(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 May 2013 (23.05.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/074412 A1

(51) International Patent Classification:
C08L 27/12 (2006.01) *C08K 5/16* (2006.01)
C08F 14/18 (2006.01)

(21) International Application Number:
PCT/US2012/064406

(22) International Filing Date:
9 November 2012 (09.11.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2011-251425 17 November 2011 (17.11.2011) JP

(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventors; and
(71) Applicants : **SUZUKI, Yuta** [JP/JP]; 33-1, Tamagawadai 2-chome, Setagaya-ku, Tokyo 158-8583 (JP). **ANDO, Nobuaki** [JP/JP]; 33-1, Tamagawadai 2-chome, Setagaya-ku, Tokyo 158-8583 (JP).

(74) Agents: **GEISE, C. Michael** et al.; 3M Center, Office of Intellectual Property Counsel Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(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, BN, 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, KE, KG, KM, KN, KP, KR, 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, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2013/074412 A1

(54) Title: FLUOROPOLYMER COMPOSITION

(57) Abstract: A fluoropolymer composition containing a fluoropolymer and a crosslinking agent. The fluoropolymer is an elastomer containing copolymerization units derived from a nitrogen-containing curing site monomer, and the crosslinking agent is a combination of two or more compounds including one or more type of amidine compound and one or more type of bis aminophenol compound.

FLUOROPOLYMER COMPOSITION

BACKGROUND

Technical Field

The present invention relates to a fluoropolymer composition containing a combined crosslinking agent.

Related Art

Perfluoroelastomers have come into use as sealants in the semiconductor market, for example, due to excellent properties such as heat resistance, chemical resistance, radical resistance, and low outgassing. In recent years, the semiconductor market has tended to shift toward higher temperatures and cleaner processes.

In Japanese Unexamined Patent Application Publication No. H6-263952 (Patent Document 1), there is described a fluorine-containing elastomer composition prepared by mixing a bis(aminophenyl) compound with a specific structure as a curing agent into a ternary copolymer of tetrafluoroethoxy-(lowerperfluoroalkyl substituted)-ethene, and cyano group-containing (perfluoro vinyl ether) of a specific structure. In Japanese Unexamined Patent Application Publication No. H8-120146 (Patent Document 2), there is described a fluorine-containing elastomer composition prepared by mixing a bis aminophenyl compound as a curing agent into a ternary copolymer of tetrafluoroethoxy-(lower perfluoroalkyl substituted)-ethene, and perfluoro (ω-cyano alkyl vinyl ether) of a specific structure.

In International Publication No. WO00/29479 Pamphlet (Patent Document 3), there is described a fluorine rubber crosslinking composition containing a fluorine-containing elastomer having carboxyl groups and/or alkoxy carbonyl groups as crosslinking groups at the end of a main chain and/or a branched chain.

In Japanese Unexamined Patent Application Publication No. 2006-502283 (Patent Document 4), there is described a composition which contains (a) a fluoropolymer containing copolymerization units derived from a nitrogen-containing curing site monomer; and (b) a curing agent containing amidine; wherein, in some cases, the fluoropolymer is perfluorinated.

[Background Documents]

[Patent Documents]

Patent Document 1: Japanese Unexamined Patent Application Publication No. H6-263952

Patent Document 2: Japanese Unexamined Patent Application Publication No. H8-120146

Patent Document 3: International Publication No. WO00/29479 Pamphlet

Patent Document 4: Japanese Unexamined Patent Application Publication No. 2006-502283.

[Summary of the Invention]

[Problem to be Solved by the Invention]

However, the present inventors discovered that a molded product (such as a sheet, for example) obtained using a conventional fluoropolymer composition may have crater-like surface defects. The present inventors further discovered that insufficient curing of the fluoropolymer is one factor contributing to these surface defects.

An object of the present invention is to obtain a fluoropolymer composition capable of providing a molded product in which surface defects are effectively reduced or prevented.

SUMMARY

A first mode of the present invention provides:

a fluoropolymer composition containing a fluoropolymer and a crosslinking agent;

wherein the fluoropolymer is an elastomer containing copolymerization units derived from a nitrogen-containing curing site monomer; and

the crosslinking agent is a combination of two or more compounds including one or more types of amidine compounds and one or more types of bis aminophenol compounds.

[Effect of the Invention]

The present invention provides a fluoropolymer composition, which enables the formation of a molded product with few surface defects.

DETAILED DESCRIPTION

Details of the embodiments of the present invention will be given hereinafter. Other characteristics, purposes, advantages, and the like of the present invention will become clear from the following descriptions and the attached Scope of the Patent Claims.

A first mode of the present invention provides:

a fluoropolymer composition containing a fluoropolymer and a crosslinking agent;

wherein the fluoropolymer is an elastomer containing copolymerization units derived from a nitrogen-containing curing site monomer; and

the crosslinking agent is a combination of two or more compounds including one or more type of amidine compound and one or more type of bis aminophenol compound.

The fluoropolymer composition of the present invention can form a cured product with high crosslinking density. Such a cured product with a high crosslinking density can be used to form a molded product with few surface defects.

In particular, with the fluoropolymer composition of the present invention, a molded product can be formed so that virtually or absolutely no depressions of a size visible to the eye are observed.

In several modes, the fluoropolymer composition may have low compression set properties due to the high crosslinking density thereof.

In the fluoropolymer composition of several modes, using a combination of an amidine compound and a bis aminophenol compound yields a higher crosslinking density while using the same amount of crosslinking agent in comparison to cases in which an amidine compound and a bis aminophenol compound are respectively used independently, for example.

In several modes, the fluoropolymer composition enables the realization of favorable surface properties while maintaining the advantages resulting from the use of an elastomer containing copolymerization units derived from a nitrogen-containing curing site monomer (for example, excellent heat resistance and excellent chemical resistance).

In this disclosure, the term "alkyl" refers to a straight-chain or branched-chain aliphatic hydrocarbon group. The term "branched-chain" refers to a substance in which one or a plurality of alkyl groups such as methyl, ethyl, propyl, or the like, for example, are attached to a straight alkyl chain. An alkyl group may be unsubstituted or may be substituted with one or a plurality of halo atoms, cycloalkyl or cycloalkenyl groups, or the like.

The term "alkenyl" refers to an aliphatic hydrocarbon group having a carbon-carbon double bond and may be a straight-chain or branched-chain substance. An alkenyl group may be unsubstituted or may be substituted with one or a plurality of halo atoms, cycloalkyl or cycloalkenyl groups, or the like.

The term "cycloalkyl" refers to a non-aromatic monocyclic or polycyclic ring system containing, for example, approximately 3 to 12 carbon atoms. Examples of cycloalkyl rings include cyclopentyl, cyclohexyl, and cycloheptyl. This cycloalkyl group may be substituted with one or a plurality of halo atoms, methylene, alkyl, cycloalkyl, heterocyclyl, aralkyl, heteroaralkyl, aryl, heteroaryl, or the like. The term "hetero" refers to oxygen, nitrogen, or sulfur substituted for one or a plurality of carbon atoms.

The term "cycloalkenyl" refers to a non-aromatic monocyclic or polycyclic ring system having a carbon-carbon double bond and containing, for example, approximately 3 to 10 carbon atoms. This cycloalkenyl group may be unsubstituted or may be substituted with one or a plurality of halo atoms, methylene, alkyl, cycloalkyl, heterocyclyl, aralkyl, heteroaralkyl, aryl or heteroaryl groups, or the like.

The term "aryl" refers to an aromatic carbon ring radical. Examples of aryl groups include phenyl or naphthyl substituted with one or a plurality of aryl group substituents which may be the same or different in some instances. Here, examples of "aryl group substituents" include hydrogen, alkyl, cycloalkyl, aryl which may be substituted in some instances, heteroaryl which may be substituted in some instances, aralkyl, aralkenyl, aralkynyl, heteroaralkyl, heteroaralkenyl, heteroaralkynyl, hydroxy, hydroxyalkyl, alkoxy, aryloxy, aralkoxy, carboxy, acyl, aroyl, halo, nitro, cyano, carboxy, alkoxycarbonyl, aryloxycarbonyl, aralkoxycarbonyl, acylamino, aroylamino, alkylsulfonyl, arylsulfonyl, and other known groups.

