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(54) Title: CURABLE BASE-RESISTANT FLUOROELASTOMERS

(57) Abstract: Compositions of specialty fluoroelastomers containing copolymerized units of tetrafluoroethylene, propylene, optionally vinylidene fluoride, and a cure site monomer selected from the group consisting of i) perfluoroalkyl ethylenes and vii) perfluoroalkoxy ethylenes are readily curable with polyhydroxy curing systems. The resulting cured articles have a combination of excellent resistance to alkaline fluids, superior tensile properties and compression set resistance.



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TITLE OF INVENTION**CURABLE BASE-RESISTANT FLUOROELASTOMERS**

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FIELD OF THE INVENTION

This invention relates to polyhydroxy curable fluoroelastomer compositions wherein the fluoroelastomer comprises copolymerized units of tetrafluoroethylene, propylene, and a cure site monomer selected from the group consisting of i) perfluoroalkyl ethylenes and ii) perfluoroalkoxy ethylenes.

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BACKGROUND OF THE INVENTION

Specialty fluoroelastomers made from copolymers of tetrafluoroethylene (TFE), propylene (P), and optionally vinylidene fluoride (VF₂) (i.e. TFE/P dipolymers or VF₂/TFE/P terpolymers) are often utilized in applications wherein resistance to alkaline fluids and other high pH chemicals is critical. The TFE/P dipolymers have the best resistance to alkaline fluids. Terpolymers containing more than about 10 wt.% vinylidene fluoride units generally do not have significantly better alkaline fluid resistance than do conventional fluoroelastomers made from copolymers of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene.

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In order to fully develop physical properties such as tensile strength, elongation, and compression set, elastomers must be cured, i.e. crosslinked. In the case of fluoroelastomers, this is generally accomplished by mixing uncured polymer (i.e. fluoroelastomer gum) with a polyfunctional curing agent and heating the resultant mixture under pressure, thereby promoting chemical reaction of the curing agent with active sites along the polymer backbone or side chains. Interchain linkages produced as a result of these chemical reactions cause formation of a crosslinked polymer composition having a three-dimensional network structure. Commonly used curing agents for fluoroelastomers include

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difunctional nucleophilic reactants, such as polyhydroxy compounds. Alternatively, peroxidic curing systems containing organic peroxides and unsaturated coagents, such as polyfunctional isocyanurates, may be employed.

5 In many cases, polyhydroxy and peroxide cure processes or curing agent formulations are unsatisfactory when used to crosslink these specialty fluoroelastomers. For example, it is known to cure elastomeric VF₂/TFE/P terpolymers with either peroxide (U.S. Patent No. 4,910,260) or
10 polyhydroxy (U.S. Patent Nos. 4,882,390 and 4,912,171) cure systems. However, when such compositions are cured using a polyhydroxy compound, the cured products exhibit undesirable high compression set. In fact, such specialty fluoroelastomers which contain less than about 10 wt.% copolymerized units of vinylidene fluoride show little to no cure
15 response with polyhydroxy cure formulations.

The peroxide cures disclosed in U.S. Patent 4,910,260 are undesirable because the curable compositions which are initially formed are extremely scorchy and would therefore be unsuitable for many commercial processes.

20 It would be particularly desirable to have an improved specialty fluoroelastomer that is resistant to alkaline fluids and which readily crosslinks with polyhydroxy cure systems to form cured articles having good tensile properties and compression set resistance.

25 SUMMARY OF THE INVENTION

It has been surprisingly found that the incorporation of a cure site monomer selected from the group consisting of i) perfluoroalkyl ethylenes and ii) perfluoroalkoxy ethylenes into TFE/P dipolymers or into VF₂/TFE/P terpolymers improves the polyhydroxy curing of these specialty
30 fluoroelastomers without significantly diminishing the resistance of these fluoroelastomers to alkaline fluids. The resulting cured fluoroelastomer articles have excellent compression set resistance and tensile properties.

Accordingly, an aspect of this invention is a curable fluoroelastomer composition comprising

5 A) a specialty fluoroelastomer comprising copolymerized units of 45 to 80 weight percent tetrafluoroethylene; 10 to 40 weight percent propylene; and 0.1 to 15 weight percent of a cure site monomer selected from the group consisting of i) perfluoroalkyl ethylenes and ii) perfluoroalkoxy ethylenes;

10 B) 0.1 to 20 parts by weight per 100 parts fluoroelastomer of a polyhydroxy curing agent;

C) 1 to 30 parts by weight per 100 parts fluoroelastomer of an acid acceptor; and

D) 0.1 to 20 parts by weight per 100 parts fluoroelastomer of a vulcanization accelerator.

