows inherent decreased combustibility. At flame action the product does not melt and is charring. The char residue yield increases with chlorine content.³¹

Numerous works^{41–45} are devoted to the study of chlorinated PE thermal decomposition. The process mechanism is more complicated compared with initial PE process mechanism. The decomposition of chlorinated PE is a multistage process, including both the rupture of main chain bonds and the substituent elimination to

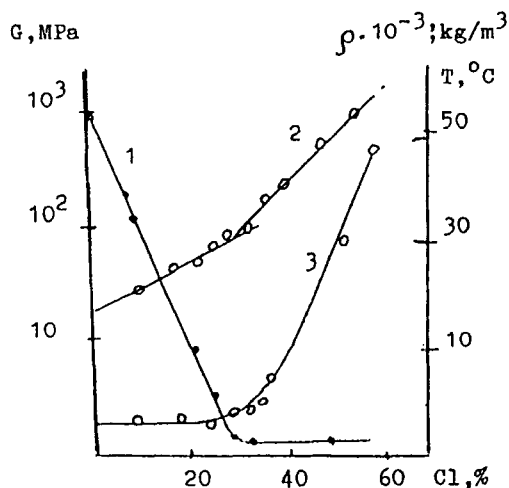


FIGURE 2 The influence of chlorine content in SCPE on the change of shear modulus (1), density (2) and glass transition temperature (3) of the polymer.

form polyene fragments capable of transformation into cross-linking and aromatic structures.

Caoutchouc-like products of PE sulfochlorination are very interesting for FHSM development. The making of sulfochlorinated polyethylene (SCPE) is carried out by barboting mixture of gaseous chlorine with sulfurous acid anhydride (in molar ratio of 2:1, preferably) through PE solution in CCl_4 at 70–75°C. Peroxides or asobisisobutyronitrile are used as radical initiators.

Domestic (Russian) industry produces 6 trade marks of SCPE based on HDPE.⁴⁶ Foreign countries produce a greater variety of such products. Du Pont Company, produces 8 trade marks of SCPE based on both HDPE and LDPE.

SCPE, produced by domestic industry, with content of 26–36% Cl and of 0.85–2% S begins to decompose at 115°–150°C. The tensile strength is about 15.0 MPa and the elongation at break is 300–350%.⁴² The mechanical properties change with increasing degree of sulfochlorination to a chlorine content of 59% and a sulfur content of 4.4%.^{30,49} The effect of structural factors on the properties of PE modified was analyzed in the study.⁴⁷ It was found that the branchings in polymer do not affect the properties of final product. Molecular weight and the molecular mass distribution of the initial polymer are more important factors. The effect of degree of chlorination on relaxation properties and phase state for SCPE was discussed in Reference 49. SCPE with chlorine content up to 59% and sulfur one up to 4.4% was obtained on the basis of HDPE ($\rho = 966 \text{ kg/m}^3$). The relaxation spectrum and phase transitions stipulated by different modes of molecular motion were determined by methods of dynamic mechanic spectrometry, linear dilatometry and DSC. The polymer crystallinity decreases with Cl content. Full amorphisation of SCPE is observed for chlorination degree of $30 \pm 2\%$ mass. Shear modulus decreases with decreasing polymer crystallinity (Figure 2, curve 1). Shear modulus was measured at temperature corresponding to the low-temperature limit for the elastic state of amorphous part in the polymer. The change in slope for curves correlating the density and glass tran-

sition temperature (Figure 2, curves 2 and 3) on degree of chlorination correspond to a completely amorphous state of polymer. DSC data prove this conclusion. Endopeak on SCPE thermograms, associated with crystal phase melting, changes its form, shifts to the lower temperature and decreases with increasing chlorine content up to 30% mass.

Sulfochlorinated PE possesses an important advantage over the chlorinated product: i.e., better ability to vulcanization. Optimum sulfur content in polymer to obtain impact-resistant product is about 1.5%. SCPE are characterized by high light-, ozone-, oil- and petrol resistance and also inherent decreased combustibility.⁵⁰ Non-vulcanized SCPE's are stored for a year without changing their properties.⁵¹ SCPE vulcanizates attract attention by their high resistance to various atmospheric influences and ionizing radiations.³⁰ In tropical conditions, they retain their properties for a long time, enduring the influence of mold and microorganisms.