The term "alkaryl" refers to an aryl-alkyl group, where aryl and alkyl are as described previously. The term "alkenylaryl" refers to an aryl-alkenyl group, where aryl and alkenyl are as described previously.

The descriptions of the chemical groups given above are publicly known in this field, and these descriptions are not intended to alter the generally recognized meanings.

Each component of the fluoropolymer composition will be further described hereinafter.

<Fluoropolymer>

The fluoropolymer used in the present invention is an elastomer containing copolymerization units derived from a nitrogen-containing curing site monomer (also called a curing elastomer hereafter). Examples of curing elastomers include fluoroelastomer rubbers. A nitrogen-containing curing site monomer is a monomer containing a nitrogen-containing curing site (that is, a structural part which contains nitrogen and participates in curing reactions). Accordingly, the nitrogen-containing curing site gives the curing elastomer curing properties. Examples of nitrogen-containing curing sites include nitrile, imidate, amidine, amide, imide, amine-oxide groups, and the like. In a preferable mode, the nitrogen-containing curing site monomer is partially or completely fluorinated.

Examples of useful nitrogen-containing curing site monomers are one or more types selected from nitrile-containing fluorinated olefin and nitrile-containing fluorinated vinyl ether. These substances are more preferably perfluorinated. Examples of nitrile-containing fluorinated vinyl ether include, for example, $CF_2=CFO(CF_2)_LCN$; $CF_2=CFO[CF_2CF(CF_3)O]q(CF_2O)yCF(CF_3)CN$; $CF_2=CF[OCF_2CF(CF_3)]rO(CF_2)_tCN$; $CF_2=CFO(CF_2)uOCF(CF_3)CN$, and the like. In the formulas, L=2 through 12; q=0 through 4; r=1 or 2; y=0 through 6; t=1 through 4; and u=2 through 6.

Representative examples of useful nitrogen-containing curing site monomers include $CF_2=CFO(CF_2)_3OCF(CF_3)CN$, perfluoro(8-cyano-5-methyl-3,6-dioxa-1-octen), and $CF_2=CFO(CF_2)_5CN$.

The copolymerization units derived from a nitrogen-containing curing site monomer preferably constitute approximately 0.1 to 5 mol % or approximately 0.3 to 2 mol % of the total polymer units of the curing elastomer. These ranges are advantageous from the perspective of providing favorable surface properties to the molded product obtained from the fluoropolymer composition of the present invention.

An example of a suitable curing elastomer is an elastomer containing copolymerization units derived from a nitrogen-containing curing site monomer and a main monomer (preferably at least two types of main monomers). Examples of candidate compounds suitable for use as main monomers include perfluoroolefins (for example, tetrafluoroethylene (TFE) and hexafluoropropylene (HFP)), other perhalogenated olefins (for example, chlorotrifluoroethylene (CTFE)), and perfluorovinyl ethers (for example, perfluoroalkyl vinyl ether and perfluoroalkoxy

vinyl ether). In some instances, a hydrogen-containing monomer such as an olefin (for example, ethylene, propylene, or the like), for example, and a partially fluorinated monomer (for example, vinylidene fluoride (VDF)) may also be used.

If the curing elastomer is perhalogenated, it is preferable for the curing elastomer to contain at least approximately 50 mol % of copolymerization units derived from one or a plurality of types of perhalogenated olefins (for example, TFE and/or CTFE as well as HFP in some instances). The remaining copolymerization units of the curing elastomer (for example, approximately 10 to 50 mol %) may consist of one or a plurality of types of perfluorovinyl ether and one or a plurality of types of nitrogen-containing curing site monomers (for example, nitrile-containing vinyl ether or imidate-containing vinyl ether). In a more preferable mode, the curing elastomer is perfluorinated.

On the other hand, in a mode in which the curing elastomer is not perhalogenated, the curing elastomer may contain, for example, approximately 5 to 90 mol % of copolymerization units derived from a perhalogenated olefin, approximately 5 to 90 mol % of copolymerization units derived from a hydrogen-containing monomer, at most 40 mol % of copolymerization units derived from vinyl ether, and approximately 0.1 to 5 mol % (more preferably approximately 0.3 to 2 mol %) of copolymerization units derived from a nitrogen-containing curing site monomer.

In a mode in which the curing elastomer is not perfluorinated, the curing elastomer may contain, for example, approximately 5 to 90 mol % of copolymerization units derived from TFE, CTFE, and/or HFP, approximately 5 to 90 mol % of copolymerization units derived from VDF, ethylene, and/or propylene, at most 40 mol % of copolymerization units derived from vinyl ether, and approximately 0.1 to 5 mol % (more preferably approximately 0.3 to 2 mol %) of copolymerization units derived from a nitrogen-containing curing site monomer.

A suitable example of a perhalogenated olefin is a perfluorinated olefin, and a particularly suitable example is a perfluorinated olefin expressed by the formula CF_2=CF-R_f (wherein R_f is fluorine or a C_1-C_8 perfluoroalkyl).

A suitable example of a hydrogen-containing olefin is a hydrogen containing C_2-C_9 olefin in which less than 1/2 or less than 1/4 of the hydrogen atoms in the molecule have been replaced with fluorine or have not been fluorinated. However, in several embodiments, copolymerization units derived from an olefin that has not been fluorinated are not contained in the curing elastomer.

A suitable example of a hydrogen-containing olefin is an olefin expressed by the formula CX_2=CX-R (wherein each X is independently hydrogen, fluorine, or chlorine, and R is hydrogen, fluorine, a C_1-C_{12} alkyl, or a C_1-C_3 alkyl). Suitable examples of these olefins are partially fluorinated monomers (for example, vinylidene fluoride) and hydrogen-containing monomers (for example, α-olefins (for example, ethylene, propylene, butene, pentene, hexene, or the like) or the like).

Two or more types of the respective raw materials described above may be used in combination.

Examples of perfluorovinyl ethers include CF_2=$CFOCF_3$, CF_2=$CFOCF_2CF_2OCF_3$, CF_2=$CFOCF_2CF_2CF_2OCF_3$, CF_2=$CFOCF_2CF_2CF_3$, CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2CF_3$, and CF_2=$CFOCF_2CF(CF_3)OCF_2CF(CF_3)OCF_2CF_2CF_3$.

In a preferable mode, the curing elastomer is a copolymer of a perfluoroolefin, a perfluorovinyl ether, and a nitrogen-containing curing site monomer. In this copolymer, a suitable example of a nitrogen-containing curing site monomer is one or more types selected from nitrile-containing fluorinated olefins and nitrile-containing fluorinated vinyl ethers.

In a more preferable mode, the curing elastomer is a copolymer of tetrafluoroethylene (TFE), at least one type of perfluoroalkyl vinyl ether, and a nitrogen-containing curing site monomer (preferably, at least one type selected from nitrile-containing fluorinated olefins and nitrile-containing fluorinated vinyl ethers).

In a particularly preferable mode, the curing elastomer is a ternary copolymer of tetrafluoroethylene (TFE), perfluoromethyl vinyl ether (PMVE), and CF_2=$CFO(CF_2)_5CN$(MV5CN).

In these copolymers, the copolymerized perfluorovinyl ether units (preferably perfluoroalkyl vinyl ether units, and more preferably PMVE units) preferably constitute approximately 1 to 60 mol % and more preferably constitute approximately 10 to 40 mol % of all of the copolymerization units of the curing elastomer.

The curing elastomer may be one type of elastomer or a blended product of two or more types of elastomers. In the case of a blended product, each elastomer contains copolymerization units derived from nitrogen-containing curing site monomers such as those described above. For example, two or more types of elastomers containing reactive sites enabling a suitable combination with the crosslinking agent used may be blended.

(Additional fluoropolymers)

In addition to the curing elastomer described above, the fluoropolymer composition may contain one or a plurality of types of additional fluoropolymers that do not contain copolymerization units derived from a nitrogen-containing curing site monomer. The additional fluoropolymers may be single polymers or copolymers. The additional fluoropolymers may be blended with the curing elastomer.

