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(71) Applicant *(for all designated States except US)*: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19899 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **LYONS, Donald F.** [US/US]; 2503 Teal Road, Wilmington, Delaware 19805 (US). **MORKEN, Peter A.** [US/US]; 6 Weilers Bend, Wilmington, Delaware 19810 (US).

(74) Agent: **KIRVAN, George E.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

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(54) Title: ACID RESISTANT FLUOROELASTOMER COMPOSITIONS

(57) Abstract: Disclosed herein is a curable composition comprising a peroxide curable fluoroelastomer, an organic peroxide, a multifunctional coagent and an acid acceptor selected from the group consisting of carboxylic acid salts of bismuth and a bismuth oxycarboxylate. Cured articles made therefrom are resistant to volume swell in acids and in biodiesel fuel and said cured articles exhibit good heat resistance.

TITLE

ACID RESISTANT FLUOROELASTOMER COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to curable fluoroelastomer compositions comprising i) a peroxide curable fluoroelastomer, ii) an organic peroxide, iii) a multifunctional coagent and iv) an acid acceptor selected from the group consisting of a carboxylic acid salt of bismuth and a bismuth oxycarboxylate.

BACKGROUND OF THE INVENTION

Fluoroelastomers having excellent heat resistance, oil resistance, and chemical resistance have been used widely for sealing materials, containers and hoses. Examples of fluoroelastomers include copolymers comprising units of vinylidene fluoride (VF_2) and units of at least one other copolymerizable fluorine-containing monomer such as hexafluoropropylene (HFP), tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), vinyl fluoride (VF), and a fluorovinyl ether such as a perfluoro(alkyl vinyl ether) (PAVE). Specific examples of PAVE include perfluoro(methyl vinyl ether), perfluoro(ethyl vinyl ether) and perfluoro(propyl vinyl ether). Other fluoroelastomers include copolymers comprising tetrafluoroethylene and perfluoro(methyl vinyl ether).

In order to fully develop physical properties such as tensile strength, elongation, and compression set, elastomers must be cured, i.e. vulcanized or 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, 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 employed curing agents for fluoroelastomers include the combination of an organic peroxide with a multifunctional coagent. A metal oxide is typically added to the composition in order to improve retention of elastomer physical properties (e.g. elongation and tensile strength) at high temperature (>200°C).

However, cured fluoroelastomer articles may exhibit unacceptably high volume swell, e.g. 50-200 vol.%, that can lead to seal failure, when seals are exposed to certain chemicals such as acids or biodiesel fuel for long periods of time or at elevated temperatures. The swelling can be minimized by eliminating metal oxides from the compositions, but elastomer physical properties at high temperature suffer. It would be desirable to have a peroxide cured fluoroelastomer that has the combination of low volume swell in acid and retention of physical properties at high temperature.

U.S. Patent No. 6,319,972 B1 discloses thermoplastic vinylidene fluoride homopolymers and copolymers that contain certain bismuth carboxylate salts as thermal stabilizers.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides a curable fluoroelastomer composition comprising:

A) a peroxide curable fluoroelastomer;

B) an organic peroxide;

C) a multifunctional coagent; and

D) 1 to 60 parts by weight, per hundred parts by weight fluoroelastomer, of an acid acceptor selected from the group consisting of a carboxylic acid salt of bismuth and a bismuth oxycarboxylate.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to curable fluoroelastomer compositions that, when cured with an organic peroxide, have reduced volume swell in acids. Exposure to nitric acid, in particular, represents a stringent test for acid resistance because of the acid's oxidizing nature and because of the high solubility of its salts in aqueous solution. Excessive swell after exposure to nitric acid indicates degradation of the crosslinked fluoroelastomer network. In addition, nitric acid solutions do not change during storage and provide a reproducible medium in which to evaluate acid resistance. The cured fluoroelastomer compositions have a variety of end uses, including turbocharger hoses and in fuel management systems having at least one fluororubber article in contact with biodiesel fuel. Because biodiesel fuel contains acidic components that either have been added deliberately or are generated by decomposition during storage or exposure to water, acid resistance is a requirement of any elastomer with which biodiesel fuel comes into contact.

