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ELASTOMERIC COMPOSITION FOR USE AS ROCKET INSULATION

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The present invention relates to an insulating lining or coating for substrates of structural members usually made of metal or reinforced plastics. More particularly the present invention relates to a flexible heat and/or pressure vulcanizable rubber-like material which is capable of protecting a substrate from the corrosive, erosive and otherwise deleterious action of flame temperature and similar temperatures such as encountered in the burning of various propellant substances.

This application is a continuation-in-part of application Ser. No. 153,675, filed Nov. 20, 1961, now abandoned.

Flame temperatures encountered in the combustion of propellants, particularly when used as source of propulsion, necessitating the confinement of the gases of combustion and ultimate release thereof through orifices, are usually accompanied by extremely turbulent flow conditions. All of these features place considerable stress and strain upon the member defining the escape passageway. While the combustion of the propellant in the case of rockets and the like will usually be of short duration, the temperatures and turbulence encountered has been found to very easily destroy even the strongest and most exotic alloys formed of iron, steel, titanium, magnesium, silicon, chromium, beryllium and the like. As a consequence, the projectile structure fails leading to total destruction thereof through explosion or in the event that only the exit passageway is destroyed, the projectile proceeds in an erratic uncontrollable path since its trajectory or path is at least in part dependent upon the contour of the passageway through which pass the gaseous products of combustion.

Various attempts have been made to protect the structural members which are exposed to such temperature and turbulence conditions. Principally, attempts have been made to protect the structural members from these deleterious effects by applying some sort of a protective coating or lining to the substrates defining the structural members. Various plastics, resins and rubbers both filled and unfilled have been tried. Among these are included phenolic resins, epoxy resins, high temperature melamine silicone coating ceramics, polyester resins and the like. Unfortunately, these resinous systems are for the most part rigid systems when cured, and as a consequence shrinkage, expansion, cracking and blistering are encountered due to the rapid temperature and pressure changes encountered. Some rubber-like elastomer systems have been attempted, but unfortunately these materials are principally hydrocarbon in nature. They are consequently inherently destroyed in and of themselves upon exposure to the conditions discussed above, particularly the flame temperatures.

It was therefore surprising that we have been able to provide a lining or coating upon the structural members adapted to be contacted by flame temperatures and the turbulent flow conditions involved from the combustion of liquid or solid propellants, which coatings or linings are capable of enduring the deleterious conditions for a time sufficient to allow complete combustion of the propellant.

It is an object of the present invention to provide a protective coating or lining for the surfaces of structural members which define a chamber for containing a propellant composition, the burning of which yields a short duration blast of flame, high temperature and high velocity gases.

It is another object of the present invention to provide a heat and/or pressure vulcanizable material which is capable of being formed into a flexible lining or coating for protection of a substrate.

It is yet another object of the present invention to provide a method of producing a material which may be easily and simply applied to a substrate for the purpose of protecting said substrate from flame temperatures and gases released by combustion of a propellant charge.

It is likewise an object of this invention to outline a method of installing the protective lining or coating to provide the optimum protection of the substrate with efficient utilization of the insulating material forming the coating or lining.

It is also an object of the present invention to provide a coating or lining which is extremely efficient in providing a balance of optimum protection and minimum weight.

In its simplest embodiment the present invention evolves out of the discovery that an intimate physical mixture of a heat and/or pressure vulcanizable elastomer and a fibrous form of asbestos filler which is retained on a 325 mesh screen (Tyler Series) as determined by a wet classification test can be applied to a substrate, and after vulcanization the resulting product will protect the substrate from short term flame blasts. The desired asbestos filler is usually employed in a mixture of fibers of which some are too fine to be retained on a 325 mesh screen. The maximum size of asbestos fibers which can be employed in this invention is limited only by the practical consideration of sizes available by production methods.

By the term elastomer is meant any rubber-like substance having some degree of flexibility in the cured, vulcanized or heat and pressure-converted state. Examples of the suitable elastomers are natural rubber, butyl rubber, butadiene-styrene copolymer rubbers, nitrile rubbers, neoprene rubbers, polyurethane rubbers, silicone rubbers, chlorosulfonated polyethylene rubbers, polybutadiene rubbers, polyisoprene rubbers, butadiene acrylonitrile rubbers, fluorocarbon polymer rubbers, ethylene-propylene copolymer rubbers and the carbon-sulfide rubbers as well as various combinations and blends of these rubbers.

