

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
1 December 2011 (01.12.2011)

PCT

(10) International Publication Number
WO 2011/149198 A9

(51) International Patent Classification:

C08L 83/07 (2006.01) *C08K 5/14* (2006.01)

C08K 3/36 (2006.01) *F16F 1/36* (2006.01)

(21) International Application Number:

PCT/KR2011/003263

(22) International Filing Date:

2 May 2011 (02.05.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10-2010-0049526 27 May 2010 (27.05.2010) KR

(71) Applicants (for all designated States except US): **INDUSTRY-ACADEMIC COOPERATION FOUNDATION GYEONGSANG NATIONAL UNIVERSITY** [KR/KR]; 900, Gajwa-dong, Jinju-si, Gyeongsangnam-do 660-701 (KR). **PAVCO** [KR/KR]; #29-17, Bonri-ri, Nongong-eup, Dalseong-gun, Daegu 711-855 (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KIM, Jin Kuk** [KR/KR]; #201-1504, Pyeonggeo 2 Cha Hyundai Apt. 454-2, Sinan-dong, Jinju-si, Gyeongsangnam-do 660-781 (KR). **SHIN, Wae Gi** [KR/KR]; #111-102, Bonri Greenville, 113-1, Bonri-ri, Nongong-eup, Dalseong-gun, Daegu 711-838 (KR). **CHOL, Han Whal** [KR/KR]; #118-602, Samsung Hangukhyeong Apt. 350bunji, Hosan-dong, Dalseo-gu, Daegu 704-741 (KR).

(74) Agents: **KWON, Oh-Sig** et al.; 4F, Joeeunleaderstel, 921, Dunsan-dong Seo-gu, Daejeon 302-120 (KR).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- with information concerning authorization of rectification of an obvious mistake under Rule 91.3 (b) (Rule 48.2(i))

(88) Date of publication of the international search report:

29 March 2012

(48) Date of publication of this corrected version:

18 May 2012

(15) Information about Correction:

see Notice of 18 May 2012

(54) Title: SILICONE VIBRATION DAMPING RUBBER COMPOSITION

(57) Abstract: Provided is rubber for damping vibration transmitted from a suspension system to frames of a vehicle, more particularly, to vibration damping rubber for a vehicle that has improved equal magnification and damping properties as well as excellent hardness, tensile strength and elongation by using silicone-based rubber containing a vinyl group.



WO 2011/149198 A9

Description

Title of Invention: SILICONE VIBRATION DAMPING RUBBER COMPOSITION

Technical Field

- [1] The present invention relates to rubber for damping vibration transmitted from a suspension system to frames of a vehicle, more particularly, to vibration damping rubber for a vehicle that improves equal magnification and damping properties by using silicone-based rubber containing a vinyl group.

Background Art

- [2] Vibration damping rubber for a vehicle damps vibration to maintain a comfortable ride in the vehicle and is applied to an engine mount insulator and a bush insulator. The vibration damping rubber for a vehicle for supporting an engine and isolating vibration as main functions is a functional component that is very important and complex. The vibration damping rubber requires static stiffness to support weights of an engine and a transmission and low dynamic stiffness to control transmission of vibration. Also, the vibration damping rubber requires heat-resisting properties to high heat generated in an engine room while a vehicle is moving and durability to repetitive load. Such vibration damping rubber has been progressed development for improving performance and obtaining reliability in order to satisfy customers who demand comfortable ride in a vehicle and improved physical properties.
- [3] In the vibration damping rubber, when physical properties such as heat-resisting properties, ageing resistance and durability are improved by mixing of the compositions, vibration insulating properties are deteriorated due to increased equal magnification, particularly due to an increased dynamic spring constant. On the other hand, there is a problem caused by a conflicting characteristic that durability is deteriorated when the equal magnification is improved. It is important to set up a mixing condition of rubber and additive in order to satisfy the conflicting and complex elements.
- [4] Since natural rubber has excellent mechanical physical properties and dynamic fatigue resistance, natural rubber has been applied to the vibration damping rubber for a vehicle. However, the natural rubber is not allowed to be used in a temperature of 100 °C or more due to development of high-performance vehicle and regulations on exhaust gas. Accordingly, rubbers having an excellent heat-resisting property and ageing resistance such as styrene butadiene rubber (SBR), Polybutadiene rubber (BR), Chloroprene rubber (CR), Nitrile butadiene rubber (NBR), Isobutylene isopropylene rubber (IIR), and Ethylene propylene diene monomer (EPDM) and synthetic rubbers thereof are applied to the vibration damping rubber. However, the physical properties

of those rubbers are disappointing.

