United States Patent Office 2,933,466
Patented Apr. 19, 1960

2,933,466

OIL RESISTANT RUBBER-LIKE MATERIAL CONTAINING A BUTADIENE-ACRYLONITRILE COPOLYMER AND CALCINED MAGNESIA

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No Drawing. Application June 6, 1956
Serial No. 589,602

17 Claims. (Cl. 260—23.7)

This invention relates to an oil-resistant rubber-like material, and to articles made therefrom, which is also resistant to breakdown at at least moderately high temperatures. More particularly the invention relates to a material of the indicated type which may be molded, or otherwise shaped, and vulcanized.

In many of the larger present day airplanes the control surfaces and engine controls are remotely operated by hydraulic devices. During servicing of the airplanes, and even during their operation, at least slight amounts of the oil or oil-like hydraulic fluid in the hydraulic motors and in the tubing connected thereto tend to leak and thus to cover the surfaces of adjacent equipment. Such fluid has a particularly deleterious effect upon natural rubber and the ordinary synthetic rubbers, with which electrical wires and similar equipment may be covered, particularly at elevated temperatures such as are encountered in engine compartments, engine fire walls, and the like.

The rubber-like material of the present invention is particularly resistant to the action of oils or oil-like fluids such as hydraulic control fluid both at atmospheric and at moderately high temperatures. The material of the invention is readily molded, or otherwise shaped, and vulcanized, and can be made into a great variety of shapes by substantially conventional procedures. Thus the material can be molded in dies to form articles such as grommets to carry electrical wiring through metal supports such as engine partitions, fire walls, and the like, or it may be extruded in the form of insulating sheaths on wires or flexible tubing.

The invention has among its objects the provision of an electrically insulating rubber-like material which sustains heating to at least moderately elevated temperatures for long periods without undue change in its hardness. The invention also includes shaped and vulcanized articles made from such material.

A further object of the invention is the provision of an electrically insulating rubber-like material which sustains heating to elevated temperatures for long periods while immersed in oil or oil-like liquids without undue change in its hardness, undue change in its volume, or undue loss in tensile strength.

Yet another object of the invention resides in the provision of an electrically insulating rubber-like material of the character indicated which has good tensile strength, high percentage elongation, and adequate hardness.

A still further object of the invention resides in the provision of an oil and high temperature resistant electrically insulating rubber-like material which has high resistance to aging and to breakdown by exposure to ozone.

Other objects of the invention are the provision of an electrically insulating rubber-like material, for the purposes indicated, which is suitable for molding in existing

molds, and for being vulcanized, without dimensional variations beyond existing tolerances, which is highly resistant to cracking when bent at low temperatures, and which does not acquire an undue set when compressed for long periods at high temperatures.

A still further object of the invention is the provision of an oil-resistant electrically insulating rubber-like material of the character indicated which may readily be extruded and which, when vulcanized, has high chafe-resistant properties.

The above and further objects of the invention will become apparent upon consideration of the following specification setting forth preferred embodiments of the composition of the material, preferred methods of compounding the material, and some permissible variations in such compositions and methods of compounding and processing them.

The oil-resistant electrically insulating rubber-like material of the invention is composed primarily of a synthetic rubber-like base compound of a butadiene-acrylonitrile copolymer and a large amount of finely divided magnesium oxide dispersed substantially uniformly throughout the base compound. To such mixture there are added small but effective amounts of other ingredients which function to give the resulting material specific desired properties upon curing and vulcanizing, and to provide in the final articles molded or shaped therefrom desired characteristics under arduous service conditions. The following table gives the permissible range of variation of a first embodiment of the composition of the invention:

Embodiment 1

	Parts by weight
Hycar #1001 (synthetic rubber base)	100
Mg O (heat resistant filler)	100–125
Zn O (accelerator activator)	5–15
Stearic acid (activator)	0.5–1.5
Methyl Tuads (primary ultra accelerator) (and vulcanizing agent)	1.5–4.0
Sulfasan R (primary accelerator) (and/or curing agent)	1.0–2.5
Thermoflex A (anti-oxidant)	2–10
Aminox (anti-oxidant)	2–10
Sunproof Jr. (inhibitor of exposure damage)	3–10
Esen (retarder)	0.25–1.5