The asbestos filler employed in accordance with the present invention must have an appreciable portion thereof composed of a relatively fibrous form in which the fibers are of definite length, and as such the asbestos filler as contemplated by the present invention is distinguishable from conventional asbestos filler materials which are made up for the most part of fines and/or floats. Asbestos, of course, is a natural occurring substance which is mined in various portions of the world. In the course of mining and processing for commercial sale the asbestos becomes exposed to degradative processing reducing the asbestos to a substantially fine, particulate condition. The commercially available asbestos materials fall into two general classes. One class consists of anhydrous metal silicates such as, for example, diopside, wollastonite, anthophyllite, tremolite, crocidolite, actinolite, mountain leather and mountain cork. The other class of asbestos materials are hydrous silicates of divalent metals. The most important of the hydrous silicates is chrysotile, which is the preferred type of asbestos in accordance with the present invention.

Preferably, the chrysotile asbestos is in a fibrous form. By the term "fibrous form" we mean the material is composed of a range of various lengths of fibers. For this purpose these asbestos materials are classified according

to grade in accordance with the amount of fibers which are of various fiber lengths as determined by the so-called Bauer-McNett Wet Classification Test. This test has been adopted by the Quebec Asbestos Mining Association. The equipment for making this determination is commercially available. In brief, the test involves forming a dilute slurry of a given weight of the asbestos and allowing it to pass through a series of vertical screens of decreasing openings. The Bauer-McNett test utilizes the Tyler Series of screens.

A preferred fibrous form of asbestos in accordance with the present invention is composed of at least 65 percent, more preferably 70 percent of fibers which are retained on a 200 mesh screen (Tyler Series) or larger as determined by the Bauer-McNett Test. In other words not over 35 percent of the fibrous form of asbestos in accordance with this invention will pass a 200 mesh screen (Tyler Series having openings 0.0029 inch). Preferably, the asbestos material to be used in accordance with this invention will be of such distribution that at least 14 percent, more preferably 25 percent, of the total amount of asbestos fibers will be retained on a 14 mesh screen (Tyler Series having openings of 0.046 inch) as determined by the Bauer-McNett Test.

It is usually desirable and preferable to pre-dry the asbestos by introducing it into a relatively large volume chamber or container and subjecting it to tumbling in order to increase the freeness of the asbestos. It is found that the tumbling together with circulating air serves to break up any bundles of individual fibers which have not become separated in the processing by the manufacturer. Care, of course, should be taken that the tumbling is not of such severity that the fibers are materially damaged or such that shortening of the fibers occurs.

The fibrous form of asbestos should be added in accordance with this invention in amounts from about 3 to 200 parts and preferably no more than about 80 parts thereof per 100 parts of the elastomer, not including the other components of the particular recipe selected. The fibrous asbestos component can be combined with the elastomeric component on a conventional rubber mill. It is expedient to have the elastomer worked gradually onto the mill. The temperature of the stock during milling usually is about 200° F. Subsequently the asbestos is added gradually and evenly to the rolling bank of stock on the mill with or followed by a suitable plasticizer or dispersing agent to aid in the incorporation of the fibrous asbestos into the elastomer with a minimum of residence on the mill. Care should be taken that the spacing of the rolls is carefully controlled to accomplish the dispersion of the asbestos into the elastomeric stock without breaking down the asbestos fibers. After the asbestos is dispersed in the elastomer, the stock can be stripped from the mill and set aside for further processing. It is of course, possible to adjust the spacing of the drums of the mill at this point and strip the material off in selected widths and thicknesses for direct use as lining material for structural substrates.

The mill incorporation of the asbestos into the elastomeric stock yields a sheet in which the asbestos fibers are oriented for the most part in a direction generally parallel to the surfaces of the sheet and in alignment with the linear dimension of the sheet of stock as removed from the mill. Preferably, these fibers are also somewhat randomly arranged with some intermeshing and entanglement. It is important that the mixing be conducted so as to avoid, or to maintain at a minimum, fiber disposition perpendicular or substantially perpendicular to the surface of the sheet material.

The sheet material stripped from the mill can be further processed by calendering to yield relatively thin sheets of the asbestos-containing stock. Alternatively the material can be taken from the mill and molded directly by heat and/or pressure in a mold having the desired contour In the latter case the stock material for molding should be preferably carefully positioned in the mold such that the flow therein is maintained at a minimum whereby the general orientation, size and form of the asbestos in the elastomeric stock is not substantially changed.

