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(54) **Title:** RUBBER COMPOUND FOR ELECTRICAL RUBBER MOLD PRODUCTS


(57) **Abstract**

A novel rubber molding composition suitable for electrical appliances, particularly for a PST, is obtained by improving the resistance to tearing of a silicone-modified EPDM inherently resistant to cold, weather conditions, and heat. A PST produced from this composition is also provided. A rubber molding composition for electrical. Appliances characterized by comprising (1) 100 parts by weight of a silicone-modified ethylene-propylene-diene terpolymer and (2) from 0.5 to 2 parts by weight of granular polytetrafluoroethylene and an amount of molybdenum disulfide effective to uniformly mix the granular polytetrafluoroethylene with the terpolymer; a rubber molding composition for electrical appliances characterized by comprising (1) 100 parts by weight of a silicone-modified ethylene-propylene-diene terpolymer, (2) from 0.5 to 2 parts by weight of granular polytetrafluoroethylene and an amount of molybdenum disulfide effective to uniformly mix the granular polytetrafluoroethylene with the terpolymer, and (3) 4 to 20 parts by weight of a 1,4-hexadiene type ethylene-propylene-diene terpolymer possessing a Mooney viscosity, [$ML_{(1+4)}$ 121 °C], in the range of from 60 to 80; electrical appliances such as, for example, PST, formed of the rubber molding composition mentioned above are provided.

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# RUBBER COMPOUND FOR ELECTRICAL RUBBER MOLD PRODUCTS

## Background of the Invention

### Field of the Invention

The present invention relates to a rubber molding composition for an electrical appliance excelling in weatherability, elongation, insulation, and resistance to tearing and permitting outdoor use.

### Description of the Related Art

The material for formed electrical rubber appliances, especially the prestretch tubing (hereinafter referred to briefly as "PST"), is required to excel in weatherability, elongation, insulation, track resistance, and resistance to tearing. A material which has an ethylene-propylene-diene terpolymer as a main component thereof and satisfies this requirement has not yet been known in the art. Here, the term "PST" means a coating tube which, for the purpose of imparting water resistance and electrical insulation to a joint of connected parts, assumes initially the form of a radially expanded tubular member. The stated qualities are imparted by first being stretched around the joint and subsequently being shrunken to form a strong coat on the joint by dint of the force of the shrinkage.

Electrical appliances using a rubber molding composition which has an ethylene-propylene-diene terpolymer (EPDM) as a main component thereof exhibit high mechanical strength and electrical insulation and have extensive utility. This material exhibits low resistance to the ultraviolet light while in a stretched state, is deficient in weatherability, and fails to acquire improved resistance to the ultraviolet light because the amount of carbon black to be incorporated therein must be increased to ensure maintenance of high insulation.

Silicone rubber excels in weatherability, resistance to cold, and resistance to heat but suffers from such drawbacks as low resistance to tearing and high cost.

The silicone-modified EPDM excels in resistance to cold, weatherability, and resistance to heat and has found utility in electrical appliances using a rubber molding composition. It nevertheless suffers from inferior resistance to tearing. This drawback gains in prominence particularly in applications that are in need of high elongation.

National Unexamined Patent Publication No. 63-501,726 (WO87/03515) discloses a composition which comprises granular polytetrafluoroethylene, molybdenum disulfide, and silicone rubber. This composition enjoys high resistance to tearing but is very expensive. The compositions of the components disclosed in the specification of this patent are suspected to exhibit inferior dispersibility of the granular polytetrafluoroethylene, inconsistency of characteristic properties, and deficiency in smoothness of the product surface.

The present invention aims to provide a novel rubber molding composition for electrical appliances, particularly a rubber molding composition suitable for use in a PST, and a PST made therefrom, comprising a silicone-modified EPDM inherently possessing resistance to cold, weatherability, and resistance to heat and surprisingly, improved resistance to tearing.

The present inventors have made various studies in search of a solution for the problems mentioned above and consequently found that the silicone-modified EPDM is improved in resistance to tearing by incorporation therein of granular polytetrafluoroethylene and molybdenum disulfide in a small total amount and further improved in resistance to tearing by additional incorporation therein of a 1,4-hexadiene type EPDM of high Mooney viscosity. The present invention has been perfected as a result.

Description of the Invention

To be specific, the present invention provides a rubber molding composition for electrical appliances comprising (1) 100 parts by weight of a silicone-modified ethylene-propylene-diene terpolymer and (2) from 0.5 to 2 parts by weight of granular polytetrafluoroethylene and an amount of molybdenum disulfide effective to uniformly mix the granular polytetrafluoroethylene with the terpolymer.