Hycar #1001 is the trade name of a butadiene-acrylonitrile copolymer having a high acrylonitrile content. The Mg O employed is finely divided extra light calcined magnesia. The Zn O is finely divided zinc oxide of the grade known as "zinc white" or "Chinese white." The stearic acid, also known as octadeconoic acid, is likewise in finely divided form.

Methyl Tuads is a trade name for tetramethylthiuram disulfide. Sulfasan R is a trade name for morpholine disulfide. Thermoflex A is the trade name of a substituted aromatic amine consisting of:

50% phenyl-beta-naphthylamine
25% di-para-methoxydiphenylamine
25% diphenyl-para-phenylenediamine

Aminox is the trade name of a low temperature reaction product of diphenylamine and acetone. Sunproof Jr. is the trade name of a specially selected mixture of waxy hydrocarbons; such material is also known as "Heliozone" and "Sunolite." Esen is a trade name of phthalic anhydride.

The functions of the ingredients are generally indicated in the first table above. More specifically, Methyl Tuads functions as a primary ultra accelerator and vulcanizing agent. As a vulcanizing agent it permits the attainment of far superior heat-aging and compression set properties than conventional agents.

Sulfasan R acts as a primary accelerator and/or curing agent, and also functions to inhibit scorching of the material. It also imparts superior aging properties in the above material. Thermoflex A acts as an antioxidant, as does also the Aminox. Sunproof Jr. protects the vulcanized material from deterioration due to exposure, inhibits cracking of the material by ozone, and also functions as an "anti-frosting" agent. Esen acts to prevent scorching of the material at processing temperatures.

It will be seen from the above that zinc oxide and stearic acid both function as an accelerator and activator, that Methyl Tuads and Sulfasan R both function as a primary accelerator, and that both Thermoflex A and Aminox function as an antioxidant. Methyl Tuads also has the further function of vulcanizing agent, Sulfasan R has the further function of inhibiting the scorching of the material, as does Esen.

From the standpoint of function the composition set out in the first table may be partially retabulated as follows:

	Parts by weight	Total
1. Accelerator and Activator:		
Zn O	5–15	5.5–16.5
Stearic acid	0.5–1.5	
2. Primary accelerator:		
Methyl Tuads	1.5–4.0	2.5–6.5
Sulfasan R	1.0–2.5	
3. Anti-oxidant:		
Thermoflex A	2–10	4–20
Aminox	2–10	
4. Vulcanizing Agent:		
See (2) Methyl Tuads	1.5–4.0	
5. Curing Agent:		
See (2) Sulfasan R	1.0–2.5	
6. Exposure Damage Inhibitor:		
Sunproof Jr	3–10	
7. Anti-scorching Agent:		
Esen	0.25–1.5	1.25–4.00
See (2) and (5) Sulfasan R	1.0–2.5	

Variation of the composition within the above defined ranges provides property characteristics within a prescribed desired range of limits. A composition lying within the above ranges, and having characteristics presently preferred for the making of grommets, is that given in the following example.

Example 1

	Parts by weight
Hycar #1001	100
Zn O	5
Stearic acid	1
Extra light calcined Mg O	100
Thermoflex A	5
Aminox	5
Methyl Tuads	1.50
Sunproof Jr.	5
Esen	1
Sulfasan R	1.5

A preferred precedure of making the material set forth in the above tables is as follows:

The Hycar is first broken down on a tight, cold mill, with roll temperature between 90° and 110° F. The zinc oxide is added first, and is thoroughly milled and blended into the base compound. The Thermoflex A, Aminox, and Esen are then added and thoroughly blended into the base compound.