It is frequently desirable to include a second auxiliary filler in the elastomeric stock in addition to the asbestos. Examples of additional fillers are carbon black, calcium carbonate, clay, formica, kaolin, metallic oxides, including zinc and titanium oxides, slate flour and silica as well as various coloring pigments and dyes. Preferably, the auxiliary filler is one which has a specific gravity not greater than and preferably less than the asbestos. As a consequence, the silica type fillers such as the silica aerogels and xerogels are usually preferred. Where an auxiliary filler is used, it may be used in equal weight amounts as the fibrous asbestos, although any proportion can be used so long as the resistance of the lining to flame temperatures and exhaust gases under turbulent flow is not materially reduced. Generally, no more than about 80 parts by weight of an auxiliary filler per 100 parts of elastomer are practical, especially with reinforcing fillers.

When using a liquid or castable type of elastomer such as a polyurethane, a nitrile, a polysulfide, a silicone system or a solvent dispersion of polymer, the asbestos filler can be incorporated therein in a dough-mixer rather than a roll mill. The viscous liquid castable systems are not conveniently mixed on a mill as they usually run through even the smallest spacing between the mill rolls. Accordingly, a dough mixer such as a Baker-Perkins Mixer can be utilized. Care must be taken in adding the asbestos to the elastomer in order to achieve the desired asbestos orientation in the stock. Of course, with these liquid castable systems asbestos fiber orientation can be achieved in the actual coating or lining operation itself.

Depending upon the viscosity of the filled stock, a brush, putty knife, trowel or the like can be so manipulated that orientation of the fibers is achieved and/or maintained during installation of the stock as a coating on a substrate. A liquid stock is permitted to flow upon the surface to be coated using careful strokes of a tool as indicated to achieve fiber orientation. Multiple coats of the material can be applied in such a system allowing sufficient time for the previous coat to set.

This type of operation provides considerable flexibility in adjusting the orientation of the fibers to meet the particular contours and design of the structural member which is being coated. In the case of a propellant chamber the coating is applied such that the asbestos fiber orientation is generally along the axis of the chamber or casing. In the case of an exit nozzle experience will determine the expected critical areas of contact by exhaust gases and turbulent flow. This critical surface area can be provided with multiple coats and with particular fiber orientation which best resist the adverse effects of heat and turbulence.

The asbestos-filled stock can contain any of the components common to elastomeric compositions such as accelerators, catalysts, tackifiers, mill lubricants, pigments, stabilizers, plasticizers, antioxidants and the like. Accelerators and catalysts are included in the more general term "vulcanizing agents." The selection of vulcanizing agents and the amounts to be used depend on the particular elastomer being used and the desired physical properties. However, such determinations are old and well-known and not a cirtical aspect of this invention. Typical systems are discussed, for example, in Vulcanization by N. Bergen, printed by P. M. Bye & Co., Oslo, Norway (1948); Hycar Manual HM–1, B. F. Goodrich (August 1958); and Hycar Manual HM–7, B. F. Goodrich (November 1960). In these references, for example, sulfur levels from 0.2 to 40 parts by weight per 100 parts of elastomer and accelerator levels from 0 to 10 or more parts by weight are disclosed. However, the total vulcanizing agents are preferably employed in a range of from

1.0 to about 20 parts by weight per 100 parts by weight of elastomer.

The asbestos filler is preferably one of the last components to be incorporated in a stock to minimize breakdown of the asbestos fibers during mixing. Generally, the composition is cured after being applied to a substrate and prior to being exposed to flame temperatures and turbulence, but the necessity for this cure can be easily determined by a simple flame test on each different composition.

The following examples are merely illustrative and are not intended to limit this invention the scope of which is properly delineated in the appended claims. All quantities are measured by weight unless otherwise stated.

EXAMPLE 1

Laminates were prepared with the compositions described below varying only in the filler as noted. Each composition was composed of a master-batch of:

	Parts
An elastomeric copolymer of butadiene and acrylonitrile in a mol ratio of 2:1 and having a Mooney viscosity of 70 to 90 (large rotor)	100
Zinc oxide	5
Symmetrical dibeta-naphthyl-p-phenylene-diamine	3
Sulfur	2
Benzothiazole disulfide (accelerator)	1
Thiuram disulfide (accelerator)	.05
Coumarone-indene based resin (tackifier)	12.5
Dioctyl phthalate	12.5
Stearic acid	1.5

In addition the fillers shown below were added.

