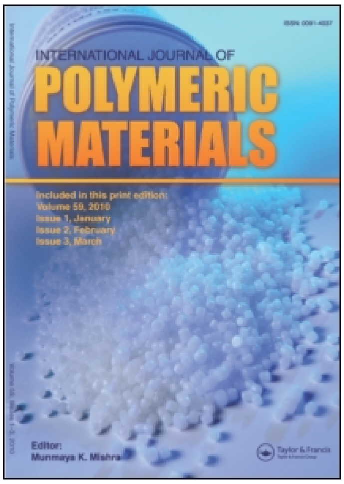

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Elastomeric Heat-Shielding Materials for Internal Surfaces of Missile Engines

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The requirements, testing procedures, compositions, and the performance characteristics of elastomeric heat-shielding materials for internal surfaces of missile engines are reviewed.

KEY WORDS Heat shielding materials, missile engines, internal surfaces, high temperature elastomers.

INTRODUCTION

Materials for shielding the walls of missile engines of solid propellant (MESP) are exposed to the gas flow of propellant combustion products under the pressure, reaching 150 and over atmospheres, and temperature up to 4000 K and the rate of tens and hundreds meters per second. In a solid propellant direct flow missile engine (DFME) the conditions at start are similar to those described above, while the engine is running, however, the medium changes to an oxidative one because of the increase of the flow rate.

Thus, the heat shielding materials (HSM) of ablation type for MESP and DFME must work at temperatures, which exceed those of their thermal decomposition. Moreover, HSM must be light, environmentally stable, resistant to vibrations and impact and resistant to vitrification. They must possess low heat conductivity and low thermal expansion coefficient.

The HSMs must be elastic to withstand the deformations under the influence of mechanical and heat stresses during manufacture of shieldings and in uses.

The most promising material for manufacturing of HSM are elastomers, which allow to produce rubbers, foamed rubbers and rubber-fabric or rubber-fiber composite materials. Since the elastomers are linear polymers, most of them form no solid carbonic residue on thermal decomposition, i.e. they possess no coking ability without introducing special additives.

RESULTS AND DISCUSSION

The problem of elastic HSM processing was first discussed in early 60s.[1]

The HSMs for internal surfaces of MESP and DFME must possess satisfactory resistance to vitrification, high mechanical strength, coking capacity, high and stable adhesion to protective surfaces and to propellant.[2,3] During engine performance shielded surfaces must not be heated over 150°C, mass and thickness of the coating should be minimum.[4] It should be noted that there are rubbers, developed in USA, which allow one to decrease the weight of engine heat shielding by a factor of two, and to use propellants possessing high temperature of combustion. High-temperature tests proved that rubber like materials are the best for heat-shielding of MESP vessels. Such materials lead under the influence of gas flow to the formation of a pored coke-like layer, possessing low heat conductivity on the surface. On thermal decomposition of the lower layers of the cover volatile products are formed, which pass through the "coke" and create a border gas layer providing additional heat resistance. The author believes that the ideal heat shielding material should be completely decomposed at the end of the propellant combustion.

Table I lists the main components of rubbers and rubber-like materials used in USA for MESP heat shielding, and their properties.[5]

As it is seen from the Table I, these materials possess very high elasticity (the elongation at break is in the range of 269–830%, excluding M808 material, filled with asbestos), and mechanical strength reaching 266 kG/cm^2.

Various elastomers are used as the basis for HSM also in France and Australia. Thus, the French Patent[6] lists a large number of materials, based on polar rubbers, such as copolymer of ethylene and vinylacetate, containing 35–60% of the latter, butadiene-nitrile rubbers, able to contain carboxile groups, for example, copolymers of butadiene acrylonitrile and acrilic acid. Highly active silicone dioxide and (or) mica-like materials are used as filler. The rubbers are vulcanized with organic peroxides or metal oxides. Adhesives are used for bonding the vulcanized plates to metal. Here is an example of the applied compound: ethylene-vinylacetate copolymer (100 parts), silicone dioxide (40 parts), 40% solution of dicumyle peroxide (4 parts), dispersing agent—stearic acid (1%), antiaging substance 0.5 phenyl-α-naphtylamine (0.5 parts), vulcanization activator—trialkylcyanurate (2 parts), antioxidant 2-polycarbodiimide (2 parts).

The materials used in Australian HSM[7] contain rubbers with ammonium perchlorate, nitrocellulose and nitroglycerin. They perform under the following conditions: propellant combustion temperature 1370–2760°C, pressure in combustion chamber 35–140 kG/cm^2. The combustion chamber cover is usually made of steel and sometimes of reinforced plastic; the wall thickness is in the range of 1–2.5 mm. The heat shielding coating is prepared from nonvulcanized sheets of elastomer compounds, adhered by special substances to the shielded surface and then vulcanized into rubbers.

The rubber mixtures are prepared using natural as well as synthetic caoutchoucs such as; chlorinated polyethylene CPE500 of Allied Chemical Company, chlorine sulfonated polyethylene Highpalone 20 of Du Pont Company, butadiene-styrene rubber SBR 1502, 1712EP, 1778 of Austrapol Company, ethylene-propylene rubber Royalene 301 of Uniroyal Company, polybutadiene 1220 of Austrapol Company.