All of the substances described above as copolymerization units which may be contained in the curing elastomer except nitrogen-containing curing site monomers can be used as examples of polymerization units of the additional fluoropolymers. For example, polytetrafluoroethylene (PTFE) and tetrafluoroethylene-perfluorovinyl ether (PFA) are useful.

For example, the fluoropolymer composition can be provided with a desired property by combining an additional fluoropolymer with an additional curing agent, which can be used as desired, other than the amidine compound and the bis aminophenol compound used as a crosslinking agent in the present invention. For example, the chemical stability of the fluoropolymer composition can be improved by combining an additional fluoropolymer suitable for peroxide curing and a peroxide curing agent. Using such an additional fluoropolymer and an additional curing agent enables a balance between the thermal stability and chemical stability of the resulting blended product and also yields economic effects.

If an additional fluoropolymer is used, the mass percentage of the curing elastomer is preferably at least approximately 25 mass % or at least approximately 50 mass % of the total of the curing elastomer and the additional fluoropolymer (also called the fluoropolymer component hereafter) contained in the fluoropolymer composition. In this case, a fluoropolymer composition, which yields a molded product having excellent surface properties, is obtained. In several modes, the fluoropolymer component contained in the fluoropolymer composition consists of only a curing elastomer.

The curing elastomer and a desired additional fluoropolymer can be prepared using a publicly known method. For example, the polymerization process can be implemented by subjecting a monomer to free-radical polymerization by means of aqueous emulsion polymerization or solution polymerization in an organic solvent. When preparing a blended product of two or more types of fluoropolymers, two or more types of fluoropolymer latex, for example, are blended at a selected ratio, coagulated, and then dried.

In the curing elastomer and the desired additional fluoropolymer, the types and amounts of end groups are not absolute. For example, the polymer may contain an $SO3^-$ end group generated by an APS/sulfite. The polymer may also contain a COO^- end group generated by an APS polymerization initiator. The polymer may also contain a "neutral" end group - for example, an end group generated by using a fluorosulfinate polymerization initiator or an organic peroxide. The number of end groups can be dramatically reduced by using a desired chain transfer agent. The presence of end groups of strong polarity such as SO_3^-, for example, can be minimized as desired for the purpose of improving processability, for example. In addition, the amount of COO^- or other unstable end groups may also be reduced as desired by post-treatment (for example, decarboxylation, post-fluorination, or the like).

The curing elastomer and/or the desired additional fluoropolymer may contain curing sites other than nitrogen-containing curing sites. These may contain halogens so as to allow participation in peroxide curing reactions. Halogens may be introduced at intermediate and/or end positions of a fluoropolymer chain. Halogens are typically bromine or iodine.

Copolymerization is a preferable method for introducing halogens at an intermediate position of a polymer chain in the fluoropolymer component. When this method is used, an appropriate fluorination curing site monomer such as a bromo- or iodo-fluoroolefin or a bromo- or iodo-fluorovinyl ether, for example, is used as a copolymerization component. Examples of bromo- or iodo-fluoroolefins include bromodifluoroethylene, bromotrifluoroethylene, iodotrifluoroethylene, 1-bromo-2,2-difluoroethylene, 4-bromo-3,3,4,4-tetrafluorobutene-1, and the like. Examples of bromo- or iodo-fluorovinyl ethers include $BrCF_2OCF=CF_2$, $BrCF_2CF_2OCF=CF_2$, $BrCF_2CF_2CF_2OCF=CF_2$, $CF_3CF(Br)CF_2OCF=CF_2$, and the like. Further, bromo- or iodo-olefins, which have not been fluorinated such as vinylbromide, 4-bromo-1-butene, and the like, may also be used.

In general, the amount of the curing sites introduced at the side chain position of the polymer in the fluoropolymer component is preferably approximately 0.05 to 5 mol % and more preferably approximately 0.1 to 2 mol % of the total polymerization units.

The curing sites may be located at the ends of a polymer chain of the fluoropolymer component. For example, a halogen may be introduced at the end position using a chain transfer agent or a polymerization initiator. Typically, a curing site is introduced at the end

position by introducing an appropriate chain transfer agent into a reaction medium or deriving the site from an appropriate polymerization initiator at the time of polymer preparation.

An example of a useful chain transfer agent is a compound expressed by the formula R_fZx (wherein R_f is a substituted or unsubstituted C_1-C_{12} fluoroalkyl radical which may be perfluorinated, Z is Br or I, and x is 1 or 2). Specific examples containing bromine include CF_2Br_2, $Br(CF_2)_2Br$, $Br(CF_2)_4Br$, $CF_2(Cl)Br$, $CF_3CF(Br)CF_2Br$, and the like.

An example of a useful polymerization initiator is a compound expressed by $NaO_2S(CF_2)_nX$ (wherein X is Br or I and n is 1 to 10).

The amount of curing sites introduced at the end position of the polymer of the fluoropolymer component is typically approximately 0.05 to 5 mol % and more preferably approximately 0.1 to 2 mol % of the total polymerization units.

Combinations of two or more types of curing sites are also useful in the present invention. For example, a useful fluoropolymer is one that contains halogens capable of participating in peroxide curing reaction along with a nitrogen-containing curing site such as a nitrile group-containing curing site, for example. The total amount of curing sites is typically approximately 0.1 to 5 mol % and preferably approximately 0.3 to 2 mol % of the total polymerization units.

Effective amounts of the crosslinking agent used in the present invention and the desired additional curing agent can be used as a curing agent to crosslink the curing elastomer and the desired additional fluoropolymer. If the amount of the curing agent is too small, the crosslinking of the fluoropolymer component will not progress sufficiently, and as a result, the desired physical properties may not be achieved and/or the crosslinking rate may be lower than expected. If the amount of the curing agent is too large, the fluoropolymer component may not be crosslinked as expected and/or crosslinking may occur more quickly than according to the expected manufacturing conditions. The amount of the curing agent required may be affected by the selection of the specific components of the composition. For example, depending on the type and/or amount of the selected filler, it may be possible to promote or suppress curing in comparison to the same composition to which a filler is not added, so it is necessary to adjust the amount of the curing agent appropriately, but this is known to people having ordinary skill in the art.

The type and amount of the curing agent that is used are influenced by the composition of the fluoropolymer component. For example, when a blended product of a nitrile group-containing fluoropolymer and an additional fluoropolymer not containing a nitrile curing site is used, an effective amount of a first selected curing agent is used to crosslink the fluoropolylmer having copolymerization units derived from a nitrile group-containing monomer, and an effective amount of a second selected curing agent is concurrently used to crosslink the additional fluoropolymer. The first and second selected curing agents may respectively be one type or combinations of two or more types of curing compounds. In addition, the first and second selected curing agents may be the same or different compositions. That is, at least one type out of a plurality of types of curing agents should have the effect of crosslinking at least one type of polymer.

<Amidine compound>

The amidine compound used in the present invention can function as a crosslinking agent. An amidine compound may typically be one type or a combination of two or more types selected from a group including mono-amidines, bis-amidines, tris-amidines, tetra-amidines, and salts thereof. One preferable mode of an amidine compound is one type or a combination of two or more types selected from a group including mono-amines, bis-amidines, and salts thereof from the perspective of availability and practicality. Here, when a mono-amidine is used, a compound having a structure capable of functioning as a crosslinking agent such as a mono-amidine salt, for example, is selected.

In a preferable mode, the amidine compound has at least one C-O-C bond. An amidine compound having at least one C-O-C bond is advantageous from the perspective of providing the molded product with particularly favorable surface properties and, in several modes, further providing favorable compression set properties.

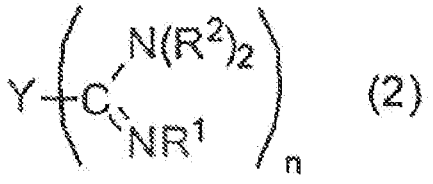
The amidine compound may contain hetero atoms such as oxygen, sulfur, phosphorus, or nitrogen present outside the amidine groups, for example.