15 The polyhydroxy curing agent and vulcanization accelerator may be present as separate components or as the salt of the curing agent and accelerator.

Another aspect of the present invention is a specialty fluoroelastomer comprising copolymerized units of 45 to 80 weight percent
20 tetrafluoroethylene; 10 to 40 weight percent propylene; and 0.1 to 15 weight percent of a cure site monomer selected from the group consisting of i) perfluoroalkyl ethylenes and ii) perfluoroalkoxy ethylenes, with the proviso that the cure site monomer may not be 4-bromo-3,3,4,4-tetrafluorobutene-1.

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DETAILED DESCRIPTION OF THE INVENTION

Specialty fluoroelastomers which may be employed in the curable compositions of this invention include the terpolymer of tetrafluoroethylene (TFE), propylene (P) and a cure site monomer selected from the group
30 consisting of i) perfluoroalkyl ethylenes and ii) perfluoroalkoxy ethylenes. Minor amounts (i.e. less than about 20 weight percent total) of other copolymerizable monomers may be present in higher order copolymer

fluoroelastomers of this invention. Examples of such monomers include, but are not limited to chlorotrifluoroethylene, vinyl fluoride, perfluoro(alkyl vinyl) ethers, perfluoro(alkoxy vinyl) ethers, perfluoro(alkoxyalkyl vinyl) ethers, perfluoroalkyl- or perfluoroalkoxy- alkenyl ethers (such as those disclosed in U.S. Patent No. 5,891,965), ethylene, isobutene, and bromine- or iodine-containing cure site monomers such as $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{Br}$; 1-bromo-2,2-difluoroethylene; bromo-trifluoroethylene; 4-bromo-3,3,4,4-tetrafluorobutene-1; 4-bromo-1,1,2-trifluorobutene-1; 2-bromoperfluoro(ethyl vinyl) ether; 3-bromoperfluoro(propyl vinyl) ether; and 4-iodo-3,3,4,4-tetrafluorobutene-1. Alternatively, bromine or iodine cure sites may be introduced onto the fluoroelastomer polymer chain ends by use of iodinated or brominated chain transfer agents such as methylene iodide or 1,4-diiodoperfluorobutane during polymerization. The presence of brominated or iodinated groups permits the fluoroelastomers of this invention to be cured by organic peroxides in addition to polyhydroxy curatives.

Generally the specialty fluoroelastomers used in the compositions of this invention contain between 45 to 80 (preferably between 50 to 78, most preferably 65 to 78) weight percent copolymerized units of tetrafluoroethylene, based on the total weight of the fluoroelastomer. Less TFE causes the polymerization to be slow, while more TFE causes the resulting polymer to be semi-crystalline plastic, rather than elastomeric.

The fluoroelastomers employed in the compositions of this invention typically contain between 10 to 40 (preferably between 12 to 30, most preferably 15 to 25) weight percent copolymerized units of propylene, based on the total weight of the fluoroelastomer. Less propylene causes the polymer to become semi-crystalline plastic, while more propylene causes the polymerization to become slow.

The specialty fluoroelastomers used in the compositions of this invention also contain 0.1 to 15 (preferably 2 to 10, most preferably 3-6) weight percent copolymerized units of a cure site monomer, based on the

total weight of the fluoroelastomer. The cure site monomer is selected from the group consisting of i) perfluoroalkyl ethylenes and ii) perfluoroalkoxy ethylenes. By "perfluoroalkyl ethylenes" is meant olefins of the formula $R_f-(CF_2)_n-CH=CH_2$, wherein R_f is a perfluorinated alkyl group containing between 1 and 7 (preferably between 1 and 4) carbon atoms and n is an integer between 1 and 7 (preferably between 1 and 4) and wherein the total number of carbon atoms in the perfluoroalkyl ethylene is less than 10 (preferably less than 7). Optionally, a fluorine atom may be replaced by a chlorine, bromine or iodine atom.