- [5] It is preferable to use silicone rubber since when the silicone rubber is mixed with the above-mentioned rubbers, the silicone rubber shows excellent physical properties such as a heat-resisting property, ageing resistance and durability in comparison with other rubbers. However, since the silicone rubber does not have a double bond in the main chain according to its chemical structure, there is a difficulty in crosslinking of sulfur to cause a problem that durability is deteriorated. Since the silicone rubber has a weak damping property and low mechanical physical properties such as tensile strength, elongation, and hardness, there is a limitation to be used as a material of the vibration damping rubber.

Disclosure of Invention

Technical Problem

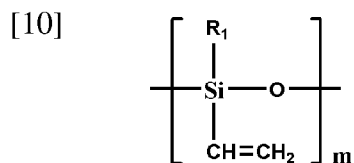
- [6] In order to solve the problem of the prior art, provided is a silicone-based vibration damping rubber composition for a vehicle that shows an excellent physical property of silicone rubber and also improves equal magnification and damping properties as a main element of the rubber for damping vibration, and vibration damping rubber for a vehicle that is prepared by using the same.

[7]

Solution to Problem

- [8] In order to solve the technical problem, provided is a silicone-based vibration damping rubber composition including 30~60 parts by weight of silica, 1~10 parts by weight of silicone oil having a hydroxyl group at a terminal thereof, and 1~10 parts by weight of organic peroxide based on 100 parts by weight of silicone gum having a structure of Chemical Formula 1 or 2 below.

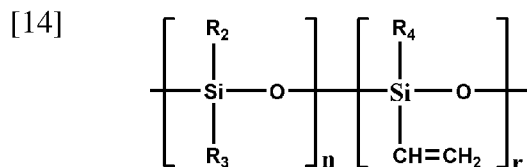
- [9] [Chemical Formula 1]



- [11] wherein

- [12] R₁ represents (C1~C10) alkyl group or (C1~C20) aryl group, and m represents an integer of 1 or greater.

- [13] [Chemical Formula 2]



- [15] wherein
- [16] R_2 and R_3 independently represent (C1~C10) alkyl group, (C1~C10) fluorinated alkyl group or (C1~C20) aryl group; R_4 represents (C1~C10) alkyl group or (C1~C20) aryl group; n and r represents an integer of 1 or greater.
- [17] In R_1 , R_2 , R_3 and R_4 of Chemical Formulas 1 and 2, as specific examples of (C1~C10) alkyl group or (C1~C20) aryl group, the alkyl group includes methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, 2-methylbutyl, pentyl, iso-amyl, hexyl, cyclohexyl, 3-methylpentyl, and octyl; and the aryl group includes phenyl, p-tolyl, 4-methoxyphenyl, 4-(tert-butoxy) phenyl, 3-methyl-4-methoxyphenyl, 4-fluorophenyl, 4-chlorophenyl, 3-nitrophenyl, 3-aminophenyl, 3-acetamidophenyl, and 4-acetamidophenyl; and the m, n and r represent an integer of 1 or greater, preferably an integer of 10~3000.
- [18] The silicone gum contains a vinyl group of 0.008~0.750mmol/g. The fact that the silicone gum contains the vinyl group, which is related to a curing reaction, is an important factor for improving a mechanical physical property of heat-resistance and durability. When the silicone gum contains a vinyl group of below 0.008mmol/g, the curing reaction is not sufficiently performed and it is difficult to expect the improvement of the physical property. When the silicone gum contains a vinyl group of over 0.750mmol/g, crosslinking density increases in curing to raise a cure value. Accordingly, brittle occurs to deteriorate the physical property of rubber.
- [19] The silica functions as a filler but other materials also may be used as a filler. The silica may be used in order to allow reinforcement, heat-resisting properties, and incombustibility. A BET specific surface area may be 120~160m²/g and precipitated silica having a particle size of 10~15nm may be used. When the silica within the above range is used, dynamic characteristics, heat-resisting property and durability, which are required for vibration damping rubber after curing, are obtained.
- [20] 30~60 parts by weight of silica based on 100 parts by weight of silicone gum may be used. More preferably, 40~55 parts by weight of silica may be used. When the content of the silica is below 30 parts by weight, the silica does not function as a filler. When the content of the silica is over 60 parts by weight, the rubber is not proper to be used for damping vibration since strength of the rubber exceeds the optimum level due to increase of crosslinking density.
- [21] Silicone oil having a hydroxyl group at its terminal may be used at an amount of 1~10 parts by weight based on 100 parts by weight of silicone gum. When the amount of silicon oil exceeds the above range, the degree of crosslinking decreases.
- [22] The organic peroxide is any one selected from the group consisting of 2,5-dimethyl-2,5-di-(t-butyl peroxy)-hexane, di-t-butyl peroxide, 5-butylcumyl peroxide, α,α' -bis(t-butyl peroxy)diisopropyl benzene, t-butyl perbenzoate and

2,5-di(t-butyl peroxy)hexyne-3. Organic peroxide may be used at an amount of 1~10 parts by weight based on 100 parts by weight of silicone gum. When the content is out of the above range, there is a problem in curing to deteriorate the degree of crosslinking.