The present invention also provides a rubber molding composition for electrical appliances comprising (1) 100 parts by weight of a silicone-modified ethylene-propylene-diene terpolymer, (2) from 0.5 to 2 parts by weight of granular polytetrafluoroethylene and such an amount of molybdenum disulfide effective to uniformly mix the granular polytetrafluoroethylene with the terpolymer, and (3) 4 to 20 parts by weight of a 1,4-hexadiene type ethylenepropylene-diene terpolymer possessing a Mooney viscosity, [$ML_{(1+4)}$ 121°C], in the range of from 60 to 80.

Further, the present invention provides electrical rubber appliances such as, for example, a pre-stretched tube (PST), which is formed of the composition mentioned above.

The silicone-modified EDPM to be used in the present invention is the product of a combination of EDPM with polysiloxane and is disclosed in Japanese Unexamined Patent Publications No. 71,737/1980 and No. 116,739/1981. It is marketed by Japan Synthetic Rubber Co., Ltd. under trademark designation of "JENIX-E." The present invention, therefore, can be worked by the use of the commercially available silicone-modified EPDM.

The granular polytetrafluoroethylene and an amount of the molybdenum disulfide effective uniformly mix the granular polytetrafluoroethylene with the silicone--modified EPDM constitutes a mixture of 25 to 50 parts by weight of polytetrafluoroethylene with about 1 to 30 parts by weight of molybdenum disulfide. It is disclosed in

National Unexamined Patent Publication No. 501,726/1988 (WO87/035151), for example. This composition is commercially available from Allphaflex Industries, Inc., U.S. under the trademark designation of "Alphaflex (α-Flex)."

In the present invention, this composition is used in a range of from 0.5 to 2 parts by weight, based on 100 parts by weight of the silicone-modified EPDM. If the amount is less than 0.5 part by weight, the resistance to tearing cannot be sufficiently improved. If the amount exceeds 2 parts by weight, the tensile stress (modulus) at an elongation of from 100% to 300% is too high and the permanent elongation is too inferior for the produced rubber molding composition to serve as a desirable material for the PST.

In another embodiment of the present invention, the aforementioned granular polytetrafluoroethylene composition such as, for example, "α-Flex", and 1,4-hexadiene type EPDM having a Mooney viscosity, [$ML_{(1+4)}$ 121°C) in the range of from 60 to 80 are used in a range of from 0.5 to 3 parts by weight, based on 100 parts by weight of the silicone-modified EPDM. In this case, the mixture of the granular polytetrafluoroethylene with the molybdenum disulfide is the same as mentioned above. If the amount of this mixture is less than 0.5 part by weight, based on 100 parts by weight, the product does not acquire sufficient resistance to tearing. If this amount exceeds 3 parts by weight, the modulus at an elongation in the range of from 100 to 300% is likewise too large for the produced rubber molding composition to serve as a desirable material for the PST.

The aforementioned 1,4-hexadiene type EPDM having a Mooney viscosity in the range of from 60 to 80 is commercially available from DuPont under the trademark designation of Nordel™.

For the purpose of improving dispersibility and miscibility, this EPDM is desired to be incorporated in

the form of a compound in the silicone-modified EPDM.

Example: A compound of 38% by weight of 1,4-hexadiene type EPDM of high Mooney viscosity, 26.5% by weight of paraffin oil, 17% by weight of carbon, 15% by weight of silica, 2.3% by weight of a co-crosslinking agent EDMA, and 1.2% by weight of working auxiliary is made. The amount of this compound to be used is in the range of from 5 to 50 parts by weight (including 1.9 to 19 parts by weight of the 1,4-hexadiene type EPDM of high Mooney viscosity), based on 100 parts weight of the silicone-modified EPDM. If the amount of the compound is less than 5 parts by weight, no effect is observed in the improvement of mechanical properties. Conversely, if this amount exceeds 50 parts by weight, the EPDM content increases to the extent of degrading the resistance to ultraviolet light.

In addition to the essential components mentioned above, the composition of the present invention can incorporate therein such additive components of popular use in the art as carbon black, antioxidant, ultraviolet absorbent, photostabilizer, and cross-linking agent.

The composition of the present invention is obtained by mixing the components described above. The production of a formed electrical appliance contemplated by this invention is accomplished by heating the composition as held in a prescribed mold to a temperature in the range of from 130 to 190°C under a pressure in the range of from 15 to 50 $kgf/cm^2$ for a period in the range of from 5 to 30 minutes.