In a particularly preferable mode, the amidine compound is a mono-amidine having at least one C-O-C bond. In a preferable mode, the mono-amidine may have alkyl groups, alkenyl groups, aryl groups, or alkaryl groups having from 1 to approximately 15 carbon atoms. These

may be straight-chain or branched-chain substances. These substances may be unsubstituted or substituted (for example, fluorinated; in particular, perfluorinated).

In a preferable mode, a preferable amidine compound is expressed by the following general formula (2):

[Formula 1]



(2)

(wherein

R^1 is a hydrogen atom; or an alkyl group, alkenyl group, aryl group, alkaryl group, or alkenyl aryl group;

R^2 is a hydrogen atom; or an alkyl group, alkenyl group, aryl group, alkaryl group, or alkenyl aryl group; or $(R^2)_2$ forms a group expressed by $H_3{}^{(+)(-)}A$, where ${}^{(-)}A$ is an anion;

Y is a single bond or a monovalent to quadrivalent group;

n is an integer of 1 to 4, wherein if n is 1, $(R^2)_2$ forms a group expressed by $H_3{}^{(+)(-)}A$; and

R^1 and R^2 may be the same or different, when a plurality of components are present in the molecule).

The alkyl group described above may have 1 to approximately 15, 1 to approximately 10, or 1 to approximately 8 carbon atoms. The alkenyl group described above may have approximately 2 to 15, approximately 2 to 10, or approximately 2 to 6 carbon atoms. The aryl group described above may have approximately 6 to 15 or approximately 6 to 12 carbon atoms.

In a preferable mode, R^1 is hydrogen and $(R^2)_2$ is $H_3{}^{(+)(-)}A$.

The anion expressed by ${}^{(-)}$ may be an inorganic anion or an organic anion. In a preferable mode, ${}^{(-)}A$ contains a Cl anion, a Br anion, an I anion, or a COO anion. A preferable example of ${}^{(-)}A$ is an anion selected from a group including COO, SO_3, SO_2, SO_2NH, PO_3, CH_2OPO_3, $(CH_2O)_2PO_2$, C_6H_4O, OSO_3, $N(SO_2)R'$, $N(SO_2)SO_2R'$, and $C(SO_2)RSO_2R'$ (wherein R and R' are respectively independently an alkyl group, alkenyl group, aryl group, alkaryl group, or alkenyl aryl group, and these may be unsubstituted or partially or completely fluorinated).

In a preferable mode, ${}^{(-)}A$ has an alkyl group having 1 to approximately 12 carbon atoms.

In a preferable mode, $^{(-)}$A has an ether bond.

In a preferable mode, $^{(-)}$A is a halogenated carboxylic acid anion, particularly a fluorocarboxylic acid anion, and more preferably a perfluorocarboxylic acid anion.

In a preferable mode, $^{(-)}$A is expressed by $CF_3O(CF_2)kCOO^{(-)}$ (wherein k is 1 to approximately 10).

In another preferable mode, $^{(-)}$A is expressed by $CF_3(CF_2)jCOO^{(-)}$ (wherein j is 1 to approximately 15, 1 to approximately 8, or 1 to approximately 3).

In a preferable mode, $^{(-)}$A is an acetic acid anion, a fluorinated acetic acid anion, or a trifluoroacetic acid anion.

Regarding Y, if n described above is 1 (that is, a mono-amidine), Y is a monovalent organic group, for example. If n is 2 (that is, a di-amidine), Y is a single bond, -O-, -S-, or a bivalent organic group, for example. If n is 3 (that is, a tri-amidine), Y is a trivalent organic group, for example. If n is 4 (that is, a tetra-amidine), Y is $N^{(+)}$ or a quadrivalent organic group, for example. These monovalent to quadrivalent organic groups may respectively contain hydrocarbon groups having 1 to approximately 15 carbon atoms, for example. The hydrocarbon groups may be unsubstituted or substituted (for example, halogenated; particularly, fluorinated; more particularly, perfluorinated) and may be straight-chain or branched-chain groups. Y preferably has at least one C-O-C bond.

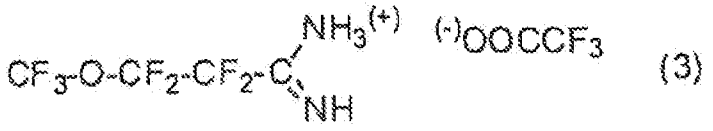
A preferable example is a mono-amidine compound in which n is 1 and Y is a group expressed by R^3OR^4- (wherein R^3 is a perfluoroalkyl group having 1 to approximately 3 carbon atoms, and R^4 is a perfluoroalkyl group having 1 to approximately 3 carbon atoms). These amidine compounds are advantageous from the perspective that the compounds are extremely easy to acquire and the perspective that the compounds are considered to have favorable crosslinking reactivity.

Another preferable example is a di-amidine compound in which n is 2 and Y is a group expressed by -$(R^5OR^6)_m$- (wherein R^5 and R^6 are respectively independently a perfluoroalkylene group having 1 to approximately 3 carbon atoms and m is an integer from 1 to 3). These amidine compounds are advantageous from the perspective that the compounds are extremely easy to acquire and the perspective that the compounds are considered to have favorable crosslinking reactivity.

Modes in which any two or more of the preferable modes described above with regard to each of R^1, R^2, Y, n, and $^{(-)}A$ in the general formula (2) are also included in this disclosure.

A preferable example among these modes is a mono-amidine compound in which R^1 is a hydrogen atom, $(R^2)_2$ is $H_3^{(+)(-)}A$, $^{(-)}A$ is a trifluoroacetic acid anion, and Y is a $CF_3OCF_2CF_2$- group. This amidine compound is expressed by the following formula (3):

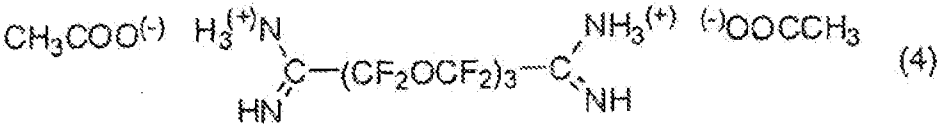
[Formula 2]



(3)

Another preferable example is a di-amidine compound in which R^1 is a hydrogen atom, $(R^2)_2$ is $H_3^{(+)(-)}A$, $^{(-)}A$ is an acetic acid anion, and Y is a $-(CF_2OCF_2)_3-$ group. This amidine compound is expressed by the following formula (4):

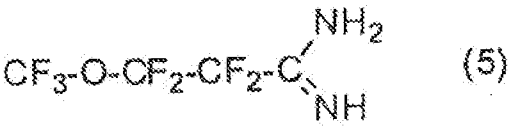
[Formula 3]



(4)

The amidine compound itself may be introduced into the fluoropolymer composition, or the amidine compound may be generated at the time of use by typically introducing the raw material or precursor of the amidine compound as a mixture. An example of the raw material or precursor of the amidine compound is a mixture of a compound expressed by the following formula (5) when an amidine compound expressed by the formula (3) described above is used:

[Formula 4]



(5)

mixed with CF_3COOH (trifluoroacetic acid).

The amount of the amidine compound used per 100 parts by mass of the curing elastomer in the fluoropolymer composition is preferably at least approximately 0.5 parts by mass from the

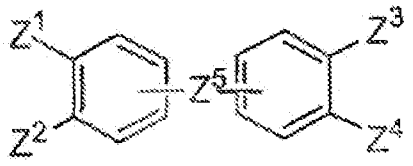
perspective of achieving a particularly favorable crosslinking density and preferably at most approximately 1.5 parts by mass from the perspective of avoiding residual unreacted curing agent in the molded product and the perspective of economic superiority.

<Bis aminophenol compound>

The bis aminophenol compound can function as a crosslinking agent in the fluoropolymer composition of the present invention. By using a bis aminophenol compound as a crosslinking agent in combination with the amidine compound as described above, it is possible to provide a higher crosslinking density than when the amidine compound and the bis aminophenol compound are respectively used alone, for example.