By "perfluoroalkoxy ethylenes" is meant olefins of the same general formula as above except wherein R_f is a perfluorinated alkoxy group containing at least one oxygen atom in the chain. Specific examples of perfluoroalkyl and perfluoroalkoxy ethylenes include, but are not limited to $CF_3CF_2CH=CH_2$; $CF_3(CF_2)_3CH=CH_2$; $BrCF_2CF_2CH=CH_2$; and $CF_3CF_2OCF_2CF_2CH=CH_2$.

It is believed that during the polyhydroxy curing process, some copolymerized units of cure site monomer, which are located adjacent to tetrafluoroethylene units in the fluoroelastomer polymer chain, dehydrofluorinate to form sites of unsaturation (i.e. C-C double bonds). These unsaturated sites are then available to react with polyhydroxy curatives to form crosslinks. Fluoroelastomers containing less than 0.1 wt.% units of cure site units do not form a sufficient number of crosslinks to yield a cured product having desirable tensile properties for most end uses. Fluoroelastomers containing more than 15 wt. % cure site units are not desirable because the polymerization is slowed and there is a reduction in the fluoroelastomer's resistance to alkaline fluids and other high pH chemicals.

Another aspect of the invention is a fluoroelastomer comprising copolymerized units of tetrafluoroethylene, propylene and a cure site monomer selected from the group consisting of i) perfluoroalkyl ethylenes and ii) perfluoroalkoxy ethylenes, with the proviso that the cure site

monomer may not be 4-bromo-3,3,4,4-tetrafluorobutene-1. The amount of each copolymerized unit is as specified above.

Preferably, the fluoroelastomers employed in this invention do not contain any copolymerized units of vinylidene fluoride. However, the fluoroelastomers may, optionally, contain up to 20 weight percent copolymerized units of vinylidene fluoride (VF_2), based on the total weight of the fluoroelastomer. If the fluoroelastomer does contain units of vinylidene fluoride, the level is preferably 2 to 20 (most preferably between 10 and 20) weight percent. Generally, the lower the level of vinylidene fluoride, the better the fluoroelastomer's resistance to alkaline fluids (also referred to as "base resistance" in the art). However, copolymers of TFE and P containing no vinylidene fluoride units generally have poor resistance to hydrocarbon fluids such as oils or fuels. The addition of VF_2 to the fluoroelastomer increases the fluorine atom content and thus improves the resistance to hydrocarbons, but at the same time reduces the resistance of the fluoroelastomer to polar fluids. Depending upon the end use application environment, fluoroelastomer base resistance and hydrocarbon fluid resistance can be balanced by adjusting the level of copolymerized vinylidene fluoride and tetrafluoroethylene in the fluoroelastomer.

The fluoroelastomers of this invention are generally prepared by free radical emulsion or suspension polymerization. Preferably, the polymerizations are carried out in batch, or semi-batch emulsion processes well known in the art. The resulting fluoroelastomer latexes are usually coagulated by addition of electrolytes. The precipitated polymer is washed with water and then dried, for example in an air oven, to produce a substantially dry fluoroelastomer gum.

In the semi-batch emulsion polymerization process of this invention, a gaseous monomer mixture of a desired composition (initial monomer charge) is introduced into a reactor which contains an aqueous solution. The aqueous solution contains a surfactant such as ammonium

perfluorooctanoate or perfluorohexylethyl sulfonic acid. Generally, the pH of the solution is controlled to between 1 and 7 (preferably 3-7), depending upon the type of fluoroelastomer being made. In addition, the initial
5 aqueous solution may contain a nucleating agent, such as a fluoroelastomer seed polymer prepared previously, in order to promote fluoroelastomer latex particle formation and thus speed up the polymerization process.

The initial monomer charge contains a quantity of a TFE, P and
10 cure site monomer and, optionally, one or more additional monomers such as VF₂. The amount of monomer mixture contained in the initial charge is set so as to result in a reactor pressure between 0.5 and 10 MPa.

The monomer mixture is dispersed in the aqueous medium and, optionally, a chain transfer agent may also be added at this point while the
15 reaction mixture is agitated, typically by mechanical stirring.

The temperature of the semi-batch reaction mixture is maintained in the range of 25°C – 130°C, preferably 50°C – 100°C. Polymerization begins when the initiator either thermally decomposes or reacts with
20 reducing agent and the resulting radicals react with dispersed monomer.

Additional quantities of the gaseous major monomers and cure site monomer (incremental feed) are added at a controlled rate throughout the polymerization in order to maintain a constant reactor pressure at a controlled temperature.