The fillers are primarily well dispersed silicone dioxide and chrizotilic asbestos of 5R04 type. In this case, the filler content must be as high as possible (usually about 50%). The combination of these two fillers is the most efficient from the

TABLE I

Composition and properties of heat shielding rubbers

No.	Material mark	Caoutchouc	Fillers	Density, g/cm^3	Strength limit at break, kGs/cm^2 (at 21°C)	Elongation at break, % (at 21°C)	Hardness by Shore (Scale A)	Heat conductivity coefficient, W/m·grad (at 93°C)	Specific heat capacity, kJ/kg·grad (at 65°C)
1	2	3	4	5	6	7	8	9	10
1	GTR-V-44	Butadien-nitril (Buna N or NBR)	Silicon dioxide, asbestos	1.28	77–105	300–450	70	0.224	1.840
	GTR-V-45	—"—	Silicon dioxide	1.22	175	400	63	0.218	1.715
	Garlock 7765	—"—	Silicon dioxide	1.25	203	610	83	0.248	1.882
2	GTR-V-62	Butadien-styrene (Buna S or SBR)	Carbon black, asbestos, graphite	1.07	110	683	70	0.170	1.630
	Goodyear M 800	—"—	Graphite, carbon black, phenil resin, silicon dioxide	1.17	266	700	58	0.172	1.674
	Goodyear M808	—"—	Asbestos	1.39	42–98	60	80	0.434	1.882
3	AGC-MMB4	Butylcaoutchouc	Silicon dioxide	1.39	40	269	65	0.242	1.674
4	EP-2005	Polysulfidic	Silicon dioxide, potassium titanate	1.08	—	—	—	0.202	1.462
5	HITCO-2800	Polyisoprene	Asbestos, silicon dioxide	1.23	84	400	85	—	—
6	PFC-11	Polypropylene	Phenolic microspheres, carbon black, graphite	1.19	105	—	—	0.105	—
7	SMR-81-15	Ethylene-propylene	Silicon dioxide, potassium titanate	1.41	52	350	—	0.202	1.674
8	P531 A	Polyurethane	Asbestos	1.19	56	830	66	—	—

Note: Carbonic and graphite fibers may be introduced into the material composition, based on caoutchoucs, mentioned in Nos. 4–8, in order to increase their erosion stability.

point of view of heat shielding. The introduction of small amounts of fillers and the type of vulcanizing system does affect the efficiency of HSM. It is interesting that only the silicone dioxide and asbestos content has been changed on the basis of investigations of materials, based on various rubbers.

The ablation indexes were obtained in accordance with ASTM No. E285-65T method using the oxygen-acethylene burner. The standard material DW-7942, based on chloro-sulfonated polyethylene, was used for the comparison. The best results were obtained with materials, based on chlorinated and chlorosulfonated polyethylenes and ethylene-propylene rubber. The evaluations of various materials showed also, that even the worst sample the series, the one based on polybutadiene possesses higher heat shielding properties than standard material DW-7942.

Table II shows the composition and heat shielding properties of Australian HSM.

The high temperature testing showed that elastomeric HSMs were promising also for internal heat shielding of the multiple use MESP. This is true particularly for those based on polyurethane rubber, butyl rubber, etc.[8] It can, therefore, be concluded that various rubbers are used as the basis for HSM. However, butadiene-nitrile, ethylene-propylene and silicone organic rubbers are the most suitable.

The physical properties of butadiene nitrile rubbers, which are the product of copolymerization of butadiene and nitrile of acrylic acid, are affected primarily by the content of the latter. The following changes take place with increasing content of acrylic acid nitrile: the intermolecular interaction between polymer chains increases, the density increases, the glass transition temperature increases, the dielectric properties decrease, the solubility in aromatic solvents decreases and the resistance to swelling in aliphatic hydrocarbons increases.[9]

The processing of butadiene-nitrile rubbers is difficult because of their high rigidity associated with high intermolecular interaction. The processibility of rubbers of different types depends on the initial viscosity and on nitrile group content. If plastificizing is required the mechanical incorporation of plasticizer using rollers at 30–40°C is most efficient.

Butadiene-nitrile rubbers may be vulcanized with sulfur in presence of accelerators. These rubbers can also be vulcanized with thyuram, organic peroxides, alkylphenolformaldehyde resins, organic chlorine compounds, etc. The vulcanization is performed at temperatures between 140–190°C. The most important reason for the wide use of butadiene-nitrile rubbers for HSM is that they are compatible with char (coke) yielding phenolformaldehyde resins. The clear products of such compositions possess relatively high mechanical strength and erosion stability. The elasticity of vulcanizates, however, decreases abruptly with the introduction of resins.

The temperature at the interface between the coating and shielding surface can be estimated.[10] Thus, for the material, based on butadiene-nitrile rubber and filled with silicone dioxide, the calculation can be made using

$$t_b - t_i = (t_d - t_i)(-Rx_i/a + R^2\theta/a).$$

Here, t_b = final temperature of the coating surface, connected with shielding surface; t_i = initial temperature of the coating; t_d = decomposition temperature (for particular

TABLE II

Composition and results of high temperature tests of heat shielding rubbers

Ingradient	230/5	232/15	234/21	235/26	236/31	241/40	DW 7942
1	2	3	4	5	6	7	8
Chlorinated polyethylene CPE500	100	-	-	-	-	-	-
Butadien-styrene caoutchouc SBR 1772EP	-	100	-	-	-	-	-
Natural rubber	-	-	100	-	-	-	-
Ethylene-propylene rubber Royalene 301	-	-	-	100	-	-	-
Butadien-styrene caoutchouc Austrapol 1200	-	-	-	-	100	-	-
Chlorsulfonated polyethylene	-	-	-	-	-	100	100
Highdispersed silicon dioxide Ultrasil VN3	44.5	44.5	44.5	44.5	44.5	44.5	Components are unknown
Asbestos of 5RC4 mark	65	65	55	55	55	55	-"-
Polyethylene AC617	1	-	-	-	-	4	-"-
Resin Stabelite	1	-	-	-	-	2.5	-"-
Magnesium oxide	5	-	-	-	-	5	-"-
Stearic acid	0.5	2	1	1	-	-	-"-
Chlorinated paraffin Cereclor 42	7.5	-	-	-	-	-	-"-
Vulcanizing agent Dicup 40	7	-	-	-	-	-	-"-
Zincum oxide	-	5	5	5	5	-	-"-

TABLE II (*Continued*)