High static strength of SCPE vulcanizates is observed even in absence of the reinforcing fillers. SCPE fragility temperature varies in the range from -55° to 60° C. SCPE vulcanizates show the satisfactory tear resistance and attrition one, retaining at increased temperature. They are characterized by high resistance to repeated tensile and bending loads, to the deterioration on heat aging. Maximum working temperatures for the most of the articles based on SCPE fall within the range of 130 – 160° C. At 100° C the products can be used for years. The properties of SCPE rubbers depend on the vulcanization conditions and vulcanizing agent type.^{52,53}

Vulcanization of elastomers is a complex process of transformation of linear macromolecules into the network structures with relatively few cross links. As result, the product loses the solubility and the thermoplasticity properties, but acquires a high elasticity, strength and a number of new valuable qualities.

The different reactive atoms and groups can participate in the net structure formation: chlorosulfonic groups, chlorine and hydrogen atoms, unsaturated double bonds formed by polymer dehydrochlorination.^{54,55} Chlorine atoms in β -position to chlorosulfonic groups are mostly labile and able to catalytic dehydrochlorination.

The presence of different reactive atoms and groups in SCPE allows us to apply a different organic and inorganic compounds as vulcanizing systems. The following substances were suggested for this purpose: metal oxides, sulfur and sulfur-containing compounds, peroxides, diisocyanates, nitrogen-containing bifunctional compounds, polyatomic alcohols, etc.^{54–58} Vulcanizing systems, including oxides of lead and magnesium, are the most effective for SCPE.⁵⁴ At present, combined vulcanizing systems, which include oxide or salt of polyvalent metal (10–50 parts mass), organic acid (2–10 parts), sulfur-containing compounds as vulcanization accelerators (0.5–10 parts), are widely used.³⁰ It has been found that the sulfur-containing accelerators of vulcanization in the systems are true cross-linking agents.

It is supposed that metal oxides make no direct influence on chemical transformation of SCPE macromolecules. Metal oxides participate in net structure formation as sorption surface, dispersator of true cross-linking agent and absorbant of gaseous products.³⁰ According to another conception, metal oxides promote the transformation of chlorosulfonic groups into more polar ones of basic salt type.⁵⁸ During polymer heating chlorosulfonic groups in presence of moisture and activators of acidic type (for example, fatty acids) or vulcanization accelerators (for example, thiurams)

hydrolyze forming HCl and $-\text{SO}_2\text{H}$ groups. The latter participate in the formation of metal-sulfonate bonds. Accelerator of sulfuric vulcanization react with chlorosulfonic groups. The cross-linkage or the voluminous side substituents are appeared. The side substituents are able to associate with each other and with polar groups on the surface of metal oxide, also. The links of polymer with metal oxide formed as the result of adsorption or hemosorption of macromolecules, are stable at usual temperatures of material exploitation.

Thiazoles, thiurams, dithiodicarbamates are used as sulfur-containing accelerators of vulcanization for SCPE. Aminoaldehyde accelerators call scorching of SCPE during its processing.^{54,55} Guanidines are used only as secondary accelerators in cooperation with thiazoles.³⁰ High vulcanizing activity for SCPE is shown by salts of hexamethylenediamine and diatomic acids (hexamethylene diammonium sebacinate, for example,⁵⁷ or the products of their condensation.⁵⁹ In this case magnesium oxide increases the cross-linking degree, and sulfur additives accelerate the process of vulcanization.⁵⁷ Dithiomorpholine was recommended.⁶⁰ The substance promotes high concentration of cross links in SCPE vulcanizate in absence of the additives and increases the strength of vulcanizate at presence of magnesium oxide. The combination of magnesium sulfide with diphenylguanidine and 2-mercaptoimidazole is very effective.^{61,62} Polyatomic alcohols (for example, pentaerythritol⁶³), chlorinated aromatic substances (as example, *p*-xylene hexachloride⁶⁴) are used as vulcanizing systems. The regimes for SCPE vulcanization by different vulcanizing agents are discussed in Reference 65. The composition formulations based on SCPE for making materials with high resistance to heat or light-ozone aging, aggressive media or water action were described.⁶⁶

Technology of SCPE processing does not differ from that for other elastomers used for a long time in rubber industry. Thus, the equipment, usual for the industry, is suitable. It should be noted that nonvulcanized SCPE is more thermoplastic than natural or many other synthetic caoutchoucs. Therefore, it needs no preliminary plasticization.^{30,48} Making rubber mixtures on roller or in the mixers is accompanied by sufficient heat release which can lead to subvulcanization of the compositions. To avoid this process it is necessary to make mixing as quick as possible. Rubber mixtures based on SCPE are formed satisfactory by pressing, extrusion, calandering or pressure molding. Vulcanization of SCPE mixtures is carried out at temperature of 120–150°C. A higher temperatures of processing can lead to the appearance of porosity, shells and other defects on the surface of the material. Vulcanization of SCPE compositions can be performed in press or by sharp vapour at pressure up to $1.8 \text{ MN}\cdot\text{m}^{-2}$. In the case there is wide plato of vulcanization and SCPE mixtures are resistant to scorching.