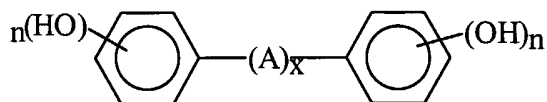
Polymerization times in the range of from 2 to 60 hours are typically
25 employed in this semi-batch polymerization process.

Curable compositions of this invention contain a specialty fluoroelastomer as defined above, a polyhydroxy curative, an acid acceptor and a vulcanization (or curing) accelerator. In the case of fluoroelastomers which contain bromine or iodine atom cure sites, the
30 curable compositions of this invention may, optionally, also contain an organic peroxide and a multifunctional curing coagent. Cured articles resulting from the latter compositions contain crosslinks due to both the

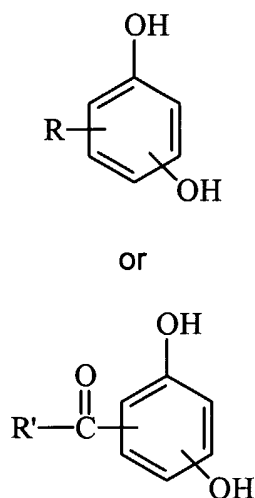
polyhydroxy and peroxide curing systems and are sometimes referred to in the art as dual cured elastomers.

The curable compositions of the invention contain between 0.1 to 20 parts by weight (preferably 1-3 parts) of polyhydroxy crosslinking agent (or a derivative thereof) per 100 parts fluoroelastomer. Typical polyhydroxy cross-linking agents include di-, tri-, and tetrahydroxybenzenes, naphthalenes, and anthracenes, and bisphenols of the formula

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where A is a difunctional aliphatic, cycloaliphatic, or aromatic radical of 1-13 carbon atoms, or a thio, oxy, carbonyl, sulfinyl, or sulfonyl radical; A may optionally be substituted with at least one chlorine or fluorine atom; x is 0 or 1; n is 1 or 2; and any aromatic ring of the polyhydroxylic compound may optionally be substituted with at least one chlorine or fluorine atom, an amino group, a -CHO group, or a carboxyl or acyl radical. Preferred polyhydroxy compounds include hexafluoroisopropylidene-bis(4-hydroxy-benzene) (i.e. bisphenol AF or BPAF); 4,4'-isopropylidene diphenol (i.e. bisphenol A); 4,4'-dihydroxydiphenyl sulfone; and diaminobisphenol AF. Referring to the bisphenol formula shown above, when A is alkylene, it can be for example methylene, ethylene, chloroethylene, fluoroethylene, difluoroethylene, propylidene, isopropylidene, tributylidene, heptachlorobutylidene, heptafluorobutylidene, pentylidene, hexylidene, and 1,1-cyclohexylidene. When A is a cycloalkylene radical, it can be for example 1,4-cyclohexylene, 2-chloro-1,4-cyclohexylene, cyclopentylene, or 2-fluoro-1,4-cyclohexylene. Further, A can be an arylene radical such as m-phenylene, p-phenylene, o-phenylene, methylphenylene, dimethylphenylene, 1,4-naphthylene, 3-fluoro-1,4-naphthylene, and 2,6-naphthylene. Polyhydroxyphenols of the formula



- 5 where R is H or an alkyl group having 1-4 carbon atoms or an aryl group containing 6-10 carbon atoms and R' is an alkyl group containing 1-4 carbon atoms also act as effective crosslinking agents. Examples of such compounds include hydroquinone, catechol, resorcinol, 2-methylresorcinol, 5-methyl-resorcinol, 2-methylhydroquinone, 2,5-
- 10 dimethylhydroquinone, 2-t-butyl-hydroquinone; and such compounds as 1,5-dihydroxynaphthalene and 2,6-dihydroxynaphthalene.

Additional polyhydroxy curing agents include alkali metal salts of bisphenol anions, tertiary sulfonium salts of bisphenol anions, quaternary ammonium salts of bisphenol anions and quaternary phosphonium salts of

15 bisphenol anions. For example, the salts of bisphenol A and bisphenol AF. Specific examples include the disodium salt of bisphenol AF, the dipotassium salt of bisphenol AF, the monosodium monopotassium salt of bisphenol AF and the benzyltriphenylphosphonium salt of bisphenol AF.

