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(54) Method for preventing the poor electrical conduction at electrical switch contacts which is caused by silicone vapor.

(57) Poor electrical conductance at switch contacts in electrical devices caused by silicone vapor generated from organosiloxane composition or its cured product used where the conditions are such that the vapor is within a sealed or semi-sealed device, can be prevented by the addition of a nitrogenous basic compound to the organopolysiloxane composition or its cured product. The results is that the poor electrical conduction does not arise at the relays, switches, micromotors and the reliability of the electrical device is increased.

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METHOD FOR PREVENTING THE POOR ELECTRICAL CONDUCTION AT ELECTRICAL SWITCH CONTACTS WHICH IS CAUSED BY SILICONE VAPOR

The present invention relates to a method for preventing the poor electrical conduction at electrical switch contacts which is caused by silicone vapor.

Organopolysiloxane-based silicone products have good heat resistance, cold resistance, and chemical resistance, as well as excellent properties as electrical insulators, and thus have entered into wide use as insulating materials. Furthermore, they are also used as electrically conductive materials when electrically conductive filler has been added.

Among silicone products, curable organopolysiloxane compositions have in the last few years entered into use as adhesives, insulators, sealants, and wire coatings in numerous electric/electronic devices. Unfortunately, these curable organopolysiloxane compositions and the cured products obtained therefrom exercise adverse effects on electrical switch contacts used in their vicinity, often causing poor electrical contact, that is, poor electrical conduction. It has been reported that this is due to the vaporization, either at room temperature or at elevated temperatures, of a silicone vapor, that is, low molecular-weight silanes and low molecular-weight organopolysiloxanes, present as a residue in such curable organopolysiloxane compositions or their cured products. This vapor, upon reaching the electrical switch contacts, is exposed to the discharge energy when the contacts open or close, and as a consequence is chemically changed into an insulating material such as silicon dioxide, silicon carbide, etc., refer, for example, to Denshi Tsushin Gakkai Gijutsu Kenkyu Hokoku (Technology Research Reports of the Institute of Electronics and Communication Engineers of Japan), Volume 76, (226) 29 - 38 (1977). With regard to methods for preventing the silicone vapor-derived poor electrical conduction at electrical switch contacts, no means for a thorough resolution has as yet been found, and proposed methods go no further than removal of the low molecular-weight organopolysiloxane by hot degassing or maintaining the voltage and current load conditions across the electrical switch contacts to within a restricted range at which poor conduction does not occur.

The present inventors, as a result of extensive investigations with a view to solving this problem, found that the problem is substantially solved by the addition and blending of a nitrogenous basic compound into the curable organopolysiloxane composition or cured product therefrom. The present invention is based on this finding. Thus, the present invention has as its object the introduction of a method for preventing poor electrical conduction at the electrical switch contacts used in relays, switches, micromotors, etc.

With regard to electrical devices which contain electrical switch contacts and a curable organopolysiloxane composition or its cured product under sealed or semi-sealed conditions and which are subject to poor electrical conduction at said electrical switch contacts due to silicone vapor generated from said organopolysiloxane composition or its cured product, the present invention relates to a method for preventing poor electrical conduction at said electrical switch contacts which comprises the addition of a nitrogenous basic compound to said organopolysiloxane composition or the cured product obtained therefrom.

The silicone vapor considered in the present invention comprises a vapor of volatile low molecular-weight silanes and low molecular-weight organopolysiloxanes which causes poor electrical conduction at electrical switch contacts. The vapor is either present in or is generated by the decomposition of the silicone rubber compositions or cured products obtained therefrom and the silicone resin compositions or cured products obtained therefrom, etc., which are used as structural or auxiliary materials in electrical devices. Typical examples or organopolysiloxanes which can generate such a vapor are cyclic dimethylpolysiloxanes with the following general formula

$\{(CH_3)_2SiO\}_n$

wherein n = an integer with a value of 3 to 10; linear dimethylpolysiloxanes with the following general formula

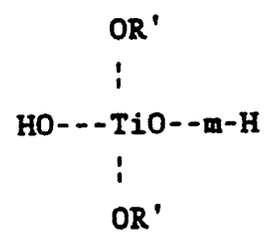
$CH_3\text{-}\{(CH_3)_2SiO\}_m\text{-}Si(CH_3)_3$

wherein m = an integer with a value of 3 to 10; low molecular-weight methylvinylpolysiloxanes, methylphenylpolysiloxanes, and methyl(3,3,3-trifluoropropyl)polysiloxanes; as well as various types of organosilanes.