4. FIRE AND HEAT SHIELD MATERIALS BASED ON SULFOCHLORINATED POLYETHYLENE

Chlorinated or sulfochlorinated PE itself or in the mixture with other caoutchoucs and thermoplastics were used for the development of flame retardant materials. For example, there were described flame retardant, impact resistant compositions based on chlorinated and sulfochlorinated PE with chlorine content of 25–45% mass.⁶⁷ The compositions and the compounds for making fire shield coatings, including addi-

TABLE I

The influence of metal oxides on the limiting oxygen index (LOI) and the flame spread rate (V_{fs}) of PESC vulcanizates

Indices	Direction of flame spread	Metal oxide content, pph of PESC						
		Sb ₂ O ₃				SiO ₂		
		0	30	50	70	30	50	70
LOI, %	↓	27.8	37.8	40.0	42.7	34.8	39.5	42.5
$V_{fs} \cdot 10$, mm/s	↓	2.01 (28)	0.56 (38)	0.52 (40)	0.85 (43)	0.7 (36)	1.18 (40)	0.73 (43)*
LOI, %	↑	20.5	34.5	35.8	37.8	27.0	29.5	30.5
LOI, %	←	26.8	38.0	40.5	43.0	33.8	38	40
$V_{fs} \cdot 10$, mm/s	Without support	0.66 (27)	0.5 (38)	0.7 (41)	0.53 (43)	0.90 (34)	0.84 (38)	0.45 (40)
LOI, %	←	31	43.5	45.5	48	41	48.5	52.8
$V_{fs} \cdot 10$, mm/s	With support	1.64 (31)	—	1.82 (46)	0.68 (48)	1.75 (41)	2.5 (49)	1.35 (53)

*Values in parentheses are oxygen content in the atmosphere.

tionally halogen-containing flame retardants, synergists and inorganic fillers, have been suggested.⁶⁸⁻⁷³ SCPE vulcanizates with low chlorine content are flame retardant ones, but they resign in this property chloroprene compositions. New types of SCPE with high chlorine content are equal to chloroprene or exceed it by flame retardancy rating. The analysis of the properties of chlorinated and sulfochlorinated PE led to the conclusion that at the development of impact resistant FHSM for FIRS, it is expedient to use an industrial SCPE with chlorine content of 27% and sulfur one of 1.3–1.5% mass.

The combined vulcanizing system included magnesium oxide, sulfur vulcanization accelerator and some other aimed components has been used to obtain the compositions with high technological properties, resistant to scorching.

The composition formulation contains silicon and antimony oxides, chloroparaffin of CP-470 trade mark with chlorine content of 47% mass. Silicon oxide (white spot) is an active filler for SCPE. The filler allows to obtain rubbers with high mechanical properties and, in particular, with high resistance to tearing and frequent bending loads. Chloroparaffin is an efficient plasticizer and simultaneously flame retardant for non-colour SCPE rubbers. Antimony oxide is synergist for halogen-containing flame retardants, increasing fire shielding effect. The compositions were obtained by rubber milling. The samples of vulcanizates are formed by pressing at temperature of 140°C and pressure of 5 kg·cm⁻².

Optimum formulation for composition has been found as the result of the variation of component content and the study of final FHSM properties. Optimum polymer to vulcanizing system ratio is 100 to 27.5 parts mass.

To understand the mechanism of fire shielding action of FIRS coatings, the effect of metal oxides and chloroparaffins on the flammability and thermal properties was investigated in detail.

The Table I shows the results illustrating the effect of the nature and the content of metal oxide in SCPE vulcanizate on the values of limiting oxygen index and flame spread rate over sample surface.