Quaternary ammonium and phosphonium salts of bisphenol anions

20 are discussed in U.S. Patents 4,957,975 and 5,648,429. Bisphenol AF salts (1:1 molar ratio) with quaternary ammonium ions of the formula $R_1R_2R_3R_4N^+$, wherein R_1 - R_4 are C_1 - C_8 alkyl groups and at least three of R_1 - R_4 are C_3 or C_4 alkyl groups are preferred. Specific examples of these preferred compositions include the 1:1 molar ratio salts of tetrapropyl

25 ammonium-, methyltributylammonium- and tetrabutylammonium bisphenol

AF. Such salts may be made by a variety of methods. For instance a methanolic solution of bisphenol AF may be mixed with a methanolic solution of a quaternary ammonium salt, the pH is then raised with sodium methoxide, causing an inorganic sodium salt to precipitate. After filtration, the tetraalkylammonium/BPAF salt may be isolated from solution by evaporation of the methanol. Alternatively, a methanolic solution of tetraalkylammonium hydroxide may be employed in place of the solution of quaternary ammonium salt, thus eliminating the precipitation of an inorganic salt and the need for its removal prior to evaporation of the solution.

In addition, derivatized polyhydroxy compounds such as mono- or diesters, and trimethylsilyl ethers are useful crosslinking agents. Examples of such compositions include, but are not limited to resorcinol monobenzoate, the diacetate of bisphenol AF, the diacetate of sulfonyl diphenol, and the diacetate of hydroquinone.

The curable compositions of the invention also contain between 1 to 30 parts by weight (preferably 1 to 7 parts) of an acid acceptor per 100 parts fluoroelastomer. The acid acceptor is typically a strong organic base such as Proton Sponge® (available from Aldrich) or an oxirane, or an inorganic base such as a metal oxide, metal hydroxide, or a mixture of 2 or more of the latter. Metal oxides or hydroxides which are useful acid acceptors include calcium hydroxide, magnesium oxide, lead oxide, zinc oxide and calcium oxide. Calcium hydroxide and magnesium oxide are preferred.

Vulcanization accelerators which may be used in the curable compositions of the invention include tertiary sulfonium salts such as $[(C_6H_5)_2S^+(C_6H_{13})][Cl]^-$, and $[(C_6H_{13})_2S(C_6H_5)]^+[CH_3CO_2]^-$ and quaternary ammonium, phosphonium, arsonium, and stibonium salts of the formula $R_5R_6R_7R_8Y^+ X^-$, where Y is phosphorous, nitrogen, arsenic, or antimony; R_5 , R_6 , R_7 , and R_8 are individually C_1 - C_{20} alkyl, aryl, aralkyl, alkenyl, and the chlorine, fluorine, bromine, cyano, -OR, and -COOR substituted

analogues thereof, with R being C₁-C₂₀ alkyl, aryl, aralkyl, alkenyl, and where X is halide, hydroxide, sulfate, sulfite, carbonate, pentachlorothiophenolate, tetrafluoroborate, hexafluorosilicate, hexafluorophosphate, dimethyl phosphate, and C₁-C₂₀ alkyl, aryl, aralkyl, and alkenyl carboxylates and dicarboxylates. Particularly preferred are benzyltri-phenylphosphonium chloride, benzyltriphenylphosphonium bromide, tetrabutylammonium hydrogen sulfate, tetrabutylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium bromide, tributylallylphosphonium chloride, tributyl-2-methoxypropylphosphonium chloride, 1,8-diazabicyclo[5.4.0]undec-7-ene, and benzyldiphenyl(dimethylamino) phosphonium chloride. Other useful accelerators include methyltrioctylammonium chloride, methyltributylammonium chloride, tetrapropylammonium chloride, benzyltrioctylphosphonium bromide, benzyltrioctylphosphonium chloride, methyltrioctylphosphonium acetate, tetraoctylphosphonium bromide, methyltriphenylarsonium tetrafluoroborate, tetraphenylstibonium bromide, 4-chlorobenzyltriphenyl phosphonium chloride, 8-benzyl-1,8-diazabicyclo(5.4.0)-7-undecenonium chloride, diphenylmethyltriphenylphosphonium chloride, allyltriphenyl-phosphonium chloride, tetrabutylphosphonium bromide, m-trifluoromethyl-benzyltrioctylphosphonium chloride, and other quaternary compounds disclosed in U.S. Patent Nos. 5,591,804; 4,912,171; 4,882,390; 4,259,463; 4,250,278 and 3,876,654. The amount of accelerator used is between 0.1 and 20 parts by weight per hundred parts by weight fluoroelastomer. Preferably, 0.5-3.0 parts accelerator per hundred parts fluoroelastomer is used.