By the term "fuel management system" is meant equipment employed in the manufacture, storage, transportation and supply, metering and control of biodiesel fuel. Fuel management systems include those contained in biodiesel manufacturing plants, motor vehicles (e.g. trucks, cars, boats), stationary diesel powered devices (e.g. electrical generators, portable pumping stations) and those associated with biodiesel fuel transportation, storage and dispensing. Specific elements of fuel management systems include, but are not limited to fuel tanks, filler neck hoses, fuel tank cap seals, fuel line hoses and tubing, valves, diaphragms, fuel sender seals and fuel injector components, o-rings, seals and gaskets. Any or all of these elements may comprise one or more fluororubber articles that contact biodiesel fuel. Cured fluororubber articles include, but are not limited to seals, gaskets, o-rings, tubing, the fuel contact layer of multilayer hoses, valve packings, diaphragms, and tank liners.

By "biodiesel fuel" is meant a fuel suitable for use in a compression ignition (diesel) engine compromising one or more fatty acid alkyl esters (FAAE) of biological origin (i.e. derived from animals or plants). These FAAEs are typically methyl or ethyl esters of fatty acids derived from vegetable oils or animal fats. Specific examples include rape seed oil methyl ester (RME), soybean oil methyl ester (SME), palm kernel oil methyl ester (PME) and the like. Also included are blends of these FAAE based materials with conventional petroleum based diesel fuel. Petroleum diesel/biodiesel blends are conventionally denoted as Bxx fuels where "xx" is the volume percent of the FAAE based biodiesel in the blend. For example, B100 denotes a biodiesel fuel containing no deliberately added petroleum component. B20 denotes biodiesel fuel containing 20 vol.% of a B100 fuel and 80 vol.% of petroleum diesel fuel.

Fluoroelastomers that are suitable for use in this invention are those that are curable by an organic peroxide and multifunctional coagent.

By "peroxide curable" is meant fluoroelastomers that contain Br or I cure sites along the polymer chain, at chain ends or in both locations.

Cure sites along the fluoroelastomer chain are typically due to copolymerized cure site monomers that contain bromine or iodine atoms. Examples of suitable cure site monomers include, but are not limited to: i) bromine -containing olefins; ii) iodine-containing olefins; iii) bromine-containing vinyl ethers; and iv) iodine-containing vinyl ethers.

Brominated cure site monomers may contain other halogens, preferably fluorine. Examples of brominated olefin cure site monomers are CF_2=$CFOCF_2CF_2CF_2OCF_2CF_2Br$; bromotrifluoroethylene; 4-bromo-3,3,4,4-tetrafluorobutene-1 (BTFB); and others such as vinyl bromide, 1-bromo-2,2-difluoroethylene; perfluoroallyl bromide; 4-bromo-1,1,2-trifluorobutene-1; 4-bromo-1,1,3,3,4,4,-hexafluorobutene; 4-bromo-3-chloro-1,1,3,4,4-pentafluorobutene; 6-bromo-5,5,6,6-tetrafluorohexene; 4-bromoperfluorobutene-1 and 3,3-difluoroallyl bromide. Brominated vinyl ether cure site monomers useful in the invention include 2-bromo-

perfluoroethyl perfluorovinyl ether and fluorinated compounds of the class CF_2Br-R_f-O-CF=CF_2 (R_f is a perfluoroalkylene group), such as CF_2BrCF_2O-CF=CF_2, and fluorovinyl ethers of the class ROCF=CFBr or ROCBr=CF_2 (where R is a lower alkyl group or fluoroalkyl group) such as CH_3OCF=CFBr or CF_3CH_2OCF=CFBr.