In a preferable mode, the bis aminophenol compound is expressed by the following general formula (1):

[Formula 5]



(1)

(wherein

Z^1, Z^2, Z^3, and Z^4 are respectively independently an $-NH_2$ group or an -OH group, one of Z^1 or Z^2 is an $-NH_2$ group while the other is an -OH group, and one of Z^3 or Z^4 is an $-NH_2$ group while the other is an -OH group; and

Z^5 is a single bond or a bivalent group selected from a group comprising -O-, -CO-, $-SO_2-$, and perfluoroalkylene groups with a carbon number of 1 to 3).

In a preferable mode, Z^5 is a perfluoroalkylene group with a carbon number of 1 to 3 from the perspective of providing the resulting molded product with particularly favorable surface properties.

In a preferable mode, the bis phenol compound is 2,2-diamino-4,4'-(perfluoropropane-2,2-diyl) from the perspective that the compound is extremely easy to acquire and the perspective that the compound is considered to have favorable crosslinking reactivity.

In another preferable mode, the bis aminophenol compound is bis(3-amino-4-hydroxyphenyl)sulfone from the perspective that the compound is extremely easy

to acquire and the perspective that the compound is considered to have favorable crosslinking reactivity.

The amount of the bis aminophenol compound used per 100 parts by mass of the curing elastomer in the fluoropolymer composition is preferably at least approximately 0.1 parts by mass from the perspective of achieving a particularly favorable crosslinking density and preferably at most approximately 1.0 parts by mass from the perspective of avoiding residual unreacted curing agent in the molded product and the perspective of economic superiority.

In a particularly preferable mode, the fluoropolymer composition contains approximately 0.5 to 1.5 parts by mass of an amidine compound and approximately 0.1 to 1.0 parts by mass of a bis aminophenol compound per 100 parts by mass of the curing elastomer. Such a composition is particularly advantageous from the perspective of providing a molded product with few surface defects by realizing a favorable crosslinking density.

<Other components>

In addition to the above, the fluoropolymer composition may arbitrarily contain one or more types of the following components, for example.

(Additional curing agents)

The properties of the fluoropolymer composition may be altered by using additional curing agents in addition to the crosslinking agents described above. Examples of additional curing agents include bis-amidoximes, ammonium salts, organic compounds (compounds containing arsenic, antimony, or tin, for example), ammonia-generating compounds, and peroxide curing agents. An example of an additional curing agent is a compound expressed by the general formula $CH_2=CHR_fCH=CH_2$ (wherein R_f is a C_1-C_8 straight-chain or branched chain alkylene, cycloalkylene, or oxyalkylene which is at least partially fluorinated). In the formula described above, one or a plurality of H atoms may be substituted with halogen atoms such as fluorine atoms, for example. Similarly, a polymer containing a lateral group of $CH_2=CHR_f$- (wherein R_f is as defined above) and a polymer in which one or a plurality of H atoms in the formula are substituted with halogen atoms such as fluorine atoms, for example, are also useful as additional curing agents in the present invention.

A desired adjuvant, which is typically used for curable fluoropolymer compositions may also be incorporated into the fluoropolymer composition. For example, a substance which is often blended into fluoropolymer compositions as a part of a curing agent system is a crosslinking aid (also sometimes called a co-curing agent), and this can work together with the peroxide curing agent to provide effective curing. Accordingly, these crosslinking aids are particularly useful when combined with the peroxide curing agent. It is typically preferable to use a crosslinking auxiliary agent in an amount between approximately 0.1 and 10 parts by mass (phr) or approximately 1 to 5 parts by mass (phr) with respect to a total of 100 parts by mass of the curing elastomer and the desired additional fluoropolymer.

For example, additives such as fillers (for example, carbon black, fluoropolymer fillers, and the like), stabilizers, plasticizers, lubricants, and processing aids ordinarily used in the compounding of a fluoropolymer composition and the like may be incorporated into the fluoropolymer composition. However, it is desirable for these additives to be sufficiently stable under the target usage conditions.

For example, the low-temperature performance can be improved by incorporating perfluoropolyether into the composition.

In addition, carbon black may be used in order to achieve a balance in the performance of the fluoropolymer composition - for example, the modulus, tensile strength, elongation, hardness, wear resistance, conductivity, processability, and the like. Suitable examples include MT blacks (medium thermal blacks) of the part numbers N-991, N-990, N-908, and N-907; FEFN-550; furnace black with a large particle size, and the like. When carbon black is used, the amount used is preferably approximately 1 to 70 parts by mass (phr) with respect to a total of 100 parts by mass of the curing elastomer and the additional fluoropolymer. This range is particularly suitable when using furnace black with a large particle size.

One type or a plurality of acid receptors may be incorporated into the fluoropolymer composition. However, in cases in which the presence of extractable metal compounds is not desirable (in semiconductor applications, for example), the use of inorganic acid receptors should be kept to a minimum and preferably forgone entirely. Examples of typically used acid receptors include zinc oxide, calcium hydroxide, calcium carbonate, magnesium oxide, silicon dioxide (silica), and the like. These compounds are typically used to bind to HF or other acids. These acids can be generated at high temperatures, which may be encountered in the curing

process when forming a molded product using the fluoropolymer composition or at the temperatures observed when exhibiting the functions of the fluoropolymer composition.

<Curing of the fluoropolymer composition]>

The fluoropolymer composition of the present invention is useful in the manufacture of molded products such as O-rings, gaskets, tubes, sheets, films, sealing materials, and the like, for example. Such molded products can be manufactured with conventionally known methods. Typically, these products can be manufactured by compounding the ingredients of the fluoropolymer composition and molding the resulting blend under increased pressure, curing the resulting product, and then further subjecting the cured product to a post-curing cycle. For example, a curable composition of a formulation, which does not use inorganic acid receptors is particularly suited to applications such as sealing materials and gaskets for manufacturing semiconductor elements and sealing materials for high-temperature parts of automobile applications.

The fluoropolymer composition can be prepared by compounding the ingredients - that is, the curing elastomer, the desired additional fluoropolymer, crosslinking agents, and various desired components (for example, one or a plurality of additional curing agents, one or a plurality of desired adjuvants used in an ordinary rubber processing device, and various other additives). More specifically, the ingredients of the fluoropolymer composition can be sufficiently mixed (that is, compounded) by adding prescribed amounts of crosslinking agents and other desired additives to the fluoropolymer component as are ordinarily used and using a desired general rubber mixing device. An example of such a device is a sealed mixer (for example, a Banbury mixer), a roll mill, or another desired simple mixing device. It is desirable for the mixing temperature at the time of mixing to be set so as to not exceed approximately 120°C. During mixing, it is preferable to uniformly disperse the other components into the fluoropolymer.

Next, the mixture is extruded (for example, when forming a shape such as a film, tube, or hose) or processed and molded with a mold (for example, when forming a shape such as a sheet or an O-ring).

The molding or pressurized curing of the compounded mixture is ordinarily performed under an appropriate pressure for a desired amount of time at a temperature sufficient for curing the mixture. The temperature is typically approximately 95°C to 230°C and preferably

approximately 150°C to 205°C, and the time is approximately 1 minute to 15 hours and typically approximately 5 minutes to 30 minutes. A pressure of approximately 700 kPa to 21,000 kPa is ordinarily applied to the mixture placed in a mold. The mold may be baked after first being coated with a release agent.

Next, the mixture molded in this way or the pressure-cured product is ordinarily post-cured over time in a heating furnace at a temperature sufficient to complete curing. This temperature is ordinarily approximately 150°C to 300°C and typically approximately 230°C, while the time is approximately 2 to 50 hours or longer, but the time typically increases as the cross-sectional thickness of the product increases. For a product with a certain thickness, the temperature at the time of post-curing is ordinarily increased gradually from the lower limit temperature to the target maximum temperature. The maximum temperature used is preferably approximately 300°C, and this temperature is maintained for approximately four or more hours. Any residual volatile components are ordinarily discharged from the composition, which is completely crosslinked or cured as a result of this post-curing process. An example of a suitable post-curing cycle is to use six-stage processing conditions to expose the product to heat in a nitrogen atmosphere. First, the product is heated from 25°C to 200°C over the course of 6 hours, the product is then held at 200°C for 16 hours, and then the product is then heated from 200°C to 250°C over the course of 2 hours. Next, the product is kept at 250°C for 8 hours and is then heated from 250°C to 300°C over the course of 2 hours. Next, the product is kept at 300°C for 16 hours. Finally, the heating of the furnace is interrupted, for example, and the product is returned to ambient temperature.