Filler

A 40 parts of loose chrysotile asbestos fibers of which about 22 percent are retained on a 4 mesh screen (Tyler Series), about 23 percent are retained on a 14 mesh screen (Tyler Series), about 20 percent are retained on a 35 mesh screen (Tyler Series) and about 7 percent are retained on a 200 mesh screen (Tyler Series) as determined by the Bauer-McNett Test and 20 parts of a hydrated reinforcing silica filler.

B 60 parts of the silica filler of A.

C 60 parts of the asbestos fibers of A.

D 80 parts of the asbestos and 20 parts of the silica of A.

E Same as A but replacing the asbestos with graphite fibers.

F Same as A but replacing the asbestos with Teflon fiber.

G Same as A but replacing the asbestos with nylon fiber.

H Same as A but replacing the asbestos with a commercial fibrous silica.

I Same as A but replacing the silica with magnesium oxide.

J Same as A but replacing the silica with aluminum oxide.

K Same as E but the graphite being a laminated woven fabric.

In each case the master-batch components except the sulfur and dioctyl phthalate were mixed on a two-roll rubber mill using conventional techniques. Cold water was circulated in the rolls while the master-batch was mixing. Any filler other than asbestos or other fiber was added together with about 30 percent of the dioctyl phthalate plasticizer. The asbestos was then slowly added with uniform distribution of the asbestos across the width of the bank. The remainder of the plasticizer was added immediately thereafter to aid in the distribution of the fibrous asbestos as it rolled into the stock. The sulfur was milled in last. The mill was maintained at a setting of about .040 inch for a laboratory mill and the rolls were kept cool. Mixing took about 20 minutes. The resulting material was stripped off of the mill and was later, in a calendering operation, formed into a sheet composed of five plies each having a thickness of 0.02 inch.

The above compositions were molded into disc-shaped test specimens 2 inches in diameter and ¼ inch thick maintaining fiber orientation generally in the plane of the disc-shaped specimens and press-cured for about 60 minutes at 300° F. These cured specimens were then subjected to an oxyacetylene flame test in order to determine the ability of the vulcanized specimens to withstand the test and to compare the performance of the various fillers. An oxyacetylene torch having a 0.075 inch diameter nozzle was positioned with the nozzle located exactly one inch above the center of the upper surface of the specimens and normal thereto. The torch was so mounted that it could oscillate through an arc of 60° from the perpendicular changing the flame direction without moving the point of contact of the flame on the specimen surface. The purpose of this oscillation was to simulate the turbulent flow conditions present during the actual firing of a propellant contained in a chamber. The oscillation was maintained at 10 cycles per minute for purposes of the test. The flow rates of oxygen and acetylene were controlled carefully so that a relative ratio of 1.1:1 was maintained to produce a neutral or slightly reducing flame. A protected thermocouple was placed under each specimen during the test. A specimen failed if it burned through in less than 90 seconds or if it provided such poor insulation that the thermocouple reached a temperature of 400° F. in less than 90 seconds. It was generally considered that if a specimen could withstand this test it was composed of a satisfactory insulating material. The specimens were weighed before and after the test to determine their weight loss. The specimens after exposure were carefully examined, particularly the surface exposed to the flame. Examination of a diametric section of each surviving specimen revealed a lower layer of apparently unaffected material, an intermediate layer of degraded material which showed the influence of the heat and turbulent flow encountered by the oscillation of the oxyacetylene torch and a "char layer" on top. The char layer was apparently composed of carbonaceous material and residues of the fibers and fillers where the compositions were in accordance with this invention as in compositions A, C and D. This fibrous network was coated and bonded in part with carbonaceous material. The thicknesses of the respective layers were also measured. From these measurements there was calculated the important determinant, the material loss rate (MLR) in inches per second, the MLR equals

$$t_o - t_v / E$$

where t_o is the original thickness in inches of the disc specimen at its center, t_v is the minimum thickness in inches of the unaffected material after exposure measured at the approximate center of the specimen and E is the time of the test in seconds.