No specific limitation arises with regard to the curable organopolysiloxane compositions and cured products therefrom which are subject to the present invention, and these encompass, for example, the organoperoxide free-radical reaction-curing organopolysiloxane compositions and cured products therefrom, condensation-curing organopolysiloxane compositions and cured products therefrom, and addition-curing organopolysiloxane compositions and cured products therefrom as known to the art. The organopolysiloxane used here can have a linear, branched, network, or slightly three-dimensional structure with the unit formula

$R_aSiO_{(4-a)/2}$ in the formula, a = 1 to 3 and R is a substituted or unsubstituted monovalent hydrocarbon group, for example, methyl, ethyl, propyl, octyl, phenyl, vinyl, or trifluoropropyl. It can be a homopolymer, copolymer, or mixture of two or more types. The viscosity is not particularly restricted, and materials can be used which range from liquids to gums at room temperature. Organopolysiloxanes having silicon-bonded vinyl groups at the molecular chain terminals and/or along the molecular chain are preferred for use in the organoperoxide free-radical reaction-curing organopolysiloxane compositions. Organoperoxides suitable for use as crosslinkers in this regard are those known in the art as crosslinkers for silicone rubbers, for example, benzoyl peroxide, dicumyl peroxide, di-t-butyl peroxide, t-butyl perbenzoate, 2,5-dimethyl-2,5-di(t-butylperoxy)hexene, etc. The organopolysiloxane used in condensation-curing organopolysiloxane compositions generally comprises hydroxyl-terminated organopolysiloxane, and the crosslinker in this case will be a silane, the partial hydrolysis condensate of a silane, a cyclic organopolysiloxane, or a linear organopolysiloxane, in each case having at least 2 silicon-bonded moisture-hydrolyzable functional groups in each molecule. These functional groups are selected from alkoxy groups, carboxyl groups, amino groups, aminoxy groups, oxime groups, amide groups, imide groups, vinyloxy groups, and lactam groups. With the exception of tetrafunctional silanes, the Si-bonded groups other than these functional groups typically consist of substituted and unsubstituted monovalent hydrocarbon groups. Catalysts which promote the condensation reaction between the above-mentioned hydroxyl-containing organopolysiloxane and functional group-containing silane or siloxane comprise the metal salts of organocarboxylic acids, for example, the salts of metals such as tin, lead, iron, antimony, zirconium, cadmium, barium calcium, titanium, bismuth, and manganese, with carboxylic acids such as acetic acid, octanoic acid, lauric acid, stearic acid, oleic acid, linoleic acid, benzoic acid, naphthoic acid, etc. Other catalysts in this regard are titanium compounds expressed by

$Ti(OR')_4$, $(R'O)_bTiO_{(4-b)/2}$, $TiOR''OTi$, and



in the formulas, R′ is a substituted or unsubstituted monovalent hydrocarbon group, R″ is a divalent organic group, n is a number with a value of 1 to 3, and m is an integer with a value of at least 1, and this encompasses titanium chelate compounds. Organopolysiloxanes having vinyl groups at the molecular chain terminals and/or along the molecular chain are used in the addition-curing organopolysiloxane compositions, and the crosslinking agents in this case comprise organohydrogensilanes and organohydrogenpolysiloxanes with the following unit formula

$R_eH_cSiO_{(4-e-c)/2}$

in the formula, R is a substituted or unsubstituted monovalent hydrocarbon group as described above, zero $< e \leq 3$, zero $< c \leq 2$, and zero $< e + c \leq 4$. Cyclic and linear organohydrogenpolysiloxanes having at least 2 SiH groups in each molecule are preferred. Platinum-based, rhodium-based, and palladium-based catalysts can be used to promote the addition reaction, and platinum and platinum compound catalysts are preferred. These latter are exemplified by supported platinum, chloroplatinic acid, alcohol-modified chloroplatinic acid, platinum-olefin complexes, platinum-ketone complexes, and platinum-vinylsiloxane complexes.