[Working Examples]

Working Examples of the present invention will be further described hereinafter.

Unless specifically stated otherwise, the displayed results were obtained using the following test method. The test results are shown in the table below.

<Mooney scorch (T5 and T35)>

The Mooney scorch time was evaluated in compliance with JIS K6300-1 2001.

<Curing rheology properties (Monsanto ODR)>

The curing rheology properties - specifically, ML, MH, Ts2, Tc10, Tc50, and Tc90 - were measured as indices of crosslinking properties.

Uncured composition samples were tested in compliance with JIS K6300-2 2001 using a model R-100 Monsanto rheometer. Both the minimum torque (ML) obtained during a prescribed period of time, as well as the highest torque (MH) for cases where a flat part or maximum torque could not be not obtained, were measured. Further, the time required to reach the 2-unit high torque from ML ("Ts2"), the time required for the torque to reach a value equal to ML+0.1 (MH-ML) ("Tc10"), the time required for the torque to reach a value equal to ML+0.5 (MH-ML) ("Tc50"), and the time required for the torque to reach a value equal to ML+0.9 (MH-ML) ("Tc90") were measured.

Similarly, after the uncured composition samples were respectively stored for 7 days and 30 days at room temperature (approximately 25°C), ML, MH, Ts2, Tc10, Tc50, and Tc90 were measured with the same method as that described above ("after 7 days" and "after 30 days" in the table).

<Curing conditions>

Pressurized curing: Unless specifically stated otherwise, sample sheets of a size of 150x150x2.0 mm for measuring physical properties were prepared by pressurizing the sheet for 30 minutes at a pressure of approximately 20 megapascal (MPa) and a temperature of 165°C.

Post-curing: The pressure-cured sample sheets were further exposed to heat in a nitrogen atmosphere. Specifically, this entails step curing in which the following steps are performed sequentially: 1) heating from room temperature to 150°C over the course of 1 hour, 2) maintenance for 7 hours at 150°C, 3) heating from 150°C to 300°C over the course of 2 hours, 4) maintenance for 4 hours at 300°C, and 5) cooling from 300°C to room temperature over the course of 2 hours. In this manner, these samples were used in tests after first being returned to the ambient temperature.

<Duro A hardness>

The Duro A hardness was measured in accordance with JIS K6253 2006 using a type A-2 shore durometer.

<Breaking tensile strength, breaking elongation, and modulus at 100% elongation>

The breaking tensile strength, breaking elongation, and modulus at 100% elongation were measured in accordance with ASTM D412 2006 for samples cut out using an ASTM die D from the sheets, which were pressure-cured and post-cured under the conditions described above. The units used in the report of the results were percentage and MPa.

<Compression set properties>

O-ring samples (half of #2140-rings) which were pressure-cured and post-cured under the conditions described above were measured in accordance with JIS K6262 2006 at the temperatures and times shown in the table. The results are reported as percentages with respect to the original compression deformation (taken as 25%).

<Surface appearance>

The sheets, which were pressure-cured and post-cured under the conditions described above were observed visually, and sheets with no irregularities on the surface were evaluated as "favorable", whereas sheets demonstrating irregularities were evaluated as "poor".

[Working Examples 1 through 13 and Comparative Examples 1 through 3]

In Working Examples 1 through 3 and Comparative Example 1, the properties of perfluoroelastomer compositions for which the content of BOAP, which is a bis aminophenol compound, was respectively 0 phr, 0.2 phr, 0.3 phr, or 0.4 phr were evaluated. In Working Examples 4 through 13 and Comparative Examples 2 and 3, the properties of perfluoroelastomer compositions consisting of various ingredients were evaluated.

The ingredients shown in the Table were mixed using a roll mill 6 inches in diameter to obtain uncured composition samples. Various tests were performed on the composition samples and samples formed by pressure-curing and post-curing the composition samples under the conditions described above. The test results are shown in Tables 1 through 3.

[Ingredients]

Fluoropolymers

Fluoropolymer A

A ternary copolymer obtained by copolymerizing 65.7 mol % of tetrafluoroethylene (TFE), 33.0 mol % of perfluoromethylvinyl ether (PMVE), and 1.3 mol % of a nitrile group-containing curing site monomer (CF_2=$CFO(CF_2)_5CN$) by emulsion polymerization.

Fluoropolymer B

A ternary copolymer obtained by copolymerizing 64.8 mol % of tetrafluoroethylene (TFE), 33.0 mol % of perfluoromethylvinyl ether (PMVE), and 2.2 mol % of a nitrile group-containing curing site monomer (CF_2=$CFO(CF_2)_5CN$) by emulsion polymerization.

Amidine compounds

Amidine compound A

[1,1,2,2-tetrafluoro-2-(trifluoromethoxy)ethyl]amidinium trifluoroacetate (available from the 3M Corporation).

Amidine compound B

Perfluoroadiponitrile bis amidine diperfluoromethoxy propionate ($CH_3OCF_2CF2COO\text{-}NH_3^+(NH{=})C(CF_2)_4C(=NH)NH_3^{+}\text{-}OOCCF_2CF_2OCF_3$); synthesized by the method described below.

Amidine compound C

Perfluorotetraethylene oxide dinitrile bis amidine diacetate ($CH_3COO^-NH_3^+(NH{=})C(CF_2OCF_2)_3C(=NH)NH_3^{+}\text{-}OOCCH_3$); synthesized by the method described below.

Bis aminophenol compounds

Bis aminophenol compound A

BOAP (2,2'-diamino-4,4'-(perfluoropropane-2,2-diyl)diphenol); available from the Aldrich Corporation.

Bis aminophenol compound B

Bis(3-amino-4-hydroxyphenyl)sulfone; available from the Aldrich Corporation.

Filler

MT Carbon; available from the CanCarb Corporation.

Synthesis of amidine compound B - perfluoroadiponitrile bis amidine diperfluoromethoxy propionate

(A) First, perfluoroadiponitrile bis amidine ($NH_2(NH{=}C(CF_2)_4C(=NH)NH_2$) was synthesized.

Methanol (188 g, 5.9 mol) was placed in a 4 L plastic flask containing a magnetic stirrer, and perfluoroadipoyl fluoride (454 g, 1.5 mol) (available from the 3M Company) was added thereto over the course of 1 hour. The hydrofluoric acid by-product was processed using a caustic scrubber. Water was added, and perfluoroadipate (446 g, 1.4 mol) was then isolated by evaporating the lower fluorochemical product phase. Perfluoroadipate (446 g, 1.4 mol), which was dissolved in methanol and placed in a 2 L flask equipped with a mechanical stirrer, was reacted with an excessive amount of ammonia (54 g, 3.2 mol), whereby perfluoroadipoylamide

(385 g, 1.3 mol, after vacuum drying) was obtained. Pyridine (508 g, 6.4 mol) and then anhydrous trifluoroacetic acid (674 g, 3.2 mol) (available from Aldrich) were reacted at -10°C in a dimethylformamide solution of perfluoroadipolyamide (385 g, 1.3 mol) placed in a 3 L flask equipped with a mechanical stirrer. Water was added, and perfluoroadiponitrile (235 g, 0.9 mol) with a boiling point of 64°C was then isolated by evaporating the lower fluorochemical product phase. When perfluoroadiponitrile (108 g, 0.4 mol) dissolved in diethyl ether was placed in a 1 L flask equipped with a mechanical stirrer and reacted with ammonia (17 g, 1.0 mol) at -10°C, perfluoroadiponitrile bis amidine (112 g, 0.9 mol) was obtained, but the melting point after vacuum drying was 132°C, and the structure of the compound was confirmed by fluorine and proton NMR.