1	2	3	4	5	6	7	8
Phenil-β-naphtil-amine	-	1	1	-	1	-	-"-
Resin Piccopal 100SF	-	13	6	-	3	-	-"-
Sulfur	-	1.5	1.5	1	1.5	-	-"-
Paraffinic wax	-	-	2	-	8	-	-"-
Vulcanization accelerators:							
Vulcafor DPG	-	0.25	-	-	-	-	-"-
Tetrone A	-	-	-	0.5	-	0.75	-"-
Tetramethyltiuramdisulfide	-	-	-	0.5	-	-	-"-
Di(2-benztiazol) disulfide	-	1.5	1.5	-	-	0.5	-"-
Vulcafor MBT	-	-	-	1	-	-	-"-
Vulcafor MBS	-	-	-	-	1.5	-	-"-
Triethanolamine	-	-	-	1	-	-	-"-
Diethyleneglycole	-	-	-	-	2	-	-"-
Aromatic naphtene oil Dutrex 95G	-	-	-	-	-	9.5	-"-
Heat shiealding properties:							
Burning out time, sec	28.47	15.34	19.41	22.74	13.18	19.81	11.86
Errosion rate (average), mm/sec	0.23	0.43	0.33	0.28	0.53	0.29	0.52

material it is about 150°C); R = average ablation rate; x_i = initial coating thickness; a = temperature conductivity coefficient; θ = heat influence duration.

The temperature estimated by means of this expression differs by approximately 1.5°C from that determined experimentally. The rubbers based on butadiene-nitrile usually contain silicone dioxide or asbestos as the main filler. They are applied for the shielding of nozzle assembly elements, internal cylindric surfaces of combustion chambers of MESP, etc.[11,12] Thus, for shielding the steel cover of MESP of "Titan 3-C" missile, Thompson Fiber Glass Company developed a rubber compound based on Hitca 6520, filled by silicone dioxide.[13] A similar material, produced by Tyokol Chemical Corporation, is bonded to the engine framework and vulcanized at 160°C for 17 hours and at a pressure of 6.3 kG/cm^2.[14] Another type of rubber used in MESP of "Titan 3-C" missile contains a combination of silicone dioxide and asbestos as the filler.[15]

Testing of highly filled rubber of similar composition, used for heat shielding the framework of the first section of "Minuteman" missile showed, that the char rate is 30% higher than that of the materials previously used.[16,17] It is pointed out, that the application of new rubber compounds led to a two-fold decrease of cover weight while simplifying the adhesion to the framework and vulcanization under pressure.

General Tire and Rubber Company has patented in Great Britain[18] and USA[19] a heat shielding rubber of the following composition (in weight parts):

Butadiene-nitrile caoutchouc	100.0
Zinc oxide	5.0
Symmetric di-β-naphtilparaphenylenediamine	3.0
Sulfur	2.0
Benzothyazolyldisulfide	1.0
Tetramethylthyuramdisulfide	0.05
Cumaron-indenic resin	12.5
Dioctylphtalate	12.5
Stearic acid	1.5
Asbestos fibers	40.0
Hydrated active silicone dioxide	20.0

Vulcanization of the composition was performed at 149°C in 60 min. During testing of disks made from this rubber and containing oriented fibers,—in an oxygen-acethylene burner flame (distance from nozzle is 25.4 mm),—the temperature at the back side of the sample reached 204°C after 90 sec. Under these conditions the material removal rate was 0.025 mm/min, i.e. it was significantly lower than that of materials, based on butyl caoutchouc, plastified butadiene-styrene rubber and methylphenylpolysiloxane elastomer, removal rate of which reached 0.07 mm/min.

Another patent discloses rubber mixtures containing butadiene-nitrile caoutchouc (35–75%, preferably 40–50%), and phenolformaldehyde resin and graphite (65–25%, preferably 60–50%) as fillers.[20] The erosion rate was determined in the engine at propellant combustion temperature of 3315°C, the initial rate of propellant combustion product of 275 m/s, the pressure in combustion chamber was 21 ± 3.5 kG/cm^2, engine running time of 31 ± 6 sec. Under these conditions the erosion rate of the heat shielding material was 0.132–0.155 mm/s, while the erosion rate in the oxygen-acetylene burner test was 0.025 mm/min. The use of a combination of phenole-formaldehyde resin and boracic acid as the filler is described in Reference 21.

High erosion resistance is reported also for heat shielding rubbers V-44 and ORSO-9250 in prenozzle zone of large scale MESP.[22]

Rock Island Arsenal Company developed a rubber compound, combining phenole-formaldehyde resin and asbestos fiber fillers.[23]

The Jet Propulsion Laboratory of California Institute of Technology developed a rubber compound of Gengard-52 type. It contains silicone oxide hydrate, asbestos and additives.[24] The material is used in MESP of Earth satellite ATS. MESP parameters are: weight = 257 kg, length = 1390 mm, diameter = 715 mm, degree of nozzle expansion = 31:1; propellant weight, based on polyurethane with ammonium perchlorate = 232 kg; pressure in combustion chamber = 18.2 kG/cm^2, engine exploitation duration = 45 s. The heat shielding cover thickness changes from 2 mm in the cylindrical part of MESP to 5 mm in the nozzle range. Preparation of covers of variable thickness is performed by applying additional 0.75 mm thick layers on the initial 2 mm thick layer.

Paper[25] points out, that in small MESP, HSM based on butadiene-nitrile caoutchoucs, are applied as nonvulcanized intermediate product are afterwards in situ vulcanized at required temperature and pressure. With large scale MESP having for example a 6.6 m diameter, the protective sheets are applied in vulcanized form.

Rubber compounds filled with asbestos for heat shielding of MESP frameworks of 6.6 m diameter, were developed by Goodyear Tire and Rubber Company.[26,27] The procedures fabricate the heat shielding covers are described in References 28–30.