Then, in that order, the Sulfasan R is added and blended, a part, preferably one-third, of the magnesia is added and thoroughly blended, a part, preferably one-half, of the stearic acid is added and blended, one-third of the magnesia and all the Sunproof Jr. are added and blended thoroughly, the remainder of the magnesia is added and blended thoroughly, and the remainder of the stearic acid is added and blended thoroughly.

The compound is then sheeted off, and allowed to cool and age for at least 24 hours. After this, the stock is warmed up on a cool mill, and Methyl Tuads are added and thoroughly blended.

Care should be taken to keep the mill roll temperatures as low as possible during the entire mixing and warm-up periods.

After the above-described addition of the Methyl Tuads, the compound is ready for the formation of articles by conventional molding and vulcanizing procedures.

Test samples made by molding and vulcanizing stock material prepared in the manner set forth above and having the composition set out in the table of Example 1 had the following initial properties:

Tensile strength	2200 p.s.i min.
Elongation	600 min.
Shore hardness	72–75
Dielectric strength	500 volts per mil.

The samples withstood continuous exposure to 10 parts per million ozone without checking for 5 minutes.

The samples possessed excellent resistance to aging at elevated temperatures. Thus, grommets heated to 250° F. for 70 hours and then cooled changed in hardness a maximum of 15 points on the Shore A hardness scale, and their sidewalls underwent a 180° flat bend without cracking.

Such grommets successfully withstood a very exacting test involving oil immersion at elevated temperature. In such test, the grommets were immersed in an oil designated in the trade as Esso Turbo #15 for a period of 70 hours at 300° F. After such heating, the grommets were withdrawn from the oil bath, cooled, and cleaned. The hardness change of the thus treated grommets was no greater than ±10 points on the Shore A scale, the volume of the grommets had changed no more than −5% to −30%, and the tensile strength of their material was no less than 1000 lbs./in.^{2}.

Embodiment 2

When the rubber-like material of the invention is to be used to make articles which during use are subject to chafing and flexing, such as hoses and electrical cables which are drawn past or through guides, the material set forth in the first table is modified to form a second embodiment thereof by adding one or more plasticizers thereto. Preferably a combination of plasticizers, as follows, are added to the compound set forth, with permissible ranges of variation of the ingredients, in the first table in forming the compound of the second embodiment:

Plasticizer	Parts by weight (based on 100 parts of Hycar)	Total
TP–95	10–20	15–35
Tricresyl phosphate	5–15	

TP–95 is a trade name of the high molecular weight polyether ester, dibutoxy ethoxy ethyl adipate. TP–95, which functions in the compound of the second embodiment as a low temperature plasticizer and softener, has no effect on the curing of the material. It imparts excellent low temperature flexibility to the vulcanized product, combined with high-temperature resistance.

Tricresyl phosphate functions as a low temperature plasticizer, softener, and flame retarder. It aids in processing the material, imparts low-temperature flexibility, and gives the material fireproofing qualities. Because of its low water solubility, TP–95 aids in giving the material moisture resistance.

A composition lying within the above indicated ranges of variation of the ingredients (the first table with the above plasticizer added), and having characteristics presently preferred for the making of the outer sheathing

layer of a flexible hose having marked anti-chafing properties, is that given in the following example.

Example 2

	Parts by weight
Hycar #1001	100
Zn O	5
Stearic acid	1
Extra light calcined Mg O	100
Thermoflex A	5
Aminox	5
Methyl Tuads	1.50
Sunproof Jr.	5
Esen	1
Sulfasan R	1.50
TP–95	10
Tricresyl phosphate	10

The material of the second embodiment of the invention is preferably processed in the same manner as the first embodiment, with the exception that the plasticizers are added slowly after all of the magnesia has been added and blended. After this, the compound is sheeted off and allowed to cool and age for at least 24 hours, following which the stock is warmed up on a cool mill, and the Methyl Tuads is added and thoroughly blended, as in the first embodiment.