Also available are three dimensionally-curing organopolysiloxane compositions which are crosslinked by exposure to high-energy radiation. These high energy radiation-curable organopolysiloxane compositions are exemplified by organopolysiloxane compositions which contain reaction initiators, sensitizers, for example, aromatic carbonyl compounds such as benzophenone, Michler's ketone, etc.; benzoyl compounds such as benzoin methyl ether, etc.; azo compounds such as azobisisobutyronitrile, etc.; organoperoxides such as benzoyl peroxide, etc.; and organopolysiloxane having unsaturated groups, for example, vinyl, allyl, acryl, etc., the mercapto group, the Si - H group, the acrylamide group, the epoxy group, halogen-substituted alkyl groups, etc., at the molecular chain terminals and/or along the molecular chain.

The form of the cured products obtained from the organopolysiloxane compositions and used in the present invention is not specifically restricted, and encompasses cured materials having the form of gels, rubbers, and high-hardness resins.

Nitrogenous basic compounds used in the present invention comprise such compounds which have a vapor pressure of at least 0.0133 Pa.s at a 25°C as well as compounds which generate the gas of a nitrogenous basic compound by decomposition within the temperature range of use of the electrical device. While the type is not specifically restricted, compound which corrode electrical switch contacts and compounds which are excessively toxic for humans should be avoided except under special circumstances.

Examples of these compounds are aliphatic primary amines such as methylamine, ethylamine, propylamine, isopropylamine, butylamine, amylamine, hexylamine, heptylamine, octylamine, etc.; aliphatic secondary amines such as dimethylamine, diethylamine, dipropylamine, diisopropylamine, dibutylamine, diamylamine, etc.; aliphatic tertiary amines such as trimethylamine, triethylamine, tripropylamine, tributylamine, etc.; aliphatically unsaturated amines such as allylamine, diallylamine, triallylamine, etc.; alicyclic amines such as cyclopropylamine, cyclobutylamine, cyclopentylamine, cyclohexylamine, etc.; aromatic amines such as aniline, methylaniline, benzylamine, etc.; guanidine and its derivatives; aliphatic diamines such as ethylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, etc.; aromatic diamines such as ortho-phenylenediamine, meta-phenylenediamine, para-phenylenediamine, etc.; triamines such as 1,2,3-triaminopropane, etc.; N-(trimethylsilyl)dimethylamine; N,N-di(trimethylsilyl)-methylamine; tetraamines such as trimethylenetetramine, etc.; and benzotriazoles.

The content of nitrogenous base is preferably a quantity which provides at least 0.0001 mole nitrogenous basic compound vapor per one mole organopolysiloxane vapor present in the curable organopolysiloxane composition or cured product therefrom.

Various methods are available for the addition of the nitrogenous base to the organopolysiloxane composition or cured product therefrom, and any method may be used which does not adversely impact the object of the invention of the present application. These methods are exemplified as follows:

The nitrogenous base is added to and blended into a curable organopolysiloxane composition as discussed above during or after the composition's production, and the obtained mixture is then cured;

The cured material obtained from an organopolysiloxane composition can be immersed in the nitrogenous base itself, or in a solution of the nitrogenous base dissolved in a solvent, in order to impregnate the cured organopolysiloxane composition with nitrogenous base;

The nitrogenous base can be directly injected into the cured material obtained from an organopolysiloxane composition using, for example, an injector;

Cured material obtained from an organopolysiloxane composition is placed in the nitrogenous base in order to carry out uptake by adsorption or absorption.