Asbestos filled rubber compounds for heat shielding of experimental MESP of 4 m diameter are produced by Lokheed Production Company.[31,32] The engine framework consists of three 5–6 m long sections. The HSM is, however, applied only to the end parts of the framework and is of variable thickness, which reaches 44.5 mm thickness near butts. The cover of such thickness is intended to perform on repeated starts of engine. The destroyed part of the cover is removed mechanically. In the case of single use, the cover thickness is 19 mm.

Very important in the study of migration of nitroglycerin and dinitrotoluene from the missile propellants NgR-005 and NgR-006F at the contact with rubbers based on butadiene-nitrile caoutchouc with different concentration and type of vulcanization, specifically with mono-, di- and polysulfide bonds.[33] In this case it was shown that high stability against the influence of missile propellants is found with rubbers based on butadiene-nitrile caoutchoucs containing after vulcanization monosulfide cross-links. The intense degradation of rubbers containing di- and polysulfide cross-links on contact with propellants is attributed to nitrogen oxides, formed during nitrocellulose decomposition.

Specific application of heat shielding rubbers, based on butadiene-nitrile rubbers are in collapsing nozzles of MESP with a high degree of expansion.[34]

The same material was considered as one of the alternatives for rubber JBT-10, silicone-phenolic composition FM 5131, graphite-phenolic composition MX 4926 for heat shielding of the nozzle block of NASA 260 SL-3 type MESP.[35]

A composition[36] based on hydrocarbonic or acrylonitrile rubber containing a dehydrogenation component, a compound of the element of 4–6 period of the VIIIth group is described in Reference 36. The composition must not contain sulfur or sulfur containing compounds as vulcanizing agents to prevent the deterioration of its properties. Silicon dioxide, asbestos or carbon are used as fillers. The use of catalysts allows to increase the char yield to $\geqslant 10\%$. Isobutylene copolymers can be used as the basis of the composition, containing $\leqslant 5$ molar % of butadiene, ethylene with propylene, styrene with butadiene butadiene with acrylonitrile. For example, 100 weight parts of isobutylene copolymer with 0.9 mol % of isoprene are mixed with 25 weight parts of the component containing 67% of nickel, and with 25 weight parts of silicone dioxide. The obtained material is treated by pyrolysis in high-frequency furnace with graphite element, allowing to heat the sample up to 1100° during 1 min. The clear yield and gas hydrogen gas for this composition is 45% and 8.2%, respectively. For the composition, based on the same copolymer, but containing only 50 weight parts of silicone dioxide, these values equal 1% and 0.9%, respectively.

Considerable interest is in HSM based on mixture of butadiene-nitrile and ethylene-propylene rubbers.[37] These materials possess high heat shielding properties. In testing of 3.5 mm thick samples heated by a quartz lamp, for 60 sec, the temperature of the surface was 428°C, while back side was heated up to 115°C only.

Ethylene-propylene rubbers are an important component of HSM because the properties of HSM compounds. If the rubber chain contains over 15% of propylene, the copolymers of ethylene and propylene display relatively high elastic properties because of low crystallinity. If 30–50 mol % of propylene is in the chain, then the polymer becomes completely amorphous and possesses the highest reported elasticity.[9]

To obtain polymers, which can be crosslinked with sulfur, ethylene and propylene are copolymerized with dienic monomer. The content of the third monomer in the rubber is 0.3–2 mol %. The increase of unsaturation content in caoutchouc causes the increases the vulcanization rate and crosslink density.

The physical properties of ethylene-propylene caoutchoucs depend only on the ratio of ethylene and propylene in the polymer but are unaffected by the existence of the third monomer. The rubbers used by HSM producers contain 30–40% of propylene and crystallize neither during storage nor on deformation.

The density of these rubbers is 0.85–0.87 g/cm^3, and their glass transition temperature is 58–65°C. They are stable at mechanical and thermooxidative incorporation of plasticizers. These rubber mixtures also possess good molding ability. The rubbers, based on ethylene-propylene elastomers, are widely used for the preparation of the articles, exposed in use to aggressive media at temperatures of up to 150°C.

Rubbers based on ethylene-propylene elastomers, are preferable as HSM if the fiber glass frameworks of MESP are fabricated by winding.[38,39]

The manufacturing process for an MESP engine HSM is described in Reference 40. The composition contained a tricomponent ethylene-propylene elastomer of GSM type and silicon dioxide as filler.

Fourteen modifications of HSM, based on ethylene-propylene elastomer were evaluated in the flame of oxygen-acethylene burner to simulate the conditions in a solid-propellant MESP. The compatibility with solid-propellant grain was investigated also.[42] The asbestos fiber was used as the filler. The optimal composition recepture R-4 is used in MESP, working according to the following parameters: combustion duration = 3.7–3.8 sec, average pressure in combustion chamber = 3.7 MPa, linear removal of coating = 0.88–1.23 mm.

Ethylene-propylene based HSMs are used also in space technology.[42,43] The Italian "Snia Viscosa" Company developed MESP for European artificial Earth Satellite GEOS. This engine must work in temperature range from −10 to 40°C at axial overloadings of 16 g, acceleration vibrations up to 10.2 g, and rotation frequency of 123 min^{-1}. The engine diameter is 684 mm, length is 1130 mm, its mass is 303 kg, propellant mass is 267 kg, specific pulse is 286 kGs·s/kg, maximum flight thrust is 2360 kGs, average pressure in combustion chamber is 23 kGs/cm^2, performance duration is 47–51 s. HSM is filled with asbestos and the temperature of shielded surface is less than 250°C after the performance of MESP is completed. The heat shield weight is 7.9 kg. The rigidly fixed cartridge consists of 14% of polybutadiene with cyclic carboxyle groups, 76% of ammonium perchlorate and 10% of aluminum.