Optionally, the curable compositions of the invention may contain a second curing agent in the form of a combination of an organic peroxide and a multifunctional (i.e. polyunsaturated) coagent compound. Examples of organic peroxides which are particularly effective curing agents for fluoroelastomers include dialkyl peroxides or bis(dialkyl peroxides) which

decompose at a temperature above 50°C. In many cases one will prefer to use a di-t-butylperoxide having a tertiary carbon atom attached to a peroxy oxygen. Among the most useful are 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3 and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane. Other peroxides can be selected from such compounds as dicumyl peroxide, dibenzoyl peroxide, t-butyl perbenzoate, and di[1,3-dimethyl-3-(t-butyl-peroxy)butyl]carbonate. Multifunctional coagents which cooperate with such peroxides to provide curing systems include methacrylates, allyl compounds, divinyl compounds, and polybutadienes. Specific examples of coagents include one or more of the following compounds: triallyl cyanurate; triallyl isocyanurate; tris(diallylamine-s-triazine); triallyl phosphite; hexaallyl phosphoramidate, N,N-diallyl acrylamide; N,N,N',N'-tetraallyl terephthalamide; N,N,N',N'-tetraallyl malonamide; trivinyl isocyanurate; 2,4,6-trivinylmethyltrisiloxane; and tri(5-norbornene-2-methylene)cyanurate. If a peroxide cure system is present in the compounds of the invention, the organic peroxide is generally at a level between 0.2 to 7 parts by weight (preferably 1 to 3 parts) per 100 parts fluoroelastomer and the coagent is present at a level of 0.1 to 10 (preferably 2 to 5) parts by weight per 100 parts fluoroelastomer.

The curable composition of the invention may contain other additives, commonly used in elastomer compounding and processing. The latter may be introduced into the composition before addition of the curative, simultaneously with it, or following the addition. Typical additives include fillers, plasticizers, processing aids, antioxidants, pigments, and the like. The amount of such ingredients which is added will depend on the particular end use applications for which the cured compositions are adapted. Fillers, such as carbon black, clays, barium sulfate, calcium carbonate, magnesium silicate, and fluoropolymers are generally added in amounts of from 5-100 parts by weight per 100 parts fluoroelastomer. The amount of plasticizer used is generally from 0.5-5.0 parts by weight per 100 parts fluoroelastomer. Typical plasticizers include esters, such as

dioctyl phthalate and dibutyl sebacate. Processing aids are generally used in amounts of from 0.1-2.0 parts by weight per 100 parts fluoroelastomer. Suitable processing aids include octadecylamine, 5 tetramethylene sulfone, p-chlorophenyl sulfone, and waxes, for example, carnauba wax, that aid in the processing of the compositions.

The fluoroelastomer, polyhydroxy curative, acid acceptor, accelerator and any other ingredients are generally incorporated into the curable compositions of the invention by means of an internal mixer or 10 rubber mill. The resulting composition may then be shaped (e.g. molded or extruded) and cured. Curing typically takes place at about 150°-200°C for 1 to 60 minutes. Conventional rubber curing presses, molds, extruders, and the like provided with suitable heating and curing means can be used. Also, for optimum physical properties and dimensional 15 stability, it is preferred to carry out a post curing operation wherein the molded or extruded article is heated in an oven or the like for an additional period of about 1-48 hours, typically from about 180°-275°C, generally in an air atmosphere.

The polymers of the invention and curable compositions of the 20 invention result in cured fluoroelastomer articles which have unusually good base resistance, tensile properties and compression set resistance. Such articles find application as gaskets, seals and tubing, particularly in automotive end uses.

The invention is now illustrated by the following embodiments in 25 which all parts are by weight unless otherwise indicated.