TABLE II

The influence of specimen thickness on oxygen index of FHSM with optimal formulation

Thickness, mm	Oxygen index, %			
	Direction of flame spread			
	↓	↑	← Without support	← With support
1.3	41.8	31.5	41.5	43.0
3.2	44.0	40.5	44.7	58.0
3.5	46.5	>42	47.0	57.5
7.3	47.0	>42	—	57.0
8.5	46.5	>42	48.0	52.0

Limiting oxygen index (LOI) was measured by standard method of GOST 12.1.044-84 and also for flame spread in horizontal or vertical directions. For these cases, the sample sizes, the reactor dimensions and the rate of nitrogen-oxygen flow corresponded to standard conditions of LOI determination. The influence of thermal insulating support on LOI and flame spread rate was estimated. LOI for nonvulcanized SCPE equals 22.5%. The Table I shows that the orientation of the samples, the direction of flame spread and the presence of support affect the flammability indices. The sample thickness at testing was equal to 4–5 mm. The effect of sample thickness on LOI value for SCPE vulcanizates of optimum formulation is shown in Table II. LOI is practically constant for sample thickness of 3.5–7.3 mm. LOI decrease at thickness lower 3.2–3.5 mm is stipulated by relative decrease of heat losses from the flame to the surroundings. LOI values for candle burning and for flame spread over horizontal surface of the samples without support are similar. The sufficient increase of LOI and the change of flame spread rate are observed when support is used (Table I). This fact confirms the presence of significant heat flow through the condensed phase and the support. The rate of flame spread along the sample surface increases with oxygen content in the surroundings. The most essential change of LOI is observed when the candle type combustion is changed to upward flame spread mode. In the latter case, the rate of flame spread increases with time. In the rigid conditions of the combustion the SCPE vulcanizates without fillers are able to ignite and to burn in air media (LOI is equal 20.5%).

The flammability of SCPE rubbers decreases on introduction of metal oxides. Antimony oxide is more effective as flame retardant than silicon oxide at filler content of up to 30 mass parts. However, the influence of metal nature levels off with the increase of metal content up to 50–70 parts, provided the LOI is determined by standard method of GOST 12.1.044-84. In this case the rate of flame spread at the extinguishing limit for SCPE filled vulcanizates is 2–4 times lower than that for the non-filled ones. High efficiency of antimony oxide as flame retardant in comparison with silicon oxide (white soot) is observed in upwards flame spread mode (Table I). It should be noted that the additional introduction of chloroparaffins into the compositions with high content of filler (antimony or silicon oxides) improves the technological properties, but it affects only insignificantly the LOI values of SCPE vul-

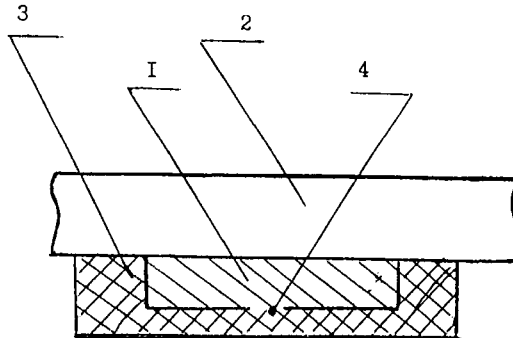


FIGURE 3 The device scheme for determination of fire and heat shield properties of materials: 1—sample; 2—heater; 3—thermal insulation; 4—thermocouple junction.

canizates. However, the positive influence of chloroparaffin on LOI increase was observed with the combination of these fillers.

SCPE rubber of optimum formulation which included all the above mentioned components, shows the highest LOI values (Table II) and the lowest rates of flame spread over the surface in comparable conditions.

The fire shielding properties of the materials for FIRS were estimated by the method of heat flow. The device with one-side heating material was used (Figure 3). Planar heater with temperature of 1100°C was contacted with the surface of sample (size of 80×80 mm, 10 mm thick). Temperature of the protected surface was recorded automatically by thermocouple. The junction of thermocouple was situated in the centre of back side of FHSM sample on the protected surface (Figure 3). The rate of temperature change of the protected surface and maximum temperature in the definite time moment were the estimating criterions. This method reproduces the simplified model of working fire shielding cover. The method allows us to perform screening FHSM and to select fastly the most efficient one. At testing fire shield properties fast ignition of the sample is observed. Flame embraces all surface contacted with the heater. Burning out of surface layer is accompanied by charring of the polymeric material and the carbonization front moves inside the sample. Reaching 450°C at shielded surface, the charring material is observed throughout the entire volume. It was found by the help of X-ray analysis that there is practically no antimony in the carbonized residue. All other metals (Mg and Si) are retained as oxides.

The testing of fire shield properties of SCPE rubbers shows that the silicon oxide decelerates the heating rate more than the antimony oxide. However, the additional introduction of chloroparaffin into the composition with Sb_2O_3 leads to a decrease of temperature on the protected surface (Figure 4).