The thus prepared material is used to sheath hoses or cables by conventional practices, as by continuously extruding the material about the central portion of the hose or cable acting as a core, after which the sheathed product is vulcanized in accordance with conventional procedure.

The sheath of a hose made in the above manner and having the composition set out in the table of Example 2 had properties which were not markedly different from those of the above described grommets.

It is to be understood that within the teaching of the invention some variations are possible. The following permissible substitutes may replace the indicated ingredient part for part.

For Hycar #1001 there may be substituted the somewhat similar butadiene-acrylonitrile copolymers designated in the trade as Paracril D, Chemigum N, Butaprene NXM, and Hycar #1041 or a mixture thereof.

For stearic acid there may be substituted zinc stearate, oleic acid, or the material designated in the trade as Laurex.

For extra light calcined magnesia there may be substituted any regular Neoprene grade of magnesia.

For Thermoflex A there may be substituted "U.O.P. 88," U.O.P. #288, Tenamene #2, Tenamene #30, Aminox, or Agerite Resin D.

For Aminox there may be substituted Thermoflex A or the other materials set forth in the preceding paragraph.

For Methyl Tuads there may be substituted Ethyl Tuads, Sulfasan R, or Dicumyl peroxide.

For Sunproof Jr. there may be substituted any microcrystalline wax or any other waxy hydrocarbons used in rubber compounding. Among these are Sunolite Wax, Crown Wax, paraffin, Carnauba, and Ceresins.

For Esen there may be substituted Vultrol, Retarder W, or salicyclic acid.

For Sulfasan R there may be substituted Tetrone A Dicumyl peroxide, or Methyl Tuads.

For TP–95 there may be substituted any low temperature plasticizer that is compatible with Buna N polymers and imparts flexibility to the compound at 65° F. One such plasticizer is Plasticizer SC.

For tricresyl phosphate there may be substituted TP–95, dioctyl phthalate, Paraplex AL–111, Paraplex G–25, or Plasticizer A–118.

Also, in accordance with the invention, the compositions of Embodiments 1 and 2 may be varied by adding 5–10 parts of U.O.P. 88, U.O.P. #288, or one of the

Tenamenes. Thermoflex A and Aminox may be omitted and replaced part by part with U.O.P. 88, U.O.P. #288, one of the Tenamenes, or Agerite Resin D. From 2 to 10 parts of a low molecular weight polyethylene may be added. Esen may be omitted. From 2 to 5 parts of Agerite Resin D may be added. Up to 5 parts of iron oxide may be added.

Although for purposes of illustration we have disclosed preferred embodiments and examples of the oil-resistant rubber-like material of our invention, and have disclosed some variations thereof, it will be understood that such embodiments and examples are illustrative only, and that the invention is defined by the claims appended hereto.

We claim:

1. A vulcanizable oil-resistant rubber-like electrically insulating material comprising about 100 parts by weight of a base compound consisting essentially of butadiene-acrylonitrile copolymer, from about 100 to 125 parts by weight of finely divided calcined magnesia, and small but effective amounts of at least one vulcanization accelerator and activator.

2. A substantially homogeneous molded and vulcanized electrically insulating article made of oil-resistant rubber-like material comprising a base compound consisting essentially of 100 parts by weight of butadiene-acrylonitrile copolymer, from about 100 to 125 parts by weight of finely divided calcined magnesia, and small but effective amounts of a vulcanization activator and a vulcanization accelerator.

3. A vulcanizable oil-resistant rubber-like electrically insulating material consisting essentially of about 100 parts of a base compound of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5.5 to 16.5 parts of a vulcanization activator, and from 2.5 to 6.5 parts of a vulcanization accelerator, all parts being by weight.

4. A vulcanizable oil-resistant rubber-like electrically insulating material comprising a base compound consisting essentially of about 100 parts by weight of butadiene-acrylonitrile copolymer, from about 100 to 125 parts by weight of finely divided calcined magnesia, and small but effective amounts of at least one vulcanization accelerator and activator, an anti-oxidant for the material, a vulcanizing agent, a material curing agent, a vulcanization retarder, and an agent inhibiting exposure damage to the material.