The present invention vests the produced rubber molding composition with high elongation, high resistance to tearing, low permanent elongation, and excellent resistance to ultraviolet light. Thus, it provides a rubber molding composition that is suitable for use in electrical appliances, particularly the PST.

The product of the present invention finds utility in outdoor rubber products such as, for example, outdoor

terminals and insulating covers that require ultraviolet-resisting properties, products such as, for example, the PST for use in the cold climates which requires shrinkage at low temperatures, products such as, for example, a rubber insulating sheath for the PST type terminal (produced by Sumitomo-3M K.K. and marketed under product code of "QT-2") which require high elongation, a high tearing property, and low permanent elongation, and semiconducting rubber and high dielectric constant stress control rubber.

Now, the present invention will be more specifically described below with reference to working examples.

Example 1:

Test sheets measuring 150 mm x 150 mm x 2 mm were produced by combining 100 parts by weight of a silicone-modified EPDM (produced by Japan Synthetic Rubber Co., Ltd. and marketed under trademark designation of "JENIX-E2151"), 5 parts by weight of a cross-linking agent (produced by Hercules Fareast K.K. and marketed under trademark designation of "VALVUP 40KE"), and varying amounts indicated in Table 1 of a mixture of granular polytetrafluoroethylene with molybdenum disulfide (produced by Alphaflex Industries, Inc. U.S. and marketed under trademark designation of "α-Flex 101") and subjecting the resultant compositions to hot compression molding at 170°C under 25 $kgf/cm^2$ for 15 minutes.

The samples were tested for hardness, 100% modulus, 300% modulus, tensile strength, resistance to tearing, and permanent elongation as follows.

The hardness was determined of samples of Japanese Industrial Standard (hereinafter referred to as "JIS") A type.

The moduli, resistance to tearing, and elongation were determined by preparing dumbbells of JIS No. 3 from the samples, setting them on a tensile tester, and

stretching them at a rate of 500 mm/min under the conditions for relevant measurement.

The permanent elongation was determined by preparing dumbbells of No. 1 from the samples, keeping them at an elongation of 100% at 100°C for 22 hours, then allowing them to stand at rest at normal room temperature for 30 minutes, removing the cooled dumbbells from the jig, and measuring the lengths thereof.

The tear strength was determined by preparing test pieces in the form of a strip 25mm in width and 100 mm in length from the samples, inserting a 50 mm cut in the longitudinal direction in the central part of the test pieces, and measuring the maximum tearing strength of each test piece.

The results are shown in the following table.

Table 1

| Amount of α-Flex added (H) | 0.1 | 0.5 | 1.0 | 1.5 | 2.0 | 3.0 |
|---|---|---|---|---|---|---|
| Hardness (Hs) | 50 | 51 | 52 | 52 | 53 | 55 |
| 100% Modulus ($kgf/cm^2$) | 10 | 12 | 16 | 17 | 19 | 22 |
| 300% Modulus ($kgf/cm^2$) | 39 | 40 | 41 | 42 | 46 | 56 |
| Tensile strength ($kgf/cm^2$) | 90 | 92 | 88 | 93 | 89 | 98 |
| Elongation (%) | 520 | 530 | 525 | 530 | 520 | 505 |
| Resistance to tearing (180 peel) (kgf/cm) | 4.1 | 5.0 | 6.2 | 8.8 | 9.2 | 12.5 |
| Permanent elongation (%) | 12.5 | 11.8 | 12.7 | 12.5 | 12.9 | 16.3 |

It is clearly noted from the table that while the effect of improving resistance to tearing was absent when the amount of "α-Flex" was 0.1 part by weight (comparative example), the improved resistance was exhibited when this amount was 0.5 part by weight or more. The amount of 3.0 parts by weight (comparative example) was undesirable

because the moduli were unduly high and the permanent elongation was unduly low.

Example 2:

Test sheets were prepared and tested by following the procedure of Example 1, excepting compositions of 100 parts by weight of a silicone-modified EPDM (produced by Japan Synthetic Rubber Co., Ltd. and marketed under the trademark designation of "JENIX E2151"), 5 parts by weight of a cross-linking agent (produced by Hercules Fareast K.K. and marketed under the trademark designation of "VALCUP 40KE"), varying amounts indicated in the following table of a mixture of granular polytetrafluoroethylene with molybdenum disulfide (produced by Alphaflex Industries, Inc. U.S. and marketed under the trademark designation of "α-Flex 101"), varying amounts indicated in the following table of a high-Mooney viscosity 1,4-dihexadiene type EPDM (produced by DuPont and marketed under the trademark designation of Nordel 1470"), 0.7 part by weight of an ultraviolet absorbent (produced by Ciba Geigy, Japan and marketed under the trademark designation of "Tinuvin 328"), and 0.7 part by weight of a photo-stabilizer (produced by Sankyo Company, Limited and marketed under the trademark designation of "Sanol LS77011) were used instead.