Suitable iodinated cure site monomers include iodinated olefins of the formula: CHR=CH-Z-CH_2CHR-I, wherein R is -H or -CH_3; Z is a C_1-C_{18} (per)fluoroalkylene radical, linear or branched, optionally containing one or more ether oxygen atoms, or a (per)fluoropolyoxyalkylene radical as disclosed in U.S. Patent 5,674,959. Other examples of useful iodinated cure site monomers are unsaturated ethers of the formula: $I(CH_2CF_2CF_2)_nOCF=CF_2$ and $ICH_2CF_2O[CF(CF_3)CF_2O]_nCF=CF_2$, and the like, wherein n=1-3, such as disclosed in U.S. Patent 5,717,036. In addition, suitable iodinated cure site monomers including iodoethylene, 4-iodo-3,3,4,4-tetrafluorobutene-1 (ITFB); 3-chloro-4- iodo-3,4,4-trifluorobutene; 2-iodo -1,1,2,2-tetrafluoro-1-(vinyloxy)ethane; 2- iodo-1-(perfluorovinyloxy)-1,1,-2,2-tetrafluoroethylene; 1,1,2,3,3,3-hexafluoro-2-iodo-1-(perfluorovinyloxy)propane; 2-iodoethyl vinyl ether; 3,3,4,5,5,5-hexafluoro-4-iodopentene; and iodotrifluoroethylene are disclosed in U.S. Patent 4,694,045. Allyl iodide and 2-iodo-perfluoroethyl perfluorovinyl ether are also useful cure site monomers.

Iodine-containing endgroups, bromine-containing endgroups or mixtures thereof may optionally be present at one or both of the fluoroelastomer polymer chain ends as a result of the use of chain transfer or molecular weight regulating agents during preparation of the fluoroelastomers. The amount of chain transfer agent, when employed, is calculated to result in an iodine or bromine level in the fluoroelastomer in the range of 0.005-5 wt.%, preferably 0.05-3 wt.%.

Examples of chain transfer agents include iodine-containing compounds that result in incorporation of a bound iodine atom at one or

both ends of the polymer molecules. Methylene iodide; 1,4-diiodoperfluoro-n-butane; and 1,6-diiodo-3,3,4,4,tetrafluorohexane are representative of such agents. Other iodinated chain transfer agents include 1,3-diiodoperfluoropropane; 1,6-diiodoperfluorohexane; 1,3-diiodo-2-chloroperfluoropropane; 1,2-di(iododifluoromethyl)-perfluorocyclobutane; monoiodoperfluoroethane; monoiodoperfluorobutane; 2-iodo-1-hydroperfluoroethane, etc. Also included are the cyano-iodine chain transfer agents disclosed in European Patent 0868447A1. Particularly preferred are diiodinated chain transfer agents.

Examples of brominated chain transfer agents include 1-bromo-2-iodoperfluoroethane; 1-bromo-3-iodoperfluoropropane; 1-iodo-2-bromo-1,1-difluoroethane and others such as disclosed in U.S. Patent 5,151,492.

Specific examples of fluoroelastomers that may be employed in the invention include, but are not limited to copolymers comprising i) vinylidene fluoride, hexafluoropropylene and optionally tetrafluoroethylene, ii) vinylidene fluoride, perfluoro(methyl vinyl ether) and optionally tetrafluoroethylene, iii) tetrafluoroethylene and perfluoro(methyl vinyl ether), and iv) tetrafluoroethylene and propylene. All of the latter polymers having iodine or bromine atoms along the polymer chain, at the ends or both.

Organic peroxides suitable for use in the compositions of the invention include, but are not limited to 1,1-bis(t-butylperoxy)-3,5,5-trimethylcyclohexane; 1,1-bis(t-butylperoxy)cyclohexane; 2,2-bis(t-butylperoxy)octane; n-butyl-4, 4-bis(t-butylperoxy)valerate; 2,2-bis(t-butylperoxy)butane; 2,5-dimethylhexane-2,5-dihydroxyperoxide; di-t-butyl peroxide; t-butylcumyl peroxide; dicumyl peroxide; alpha, alpha'-bis(t-butylperoxy-m-isopropyl)benzene; 2,5-dimethyl-2,5-di(t-butylperoxy)hexane; 2,5-dimethyl-2,5-di(t-butylperoxy)hexene-3; benzoyl peroxide, t-butylperoxybenzene; 2,5-dimethyl-2,5-di(benzoylperoxy)-hexane; t-butylperoxymaleic acid; and t-butylperoxyisopropylcarbonate. Preferred examples of organic peroxides include 2,5-dimethyl-2,5-di(t-