Another MESP was developed by Tyokol Chemical Corporation for space exploration.[44] Light material, based on phenolic resin, is used as heat shielding, the filled is cork. To prevent cork chipping the shield is covered with rubber, based on ethylene-propylene elastomer. Several HSMs based on ethylene-propylene elastomers are disclosed in patents. For example,[45] discloses a composition consisting of 80–100 weight parts of copolymer of ethylene, propylene and diene with non-conjugated double bonds, 5–20 (preferably 10) weight parts of polybutadiene with COOH end groups, 40 weight parts of perchloropentacyclodecane and 20 weight parts of antimony oxide to increase the combustion strength, 75–150 (preferably 100) weight parts of asbestos and 7.5 weight parts of 2.5-dimethyl-2.5-(*ter*-butylperoxi)hexane as vulcanizing agent. The density of hardened HSM is ≈1.4 g/cm^3, the Barckol hardness is 32–42, the strength is 9.8 kGs/cm^2, the elongation is 36% and modulus is 57.89 kGs/cm^2. The Shore hardness is 77 after the second stage of vulcanization at 121°C for hours. To determine the clear (coke) yield the vulcanized samples of 50.8·50.8·5.0 8 mm size, are placed in MESP, working with the propellant having the combustion temperature of 3204°C at the rates of solid propellant combustion product flow of 20.09 and 137.9 $\text{g/cm}^2\cdot\text{s}$. Under these conditions, the rate of coking of HSM samples at 20.09 $\text{g/cm}^2\cdot\text{s}$ was 0.2794 mm/s, and at 137.9 $\text{g/cm}^2\cdot\text{s}$ 0.762 mm/s.

Other patents[46,47] disclose materials, based on copolymer of isobutadiene and isoprene, butadiene-styrene, chloroprene and other elastomers along with HSMs based on ethylene-propylene elastomer. An HSM based on chlorine containing elastomer was also used in MESP.[48]

A typical HSM based on synthetic chlorinated elastomer (preferably chloroprene), contains 25–100 weight parts of a thermostable fiber (silicon dioxide, asbestos, etc.) and various additives per 100 weight parts of elastomer. For example (in weight parts): neoprene WRT—50, asbestos—50, Permanax 45—1, stearic acid—1, magnesium—4, zinc oxide—5, ethylene-tiocarbamide—0.5. After mixing on rollers the rubber mixture is calandered to the thickness of 2 mm, and sheets of required sizes and shapes are cut to conform to the shape of the protected surface. After that, molding of coatings is carried out for 30 minutes at 160°C.

Tyokol Corporation heat shielding coatings, based on polyisoprene with asbestos and carbon black as fillers, possesses sufficiently high mechanical strength (1120 kGs/cm^2) at required elongation and good heat shielding characteristics. At testing in the flame of oxygen-acethylene burner (distance between sample and nozzle was 19 mm, inclination angle of the flame was 45°) the mass removal was 20% after 60 sec, ablation rate = 0.135 mm/s, and temperature of back side of the sample increased by only 12°C.[49]

Rubbers, based on butyl- and polyurethane elastomers, were developed for internal heat shielding of MESP capable of multiple starts. Such coatings were tested successfully under repeated (up to 12) starts of the engine.[8]

Rubbers, based on polyurethene elastomers can be used for heat shielding coatings working in the flow of solid propellant combustion products, having combustion temperatures of up to 3300°C and forming mechanically stable layer of coke.[50]

USA patents disclose fillers for HSM which are unusual for rubber industry. Thus, patent[51] and notes[52,53] discuss a material, containing chromium oxide as the filler. Patent[54] discloses a metal haloid (zinc chloride), possessing boiling temperature of 500°C and high pressure of vapours in the range of 500–1200°C.

Materials have also been developed possessing improved erosion stability with resistance to vitrification to −40°C.[55] They are produced on the basis of elastomers participating in the composition of solid propellant. They are suitable for applications where the propellant is in direct contact with the heat shielding in the engine. The application of such materials is mostly advisable in large size engines. In this case the coating is applied to the walls as partly vulcanized intermediate and the complete vulcanization is performed simultaneously with the elastomer, on which the propellant is based.

Materials, produced by Goodreach Company, are intended for use at temperature up to 3850°C and propellant combustion time of up to 2 min.[56,57]

Rubber-like HSM applicable in a wide range of temperatures (1360–2760°C) and pressures (35–140 kGs/cm^2) are discussed in Reference 58.

Figure 2 shows multilayer rubber coating, applied to spheric lid of large MESP.[59] Specific feature of this coating is smoothly changing thickness, that provides effective shielding of various parts of the framework in accord with the intensity of the influence of the flow of solid propellant combustion products. The rubber is applied by layers, whose number can reach 20 on sections exposed to maximum erosion.

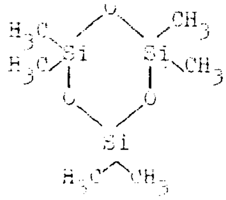
Not much is written about rubber-fabric (reinforced) elastic materials, based on organic elastomers, despite the fact, that they possess increased erosion strength in comparison with unreinforced rubbers. It is pointed out,[60] that chared rubber-resin compositions reinforced with fabrics show higher erosion strength that plastics at lower densities. The temperature range of working ability is also wider for reinforced systems than for plastics.

Apparently, "Astracan" material, based on Hitco-158 type rubber and Pliofen 5900 resin, reinforced with carbonic fiber and worked out for the nozzle systems of some engines,[61] belongs to similar systems. The material possesses the density of 1.4 ± 0.05 g/cm and is vulcanized during 4 hours at 160°C and 150 bar pressure.

In some cases HSM must meet additional requirements. Thus, for example, sometimes HSM must protect blocks from splitting during mounting on the engine framework as well as to protect the MESP framework from high temperature flows of solid propellant combustion products. In this case it is suggested heat shielding coating, consisting of two thin layers of rubber, based on natural or synthetic elastomers, between which a perforated sheet with holes filled by the same rubber is placed.[62] Such composite coating may be deformated on shrinkage of blocks can withstand the pressure formed during propellant combustion. The above mentioned two layers of rubber are not adhered to each other over the entire contact surface. The adhered sections have the form of separated longitudinal belts whose width is approximately 3 times lower, than that of longitudinal belts where the adhesion is not performed. Such adhesion free zones, are obtained applying silicon and polytetraethylene belts.