5. A vulcanizable oil-resistant rubber-like electrically insulating material comprising a base compound consisting essentially of about 100 parts of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5.5 to 16.5 parts of a vulcanization activator, from 2.5 to 6.5 parts of a vulcanization accelerator, from 4 to 20 parts of an anti-oxidant for the material, from 1.5 to 4.0 parts of a vulcanizing agent, from 1.0 to 2.5 parts of a material curing agent, from .25 to 1.5 parts of a vulcanization retarder, and from 3 to 10 parts of an agent inhibiting exposure damage to the material, all parts being by weight.

6. A vulcanizable oil-resistant rubber-like electrically insulating material comprising a base compound consisting essential of about 100 parts of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5.5 to 16.5 parts of a vulcanization activator composed of zinc oxide and stearic acid, and from 2.5 to 6.5 parts of a vulcanization accelerator composed of tetramethylthiuram disulfide and morpholine disulfide, all parts being by weight.

7. A substantially homogeneous molded and vulcanized electrically insulating article made of oil-resistant rubber-like material comprising a base compound consisting essentially of about 100 parts of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5.5 to 16.5 parts of a vulcanization activator composed of zinc oxide and stearic acid,

and from 2.5 to 6.5 parts of a vulcanization accelerator composed of tetramethylthiuram disulfide and morpholine disulfide, all parts being by weight.

8. A vulcanizable oil-resistant rubber-like electrically insulating material comprising a base compound consisting essentially of about 100 parts of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5.5 to 16.5 parts of a vulcanization activator, from 2.5 to 6.5 parts of a vulcanization accelerator, from 4 to 20 parts of an anti-oxidant for the material, from 1.5 to 4.0 parts of a vulcanizing agent, from 1.0 to 2.5 parts of a material curing agent, from .25 to 1.5 parts of a vulcanization retarder, and from 3 to 10 parts of an agent inhibiting exposure damage to the material, all parts being by weight.

9. A vulcanizable oil-resistant rubber-like electrically insulating material comprising a base compound consisting essentially of about 100 parts of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5.5 to 16.5 parts of a vulcanization activator, from 2.5 to 6.5 parts of a primary vulcanization accelerator, minor but effective amounts of an anti-oxidant for the material composed of a substituted aromatic amine and a low temperature reaction product of diphenylamine and acetone, of a vulcanizing agent composed of tetramethylthiuram disulfide, a material curing agent composed of morpholine disulfide, a vulcanization retarder composed of phthalic anhydride, and a mixture of waxy hydrocarbons inhibiting exposure damage to the material, all parts being by weight.

10. A vulcanizable oil-resistant rubber-like electrically insulating material comprising a base compound consisting essentially of about 100 parts of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5.5 to 16.5 parts of a vulcanization activator, from 2.5 to 6.5 parts of a primary vulcanization accelerator, from 4 to 20 parts of an anti-oxidant for the material composed of a substituted aromatic amine and a low temperature reaction product of diphenylamine and acetone, from 1.5 to 4.0 parts of a vulcanizing agent composed of tetramethylthiuram disulfide, from 1.0 to 2.5 parts of a material curing agent composed of morpholine disulfide, from .25 to 1.5 parts of a vulcanization retarder composed of phthalic anhydride, and from 3 to 10 parts of a mixture of waxy hydrocarbons inhibiting exposure damage to the material, all parts being by weight.

11. A vulcanizable oil-resistant rubber-like electrically insulating material comprising a base compound consisting essentially of about 100 parts of a base compound of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5.5 to 16.5 parts of a vulcanization activator composed of zinc oxide and stearic acid, from 2.5 to 6.5 parts of a vulcanization accelerator comprising tetramethylthiuram disulfide, from 4 to 20 parts of an anti-oxidant for the material composed of a substituted aromatic amine and a low temperature reaction product of diphenylamine and acetone, from 1.5 to 4.0 parts of a vulcanizing agent composed of tetramethylthiuram disulfide, from 1.0 to 2.5 parts of a material curing agent composed of morpholine disulfide, from .25 to 1.5 parts of a vulcanization retarder composed of phthalic anhydride, and from 3 to 10 parts of a mixture of waxy hydrocarbons inhibiting exposure damage to the material, all parts being by weight.