butylperoxy)hexane, dicumyl peroxide, and alpha, alpha'-bis(t-butylperoxy-m-isopropyl)benzene. The amount compounded is generally in the range of 0.05-5 parts by weight, preferably in the range of 0.1-3 parts by weight per 100 parts by weight of the fluoroelastomer. This particular range is selected because if the peroxide is present in an amount of less than 0.05 parts by weight, the vulcanization rate is insufficient and causes poor mold release. On the other hand, if the peroxide is present in amounts of greater than 5 parts by weight, the compression set of the cured polymer becomes unacceptably high. In addition, the organic peroxides may be used singly or in combinations of two or more types.

Multifunctional coagents employed in the curable compositions of this invention are polyfunctional unsaturated compounds such as triallyl cyanurate, trimethacryl isocyanurate, triallyl isocyanurate, trimethallyl isocyanurate, triacryl formal, triallyl trimellitate, N,N'-m-phenylene bismaleimide, diallyl phthalate, tetraallylterephthalamide, tri(diallylamine)-s-triazine, triallyl phosphite, bis-olefins and N,N-diallylacrylamide. The amount compounded is generally in the range of 0.1-10 parts by weight per 100 parts by weight of the fluoroelastomer. This particular concentration range is selected because if the coagent is present in amounts less than 0.1 part by weight, crosslink density of the cured polymer is unacceptable. On the other hand, if the coagent is present in amounts above 10 parts by weight, it blooms to the surface during molding, resulting in poor mold release characteristics. The preferable range of coagent is 0.2-6 parts by weight per 100 parts fluoroelastomer. The unsaturated compounds may be used singly or as a combination of two or more types.

The curable compositions of the invention also contain 1 to 60 parts by weight (preferably 4 to 40 parts) of at least one acid acceptor selected from the group consisting of a carboxylic acid salt of bismuth and a bismuth oxycarboxylate per hundred parts by weight fluoroelastomer. The

bismuth compound acts as both an acid acceptor in order to facilitate the curing (crosslinking) reaction and as an anion exchange compound for scavenging any acidic substances such as HF or carboxylic acids. It is well known that bismuth salts have variable stoichiometry and that various amounts of water or hydroxide ions will be incorporated into a bismuth compound depending on the exact preparation and isolation conditions. The "sub" prefix is used when the formation of the bismuthyl (BiO+) ion is formally present. (*Chemical Reviews*, **1999**, 2601). Suitable bismuth carboxylate compounds include bismuth acetate, bismuth benzoate, bismuth carbonate, bismuth citrate, bismuth 2-ethylhexanoate, bismuth neodeconate, and bismuth oxalate. Suitable bismuth oxycarboxylate compounds include bismuth subgallate, bismuth subcarbonate, and bismuth subsalicylate.

Optionally other acid acceptors (e.g. zinc oxide, magnesium oxide, calcium hydroxide) in addition to bismuth carboxylate salts or bismuth oxycarboxylate may be present in the curable compositions of the invention. If present, the level of other acid acceptor is between 1 and 30 parts by weight per 100 parts by weight fluoroelastomer.

The fluoroelastomer, curative, acid acceptor and any other ingredients are generally incorporated into a curable composition by means of an internal mixer or rubber mill. The resulting composition may then be shaped (e.g. molded or extruded) and cured to form a fluororubber article. 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 stability, it is preferred to carry out a post curing operation wherein the molded or extruded fluororubber article is heated in an oven or the like for an additional period of about 1-48 hours, typically from about 180°-275°C.

EXAMPLES

TEST METHODS

Volume Swells (%) after immersion in acidic media were determined by ASTM D471-96 on standard ASTM D471 coupons. The coupons were prepared from cured fluororubber slabs and immersed in acidic media under the conditions noted in the Examples.

Tensile properties were determined by ASTM D412.

Compression set resistance was measured according to ASTM D395.

The invention is further illustrated by, but is not limited to, the following examples.

Fluoroelastomer FKM1 employed in the examples was Viton® GF-600S, a 70 weight percent fluorine content copolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene containing iodine cure sites, available from DuPont.