With the combination of two metal oxides and chloroparaffin the efficiency of fire shielding action of the coating increases. The substitution of chloroparaffin by chlorobromoparaffin with equal total halogen content and $\text{Br} = 25\%$ mass produces large decreases of the heating rate of the protected surface (Figure 4, curve 6). However, this effect appears only at test durations, exceeding 6–8 min. Apparently, at lower duration of the testing, there is not enough time to form the layer of foamed coke

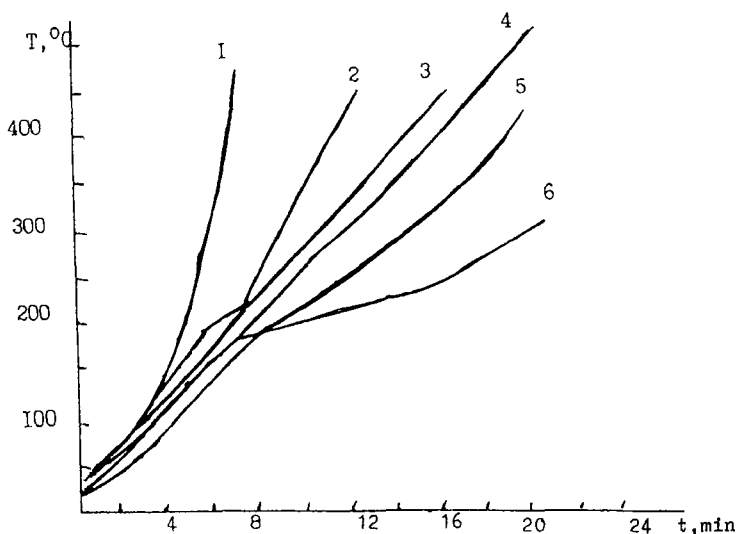


FIGURE 4 Fire and heat shield properties of the compositions based on SCPE: 1—vulcanized SCPE; 2—SCPE with 50 mass parts of Sb_2O_3 ; 3—SCPE with 50 mass parts of SiO_2 ; 4—SCPE with 50 mass parts of Sb_2O_3 and CP-47; 5—optimum formulation; 6—the composition with chlorobromoparaffin.

sufficient thickness. At this stage the heat shield is determined by thermophysical properties of the initial material and its thermal inertia.

The mechanism of heat shielded action of the cover is complex. To elucidate the physical and chemical processes in this mechanism, the thermal properties of SCPE vulcanizates were studied. Heat flows from flame to the FHSM sample surface were also estimated.⁷⁴

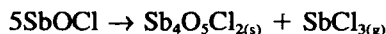
The thermooxidative decomposition of initial polymer and SCPE vulcanizates represent multistage process at dynamic heating (7 degree/min). Metal oxide nature affects the temperature range and the rate of volatalization, as well as the yield of char residue. The transition temperature of initial polymer into high elastic state is observed above 100°C. Endopeak with the maximum at 125°C on the DTA curve for the sample corresponds to this transition. Small mass losses (about 4% mass) below 200°C are stipulated by the volatalization of low molecular substances, which are present in the initial polymer. The intensive decomposition of SCPE is observed in temperature range between 230°–400°C. The process proceeds according to the first order reaction with the rate constant of $k = 4.3 \times 10^8 \exp(-94700 J/RT)$, min^{-1} . The elimination of side substituents in the main chain and the degradation of chlorosulfonic groups with the formation of sulfur dioxide and hydrogen chloride take place during this stage. Vulcanized SCPE decomposes intensely at temperatures over 182°C. The mass losses at heating up to 182°C do not exceed 2%. The first stage of the decomposition in the range of 182°–360°C is practically thermoneutral unlike that at high temperature stages. It should be noted that despite the decrease of temperature of SCPE decomposition onset after vulcanization of polymer, the rate of the process at the first stage is retarded. Activation energy of the decomposition of SCPE vulcanizate increases up to 100 kJ/mole. The reaction becomes of the second order (Table III). It is connected with conformational and spatial changes in

TABLE III
Kinetic parameters of thermooxidative decomposition for SCPE compositions