EXAMPLES

Test Methods

Curing characteristics of the compositions described in the 30 examples are measured according to the following test procedure:

Moving Disc Rheometer (MDR)

ASTM D5289

Example 1

A polymer of the invention (Polymer 1) is prepared by a semi-batch emulsion polymerization, carried out at 60°C in a well-stirred reaction vessel. A 33-liter, horizontally agitated reactor is charged with 20 liters of deionized, deoxygenated water, 150 g of ammonium perfluorooctanoate and 70 g of sodium phosphate dibasic heptahydrate. The reactor is heated to 60°C and then pressurized to 1.93 MPa with a mixture of 96 wt.% tetrafluoroethylene (TFE), 2 wt.% propylene (P), and 2 wt.% CF₃CF₂CH=CH₂ cure site monomer. A 250 ml aliquot of an aqueous 10 wt.% ammonium persulfate initiator solution is then added. A mixture of 70.0 wt.% TFE, 20.0 wt.% P, and 10.0 wt.% CF₃CF₂CH=CH₂ is supplied to the reactor to maintain a pressure of 1.93 MPa throughout the polymerization. The initiator solution is fed continuously at 5 ml/hour through the end of the reaction period. After a total of 6000 g of monomer mixture has been supplied to the reactor, monomer addition is discontinued and the reactor is purged of residual monomer. The total reaction time is about 60 hours. The resulting fluoroelastomer latex is coagulated by addition of aluminum potassium sulfate solution, filtered and then washed with deionized water. The polymer crumb is dried for two days at 60°C. The product, composed of about 70 wt.% TFE units, 20 wt.% P units, and 10 wt.% CF₃CF₂CH=CH₂ units, is an amorphous elastomer. Mooney viscosity, ML-10 (121°C), is about 19.

Control A

A control polymer of the prior art (Control Polymer A) is prepared by a semi-batch emulsion polymerization, carried out at 60°C in a well-stirred reaction vessel. A 33-liter, horizontally agitated reactor is charged with 20 liters of deionized, deoxygenated water, 200 g of perfluorohexylethyl sulfonic acid and 18 g of sodium hydroxide. The reactor is heated to 60°C and then pressurized to 2.07 MPa with a mixture of 95.0 wt.% TFE and 5.0 wt.% P. A 326 ml aliquot of an aqueous initiator solution is then added.

10 The solution contains 10 wt.% ammonium persulfate and 3.5 wt.% sodium hydroxide. A mixture of 77.8 wt.% TFE and 22.2 wt.% P is supplied to the reactor to maintain a pressure of 2.07 MPa throughout the polymerization. The initiator solution is fed continuously at 6 ml/hour through the end of the reaction period. After a total of 8000 g monomer mixture has been

15 supplied to the reactor, monomer addition is discontinued and the reactor is purged of residual monomer. The total reaction time is 14 hours. The resulting emulsion is coagulated by addition of aluminum potassium sulfate solution and then washed with deionized water. The polymer crumb is dried for two days at 60°C. The product, composed of about 78

20 wt.% TFE units and 22 wt.% P units, is an amorphous fluoroelastomer. Mooney viscosity, ML-10 (121°C), is about 32.

Example 2

A curable composition of the invention (Sample 1) is made by mixing 100 parts by weight per hundred parts rubber (phr) fluoroelastomer of the invention (Polymer 1 prepared above) with 2 phr Bisphenol AF, 6 phr Maglite® D magnesium oxide (available from C.P. Hall), 2.3 phr of tetrabutylammonium hydroxide and 30 phr MT carbon black on a conventional two-roll rubber mill, using standard mixing techniques

25 employed in the elastomer industry. A comparative curable composition (Comparative Sample A) is made by the same procedure except that a

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fluoroelastomer of the prior art (Control Polymer A prepared above), not containing $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$ cure site monomer units is used.

Curing characteristics are measured by MDR (at 177°C , 24
5 minutes) according to the Test Methods. Sample 1 cures, as indicated by an increase in torque (M) during the test. However, Control Polymer B, which does not contain copolymerized units of $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}_2$ cure site monomer, does not cure under these conditions as indicated by the lack of a measurable increase in torque (M) when Comparative Sample A is run
10 in the MDR.

CLAIMS

What is claimed is:

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1. A specialty fluoroelastomer comprising copolymerized units of 45 to 80 weight percent tetrafluoroethylene; 10 to 40 weight percent propylene; and 0.1 to 15 weight percent of a cure site monomer selected from the group consisting of i) perfluoroalkyl ethylenes and ii) perfluoroalkoxy ethylenes, with the proviso that the cure site monomer may not be 4-bromo-3,3,4,4-tetrafluorobutene-1.