For the determination of ultraviolet resistance, PST samples were prepared by forcing each composition through an extruding device thereby obtaining a hollow cylindrical tube 13.5 mm in its inside diameter and 4 mm in wall thickness, cross-linking the composition forming the hollow cylindrical tube with steam, cutting the cross-linked cylindrical tube into lengths of 75 mm, and fitting the cylindrical tube on a cable in such a manner that the maximum inside diameter thereof would undergo elongation to 225%. The samples thus obtained were tested for crack resistance by the use of a sunshine weather meter produced by Suga Shikenki K.K. under the following

conditions: 120 minutes of cycle time, 18 minutes of rainfall, and 63°C of black panel temperature.

The results are shown in Table 2 below.

Table 2

| Amount of α-Flex added (PHR) | 0.5 | 0.5 | 1 | 1 | 1.35 | 3 | 3 |
|---|---|---|---|---|---|---|---|
| Amount of HSR added (PHR) | 5 | 10 | 20 | 30 | 40 | 50 | 70 |
| Content of high-Mooney 1,4HD EDPM | 1.9 | 3.8 | 7.6 | 11.4 | 15.2 | 19.0 | 26.6 |
| Hardness (Hs) | 51 | 50 | 50 | 49 | 50 | 53 | 52 |
| 100% modulus ($kgf/cm^2$) | 13 | 13 | 11 | 9 | 13 | 14 | 9 |
| 300% modulus ($kgf/cm^2$) | 42 | 41 | 38 | 35 | 37 | 38 | 33 |
| Tensile strength ($kgf/cm^2$) | 92 | 96 | 90 | 87 | 95 | 97 | 92 |
| Elongation (%) | 540 | 550 | 585 | 595 | 590 | 600 | 620 |
| Resistance to tearing (180 peel)(kgf/cm) | 4.8 | 5.5 | 7.7 | 8.4 | 11.5 | 13.5 | 14.1 |
| Permanent elongation (%) | 12.8 | 13.3 | 13.1 | 13.0 | 13.5 | 14.2 | 15.3 |
| UV resistance (1000 hr) | No crack | No crack | No crack | No crack | No crack | No crack | Minute crack |

The effect in improving resistance to tearing was present when the amount of high-Mooney viscosity 1,4 HD type EPDM was in the range of from 4 to 20 parts by weight and the amount of α-Flex was in the range of from 0.5 to 3.0 parts by weight. Virtually no improvement in either elongation or moduli was observed when the amount of high-Mooney 1,4 HD type EPDM was 2 parts by weight or less. The UV resistance was adversely affected when this amount was 20 parts by weight or more.

**What Is Claimed Is:**

1. A rubber molding composition for electrical appliances characterized by comprising (1) 100 parts by weight of a silicone-modified ethylene-propylene-diene terpolymer and (2) from 0.5 to 2 parts by weight of granular polytetrafluoroethylene and an amount of molybdenum disulfide effective to uniformly mix said granular polytetrafluoroethylene with said terpolymer.

2. A rubber molding composition for electrical appliances characterized by comprising (1) 100 parts by weight of a silicone-modified ethylene-propylene-diene terpolymer, (2) from 0.5 to 2 parts by weight of granular polytetrafluoroethylene and an amount of molybdenum disulfide effective to uniformly mix said granular polytetrafluoroethylene with said terpolymer, and (3) 4 to 20 parts by weight of a 1,4-hexadiene type ethylene-propylene-diene terpolymer possessing a Mooney viscosity, [$ML_{(1+4)}$ 121°C], in the range of from 60 to 80.

3. An electrical rubber appliance made from a rubber molding composition for an electric appliance according to claim 1 or claim 2.

4. An electrical rubber appliance according to claim 3, wherein said electrical rubber appliance is a prestretched tube.

# INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 94/00064

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08L23/26 C08L43/04 C08K3/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | WO,A,87 03515 (PETERS W. E.) 18 June 1987<br>cited in the application<br>see claims 1-4 | 1-4 |
| Y | DATABASE WPI<br>Week 8028,<br>Derwent Publications Ltd., London, GB;<br>AN 80-49013C<br>& JP,A,55 071 737 (TOSHIBA SILICONE K K)<br>31 May 1980<br>cited in the application<br>see abstract | 1-4 |
| A | WO,A,87 01309 (PETERS W. E.) 12 March 1987 | |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.
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| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
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