Sample	Temperature range, °C	$E_{et} \pm 2$, kJ/mol	Z , min ⁻¹	n
PESC	230–400	94.7	$4.3 \cdot 10^8$	1
PESC vulcanizate (I)	182–362	110.0	$1.6 \cdot 10^{11}$	2
1 + SiO ₂ (50)	195–380	130.0	$1.2 \cdot 10^{13}$	2
1 + Sb ₂ O ₃ (50)	220–400	167.2	$8.1 \cdot 10^{17}$	2
1 + Sb ₂ O ₃ + CP - 470	110–385	145.0	$7.2 \cdot 10^{14}$	1.5
1 + Sb ₂ O ₃ + SiO ₂ + CP-470	120–400	140.0	$2.8 \cdot 10^{13}$	2

E_{et} = activation energy, Z = preexponential factor and n = orders of reaction.

net polymer structure leading to a decrease of the macromolecule mobility after vulcanization. Magnesium oxide included into vulcanizing system affect the change of macromolecular mobility. Additional introduction of fillers (silicon or antimony oxides) causes the increase of SCPE rubber stability. The opposite effect is observed on addition of plasticizers-chloroparaffins or other compounds (Table III). It is known that the effective activation energy of polymer decomposition depends on the initiation reaction. The data obtained indicate a different type of molecular interaction of polymeric matrix with the surface atoms or groups of metal oxides. In our opinion this interaction causes the inactivation of labile SCPE centers, initiating the degradation of cross-linking polymer. The plasticizers promote the polymer decomposition by the deterioration of the interaction with the surface of metal oxides. However, it should be taken into account that chloroparaffin and antimony oxide are reactive compounds. Chloroparaffin of CP-470 mark decomposes at temperature above 130°C on dynamic heating. Its LOI is 25%.⁷⁵ The interaction of antimony oxide with hydrogen chloride (the product of SCPE and CP-470 dehydrochlorination) leads to the formation of oxychlorides and volatile antimony chloride.^{76,77} The initial intermediate product—antimony oxychloride SbOCl—is unstable and decomposes at 240–280°C according to the following reaction:



The following decomposition of Sb₄O₅Cl₂ at higher temperature (400°–570°C) limits the transfer of SbCl₃ into gas phase.^{76–78}

Similar antimony oxybromides are formed in the presence of bromine-containing compounds and Sb₂O₃. Sb₄O₅Br₂ was found in the condensed phase of the combustion products for polyolefine compositions with synergetic mixtures of Sb₂O₃ and bromine-containing flame retardant.⁷⁹

The efficiency of flame retardants depends on the ratio of Sb:Hal in the composition, the interaction of Sb₂O₃ and halogen-containing compound and the type of polymer. These factors affect the amount of SbHal₃, coming to gas phase because the SbHal₃ is an efficient inhibitor of flame radical reactions. A characteristic feature of the thermooxidative decomposition of SCPE rubbers are the secondary reactions of polymer charring and the oxidation of carbonized residue at temperature over 500°C. Polymer transformation into carbonized structure with fragments of con-

densed aromatic cycles is carried out after dehydrochlorination and the appearance of unsaturated π -conjugated double bonds in macromolecules.

Magnesium and silicon oxides do not practically affect the char residue yield. Antimony oxide increases the char residue, if we take into account the elimination of antimony from the system as volatile derivatives. It is interesting to investigate the effect of atomic ratio of chlorine and antimony in the compositions on flammability indices of SCPE rubbers. The compositions, containing only antimony oxide, have Cl:Sb ratio from 7.46 (for 30 mass parts of Sb_2O_3) to 1.6 (for 70 mass parts of one).

The additional introduction of chloroparaffin in a high filled system increases the ratio to 2.16, which is close to the value of 2.26 for SCPE composition with 50 mass parts of Sb_2O_3 . It is known that the largest effect of flame retardancy is reached at the optimum ratio of Cl:Sb required for the formation of SbCl_3 . There is no surprise that the highest change of LOI is observed for the system with 30 mass parts of Sb_2O_3 . Additional introduction of chloroparaffin into highly filled composition does not provide optimum ratio of Cl:Sb = 3 and does not lead to LOI increase. At the same time, the ratio Cl:Sb comes close to the optimum one (3.04), if the chloroparaffin is used in the composition with 50 mass parts of Sb_2O_3 . Thus, the efficiency of fire shielding action of FHSM increases (Figure 4, curves 2 and 4). The largest fire shield effect was observed when chloroparaffin was substituted by chlorobromoparaffin in SCPE composition. However, atomic ratio Hal:Sb decreases to 2:1 in this case.

The analysis of FHSM thermogravimetric curves shows that only low temperature stages of the decomposition exhibit essential differences. Slow decrease of weight of FHSM sample with chlorobromoparaffin begins over 130°C . At 220°C (the start of intensive decomposition) weight losses are 6% (instead of 2% for the composition with CP-470).