Wide applications for heat shielding of internal surfaces of MESP and direct-flow missile engines (DME) exist for HSM based on silicon-organic elastomers. These materials work successfully under conditions existing in MESP and during the 1-st starting stage of DFME, as well as during the oxidative phase which exist in DFME during the 2nd stage of performance. This is explained on the basis of thermal decomposition characteristics of silicon-organic elastomers.

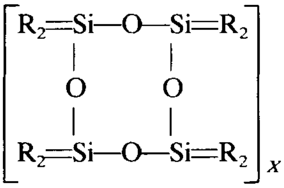
Comparing with hydrocarbonic elastomers, possessing equal energies of carbon-carbon bond (58.6 kcal/mole) in the main chain, the silicon-organic elastomers possess sufficiently higher bond energy of silicon-carbon type (from 101 to 118 kcal/mole) in the main chain, calculated from combustion heats.[63] Polar silicon-carbon bond stipulates high ability for rearrangement under thermal influence. The silicon-organic elastomers are suitable as the basis of HSM because of their ability to form under the influence of high temperatures cyclic low molecular compounds possessing high thermoabsorption.[64–66] For example, cyclic trimer is formed during the decomposition of dimethylpolysiloxane elastomer.[67]



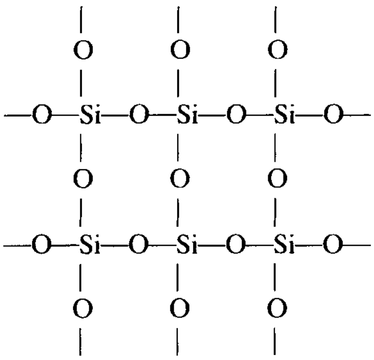
Besides this trimer, content of which can reach 44%, the following dimethylcyclosiloxanes can be formed at polydimethylsiloxane heating over 400°C in vacuum: $[(H_3C)_2SiO]_4$—24%; $[(H_3C)_2SiO]_5$—9%; $[(H_3C)_2SiO]_6$—10%, $[(H_3C)_2SiO]_{n>6}$—13%.[68] Further decomposition of cyclosiloxanes into low molecular products requires additional amounts of heat energy.

The ability to high temperature transformations of silicon-organic elastomers into cyclic compositions is stipulated also by molecule structure.[69] Molecules of polydimethylsiloxanes possess spiral-like form with six or eight chain units in single loop of the spiral as a consequence of high flexibility of molecular chains and low sizes of methyl groups. Polysiloxane chain break occurs at silicon-oxygen bond. In this case spiral-like structure of the molecule creates conditions for closing parts of the molecule into cycles provide the ends come sufficiently close after the break.

The experience with organic polymers shows that one of the most important conditions for char formation is the ability to form cyclic structures on heating. Contrary to organic cycles, where 5- and 6-unit cycles are the most stable, on the silicon-organic polymers under the influence of high temperatures and in inert medium form cyclic low molecular weight polymers. In presence of oxygen, however, polymeric silicon oxides are formed the typical representative of which is silicon dioxide $(SiO_2)_n$. For example:



is transformed into



In this case each silicon atom is linked with four atoms of oxygen, whereas carbon does not form similar stable structures. This is explained by the fact, that silicon, possessing larger atomic size and higher charge than carbon, forms stable polymeric formations while those of carbon are thermally instable. Thus, for example polyoximethylenes with similar molecule structure $—CH_2O—CH_2O—$ are thermally instable and can decompose easily already at 170°C.

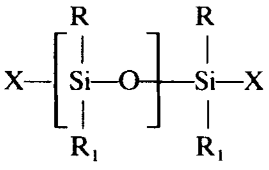
Because of the higher energy of silicon-carbon bond in comparison with the energy of carbon-carbon we can expect that more severe conditions of flow are required for decomposition of polymeric compositions of $[R_2SiO]_m$ and $[SiO_2]_n$ type in comparison with carbonic chars. Moreover, at high temperatures materials, based on polysiloxanes, carbonic residues are also formed, their yield depends on chemical structure as the nature of fillers.[70]

The important feature of the compositions, based on silicon-organic elastomers is the resistance to aging under severe climatic conditions. This is stipulated by the absence of double bonds in the macro molecule of the elastomer.[71] Because of the absence of double bonds this elastomer does not enter addition reactions. After vulcanization silicon-organic compositions are completely nontoxic, possess good stability against the influence of oxidating agents, solutions of salts, acids, and alkali.

The vulcanizates of dimethylpolysiloxane elastomer possess elastic properties in sufficiently wide range of temperatures (from −70° to 300°C), that attributed to large interatomic distance in silicon-oxygen unit in comparison with the carbon-carbon bond.[9]

It should be mentioned, that vulcanization of compositions, based on silicon-organic elastomers, according to methods, worked out for the first time by N. B. Baranovsky *et al.*,[72,73] may be performed without heating. In addition to the containing systems, other classes of vulcanizing systems[74-79] were developed.

Silicon-organic linkages represent great interest for rubber-fabric reinforced materials as well as for porous structures, this is because these elastomers are produced both as rubber-like material, and as relatively fluid liquids which are called liquid rubbers. Thus liquid rubbers simplify the impregnation of various types of preforms.[79] The liquid silicon-organic rubbers possess linear structure with molecular weight in the range from 20,000 to 100,000 and viscosity between 0.5–80 Pa. Their general formula is:



$$X-\left[\begin{matrix} R \\ | \\ \mathrm{Si}-O \\ | \\ R_1 \end{matrix}\right]-\overset{\displaystyle R}{\underset{\displaystyle R_1}{\mathrm{Si}}}-X$$

where R and R_1 = methylic, phenylic, vinylic and other radicals; X = functional groups, for example OH.[80] The methods of obtaining linear polysiloxanes are described in References 81 and 83.