(B) Next, perfluoroadiponitrile bis amidine (26 g, 0.1 ml) prepared as described above and dissolved in methanol was placed in a 100 mL flask containing a magnetic stirrer, and perfluoromethoxy propionic acid (46 g, 0.2 mol) prepared by hydrolyzing perfluoromethoxy propionyl fluoride as described in the pamphlet of International Publication No. WO01/46116 was dripped into the solution. The solution was vacuum-dried, and perfluoroadiponitrile bis amidine diperfluoromethoxy propionate (59 g, 0.8 mol) was isolated. The structure of the compound was confirmed by fluorine and proton NMR.

Synthesis of amidine compound C - Perfluorotetraethylene oxide dinitrile bis amidine diacetate

(C) Tetraethylene glycol diacetate was directly fluorinated as described in the specification of US Patent No. 5,488,142, and perfluorotetraethylene oxide dimethyl ester was isolated. Next, bis amide was first synthesized by reacting the compound with ammonia in accordance with the synthesis procedure described in (A) above, and bis nitrile was formed by dehydration. Next, the compound was reacted with ammonia to obtain fluorochemical bis amidine.

(D) Next, when acetic acid was dripped into this fluorochemical bis amidine as described in (B) above, perfluorotetraethylene oxide dinitrile bis amidine diacetate was obtained.

[Table 1]

	Comparative Example 1	Working Example 1	Working Example 2	Working Example 3
Formulation (parts by mass)				
Fluoropolymers				
Ternary copolymer of 64.8 mol% of TFE, 33.0 mol% of PMVE, and 2.2 mol% of CF_2=CFO(CF_2)$_5$	100	100	100	100
Amide compounds				
[1,1,2,2-tetrafuoro-2-(trifluoromethoxy)ethyl] amidinium trifluoroacetate	1.1	1.1	1.1	1.1
Bis aminophenol compounds				
2,2'-diamino-4,4'-(perfluoropropane-2,2-diyl)diphenol		0.2	0.3	0.4
Filler				
MT Carbon	20	20	20	20
Monsanto ODR				
Test conditions	30 min (165°C)	30 min (165°C)	30 min (165°C)	30 min (165°C)
ML (dNm)	16.99	17.31	19.01	17.00
MH (dNm)	74.94	98.48	99.05	96.95
M-ML (dNm)	57.95	81.17	80.04	79.95
Ts2 (min)	1.39	1.16	1.44	1.14
Tc10 (min)	1.67	1.53	1.83	1.50
Tc50 (min)	2.94	3.17	3.49	3.06
Tc90 (min)	6.16	17.19	18.24	17.65
Cured product properties				
Duro A hardness	74	76	77	79
100% modulus (MPa)	12.1	15.1	15.7	16.5
Breaking tensile strength (MPa)	21	24.3	25.0	24.5
Breaking elongation (%)	140	140	140	130
Compression set (%) for 70 hours at 250°C	12	8	7	7
Compression set (%) for 70 hours at 300°C	12	11	10	10
Surface appearance	Poor	Favorable	Favorable	Favorable

[Table 2]

	Comparative Example 1	Working Example 1	Working Example 2	Working Example 3
Mooney scorch ML (121°C)				
T5	10.09	8.49	8.06	7.99
T35	20.84	15.18	14.01	13.52
Monsanto ODR				
Test conditions	30 min (165°C)	30 min (165°C)	30 min (165°C)	30 min (165°C)
Initial composition				
NL (dNm)	16.99	17.31	19.01	17.00
MH (dNm)	74.94	98.48	99.05	96.95
MH-ML (dNm)	57.95	81.17	80.04	79.95
T2 (min)	1.39	1.16	1.44	1.14
Tc10 (min)	1.67	1.53	1.83	1.50
Tc50 (min)	2.94	3.17	3.49	3.06
Tc90 (min)	6.16	17.19	18.24	17.65
Composition after 7 days				
ML (dNm)	15.96	17.74	18.56	18.04
MH (dNm)	92.77	93.1	95.11	97.32
MH-ML (dNm)	76.81	75.36	76.55	79.28
T2 (min)	1.23	1.15	1.23	1.12
Tc10 (min)	1.61	1.48	1.57	1.45
Tc50 (min)	3.30	2.91	3.03	2.88
Tc90 (min)	17.37	16.48	16.86	17.06
Composition after 30 days				
ML (dNm)	16.40	18.32	20.23	19.07
MH (dNm)	94.91	97.72	101.17	102.73
MH-ML (dNm)	78.51	79.40	80.94	83.66
Ts2 (min)	1.24	1.16	1.48	1.19
Tc10 (min)	1.61	1.53	1.86	1.55
Tc50 (min)	3.28	3.13	3.38	3.01
Tc90 (min)	17.77	18.48	18.55	18.12

[Table 3]

	Comparative Example 2	Working Example 4	Comparative example 3	Working Example 5	Working Example 6	Working Example 7	Working Example 8	Working Example 9	Working Example 10	Working Example 11	Working Example 12	Working Example 13
Formulation (parts by mass)												
Fluoropolymers												
A Ternary copolymer of 65.7 mol% of TFE, 33.0, mol% of PMVE and 1.3 mol% of CF_2=CFO(CF_2)$_5$CN	100	100										
B Ternary copolymer of 64.8 mol% of TFE, 33.0 mol% of PMVE, and 2.2 mol% of CF_2=CFO(CF_2)$_5$CN			100	100	100	100	100	100	100	100	100	100
Amidine compounds												
A [1,1,2,2-tetrafuoro-2-(trifuoromethoxy)ethyl] amidium trifuoroacetate	1.1	1.1	1.1	1.1			0.5	1.5	1.1	1.1	1.1	1.1
B perfluorodiponitrile bis amidine diperfluoromethoxy propionate					0.5							
C Perfluorotetraethylene oxide dinitrile bis amidine perfluorotetraethylene oxide						0.5						
Bis aminophenol compounds												
A 2,2'-diamino-4,4' -(perfluoropropane-2,2- diyl) diphenol		0.3		0.3	0.3	0.3	0.3	0.3	0.1	0.5	1	
B Bis(3-amino-4-hydroxyphenyl) sulfone												0.3
Filler												
MT Carbon	20	20	20	20	20	20	20	20	20	20	20	20

Monsanto ODR												
Test conditions	30 min (165 °C)	30 min (165 °C)	30 min (165 °C)	30 min (165 °C)	30 min (165 °C)	30 min (165 °C)	30 min (165 °C)	30 min (165 °C)	30 min (165 °C)	30 min (165 °C)	30 min (165 °C)	30 min (165 °C)
ML (dNm)	13.64	19.32	17.79	19.71	18.60	28.44	18.47	20.17	19.40	20.48	21.97	15.60
MH (dNm)	63.99	114.63	87.07	97.23	91.79	103.57	74.64	108.41	97.59	104.00	111.75	72.18
MH-ML (dNm)	50.35	95.19	69.28	77.52	73.19	75.13	56.17	88.24	78.19	83.52	89.78	56.58
Ts2 (min)	1.57	1.07	1.19	1.11	2.13	8.91	1.18	1.23	1.20	1.08	0.98	1.43
Tc10 (min)	1.91	1.43	1.51	1.43	3.21	1.19	1.45	1.51	1.55	1.41	1.31	1.77
Tc50 (min)	4.02	2.90	3.16	2.92	7.36	2.60	3.42	3.46	3.20	2.88	2.72	3.68
Tc90 (min)	16.12	17.66	18.76	18.09	17.21	12.60	17.65	19.57	18.47	18.27	18.50	16.97
Cured product properties												
Duro A hardness	71	73	78	80	80	80	79	79	79	78	78	79
Breaking tensile strength (MPa)	20.9	20.4	24.0	21.4	19.4	22.1	22.4	24.0	22.3	22.7	21.5	22.6
Breaking elongation (%)	220	190	150	120	100	100	130	130	130	120	90	130
Compression set (%) for 70 hours at 250°C	18	15	13	7	11	11	11	8	5	8	8	9
Surface properties	Poor	Favor-able	Poor	Favor-able	Poor	Favor-able	Favor-able	Favor-able	Favor-able	Favor-able	Favor-able	Favor-able

[Field of Industrial Application]

The fluoropolymer composition of the present invention can be suitably applied to the formation of various molded products such as sheets, films, hoses, gaskets, O-rings, and the like, for example.