The additional stage with neutral heat effect and low weight loss is observed in the range of $330^\circ\text{--}403^\circ\text{C}$. The yield of nonvolatile residue is similar at 490° and 535°C (Figure 5).

These data allow us to conclude that the efficiency of FHSM depends on the reactions in condensed phase and the chemical nature and the amount of flame retardant transferred in gas phase.

At halogen surplus HHal and SbHal_3 appears in the gas phase. At halogen deficiency SbHal_3 is the main volatile product. Nonreacted antimony oxide is the inert diluent of the combustible part in the condensed phase. It is known, that SbHal_3 is more efficient flame retardant of radical gas reactions than HHal . The latter acts usually as inert diluent in the gas phase. Antimony halides (SbCl_3 and SbBr_3) show a double function in the flame. First, they are the source of HHal , and second they form antimony monooxide, SbO , which participates in the catalysis of recombination reactions of active radical (H , O , OH) in the flame. This latter process involves intermediate particles, such as SbOH .⁸⁰ The residence time of inhibitor particles in flame increases with increasing boiling temperature of antimony halides (223°C for SbCl_3 and 288°C for SbBr_3).

To determine the mechanism of flame spread over FHSM surface the temperature distribution in the combustion wave has been measured. Oxygen concentration in

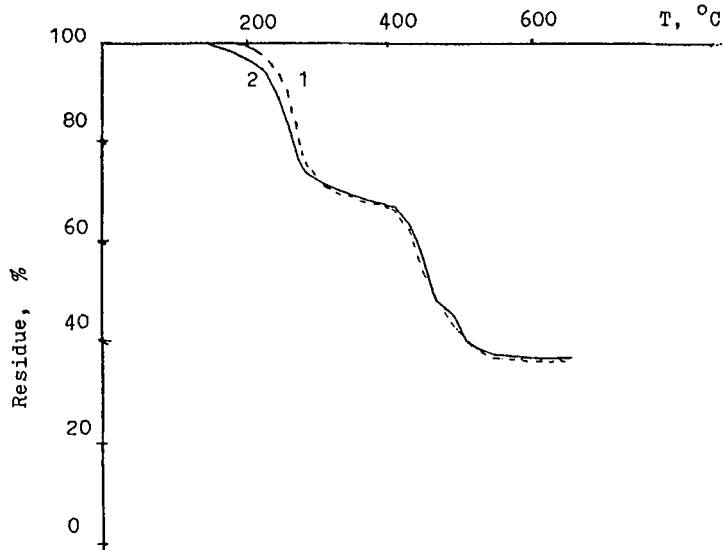


FIGURE 5 Thermogravimetric curves for FHSM composition containing CP-470 (1) and chlorobromoparaffin (2) at air heating with the rate of 7 degree/min.

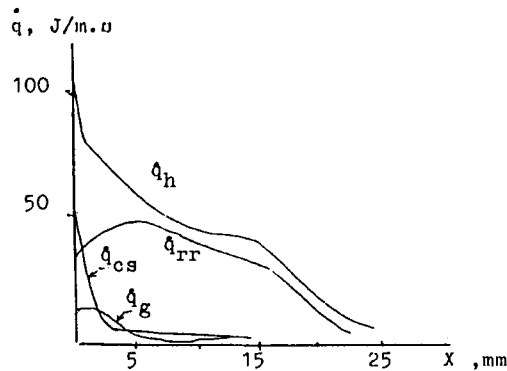


FIGURE 6 The distribution of heat flows at downward flame spread on the surface of SCPE vulcanizate sample containing 30 mass parts of Sb_2O_3 .

nitrogen-oxygen media was equal to 46%. The details of the measurement and the calculation of heat flux are given in Reference 74. The next thermal-physical properties of SCPE composition were used for the treatment of experimental results: thermal conductivity $\lambda = 0.33 \text{ W/m.K}$; specific heat capacity $c_p = 1.3 \text{ kJ/kg.K}$; thermal diffusivity $a = 1.6 \times 10^{-7} \text{ m}^2/\text{s}$; density $\rho = 1550 \text{ kg/m}^3$.

The temperature reaches 830°C in the flame edge at the distance of 3 mm from the sample surface. Maximum temperature of the flame outside the edge is 1230°C . The temperature of the surface under the flame edge is 620°C . However, in a far distance from the flame edge, the temperature on the surface increases up to 960°C because of charring and char oxidation.