Fluoroelastomer FKM2 employed in the examples was Viton® GBL-600S, a 68 weight percent fluorine content copolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene containing iodine cure sites, available from DuPont.

Fluoroelastomer FKM3 employed in the examples was Viton® GF, a 69.5 weight percent fluorine content copolymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene containing bromine cure sites, available from DuPont.

Fluoroelastomer FKM4 employed in the examples was Viton® GLT-600S, a 64 weight percent fluorine content copolymer of vinylidene fluoride, tetrafluoroethylene and perfluoro(methyl vinyl ether) containing iodine cure sites, available from DuPont.

Fluoroelastomer FFKM1 employed in the examples was a copolymer of tetrafluoroethylene and perfluoro(methyl vinyl ether)

containing iodine cure sites and prepared by semi-batch emulsion polymerization.

All bismuth compounds employed in the examples were from Alfa Aesar.

Example 1 and Comparative Examples A, B, and C

Curable compositions for Example 1 and Comparative Examples A, B, and C were made by compounding the ingredients on a two-roll mill. Formulations are shown in Table I.

The compositions were molded into slabs and press cured at 177°C for 10 minutes. The cured slabs were then post-cured for 4 hours at 232°C.

Coupons made from cured slabs were exposed to 70% nitric acid for 70 hours at 70°C.

This example demonstrates that compositions containing bismuth subsalicylate display both adequate acid resistance and acceptable heat resistance. Compositions containing zinc oxide display adequate heat resistance, but poor acid resistance. A metal oxide-free composition displays adequate acid resistance but poor heat resistance.

TABLE I

Ingredient, phr[1]	Ex. 1	Comp. Ex. A	Comp. Ex. B	Comp. Ex. C
FKM1	100	100	100	100
ZnO	0	15	7.5	0
Bismuth subsalicylate	15	0	7.5	0
Carbon black N990	8	8	8	8
Diak 7[2]	3	3	3	3
Varox DBPH-50[3]	1.5	1.5	1.5	1.5
Original tensile properties				
T_B, MPa	17.6	18.1	16.1	19.8
E_B, %	376	368	360	408
Percent change in tensile properties after 70 hours @ 250°C				
T_B	-12	+28	+11	-35
E_B	+3	+29	+13	+23
Percent change in tensile properties after 168 hours @ 250°C				
T_B	-17	0	+9	-55
E_B	+11	+18	+26	+7
Volume swell in 70% nitric acid				
70 hours at 70°C	32	107	71	5

[1] parts by weight per hundred parts rubber (i.e. fluoroelastomer)

[2] triallyl isocyanurate coagent available from DuPont

[3] organic peroxide available from R. T. Vanderbilt

Example 2 and Comparative Examples D, E, and F

Curable compositions for Example 2 and Comparative Example D, E, and F were made by compounding the ingredients on a two roll mill. Formulations are shown in Table II.

The compositions were molded into slabs and press cured at 177°C for 10 minutes. The cured slabs were then post-cured for 4 hours at 232°C.

Coupons made from cured slabs were exposed to 70% nitric acid for 70 hours at 70°C and 100% acetic acid for 168 hours at 100°C.

This example demonstrates that fluororubber containing bismuth subsalicylate displays better acid resistance than fluororubber containing either zinc oxide or magnesium oxide in a compound based on a 68 weight percent fluorine content polymer.

TABLE II

Ingredient, phr[1]	Ex. 2	Comp. Ex. D	Comp. Ex. E	Comp. Ex. F
FKM2	100	100	100	100
ZnO	0	5	0	0
Elastomag 170[4]	0	0	5	0
Bismuth subsalicylate	5	0	0	0
Carbon black N990	30	30	30	30
Diak 7[2]	2.5	2.5	2.5	2.5
Varox DBPH-50[3]	1.75	1.75	1.75	1.75
Original tensile properties				
T_B, MPa	20.4	19.0	20.0	21.1
E_B, %	264	249	201	251
Percent change in tensile properties after 70 hours @ 250°C				
T_B	-13	+13	-15	-35
E_B	+27	+25	+39	+23
Percent change in tensile properties after 168 hours @ 250°C				
T_B	-36	-76	-35	-55
E_B	+35	+24	+57	+57
Volume swell				
70% nitric acid for 70 hours at 70°C	10	22	23	6
100% acetic acid for 168 hours at 100°C	29	33	40	28

[4] magnesium oxide available from Martin Marietta Magnesium Specialties

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Examples 3 and Comparative Examples G, H and I

Curable compositions for Example 3 and Comparative Examples G, H and I were made by compounding the ingredients on a two roll mill. Formulations are shown in Table III.