The results of the tests of the above compositions were as follows:

TABLE I

Composition	Exposure Time E (sec.)	Material Loss Rate (inches per second)	Weight Loss (lbs.)
A	90	0.0010	0.0109
B	[1] 71	.0035	.0180
C	90	.0021	.0117
D	90	.0017	.0115
E	[1] 86	.0029	.0175
F	[1] 73	.0034	.0137
G	[1] 58	.0043	.0099
H	[1] 68	.0036	.0132
I	90	.0025	.0132
J	90	.0024	.0104
K	90	[2]	.0127

[1] Specimens burned through at exposure times noted.
[2] Value not obtained because of severe delamination.

EXAMPLE 2

The composition employed in this example consisted of:

	Parts
A copolymer of isobutylene and isoprene containing an average of from 1.5 to 2 isoprene units per 100 monomer units, said copolymer having a Mooney viscosity of 50 to 60 (large rotor)	100
Zinc oxide	3
Stearic acid	1
Thiuram disulfide accelerator	1
2-mercaptobenzothiozole (accelerator)	0.05
Sulphur	1.5
Tributoxyethyl phosphate (stabilizer)	1.5
Chrysotile asbestos fibers like those employed in Example 1	75

All of the above ingredients with the exception of the sulphur and the asbestos fibers were milled together on a conventional two-roll rubber mill. When an even blend had formed, the asbestos fibers were added uniformly and slowly across the lip of the band until completely incorporated. Care was taken to insure good dispersion without degradation of the fibers. The sulfur was then milled in. The composition was then sheeted from the mill, laminated, molded into test specimens, press-cured and tested by the oxyacetylene flame test as described in Example 1. The specimens withstood 90 second exposure and showed an average MLR of 0.0023 inch per second approximating that of the composition employing filler C in Example 1.

EXAMPLE 3

Another composition of this invention was prepared from the following formulation:

	Parts
An oil-extended butadiene-styrene gum copolymer having 23.5% bound styrene and containing 37.5% highly aromatic processing oil	100
Silica filler like that employed in Example 1	34.1
Chrysotile asbestos fibers like those employed in Example 1	34.1
Zinc oxide	3.0
Stearic acid	1.5
N-cyclohexyl-2-benzothiazyl sulfanamide	1.1
Sulphur	2.2
Triethanolamine	3.0
Symmetrical dibeta-naphthyl-p-phenylene-diamine	1.5

All of the ingredients with the exception of the sulphur and the abestos fibers were milled together on a conventional two-roll rubber mill. When an even blend had formed, the asbestos fibers were added slowly until completely incorporated. Care was taken to insure good dispersion without degradation of the fibers. The sulfur was then milled in. The composition was then sheeted from the mill, laminated, molded into test specimens, press-cured and tested by the oxyacetylene flame test described in Example 1. The specimens withstood 90 second exposure and showed an average MLR of 0.0020 inch per second approximating that of the composition employing filler C in Example 1.

EXAMPLE 4

When a composition consisting of:

	Parts
A poly(methylphenylsiloxane) endblocked with methylphenylvinylsiloxane units and having a Williams plasticity of about 0.065 inch	100
A hydrophobed reinforcing silica filler	25
Dibenzoyl peroxide	2
Chrysotile asbestos fibers like those employed in Example 1	70

is mixed together by milling the components together on a conventional two-roll rubber mill in the order shown, care being taken to insure good dispersion without degradation of the fibers, and the composition is then sheeted from the mill, laminated, molded into test specimens, press-cured and tested by the oxyacetylene flame test as described in Example 1, the specimens withstand 90 second exposure and have a satisfactorily low material loss rate.

EXAMPLE 5

When crocidolite, tremolite and actinolite are each substituted for the chrysotile asbestos in Example 1–A in fibrous form such that about 15% of the fibers are retained on a 14 mesh screen (Tyler Series) and 55% are retained on a 200 mesh screen (Tyler Series) as determined by the Bauer-McNett Test, and extreme care is taken in milling in these fibers, satisfactory insulating materials are produced as determined by the oxyacetylene flame test described in Example 1.

EXAMPLE 6

When anthophyllite fibers 80% of which are retained on a 200 mesh screen (Tyler Series) as determined by the Bauer-McNett Test are substituted for the silica filler in Example 1–A, a satisfactory insulating material is produced as determined by the oxyacetylene flame test described in Example 1.

When loose chrysotile asbestos fibers of each of the following types are substituted for the asbestos fibers in Example 1–A, similar results are obtained:

Asbestos fibers of which about 59 percent are retained on a 14 mesh screen (Tyler Series) and about 26 percent are retained on a 200 mesh screen (Tyler Series) as determined by the Bauer-McNett Test.