The flame edge was determined by the position of maximum temperature gradient in the gas phase. Figure 6 shows the distribution of heat flows on the FHSM surface.

The heat balance at the combustion has taken into account; 1) the heat flows transferred to the surface from flame by convection through the gas phase (\dot{q}_g''), 2) the heat conductivity through condensed phase (\dot{q}_{cs}'') and 3) heat flow through radiation (\dot{q}_{fr}''). Heat losses are probable because of irradiation and reflection of heat energy by FHSM surface:

$$\dot{q}_i'' = \dot{q}_{rr}'' + \dot{q}_{ref}''$$

Thus, heat balance can be presented by the equation:

$$\dot{q}_s'' = \dot{q}_g'' + \dot{q}_{cs}'' + \dot{q}_{fr}'' - \dot{q}_i''$$

The heat flow before the pyrolysis front is expended in the enthalpy change of the surface layer, \dot{q}_h'' . Radiation energy absorbed by FHSM was estimated by the difference between \dot{q}_h'' and $(\dot{q}_g'' + \dot{q}_{cs}'')$. As it is seen from Figure 6, the main contribution into the surface layer enthalpy near the flame edge is due to radiation heat transfer from the flame and by conduction through the condensed phase. Far from the edge this contribution is mainly due to the radiation from flame. Heat transfer through the gas phase near the flame edge by convection is 9.5% of the total heat flow. The contribution of the radiation energy is 49.1% and that of heat transfer through condensed phase is 41.4%. Probably, a large contribution of radiation to the total heat transfer is connected with carbon soot formation during FHSM combustion. The change to radiative heat flow in preflame zone (5 mm from flame edge) shows significant heat losses due to reflection of energy and irradiation from material surface. The metal oxides with high reflection coefficients for IR range⁷ increase the reflective ability of FHSM.

The data obtained show the complex mechanism of heat shielding action for the developed FHSM. Both physical and chemical factors are important. The processes proceeding in the condensed and gas phase, at the interface affect the heat and mass transfer at FHSM combustion.

This investigation allowed us to develop the rubber-like impact-resistant FHSM of high efficiency. Coatings for FIRS, made of developed material, were tested in the conditions modelling those in actual use.

During testing the following indices were estimated: the resistance to distributed static load of 1000 kg at 30 min exposure. This index was determined for two axes of device; the resistance to impact of 250 kg load, falling from 1 m height. The contact square was equal 1.6 cm². The impact overloads approach a factor of 1000. During these tests there were no breakdown of FHSM structural integrity. The information tape was fully protected and the recording was reproduced without any disturbances.

The influence of thermal impact of 1000°C with 15 min exposure to all surfaces of device was estimated for two types of FIRS construction: 1) the usual construction with internal heat insulation and 2) the construction without internal insulating layer. The newly developed coatings and traditionally used rubber-fiber FHSM were compared. In testing, the following parameters were controlled: the temperature at titanium FIRS box and the time of reaching the maximum temperature.

TABLE IV

Testing results of thermal impact stability of FIRs with two types of fire and heat shield coatings

Shield Material	Temperature, °C			
	Outside Ti FIR box		Inside the box	
	T _{max}	After 15 min	T _{max}	After 15 min
Silicone				
Rubber Textile	890	810*	420*	not determined*
SCPE based				
material	380	248	190 - 280	150 - 180*

* Heating discontinued after 7 minutes because of too high box outside temperature. Therefore, the inside temperature after 15 min. exposure is meaningless.

** T_{max} reached after 20 - 35 minutes

After a 15 min exposure to 1000°C, the temperature was measured at the surface of the titanium box and inside the FIRS container. In addition, the maximum temperature was recorded along with the time for reaching this temperature.

The advantages of the developed materials based on SCPE are shown in Table IV. With the commonly used silicone rubber textile shield, the heating had to be discontinued after seven minutes because of too high box surface temperature of 810°C. But even under these conditions (i.e. of seven minutes heating), the temperature in the box reached 420°C. With the testing device of the SCPE type, the maximum surface temperature of 380°C was reached 34 min after the start of testing, the increase of temperature inside the box after 15 min was reduced to 150–180°C. The maximum temperatures with SCPE type system reached 190–280°C in 20–35 min depending on the SCPE composition. Thus, we demonstrated the high level of heat shielding potential for the SCPE type materials.

In addition, the developed FHSMs allow us to replace the complex FIRS constructions with the internal thermal insulation based on SCPE materials.

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