The compositions were molded into slabs and press cured at 177°C for 10 minutes. The cured slabs were then post-cured for 4 hours at 232°C.

This example demonstrates that bismuth subsalicylate can induce the cure of a bromine-containing fluoroelastomer. Metal oxide-free compositions do not cure. It also demonstrates that bismuth subsalicylate behaves differently than bismuth oxide, which also does not induce the cure of a bromine-containing fluoroelastomer.

TABLE III

Ingredient, phr[1]	Ex. 3	Comp. Ex. G	Comp. Ex. H	Comp. Ex. I
FKM3	100	100	100	100
ZnO	0	4	0	0
Bismuth oxide	0	0	4	0
Bismuth subsalicylate	4	0	0	0
Diak 7[2]	3	3	3	3
Varox DBPH-50[3]	1.5	1.5	1.5	1.5
Original tensile properties				
T_B, MPa	8.0	10.6	Did not cure	Did not cure
E_B, %	346	327	xxx	xxx
Percent change in tensile properties after 70 hours @ 250°C				
T_B	27.9	82.7	xxx	xxx
E_B	26.6	22.2	xxx	xxx
Percent change in tensile properties after 168 hours @ 250°C				
T_B	29.1	64.7	xxx	xxx
E_B	59.8	35.8	xxx	xxx

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Examples 4 and 5 and Comparative Example J

Curable compositions for Examples 4 and 5 and Comparative Example J were made by compounding the ingredients on a two roll mill. Formulations are shown in Table IV.

The compositions were molded into slabs and O-rings (for compression set testing) and press cured at 177°C for 10 minutes. The cured slabs and O-rings were then post-cured for 4 hours at 232°C.

Coupons made from cured slabs were exposed to 70% nitric acid for 70 hours at 70°C.

This example demonstrates that compositions containing bismuth subsalicylate display both adequate acid resistance and acceptable heat resistance in a perfluoro(methyl vinyl ether)-containing fluoroelastomer. A metal oxide-free composition displays adequate acid resistance but poor heat resistance.

TABLE IV

Ingredient, phr[1]	Ex. 4	Ex. 5	Comp. Ex. J
FKM4	100	100	100
Bismuth subsalicylate	3	5	0
Carbon black N990	30	30	30
Diak 7[2]	3	3	3
Varox DBPH-50[3]	1.5	1.5	1.5
Original tensile properties			
T_B, MPa	18.7	17.9	18.8
E_B, %	285	277	280
Percent change in tensile properties after 70 hours @ 250°C			
T_B	-3	-9	-29
E_B	+14	+2	+23
Percent change in tensile properties after 168 hours @ 250°C			
T_B	-28	-24	-45
E_B	+17	+14	+24
Volume swell			
70% nitric acid for 70 hours at 70°C	13	15	8
Compression set			
70 hours @ 200°C	24	27	26

Example 6

The curable composition for Example 6 was made by compounding the ingredients on a two roll mill. The formulation is shown in Table V.

The composition was molded into slabs and O-rings (for compression set testing) and press cured at 165°C for 10 minutes. The cured slabs and O-rings were then post-cured for 4 hours at 232°C.

Coupons made from cured slabs were exposed to 70% nitric acid for 70 hours at 70°C.

This example demonstrates that a composition containing bismuth subsalicylate displays both adequate acid resistance and acceptable heat resistance in a perfluoroelastomer.