Asbestos fibers of which about 15 percent are retained on a 14 mesh screen (Tyler Series) and about 57 percent are retained on a 200 mesh screen (Tyler Series) as determined by the Bauer-McNett Test.

EXAMPLE 7

A stock was prepared essentially in accordance with the procedure set forth in Example 1 but with the following formulation:

	Parts
An elastomeric butadiene-acrylonitrile copolymer such as that employed in Example 1 except the copolymer is of low enough molecular weight to be a viscous liquid at room temperature	100
Zinc oxide	3
Stearic acid	1.5
Symmetrical dibeta-naphthyl-p-phenylene-diamine	1.5
Tetramethyl thiuram disulfide	1
Benzothiazyl disulfide	2
Hydrated reinforcing silica filler like that employed in Example 1–A	30
Chrysotile asbestos fibers like those employed in Example 1–A	5
Sulfur	10

This stock was prepared in a Baker-Perkins mixer, molded into test specimen, press-cured and tested by the oxyacetylene flame test in accordance with the procedures described in Example 1. The test specimen withstood the test for 90 seconds having a material loss rate of 0.0020 inch per second.

EXAMPLE 8

The composition employed in this example consisted of the materials of Example 1 with the addition of 18 parts of loose crysotile asbestos fiber of which about 25% are retained on a 325 mesh screen (Tyler Series) as determined by the Bauer-McNett Test and 20 parts of a hydrated reinforcing silica filler. The press-cured test specimens withstood the 90 second exposure to the oxyacetylene flame test described in Example 1 with a satisfactory low material loss rate.

The lining or coating compositions in accordance with the present invention and which include a fibrous form of asbestos, preferably chrysotile, which is of a fiber length as to be retained on at least a 325 mesh screen (Tyler Series), preferably a 200 mesh screen (Tyler Series), provides resistance to flame temperatures and turbulent gas flow conditions. While the exact reasons for the desirable performance of the composition of this dimension are not known, it is believed that the combination of the elastomers and the specified type of asbestos forms, upon application to the structural substrate, a layer which is ideally suited to meet the rigorous conditions to be encountered. In the first place, the lining or insulating coating is flexible and therefore is not subject to cracking when subjected to thermal and pressure shock conditions. Secondly, it is believed that the hydrocarbon portions burn away permitting the heat to be thus dissipated very efficiently by means of the thermodynamic phenomena of sublimation. In other words, it appears that the extremely high temperatures and the turbulent flow involved causes portions of the elastomer constituent to convert directly from the solid to the gas. This is one facet of the mechanism that has also been referred to in the art as the phenomena of ablation. At the same time, however, the fibrous form of asbestos is by reason of the amounts thereof present in the lining and the nature of the orientation of the fiber residue, after deterioration of the elastomer, able to provide a char-like network which slows down the material loss rate while at the same time protecting the substrate. It can thus be seen that the compositions of the present invention permit structural members for rockets, missiles and the like to be fabricated into assemblies having a lower over-all tare because these compositions are more effective insulators.

It is to be understood that in accordance with the provisions of the patent statutes, variations and modifications of the specific devices herein shown and described may be made without departing from the spirit of the invention.

What we claim is:

1. A method of producing an insulated substrate comprising (1) mixing a vulcanizable elastomeric composition consisting essentially of an elastomer, vulcanizing agents for said elastomer, and from about 3 to 80 parts by weight per 100 parts by weight of elastomer of asbestos fibers which are sufficiently large to be retained on a 325 mesh screen (Tyler Series) to form a uniform heterogeneous mixture without appreciable breakdown in size of said asbestos fibers, (2) orienting said fibers primarily in a preselected direction approximately parallel to the surface of said substrate, (3) applying said composition as a coating to a substrate, and (4) vulcanizing said composition on said substrate to form a composite article containing a protective, flexible, vulcanized coating.

2. A method of producing an insulated substrate for rockets comprising (1) mixing a vulcanizable elastomeric composition consisting essentially of an elastomer, vulcanizing agents for said elastomer, and from about 3 to 80 parts by weight per 100 parts by weight of elastomer of asbestos fibers which are sufficiently large to be retained on a 325 mesh screen (Tyler Series) to form a uniform heterogeneous mixture without appreciable breakdown in size of said asbestos fibers, (2) forming said composition into a sheet, (3) orienting said fibers in said composition primarily in a pre-selected direction approximately parallel to the surfaces of said sheet, (4) applying said sheet as a coating to a substrate, and (5) vulcanizing said composition in the substantial absence of added resins on said substrate to form a composite article containing a protective, flexible, vulcanized coating.