When applied to electrical devices which contain electrical switch contacts and an organopolysiloxane composition or its cured product under sealed or semi-sealed conditions and which are subject to poor electrical conduction at the electrical switch contacts due to silicone vapor generated from said organopolysiloxane composition or cured product therefrom, the above-described method of the present invention prevents this poor electrical conduction at the electrical switch contacts and thus is extremely useful.

EXAMPLES

The present invention will be explained below with reference to illustrative examples. The load switching tests on electrical switch contacts were carried out as follows.

Load switching test method for electrical switch contacts in a sealed system

A microrelay with 8 electrical switch contacts was installed in a sealable 1 L container, and a device was set up which could operate these contacts from the exterior. The cured product obtained from the organopolysiloxane composition was placed in the container and the container was then sealed. Switch testing was then conducted under the following conditions.

Voltage applied across each contact:	24 V DC
Load applied across each contact:	1 kiloohm (R load)
Switching frequency for each contact:	5 cycles per second (5 Hz)
Test temperature:	70 degrees Centigrade

The contact-resistance value at the contact was measured by the voltage drop method and was recorded using a multipen recorder. The contact was rated as faulty when the contact-resistance value reached 10 ohms. The number of contact switching cycles until contact fault was designated at the contact fault life, the number of switching cycles until the first fault among the 8 contacts was designated as the initial fault life, and the number of switching cycles until fault at 4 contacts was designated as the 50% fault life.

Load switching test method for electrical switch contacts in a semi-sealed system

This testing was conducted by the procedure described above under "Load switching test method for electrical switch contacts in a sealed system," with the modification that an otherwise identical 1 L container having two holes (diameter = 1 cm) placed opposite each other at the center of the sides was used in place of the 1 L sealable container.

EXAMPLES 1 AND 2

3 Parts dicumyl peroxide was mixed to homogeneity with 100 parts trimethylsiloxy-terminated dimethylpolysiloxane having a viscosity of 30,000 centistokes and containing 96 mole% dimethylsiloxane units and 4 mole% methylvinylsiloxane units to afford a radical reaction-curing organopolysiloxane composition. Each of the nitrogenous bases listed in Table 1 was then respectively added in the quantity reported in Table 1 to 100 parts of this composition with mixing to homogeneity. The obtained mixture was press-vulcanized at 20 kg/cm2/170 degrees Centigrade for 10 minutes to prepare sheets of cured organopolysiloxane. The cured products were then subjected to the sealed-system load switching tests on electrical switch contacts, and these results are reported as Examples 1 and 2 in Table 1.

For comparison, the radical reaction-curing organopolysiloxane composition prepared as above was cured as above without the additive and was then subjected to load switching testing as described above. These results are also reported in Table 1 as Comparison Example 1.

TABLE 1

Composition and Contact fault lives	Example 1	Example 2	Comparison Example 1
Vinyl group-containing dimethylpolysiloxane	100	100	100
Dicumyl peroxide	3	3	3
Triethylenetetramine	0.15	-	-
Nonylamine	-	0.15	-
Initial contact fault life (cycles)	77300	73700	20700
50% contact fault life (cycles)	153700	143500	28500

EXAMPLES 3 AND 4

A condensation-curing organopolysiloxane composition was prepared by mixing the following to

homogeneity: 100 parts hydroxyl-terminated dimethylpolysiloxane having a viscosity of 2,000 centistokes, 4 parts ethyl silicate, and 0.4 parts dibutyltin dilaurate. Each of the nitrogenous bases listed in Table 2 was respectively added in the quantity given in Table 2 to this composition with mixing to homogeneity. The obtained mixture was coated on a teflon sheet and cured by standing at room temperature for 24 hours. The obtained cured organopolysiloxane sheets were subjected to sealed-system load switching testing of electrical switch contacts, and these results are respectively reported as Examples 3 and 4 in Table 2.

For comparison, the condensation-curing organopolysiloxane composition prepared as described above was cured as described above without the additive, and load switching testing was conducted as described above. These results are also reported in Table 2 as Comparison Example 2.