TABLE V

Ingredient, phr[1]	Ex. 6
FFKM1	100
Bismuth subsalicylate	3
Carbon black N990	15
Diak 7[2]	2
Varox DBPH-50[3]	1.25
Original tensile properties	
T_B, MPa	20.9
E_B, %	188
Percent change in tensile properties after 70 hours @ 250°C	
T_B	-1
E_B	+24
Percent change in tensile properties after 168 hours @ 250°C	
T_B	-22
E_B	+29
Volume swell	
70% nitric acid for 168 hours at 85°C	11
100% acetic acid for 168 hours at 100°C	21
Compression set	
70 hours at 200°C	8

Examples 7 - 9

Curable compositions for Examples 7, 8, and 9 were made by compounding the ingredients on a two-roll mill. Formulations are shown in Table VI.

The compositions were molded into slabs and press cured at 177°C for 10 minutes. The cured slabs were then post-cured for 4 hours at 232°C.

Coupons made from cured slabs were exposed to 70% nitric acid for 70 hours at 70°C.

These examples demonstrate that the carboxylic acid salts of bismuth are also effective at improving the acid resistance of fluoroelastomer compositions while maintaining adequate heat resistance.

Table VI

Ingredient, phr[1]	Ex. 7	Ex. 8	Ex. 9
FKM1	100	100	100
Bismuth subsalicylate	5	0	0
Bismuth citrate	0	5	0
Bismuth subcarbonate	0	0	5
Carbon black N990	30	30	30
Diak 7[2]	3	3	3
Varox DBPH-50[3]	1.5	1.5	1.5
Original tensile properties			
T_B, MPa	18.6	18.6	19.9
E_B, %	309	282	325
Percent change in tensile properties after 70 hours @ 250°C			
T_B	+1	-3	-9
E_B	+16	+23	+5
Percent change in tensile properties after 168 hours @ 250°C			
T_B	-24	-28	-32
E_B	+32	+37	+12
Volume swell			
70% nitric acid for 70 hours at 70°C	12	14	15

WHAT IS CLAIMED IS:

1. A curable fluoroelastomer composition comprising:

A) a peroxide curable fluoroelastomer;

B) an organic peroxide;

C) a multifunctional coagent; and

D) 1 to 60 parts by weight, per hundred parts by weight fluoroelastomer, of an acid acceptor selected from the group consisting of a carboxylic acid salt of bismuth and a bismuth oxycarboxylate.

2. The curable fluoroelastomer composition of claim 1 wherein said acid acceptor is a carboxylic salt of bismuth selected from the group consisting of bismuth acetate, bismuth benzoate, bismuth carbonate, bismuth citrate, bismuth 2-ethylhexanoate, bismuth neodeconate, and bismuth oxalate.

3. The curable fluoroelastomer composition of claim 1 wherein said acid acceptor is a bismuth oxycarboxylate selected from the group consisting of bismuth subgallate, bismuth subcarbonate, and bismuth subsalicylate.

4. The curable fluoroelastomer composition of claim 3 wherein said acid acceptor is bismuth subcarbonate.

5. The curable fluoroelastomer composition of claim 3 wherein said acid acceptor is bismuth subsalicylate.

6. The curable fluoroelastomer composition of claim 1 wherein said peroxide curable fluoroelastomer comprises copolymerized units of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene.

7. The curable fluoroelastomer composition of claim 1 wherein said peroxide curable fluoroelastomer comprises copolymerized units of vinylidene fluoride, perfluoro(methyl vinyl ether) and tetrafluoroethylene.

8. The curable fluoroelastomer composition of claim 1 wherein said peroxide curable fluoroelastomer comprises copolymerized units of tetrafluoroethylene and perfluoro(methyl vinyl ether).

9. A cured fluoroelastomer article made from the composition of claim 1.

10. A fuel management system comprising a cured fluoroelastomer article of claim 9.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/044108

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/098
ADD.

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)
C08K C08L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/068835 A1 (DUPONT PERFORMANCE ELASTOMERS [US]; STEVENS RONALD D [US]) 9 June 2011 (2011-06-09) page 1, line 29 - page 2, line 4 examples; tables I-III	1-10
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A	US 5 696 189 A (LEGARE JOHN MICHAEL [US]) 9 December 1997 (1997-12-09) examples 4-7 claims 1-5,10,11,12-15	1-10

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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"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
3 September 2012	17/09/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Russell, Graham

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/044108

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No
PCT/US2012/044108

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