The attempts of developers of silicon-organic elastomers are aimed, generally, to the increase of freezing, heat-, thermo- and oil stability.[84] It was found, that the increase of freezing stability may be provided by suppression of the ability of polyorganosiloxanes to crystallize. For this purpose regularity of their structure is broken by the introduction besides dimethylic groups also methylphenilic, diphenilic and diethylic groups.[85-88] The most effective freeze resistant siloxane elastomers are polydimethyldiethylsiloxanes, with the glass transition temperature in the range between −135 to −140°C.

Heat- and thermostability of silicon-organic elastomers is increased by the introduction of aromatic side groups into their structure.[89,90] Another way for increasing these properties is the synthesis of polyblock copolymers, consisting of rigid and elastic blocks.[91]

Polyorganosiloxanes are also known for their resistance to ozone, radiation and high vacuum.[92-94]

Silicon-organic materials for MESP show significant advantages over HSMs based on polychloroprene, butyl rubber, polyurethanes,[95] fluorine elastomers, polysulfides, epoxy resins,[96] and before phenol-neilon erosion stable material, also.[97-101]

The conclusions about the advantage of silicon-organic materials with organic and mineral fillers are based on performance testing in high temperature gas flow of solid propellant combustion products, flowing from MESP at high rates. The investigations showed, that erosion resistance of the materials depends on the chemical nature and amount of the filler, which can vary from 10 to 100% depending on application. The higher the intensity of heat- and mass transfer and erosion influence of the flow, the larger is the required amount of filler.

Silicon-organic rubbers have found wide application for shielding the combustion chambers and gas ducts for combustion products of solid propellant in "Minuteman," "Bomark," "Polaris," "Saturn," "Titan IIIC" type missiles etc.[102-106] In this case the weight of silicon-organic heat shielding, for example on "Minuteman" missile, is 250 kg, and that of the first section of the "Polaris" missile—50 kg.[107]

One of such silicon-organic rubbers is USR material, filled by phenolic resin and inorganic hydrates.[108] Its properties are shown below:

Density, g/cm^3	1.24
Strength limit at break (at 21°C), kGs/cm^2	56–84
Relative elongation at stretching (at 21°C), %	200–400
Hardness according to Shore (scale D, at 21°C)	45
Heat conductivity coefficient (at 93°C), W/m·grad	0.26
Specific heat capacity (at 65°C), kJ/kg·grad	2.3

A slightly higher density is found with silicon organic rubber AMS 3345–1.32 g/cm^3. This rubber was applied in "Minuteman III" missile.[109] Heat shielding coating thickness is 1.65 ± 0.13 mm. High temperature tests of samples of 38 mm diameter were performed on stationary reactive engine at pressure in combustion chamber of 7–12.2 kGs/cm.^{2} The tests were performed according to the following scheme: 4.2 sec at heat flow of 4800–5480 kJ/m^2, 1.3 sec at 798–1370 kJ/m^2. Table III shows the erosion results.

The material is applied to the shielding surface through the support from fiber glass fabric. It provides heat shielding of internal surfaces of PBPS engine from the influence of high temperature gas flow with solid particles during the engine performance and separation of the third section of the missile.

Another material suitable for nozzle block is the composition based on dimethylpolysiloxane elastomer DC 93-022 of Dow Corning Company, which is hardened at elevated temperatures.[110] Further investigations of the material modifications were performed at values of heat flow of 8631, 11858 and 17598 kW/m^2

TABLE III

Erosion strength of AMS 3345 material

Exposition duration, s	Heat flow, kJ/m^2	Material moving away	
		g	mm
4.2	4800 - 5480	1.00	1.15
3.0	2970 - 3310	0.97 - 1.17	0.75 - 0.90
1.3	798 - 1370	0.19 - 0.43	1.52 - 0.33

and the rate of high temperature gas flow up to 3.0 M/s. The best results were obtained when dimethylpolysiloxane was substituted with methylphenylpolysiloxane and filled with silicon carbide. Testing included the following substances: aluminum oxide, boron carbide, boron nitride, molibdenum carbide, niobium carbide, titanum carbide, zirconium boride, tungsten carbide, boron nitride, zirconium carbide, zirconium silicate. The material was designated as 93-104, its heat conductivity coefficient is 0.33 W/m·grad. The material 93-104 can be reinforced with asbestos or aromatic polyimide or polyester fabrics to broaden the range of its application. The reinforcement also increases the shielding potential of the base polymeric compound.[111] Antioxidants and antiozonants may also be incorporated into the material. The same material can also be used for the preparation of coatings by rolling. In this case, the material is reinforced with steel network belts.[112]

The synthetic fibers are used as a reinforcing component, while the wood fillers are usually used as powders.[113]

The DC-93-118 material of Dow Corning Company is intended for shielding the cylindric internal surfaces of MESP. However, some other materials produced by this company, made on the basis of silicon-organic elastomers can also be used for the same purpose.[114]

The customers receive the silicon-organic rubbers as calandered sheets, belts or extrused fabrics.[115] As a rule, such materials are applied in MESPs with low rate high temperature gas flows of products of solid propellant combustion.

Vulcanized mixtures can be stored in closed containers at 25°C without any change in performance for at least 6 months. Molded coatings, however, possess longer storage time. Pressure is not required for vulcanization, but small pressure is necessary densification of material and application of molded coating. The vulcanization is performed at 160–190°C, its duration depends on temperature and configuration of rubber articles.

Silicon-organic HSM are produced also as molding compositions, filled with short dropped fibers. Such compositions can be processed into articles of complicated form without heating under pressure. Articles, possessing high mechanical strength in low rate high temperature gas flows of the products of solid propellant combustion can be obtained from these materials by compression molding.

