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(54) **FUEL MANAGEMENT SYSTEMS HAVING A  
FLUORORUBBER COMPONENT IN  
CONTACT WITH BIODIESEL FUEL**

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(57) **ABSTRACT**

Disclosed herein is a fuel management system having at least one fluororubber component in contact with biodiesel fuel wherein said 5 fluororubber component comprises i) a peroxide cured fluoroelastomer comprising copolymerized units of vinylidene fluoride and at least one other fluoromonomer, said fluoroelastomer having cure sites selected from the group consisting of iodine and bromine atoms, and ii) 0 to 5000 parts by weight of an inorganic acid acceptor per million parts fluoroelastomer.

**FUEL MANAGEMENT SYSTEMS HAVING A  
FLUORORUBBER COMPONENT IN  
CONTACT WITH BIODIESEL FUEL**

FIELD OF THE INVENTION

**[0001]** This invention relates to fuel management systems having fluororubber components in contact with biodiesel fuel wherein said fluororubber component comprises i) a peroxide cured fluoroelastomer comprising copolymerized units of vinylidene fluoride and at least one other fluoromonomer, said fluoroelastomer having cure sites selected from the group consisting of iodine and bromine atoms, and ii) 0 to 5000 parts by weight of an inorganic acid acceptor per million parts fluoroelastomer.

BACKGROUND OF THE INVENTION

**[0002]** 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<sub>2</sub>) 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 examples of fluoroelastomers include the copolymers of tetrafluoroethylene with a perfluoro(alkyl vinyl ether) such as perfluoro(methyl vinyl ether) (PMVE).

**[0003]** In order to develop the physical properties necessary for most end use applications, fluoroelastomers must be crosslinked. A preferred curing system for many end uses is the combination of an organic peroxide and a multifunctional unsaturated coagent. The coagent forms crosslinks by reacting with bromine or iodine atom cure sites on the fluoroelastomer polymer chain. A preferred cure site is an iodine atom bonded to a carbon atom on the fluoroelastomer chain.

**[0004]** Typical peroxide curable fluoroelastomer compositions contain 1 to 10 parts by weight of an inorganic acid acceptor per hundred parts by weight fluoroelastomer. Inorganic acid acceptors include metal oxides, metal hydroxides and hydrotalcite compounds. The function of inorganic acid acceptors in a peroxide curable fluoroelastomer compound is to neutralize acids that are byproducts of the curing process.

**[0005]** However, peroxide cured fluoroelastomer articles containing inorganic acid acceptors generally exhibit unacceptably high volume swell, that may lead to seal failure, when seals are exposed to biodiesel fuel for long periods of time or at elevated temperatures, especially when the fuel contains a minor amount of water. Biodiesel fuels often contain water as an impurity. The source of the water may be a washing step in the fuel manufacturing process or exposure to moist air during storage. Typical specifications for manufactured biodiesel allow for some water impurity, e.g. ASTM D6751.

SUMMARY OF THE INVENTION

**[0006]** In one aspect, the present invention provides a fuel management system having at least one fluororubber component in contact with biodiesel wherein said fluororubber component has excellent (i.e. low) volume swell in biodiesel fuel. Said fluororubber component comprises i) a peroxide cured

fluoroelastomer comprising copolymerized units of vinylidene fluoride and at least one other fluoromonomer, said fluoroelastomer having cure sites selected from the group consisting of iodine and bromine atoms, and ii) 0 to 5000 parts by weight of an inorganic acid acceptor per million parts fluoroelastomer.

DETAILED DESCRIPTION OF THE INVENTION

**[0007]** The present invention is directed to fuel management systems having at least one fluororubber component in contact with biodiesel fuel. The fluororubber component comprises a peroxide cured fluoroelastomer composition and is substantially free of inorganic acid acceptors. By "substantially free" is meant 0 to 5000 (preferably 0 to 1000, more preferably 0 to 500, most preferably 0) parts by weight of an inorganic acid acceptor per million parts by weight fluoroelastomer. Such fluororubber components have surprisingly low volume swell when exposed to biodiesel fuel for long periods of time and/or at elevated temperatures.

**[0008]** 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 and fuel injector components, o-rings, seals and gaskets. Any or all of these elements may comprise one or more fluororubber component that contacts biodiesel fuel.

**[0009]** By "biodiesel fuel" is meant a fuel suitable for use in a compression ignition (diesel) engine comprising 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 FME 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.

**[0010]** By "inorganic acid acceptor" is meant metal oxides, metal hydroxides and hydrotalcite compounds, e.g. CaO, Ca(OH)<sub>2</sub>, MgO, ZnO, etc.

**[0011]** Fluororubber components of this invention include, but are not limited to seals, gaskets, o-rings, tubing, the fuel contact layer of multilayer hoses, valve packings, diaphragms, and tank liners.

**[0012]** The fluoroelastomers employed in this invention comprise copolymerized units of vinylidene fluoride (VF<sub>2</sub>) and one or more additional fluoromonomers such as those selected from the group consisting of fluorine-containing olefins, fluorine-containing ethers and mixtures thereof.

**[0013]** According to the present invention, fluorine-containing olefins copolymerizable with vinylidene fluoride include, but are not limited to hexafluoropropylene (HFP),

tetrafluoroethylene (TFE), 1,2,3,3,3-pentafluoropropene (1-HPFP), chlorotrifluoroethylene (CTFE) and vinyl fluoride.