3. The method of protecting a shaped surface from the deteriorating effect thereon from burning of a solid propellant for rockets and jets, which comprises disposing over said surface, interposed between said surface and the source of said heat, a layer of flexible, vulcanized, non-resinous elastomeric composition shaped in conformity with said surface, said vulcanized elastomeric composition controlling the burning area of said propellant and containing per 100 parts by weight of the elastomer in said composition from about 3 to 80 parts by weight of chrysotile asbestos fibers which before incorporation in said composition were sufficiently large to be retained on a 325 mesh screen (Tyler Series), said vulcanized elastomeric composition containing prior to vulcanization from about 1.0 to about 20 parts by weight vulcanizing agents per 100 parts by weight of the elastomer in said composition, said fibers being primarily oriented in a pre-selected direction approximately parallel to the surface of said shaped layer.

4. In a rocket or jet motor adapted to provide thrust in a desired direction by discharge of products of combustion from a combustion chamber under pressure through a nozzle, the improvement which comprises a lining internally-around and disposed upon the inner surface of said combustion chamber and bearing against solid products for combustion of a flexible, vulcanized elastomeric resin-free composition which prior to vulcanization contained evenly dispersed therein per 100 parts by weight of the elastomer in said composition from about 1.0 to 20 parts by weight of vulcanizing agents and from about 3 to 80 parts by weight of asbestos fibers which before incorporation in said composition were sufficiently large to be retained on a 325 mesh screen (Tyler Series), said fibers being primarily oriented in a pre-selected direction approximately parallel to the surfaces of said lining and adjacent said direction said products of combustion are discharged.

5. In a rocket or jet motor adapted to provide thrust in a desired direction by burning a solid propellant and by discharge of products of combustion thereof from a combustion chamber under pressure through a nozzle, the improvement which comprises a lining over the inner surface of said combustion chamber bearing against the surface of said solid propellant, said lining consisting essentially of a flexible, vulcanized unreclaimed elastomeric composition which prior to vulcanization contained evenly dispersed therein per 100 parts by weight of the elastomer from about 1.0 to about 20 parts by weight of vulcanizing agents and about 3 to 80 parts by weight of abestos fibers which before incorporation in said composition were sufficiently large to be retained on a 325 mesh screen (Tyler Series), said fibers being primarily oriented in a pre-selected direction approximately parallel to the surfaces of said lining, said elastomer being selected from the group consisting of (a) a copolymer derived from about 90 to 99 mol percent isobutylene and 1 to 10 mol percent isoprene, (b) a copolymer derived from at least 50 mol percent butadiene, the remaining component being acrylonitrile, (c) a copolymer derived from at least 50 mol percent butadiene, the remaining component being styrene and (d) a diorganopolysiloxane.

6. In a rocket or jet motor adapted to provide thrust in a desired direction by discharge of products of combustion from a combustion chamber under pressure through a nozzle, the improvement which comprises a lining over the inner surface of said combustion chamber bearing against said surface, said lining consisting essentially of a flexible, vulcanized elastomeric composition which prior to vulcanization contained evenly dispersed therein per 100 parts by weight of the elastomer in said composition from about 1.0 to about 20 parts by weight of vulcanizing agents and from about 3 to 80 parts by weight of chrysotile asbestos fibers which before incorporation in said composition were sufficiently large to be retained on a 325 mesh screen (Tyler Series), said fibers being primarily oriented in a pre-selected direction approximately parallel to the surfaces of said lining.

7. The method of claim **3** wherein the elastomeric composition comprises natural rubber.

8. The method of claim 3 wherein the elastomer in said composition is principally natural rubber.

9. The method of claim 3 wherein the elastomer in said composition comprises a butadiene acrylonitrile copolymer.

10. The product according to claim 4 wherein the vulcanized elastomeric composition comprises natural rubber.

11. The product of claim 6 wherein a major part of said elastomer is natural rubber.

12. A product according to claim 6 wherein the elastomer comprises a copolymer of a major portion of butadiene and a minor portion of acrylonitrile.

13. The product of claim 6 wherein the elastomer is principally a copolymer of a major portion of butadiene and a minor portion of acrylonitrile.

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