TABLE 2

Composition and Contact fault lives	Example 3	Example 4	Comparison Example 2
Hydroxyl-terminated dimethylpolysiloxane	100	100	100
Ethyl silicate	4	4	4
Dibutyltin dilaurate	0.5	0.5	0.5
Tributylamine	0.5	-	-
Benzotriazole	-	0.2	-
Initial contact fault life (cycles)	126400	82100	38500
50% contact fault life (cycles)	385000	204200	64300

EXAMPLES 5 AND 6

A condensation-curing organopolysiloxane composition was prepared by mixing the following to homogeneity: 100 parts hydroxyl-terminated dimethylpolysiloxane having a viscosity of 10,000 centistokes, 5 parts of the oximesilane given in Table 3, and 0.5 parts dibutyltin dilaurate as catalyst. 0.01 Part tetraethylethylenediamine was mixed to homogeneity into 100 weight parts of this composition, and the obtained mixture was applied on a teflon sheet and cured by standing at room temperature for 120 hours. The resulting cured organopolysiloxane sheet was subjected to the sealed-system load switching test of electrical switch contacts, and the results are reported as Example 5 in Table 3.

Cured organopolysiloxane was also prepared as described above using 0.1 part benzotriazole in place of the 0.01 part tetraethylethylenediamine, and this was subjected to load switching testing as above. These results are reported as Example 6 in Table 3.

For comparison, a condensation-curing organopolysiloxane composition prepared as above was cured as above without the additive, and the resulting cured product was subjected to load switching testing as above. These results are reported as Comparison Example 3 in Table 3.

TABLE 3

Composition and Contact fault lives	Example 5	Example 6	Comparison Example 3
Hydroxyl-terminated dimethylpolysiloxane	100	100	100
$CH_3Si(-ON=C(C_2H_5)(CH_3))_3$	5	5	5
Dibutyltin dilaurate	0.5	0.5	0.5
Tetraethylenediamine	0.01	-	-
Benzotriazole	-	0.1	-
Initial contact fault life (cycles)	40300	94300	23200
50% contact fault life (cycles)	81600	196500	29400

EXAMPLES 7 AND 8

0.1 Part divinyltetramethyldisiloxane and 3 parts trimethylsiloxy-terminated methylhydrogenpolysiloxane having a viscosity of 10 centistokes were stirred and mixed into 100 parts dimethylvinylsiloxy-terminated dimethylpolysiloxane having a viscosity of 2,000 centistokes. An addition-curing organopolysiloxane composition was obtained by the addition with mixing of an ethanolic chloroplatinic acid solution as the catalyst

in a quantity providing 15 ppm as platinum metal based on the total quantity of polysiloxane. 0.1 Part tetraethylethylenediamine was added to 100 parts of this composition with mixing to homogeneity, and this mixture was cured by heating for 30 minutes in an oven held at 150 degrees Centigrade. The cured product was subjected to the sealed-system load switching test by the method described above, and the results are reported as Example 7 in Table 4. Another cured organopolysiloxane material was prepared as described above, but using 0.1 part cyclohexylamine in place of the 0.1 part tetraethylethylenediamine, and this was also subjected to load switching testing as above. These results are reported as Example 4 in Table 4. For comparison, the addition-curing organopolysiloxane prepared as above was cured as above without the additive, and the resulting cured material was then subjected to load switching testing as above. These results are reported as Comparison Example 4 in Table 4.

TABLE 4

Composition and Contact fault lives	Example 7	Example 8	Comparison Example 4
Dimethylvinylsilyl-terminated dimethylpolysiloxane	100	100	100
Methylhydrogenpolysiloxane	3	3	3
Chloroplatinic acid (quantity as amount of platinum metal)	15 ppm	15 ppm	15 ppm
Divinyltetramethyldisiloxane	0.1	0.1	0.1
Tetraethylethylenediamine Cyclohexylamine	-	0.1	-
Initial contact fault life (cycles)	48000	41300	25600
50% contact fault life (cycles)	136500	128400	41300