2. A specialty fluoroelastomer of Claim 1 wherein said copolymerized units of tetrafluoroethylene are present in an amount between 65 and 78 weight percent; said copolymerized units of propylene in an amount between 15 and 25 weight percent; and said copolymerized units of cure site monomer in an amount between 2 and 10 weight percent.

3. A specialty fluoroelastomer of Claim 2 further comprising copolymerized units of vinylidene fluoride present in an amount between 2 and 20 weight percent.

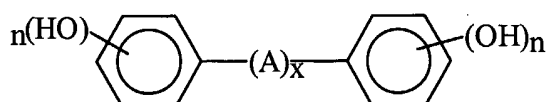
4. A curable fluoroelastomer composition comprising
A) a specialty fluoroelastomer comprising copolymerized units of 45 to 80 weight percent tetrafluoroethylene; 10 to 40 weight percent propylene; and 0.1 to 15 weight percent of a cure site monomer selected from the group consisting of i) perfluoroalkyl ethylenes and ii) perfluoroalkoxy ethylenes;

B) 0.1 to 20 parts by weight per 100 parts fluoroelastomer of a polyhydroxy curing agent;

C) 1 to 30 parts by weight per 100 parts fluoroelastomer of an acid acceptor; and

D) 0.1 to 20 parts by weight per 100 parts fluoroelastomer of a vulcanization accelerator.

5. A curable fluoroelastomer composition of Claim 4 wherein said polyhydroxy curing agent B is a curing agent selected from the group consisting of i) dihydroxy-, trihydroxy-, and tetrahydroxy- benzenes, - naphthalenes, and -anthracenes;
- ii) bisphenols of the formula



- where A is a stable divalent radical; x is 0 or 1; and n is 1 or 2;
- iii) dialkali salts of said bisphenols, iv) quaternary ammonium and phosphonium salts of said bisphenols, v) tertiary sulfonium salts of said bisphenols, and vi) esters of phenols.

6. A curable fluoroelastomer composition of Claim 4 wherein said vulcanization accelerator D is chosen from the group consisting of quaternary ammonium salts, tertiary sulfonium salts and quaternary phosphonium salts.

7. A curable fluoroelastomer composition of Claim 6 wherein said cure accelerator D is selected from the group consisting of i) quaternary ammonium salts of said polyhydroxy crosslinking agent (B), ii) quaternary phosphonium salts of said polyhydroxy crosslinking agent (B) and iii) tertiary sulfonium salts of said polyhydroxy crosslinking agent.

8. A curable fluoroelastomer composition comprising
- A) a specialty fluoroelastomer comprising copolymerized units of 45 to 80 weight percent tetrafluoroethylene; 10 to 40 weight percent propylene; and 0.1 to 15 weight percent of a cure site monomer selected from the group consisting of i) perfluoroalkyl ethylenes and ii) perfluoroalkoxy ethylenes;
- B) a compound selected from the group consisting of i) quaternary ammonium salts of a bisphenol, ii) quaternary

phosphonium salts of a bisphenol and iii) tertiary sulfonium salts of a bisphenol; and

C) an acid acceptor.

5 9. A curable fluoroelastomer composition of Claim 8 wherein said quaternary ammonium salt of a bisphenol is selected from the group consisting of a) a tetrapropylammonium/bisphenol AF salt, b) a methyltributylammonium/bisphenol AF salt, and c) a tetrabutylammonium/bisphenol AF salt.

10 10. A curable fluoroelastomer composition of Claim 8 wherein said quaternary ammonium salt of a bisphenol is a 1:1 molar ratio salt of a quaternary ammonium compound and bisphenol AF.

15 11. A curable fluoroelastomer composition of any one of Claims 4 to 10 wherein said specialty fluoroelastomer comprises copolymerized units of tetrafluoroethylene present in an amount between 65 and 78 weight percent; copolymerized units of propylene in an amount between 15 and 25 weight percent; and copolymerized units of cure site monomer in an amount between 2 and 10 weight percent.

20 12. A curable fluoroelastomer composition of any one of Claims 4 to 10 wherein said specialty fluoroelastomer further comprises copolymerized units of vinylidene fluoride present in an amount between 2 and 20 weight percent.

25 13. A curable fluoroelastomer composition of any one of Claims 4 to 10 further comprising E) 0.2 to 7 parts by weight per 100 parts fluoroelastomer of an organic peroxide and F) 0.1 to 10 parts by weight per 100 parts fluoroelastomer of a multifunctional coagent.