[23] Also, the vibration damping rubber composition may further include diverse additives such as antioxidants, retarders, and releasing agents according to usages thereof.

[24] Provided is the vibration damping rubber for a vehicle that is prepared by curing the above-mentioned silicone-based vibration damping rubber composition. Equal magnification of the vibration damping rubber may be 1.6~2.0.

Advantageous Effects of Invention

[25] As described above, a silicone-based vibration damping rubber composition for a vehicle according to the present invention has excellent mechanical physical properties such as tensile strength, elongation, and hardness of silicone rubber. In addition, a damping property, which is proper to vibration damping rubber for a vehicle, i.e., equal magnification, is controlled to a range of 1.6~2.0. A damping property ($\tan\delta$) is also improved to a range of 0.10~0.13. In particular, the silicone-based vibration damping rubber composition shows remarkably improved heat-resisting properties, ageing resistance and durability in comparison with other conventional rubbers.

Best Mode for Carrying out the Invention

[26] Hereinafter, the present invention will be described in detail according to following examples.

[27] It is apparent that the following examples are only provided for the purpose of description on the present invention and the content of the present invention is not limited to the following examples.

[28]

[29] (Example 1)

[30] 55 parts by weight of precipitated silica (Zeosil 142 of Rhodia Company) having a BET specific surface area of 180m²/g, 5 parts by weight of silicone oil having a hydroxyl group at its terminal (HEO-60 of KCC Company) and 3 parts by weight of HC-8, based on 100 parts by weight of silicone gum containing a vinyl group of 0.750mmol/g were mixed by a mixer. Subsequently, a curing reaction was performed for 10 minutes at 170°C to obtain a sample of vibration damping rubber. Table below showed a result of physical properties.

[31]

[32] (Example 2)

[33] 40 parts by weight of precipitated silica (Zeosil 142 of Rhodia Company) having a

BET specific surface area of 180m²/g, 5 parts by weight of silicone oil having a hydroxyl group at its terminal (HEO-60 of KCC Company) and 3 parts by weight of HC-8, based on 100 parts by weight of silicone gum containing a vinyl group of 0.750mmol/g were mixed by a mixer. Subsequently, a curing reaction was performed for 10 minutes at 170°C to obtain a sample of vibration damping rubber. Table below showed a result of physical properties.

[34]

[35] (Example 3)

[36] Based on 100 parts by weight of silicone gum containing a vinyl group of 0.750mmol/g, 50 parts by weight of precipitated silica (Zeosil 132 of Rhodia Company) having a BET specific surface area of 205m²/g, 5 parts by weight of silicone oil having a hydroxyl group at its terminal (HEO-60 of KCC Company) and 3 parts by weight of HC-8 were mixed by a mixer. Subsequently, a curing reaction was performed for 10 minutes at 170°C to obtain a sample of vibration damping rubber. Table below showed a result of physical properties.

[37]

[38] (Comparative Example 1)

[39] Based on 100 parts by weight of ethylene-alpha-olefin resin, 50 parts by weight of precipitated silica (Zeosil 142 of Rhodia Company) having a BET specific surface area of 180m²/g and 5 parts by weight of silicone oil having a hydroxyl group at its terminal (HEO-60 of KCC Company) were mixed by a mixer. Subsequently, a curing reaction was performed for 10 minutes at 170°C to obtain a sample of vibration damping rubber. Table below showed a result of physical properties.

[40] Tests on following items were performed in order to evaluate the rubber sample prepared in Examples 1 to 3 and Comparative Example 1, and test results were shown below.

[41] Hardness of the vibration damping rubber was measured according to KS M 6784.

[42] Tensile strength, tearing strength, elongation and a modulus of the vibration damping rubber were measured according to KS M 6782.

[43] After aging of the vibration damping rubber, a physical property was measured at 120°C, 48 hours later.

[44]

[45]

[45] Table 1. Measurement Result of Physical Properties

	Example 1	Example 2	Example 3	Comparative Example 1
Tensile (Mpa)	5.6	7.3	4.0	11.5
Elongation (%)	354	502	470	645
M100 (%)	1.3	1.4	0.8	1.6
M200 (%)	2.7	2.2	1.4	3.0
M300 (%)	4.5	3.4	2.3	5.1
Tear (N/mm)	19.01	23.0	14.87	32
Hardness	46	45	36	46
Tan δ (,15Hz)	0.067	0.060	0.124	0.11
Dynamic ratio	1.98	1.92	1.83	2.17
After aging				
Tensile (Mpa)	5.5	7.5	4.6	10.0
Elongation (%)	318	495	438	560
M100 (%)	1.4	1.4	0.9	0.6
M200 (%)	2.9	2.5	1.7	1.9
M300 (%)	5.0	3.7	2.8	2.4
Hardness	47	46	38	46

[46]

[47] As shown in Table 1, the silicone-based vibration damping rubber containing a lot of vinyl groups in Examples 1 to 3 according to the present invention is proper to be used as vibration damping rubber. More preferably, Example 3 according to the present invention showed a superior vibration damping characteristic that equal magnification was 1.83 and a damping property was 0.124. According to the above measurement result of physical properties of tensile strength, elongation, hardness and modulus of elasticity, the silicone-based vibration damping rubber according to the present invention has excellent mechanical physical properties and improved durability in comparison with Comparative Example 1.