EXAMPLES 9 AND 10

A high energy radiation-curable organopolysiloxane composition was prepared by mixing 100 parts trimethylsiloxy-terminated methylvinylpolysiloxane having a viscosity of 6,000 centistokes and composed of 90 mole% dimethylsiloxane units and 10 mole% methylvinylsiloxane units, 5 parts methylhydrogenpolysiloxane having a viscosity of 20 centistokes, and 1.5 parts benzophenone as sensitizer. 0.05 Part dimethyloctylamine was mixed to homogeneity into 100 parts of this composition, and this was filled into a 1 mm-deep metal frame. It was then exposed to ultraviolet radiation for 20 seconds from an ultrahigh-pressure mercury lamp (160 w/cm, lamp length = 20 cm, radiation wavelength = 200 to 500 nanometers) placed 10 cm from the metal frame to obtain the cured organopolysiloxane. This cured product was subjected to sealed-system load switching testing of electrical switch contacts, and the results are reported in Table 5 as Example 9. A cured organopolysiloxane was also prepared as above using 0.1 part benzylamine in place of the 0.05 parts dimethyloctylamine and was subjected to the load switching test. These results are reported in Example 10 in Table 5. For comparison, the above organopolysiloxane composition without the additive was cured by irradiation as described above, and the obtained cured product was also subjected to load switching testing as above. These results are reported in Table 5 as Comparison Example 5.

TABLE 5

Composition and Contact fault lives	Example 9	Example 10	Comparison Example 5
Vinyl group-containing dimethylpolysiloxane	100	100	100
Methylhydrogenpolysiloxane	5	5	5
Benzophenone	1.5	1.5	1.5
Dimethyloctylamine	0.05	-	-
Benzylamine	-	0.1	-
Initial contact fault life (cycles)	46600	73800	19400
50% contact fault life (cycles)	104000	213100	32500

EXAMPLE 11

The semi-sealed-system load switching test of electrical switch contacts was run using the cured organopolysiloxane sheet prepared in Example 1, and these results are reported in Table 6. For comparison, the semi-sealed-system load switching test was also conducted using the radical reaction-curing organopolysiloxane composition from Example 1 without the additive, and these results are reported in Table 6 as Comparison Example 6.

Table 6

Composition and Contact fault lives	Example 11	Comparison Example 6
Vinyl group-containing dimethylpolysiloxane	100	100
Dicumyl peroxide	3	3
Triethylenetetramine	0.15	-
Initial contact fault life (cycles)	154000	4000
50% contact fault life (cycles)	307000	562000

With respect to electrical devices which contain electrical switch contacts and a curable organopolysiloxane composition or its cured product under sealed or semi-sealed conditions and which are subject to poor electrical conduction at said electrical switch contacts due to silicone vapor generated from said organopolysiloxane composition or its cured product, the method of the present invention for preventing poor electrical conduction at said electrical switch contacts comprises the addition of a nitrogenous basic compound to said organopolysiloxane or the cured product obtained therefrom. As a result, it is characteristic of the present invention that poor electrical conduction does not arise at the relays, switches, micromotors, etc., which may be installed in the sealed or semi-sealed electrical device, and the reliability of the electrical device is increased as a consequence.

Claims

1. With regard to an electrical device which contains electrical switch contacts and a curable organopolysiloxane composition or its cured product under sealed or semi-sealed conditions and which is subject to poor electrical conduction at said electrical switch contacts due to silicone vapor generated from said organopolysiloxane composition or its cured product, the method for preventing poor electrical conduction at electrical switch contacts comprises the addition of a nitrogenous basic compound to said organopolysiloxane composition or its cured product.

2. The method as described in claim 1 wherein the nitrogenous basic compound is an aliphatic amine.

3. The method as described in claim 1 wherein the nitrogenous basic compound is an aromatic amine.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 11 1959

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0266183 (TORAY SILICONE COMPANY LTD.) * the whole document *	1-3	H01H1/60

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

H01H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03 APRIL 1989	OVERDIJK J.

CATEGORY OF CITED DOCUMENTS

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