12. A vulcanizable oil-resistant rubber-like electrically insulating material consisting essentially of about 100 parts of a base compound of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5 to 15 parts of zinc oxide, from 0.5 to 1.5 parts of stearic acid, from 1.5 to 4.0 parts of tetramethylthiuram disulfide, from 1.0 to 2.5 parts of morpholine disulfide, from 2 to 10 parts of a mixture composed of

50% phenyl-beta-naphthylamine
25% di-para-methoxydiphenylamine
25% diphenyl-para-phenylenediamine

minor but effective amounts of a low temperature reaction product of diphenylamine and acetone, an inhibitor of exposure damage composed of a mixture of waxy hydrocarbons, and phthalic anhydride, all parts being by weight.

13. A vulcanizable oil-resistant rubber-like electrically insulating material consisting essentially of about 100 parts of a base compound of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5 to 15 parts of zinc oxide, from 0.5 to 1.5 parts of stearic acid, from 1.5 to 4.0 parts of tetramethylthiuram disulfide, from 1.0 to 2.5 parts of morpholine disulfide, from 2 to 10 parts of a mixture composed of

50% phenyl-beta-naphthylamine
25% di-para-methoxydiphenylamine
25% diphenyl-para-phenylenediamine

from 2 to 10 parts of a low temperature reaction product of diphenylamine and acetone, from 3 to 10 parts of an inhibitor of exposure damage composed of a mixture of waxy hydrocarbons, and from .25 to 1.5 parts of phthalic anhydride, all parts being by weight.

14. A vulcanizable oil-resistant rubber-like electrically insulating material comprising a base compound consisting essentially of about 100 parts by weight of butadiene-acrylonitrile copolymer, from about 100 to 125 parts by weight of finely divided calcined magnesia, a minor amount of at least one low temperature plasticizing agent for the material, and small but effective amounts of at least one vulcanization accelerator and activator.

15. A vulcanizable oil-resistant rubber-like electrically insulating material comprising a base compound consisting essentially of about 100 parts of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 15 to 35 parts of a plasticizer for the material composed of dibutoxy ethoxy ethyl adipate and tricresyl phosphate, from 5.5 to 16.5 parts of a vulcanization activator, and from 2.5 to 6.5 parts of a vulcanization accelerator, all parts being by weight.

16. A vulcanizable oil-resistant rubber-like electrically insulating material consisting essentially of about 100 parts of a base compound of butadiene-acrylonitrile copolymer, from about 100 to 125 parts of finely divided calcined magnesia, from 5 to 15 parts of zinc oxide, from 0.5 to 1.5 parts of stearic acid, from 1.5 to 4.0 parts of tetramethylthiuram disulfide, from 1.0 to 2.5 parts of morpholine disulfide, from 2 to 10 parts of a mixture composed of

50% phenyl-beta-naphthylamine
25% di-para-methoxydiphenylamine
25% diphenyl-para-phenylenediamine

from 2 to 10 parts of a low temperature reaction product of diphenylamine and acetone, from 3 to 10 parts of an inhibitor of exposure damage composed of a mixture of waxy hydrocarbons, from .25 to 1.5 parts of phthalic anhydride, and a plasticizing agent for the material composed of from 10 to 20 parts of dibutoxy ethoxy ethyl adipate and from 5 to 15 parts of tricresyl phosphate, all parts being by weight.

17. A vulcanizable oil-resistant rubber-like material consisting essentially of a base compound of butadiene-acrylonitrile copolymer, about an equal amount by weight of finely divided calcined magnesia, and small but effective amounts of at least one vulcanization accelerator and activator.

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