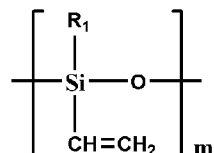
[48] The idea of the invention should not be construed to be restricted to the Examples, but any equivalency or equivalent modifications of claims, as well as claims

themselves described here-in-below are intended to fall under the scope of the idea of the invention.

Claims

- [Claim 1] A silicone-based vibration damping rubber composition, comprising: 30~60 parts by weight of silica, 1~10 parts by weight of silicone oil having a hydroxyl group at a terminal thereof, and 1~10 parts by weight of organic peroxide based on 100 parts by weight of silicone gum having a structure of Chemical Formula 1 or 2 below:

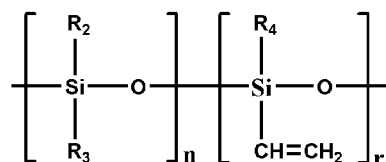
[Chemical Formula 1]



wherein

R₁ represents (C1~C10) alkyl group or (C1~C20) aryl group, and m represents an integer of 1 or greater.

[Chemical Formula 2]



wherein

R₂ and R₃ independently represents (C1~C10) alkyl group, (C1~C10) fluorinated alkyl group or (C1~C20) aryl group; R₄ represents C1~C10 alkyl group or (C1~C20) aryl group; n and r represents an integer of 1 or greater.

- [Claim 2] The rubber composition of claim 1, wherein the silicone gum contains a vinyl group of 0.008~0.750mmol/g.
- [Claim 3] The rubber composition of claim 1, wherein the silica includes precipitated silica having a BET specific surface area of 120~160m²/g, and a particle size of 10~15nm.
- [Claim 4] The rubber composition of claim 1, wherein the organic peroxide is any one selected from the group consisting of 2,5-dimethyl-2,5-di-(t-butyl peroxy)-hexane, di-t-butyl peroxide, 5-butylcumyl peroxide, α,α'-bis(t-butyl peroxy)diisopropyl benzene, t-butyl perbenzoate and 2,5-di(t-butyl peroxy)hexyne-3.
- [Claim 5] Vibration damping rubber for a vehicle prepared by curing the rubber composition according to any one of claims 1 to 4.
- [Claim 6] The vibration damping rubber of claim 5, wherein the vibration

damping rubber has equal magnification of 1.6~2.0.

A. CLASSIFICATION OF SUBJECT MATTER*C08L 83/07(2006.01)i, C08K 3/36(2006.01)i, C08K 5/14(2006.01)i, F16F 1/36(2006.01)i*

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)

C08L 83/07; C08K 5/24; C08L 83/04; C08F 283/00; B29C 35/04; C08L 43/00

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 practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: vibration damping silicone composition, silicone gum, peroxide curing silicone composition

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4678828 A (NAKAMURA, T. et al.) 07 July 1987 See abstract, examples.	1-6
A	US 4052357 A (MARINIK, J. A.) 04 October 1977 See the whole document.	1-6
A	US 5840220 A (AKAMATSU, S. et al.) 24 November 1998 See the whole document.	1-6
A	US 5268433 A (IKENO, M, et al.) 07 December 1993 See the whole document.	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

19 JANUARY 2012 (19.01.2012)

Date of mailing of the international search report

19 JANUARY 2012 (19.01.2012)

Name and mailing address of the ISA/KR

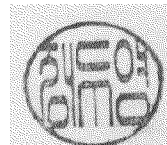
Korean Intellectual Property Office
Government Complex-Daejeon, 189 Cheongsu-ro,
Seo-gu, Daejeon 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

Jung Doo Young

Telephone No. 82-42-481-8699



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2011/003263

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4678828 A	07.07.1987	None	
US 4052357 A	04.10.1977	JP 52-140561 A JP 53-037377 B JP 955058C	24.11.1977 07.10.1978 31.05.1979
US 5840220 A	24.11.1998	EP 0635549 A1 EP 0635549 B1 JP 07-026145 A US 5661203 A	25.01.1995 11.06.1997 27.01.1995 26.08.1997
US 5268433 A	07.12.1993	JP 02646046 B2 JP 05-112722 A	25.08.1997 07.05.1993