Claims

What is claimed is:

1. A fluoropolymer composition comprising a fluoropolymer and a crosslinking agent;

wherein the fluoropolymer is an elastomer containing copolymerization units derived from a nitrogen-containing curing site monomer; and

the crosslinking agent is a combination of two or more compounds including one or more type of amidine compound and one or more type of bis aminophenol compound.

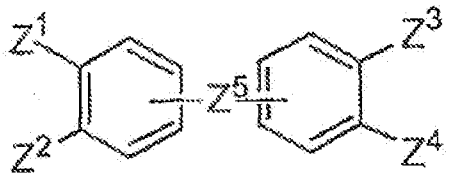
2. The fluoropolymer composition of claim 1, wherein the nitrogen-containing curing site monomer is one or more type selected from nitrile-containing fluorinated olefins and nitrile-containing fluorinated vinyl ethers; and

the fluoropolymer is a copolymer of a perfluoroolefin, a perfluorovinyl ether, and a nitrogen-containing curing site monomer.

3. The fluoropolymer composition of claim 1 or 2, wherein the amidine compound is one type or a combination of two or more types selected from a group comprising mono-amidines, bis-amidines, and salts thereof.

4. The fluoropolymer composition of any one of claims 1 through 3, wherein the bis aminophenol compound is expressed by the following general formula (1):

[Formula 1]



(1)

(wherein

Z^1, Z^2, Z^3, and Z^4 are respectively independently an $-NH_2$ group or a -OH group, one of Z^1 or Z^2 is an $-NH_2$ group while the other is an -OH group, and one of Z^3 or Z^4 is an $-NH_2$ group while the other is an -OH group; and

Z^5 is a single bond or a bivalent group selected from a group comprising -O-, -CO-, $-SO_2-$, and perfluoroalkylene groups with a carbon number of 1 to 3).

5. The fluoropolymer composition of any one of claims 1 through 4, further comprising from 0.5 to 1.5 parts by mass of the amidine compound and from 0.1 to 1.0 parts by mass of the bis aminophenol compound per 100 parts by weight of the fluoropolymer.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/064406

A. CLASSIFICATION OF SUBJECT MATTER

C08L 27/12(2006.01)i, C08F 14/18(2006.01)i, C08K 5/16(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 27/12; C08K 5/16; C08K 5/17; C08F 8/00; C08K 5/19; C08K 5/50; C08K 5/29

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

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: fluoropolymer, fluoroelastomer, composition, crosslinking, cure, curing agent, nitrogen, amidine, bis-aminophenol, fluoroolefin, fluorovinyl ether

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6638999 B2 (BISH; CHRISTOPHER JOHN et al.) 28 October 2003 See abstract and claims 1 to 12	1-3
X	US 2004-0072959 A1 (WERNER, M.A. GROOTAERT et al.) 15 April 2004 See abstract and claims 1 to 30	1-3
A	KR 10-2007-0087072 A (3M Innovative Properties Company) 27 August 2007 See whole document	1-3
A	KR 10-2009-0033242 A (3M Innovative Properties Company) 01 April 2009 See whole document	1-3

☐ 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	Date of mailing of the international search report
12 MARCH 2013 (12.03.2013)	**13 MARCH 2013 (13.03.2013)**

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

KANG, Huiman

Telephone No. 82-42-481-8290

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/064406

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4, 5
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2012/064406

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6638999 B2	28.10.2003	DE 60139185 D1	20.08.2009
		EP 1263857 A2	11.12.2002
		EP 1263857 B1	08.07.2009
		JP 05-031166 B2	06.07.2012
		JP 2004-500459 A	08.01.2004
		JP 2004-500459 T	08.01.2004
		US 2002-0026014 A1	28.02.2002
		WO 01-59005 A2	16.08.2001
		WO 01-59005 A3	07.03.2002
		WO 01-59005 A3	16.08.2001
US 2004-0072959 A1	15.04.2004	AT 388195 T	15.03.2008
		AU 2003-267301 A1	04.05.2004
		CN 1302059 C	28.02.2007
		CN 1302059 C0	28.02.2007
		CN 1688646 A	26.10.2005
		DE 60319552 D1	17.04.2008
		DE 60319552 T2	26.03.2009
		EP 1549705 A1	06.07.2005
		EP 1549705 B1	05.03.2008
		JP 04-777652 B2	08.07.2011
		JP 2006-502283 A	19.01.2006
		JP 2006-502283 T	19.01.2006
		JP 4777652 B2	21.09.2011
		RU 2005108346 A	27.02.2006
		US 6846880 B2	25.01.2005
		WO 2004-033546 A1	22.04.2004
KR 10-2007-0087072 A	27.08.2007	CN 101080448 A0	28.11.2007
		EP 1824918 A1	29.08.2007
		EP 1824918 B1	03.12.2008
		JP 05-001168 B2	25.05.2012
		JP 2008-524375 A	10.07.2008
		US 2006-0135827 A1	22.06.2006
		US 2008-0262138 A1	23.10.2008
		US 2009-0088517 A1	02.04.2009
		US 7402630 B2	22.07.2008
		US 7666949 B2	23.02.2010
		US 7989552 B2	02.08.2011
		WO 2006-065334 A1	22.06.2006
KR 10-2009-0033242 A	01.04.2009	AU 1999-60192 A1	03.04.2000
		AU 2002-307045 A8	15.10.2002
		CA 2343056 A1	23.03.2000
		CA 2343056 C	09.01.2007
		CA 2556195 A1	23.03.2000
		CA 2556195 C	16.11.2010
		CA 2716246 A1	23.03.2000
		CN 101490154 A	22.07.2009

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/064406

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		CN 101490154 B	08.02.2012
		EP 1113943 A2	11.07.2001
		EP 1113943 B1	24.11.2004
		EP 1522450 A2	13.04.2005
		EP 1522450 A3	22.06.2005
		EP 1932704 A2	18.06.2008
		EP 1932704 A3	26.11.2008
		EP 1932704 B1	26.10.2011
		EP 2044146 A1	08.04.2009
		EP 2289750 A1	02.03.2011
		JP 03-676235 B2	27.07.2005
		JP 03-779676 B2	31.05.2006
		JP 04-459876 B2	19.02.2010
		JP 2002-525022 A	06.08.2002
		JP 2004-007944 A	08.01.2004
		JP 2006-044649 A	16.02.2006
		JP 2009-544814 A	17.12.2009
		JP 4459876 B2	28.04.2010
		KR 10-0466165 B1	14.01.2005
		US 2001-0039230 A1	08.11.2001
		US 2003-217876 A1	27.11.2003
		US 2006-0100057 A1	11.05.2006
		US 2006-0231304 A1	19.10.2006
		US 2006-0231305 A1	19.10.2006
		US 2006-0231306 A1	19.10.2006
		US 2006-0237246 A1	26.10.2006
		US 2006-0237247 A1	26.10.2006
		US 2008-0021148 A1	24.01.2008
		US 2009-0177345 A1	09.07.2009
		US 2011-0004363 A1	06.01.2011
		US 6209672 B1	03.04.2001
		US 6338391 B1	15.01.2002
		US 6554088 B2	29.04.2003
		US 7104347 B2	12.09.2006
		US 7237634 B2	03.07.2007
		US 7392871 B2	01.07.2008
		US 7455134 B2	25.11.2008
		US 7520353 B2	21.04.2009
		US 7559388 B2	14.07.2009
		US 7597164 B2	06.10.2009
		WO 00-15455 A2	23.03.2000
		WO 00-15455 A3	23.03.2000
		WO 02-078987 A2	10.10.2002
		WO 02-078987 A3	10.10.2002
		WO 2008-014119 A1	31.01.2008