Compositions, based on silicon-organic elastomers, can also be used as matrix for rubber-fabric materials. Carbon, silica, quartz, aramide and other fabrics are used as fabric preforms. For this purpose the same processes are suitable, which are used for the production of the materials from fabric, impregnated by organic resins. Materials possess outstanding mechanical characteristics produced from carbon fiber fabrics, and consequently form strong coherent layers of coke. Materials with silica and quartz fabrics perform better in oxidating atmosphere, encountered in the flow of fluid reactive engines.

The main material among silicon-organic elastomers is the very inexpensive polymer polydimethylsiloxane. It can be modified by vinylic, phenylic and (or) fluorine-containing groups. These modified elastomers possess increased oil stability and lowered crystallization temperature, coupled with high mechanical strength and low residual shrinkage. The following materials are usually applied as vulcanizing agents of these elastomers: organic peroxides of bis-2,4-dichlorbenzoile, dibenzoile, dicumyle and di-*tert*-butyl. The following materials are used as fillers: powder glass, silica, quartz, carbon, silicon carbide, iron oxide.

The screening of silicon-organic rubbers compounds is carried with 30 cm long cylindric samples having the initial diameter of 1.5 cm. They are tested in the standard solid-propellant device which is 81.4 cm long and 15.2 cm diameter.

Mixed propellants, containing 20% of aluminum, are used for the tests. Average pressure in combustion chamber is 53 atm., the testing time is 8.8 s. The results of tests of HSM, based on various materials, are shown in Table IV.

A thin metal foil is bonded to the surface of silicon-organic rubber to prevent the diffusion of polybutadiene propellant components (such as vulcanizing isocyanate agent) into it.[116]

The use of foil solved the problem of application of silicon-organic rubbers in solid-propellant jet engines, because good adhesion between silicon-organic materials and propellant, based on organic rubbers, is difficult to achieve. There is no difficulty, however, in bonding these two materials to the metal foil. To avoid the additional manufacturing costs, direct adhesion (without the foil) of such heterogeneous materials was first described in Reference 117. For this purpose silicon-organic elastomer is combined with polybutadiene containing hydroxyl end groups which migrate to the coating surface. The propellant is also prepared on the basis of polybutadiene with hydroxyl end groups and with isoforondiisocyanate. This leads to the formation of a long-chain polymer, which is insoluble in silicon-organic material but forms a bond with the propellant through action of isocyanate. In this case hydroxyl groups of butadiene do not interact with functional groups of silicon-organic elastomer. The detailed preparation of this propellant-shield system is described in Reference 117.

High temperature tests showed that the erosion rate of the coating is 1 mm/s and that the coating is not separated into layers, when the coke layer is formed. Under this coke layer, the material preserves its plasticity.[118]

An important technological advantage of silicon-organic compositions based on liquid elastomers, is their ability to form the coatings by centrifugal method or by pouring into mold cavity under pressure.[119] Such methods are used for the prep-

TABLE IV

Erosion stability of HSM

Material basis	Filler	Density, g/cm^3	Ablation rate, mm/s
Polydimethylsiloxane elastomer	Carbon	1.16	0.020
Ethylene-propylene rubber	Aramide fiber	1.14	0.025
	Asbastos fiber	1.28	0.015
Butadiene-nitrile rubber	Asbastos fiber	1.23	0.030
Propylene rubber	Carbon	1.24	0.015
	Carbonic fabric	1.23	0.007
	Carbonic tricot	1.33	0.006
	Silica	1.45	0.019
	Quartz	1.49	0.020
Phenolic resin	Carbonic fabric	1.48	0.005
	Silica	1.60	0.020

aration of coatings from the Dow Corning materials DC-93-104, DC Sygard 184, DC E691-22E and General Electric RTV-560 for internal surfaces of MESP and DFME.

Comparative high temperature tests of HSMs based on silicon-organic elastomers and phenolic asbestos and fiber glass reinforced plastics are reported in References 120–122. It was found, that DC 93-104 material provides the best heat shielding against the influence of the flow with 1980°C temperature.

Martin Marietta decided to use silicon-organic rubber for "ground-ground" and "ground-air" missiles equipped with the direct flow engine "Seram."[123]

For long performance time (up to 9 min) direct flow missile engines working below 2080 K temperature, the possibility was considered to use rubber-fabric material with silicon-organic matrix while the fabric carcass was made from three-dimensional fabric.[124]

The application of two types of materials for shielding the combustion chamber of direct flow missile engines is discussed in Reference 125. One type are rubber-fabric materials with silica carcasses, treated with phenolic, epoxy, polyimide and other resins and impregnated with silicon-organic binders. However, for these materials the problem is the increase of heat conductivity coking of binders under the influence of high temperature flow. In this case, the rubber-like materials such as DC 93-104 are preferable because they are stable under the influence of high temperature oxidating flow, while the heat conductivity of the coke layer remains sufficiently low.

To provide safe heat shielding of afterburner in ASALM missile, silicon-organic rubber is reinforced with stainless steel cells.[121] The material performs adequately under the influence of the flow having temperature of 1980°C.

Materials, based on silicon-organic elastomers, are selected also for heat shielding coatings of engines for invisible tactical missiles.[126]

Methods to study the pyrolysis HMSs with further analysis of volatile products and solid residue with the help of mass-spectrography and γ-diffraction technique are described in Reference 127. With the help of these techniques we can obtain the plots of temperature change as a function of sample thickness, duration of test, heat conductivity and specific heat capacity of coke and initial material, heat of formation and the order of kinetic reactions.

CONCLUSIONS

1. The elastomeric HSMs are widely used for shielding surfaces of small- and large-scaled MESPs, on "Minuteman," "Polaris," "Titan," "Saturn," etc. missiles.
2. The heat shielding coatings are produced from intermediate products of condensed or porous rubbers. They may be reinforced with fibers, fabrics, etc.
3. The elastomeric HSMs possess high performance characteristics and do not crack on deformations of shielding surfaces, exposure to heat and mechanical impact, vibrations, and during storage and transportation.

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