[0014] The fluorine-containing ethers that may be employed in the fluoroelastomers include, but are not limited to perfluoro(alkyl vinyl ethers), perfluoro(alkyl alkenyl ethers) and perfluoro(alkoxy alkenylethers).

[0015] Perfluoro(alkyl vinyl ethers) (PAVE) suitable for use as monomers include those of the formula



where  $\text{R}_f$  and  $\text{R}_f$  are different linear or branched perfluoroalkylene groups of 2-6 carbon atoms,  $m$  and  $n$  are independently 0-10, and  $\text{R}_f$  is a perfluoroalkyl group of 1-6 carbon atoms.

[0016] A preferred class of perfluoro(alkyl vinyl ethers) includes compositions of the formula

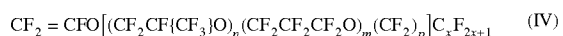


where  $\text{X}$  is  $\text{F}$  or  $\text{CF}_3$ ,  $n$  is 0-5, and  $\text{R}_f$  is a perfluoroalkyl group of 1-6 carbon atoms. A most preferred class of perfluoro(alkyl vinyl ethers) includes those ethers wherein  $n$  is 0 or 1 and  $\text{R}_f$  contains 1-3 carbon atoms. Examples of such perfluorinated ethers include perfluoro(methyl vinyl ether) (PMVE) and perfluoro(propyl vinyl ether) (PPVE). Other useful monomers include compounds of the formula



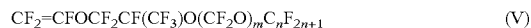
where  $\text{R}_f$  is a perfluoroalkyl group having 1-6 carbon atoms,  $m=0$  or 1,  $n=0-5$ , and  $\text{Z}=\text{F}$  or  $\text{CF}_3$ . Preferred members of this class are those in which  $\text{R}_f$  is  $\text{C}_3\text{F}_7$ ,  $m=0$ , and  $n=1$ .

[0017] Additional perfluoro(alkyl vinyl ether) monomers include compounds of the formula



where  $m$  and  $n$  independently=0-10,  $p=0-3$ , and  $x=1-5$ . Preferred members of this class include compounds where  $n=0-1$ ,  $m=0-1$ , and  $x=1$ .

[0018] Other examples of useful perfluoro(alkyl vinyl ethers) include



where  $n=1-5$ ,  $m=1-3$ , and where, preferably,  $n=1$ .

[0019] Perfluoro(alkyl alkenyl ethers) suitable for use as monomers include those of the formula VI



where  $\text{R}_f$  is a perfluorinated linear or branched aliphatic group containing 1-20, preferably 1-10, and most preferably 1-4 carbon atoms and  $n$  is an integer between 1 and 4. Specific examples include, but are not limited to perfluoro(propoxyallyl ether) and perfluoro(propoxybutenyl ether).

[0020] Perfluoro(alkoxy alkenyl ethers) differ from perfluoro(alkyl alkenyl ethers) in that  $\text{R}_f$  in formula VI contains at least one oxygen atom in the aliphatic chain. A specific example includes, but is not limited to perfluoro(methoxyethoxyallyl ether).

[0021] If copolymerized units of a fluorine-containing ether are present in the fluoroelastomers of the invention, the ether unit content generally ranges from 25 to 75 weight percent, based on the total weight of the fluoroelastomer. If

perfluoro(methyl vinyl) ether is used, then the fluoroelastomer preferably contains between 30 and 55 wt. % copolymerized PMVE units.

[0022] The fluoroelastomers of the present invention also contain cure sites of bromine atoms, iodine atoms or both. The cure sites may be along the fluoroelastomer chain (i.e. due to copolymerized units of cure site monomer), at chain ends (i.e. due to polymerization in the presence of a chain transfer agent), or both along fluoroelastomer chains and at chain ends.

[0023] Brominated cure site monomers may contain other halogens, preferably fluorine. Examples of brominated olefin cure site monomers are  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{Br}$ ; 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  $\text{CF}_2\text{Br}-\text{R}-\text{O}-\text{CF}=\text{CF}_2$  ( $\text{R}_f$  is a perfluoroalkylene group), such as  $\text{CF}_2\text{BrCF}_2\text{O}-\text{CF}=\text{CF}_2$ , and fluorovinyl ethers of the class  $\text{ROCF}=\text{CFBr}$  or  $\text{ROCF}=\text{CF}_2$  (where  $\text{R}$  is a lower alkyl group or fluoroalkyl group) such as  $\text{CH}_3\text{OCF}=\text{CFBr}$  or  $\text{CF}_3\text{CH}_2\text{OCF}=\text{CFBr}$ .

[0024] Suitable iodinated cure site monomers include iodinated olefins of the formula:  $\text{CHR}=\text{CH}-\text{Z}-\text{CH}_2\text{CHR}-\text{I}$ , wherein  $\text{R}$  is  $-\text{H}$  or  $-\text{CH}_3$ ;  $\text{Z}$  is a  $\text{C}_1-\text{C}_{18}$  (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:  $\text{I}(\text{CH}_2\text{CF}_2\text{CF}_2)_n\text{OCF}=\text{CF}_2$  and  $\text{I}(\text{CH}_2\text{CF}_2\text{O})_n[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_m\text{CF}=\text{CF}_2$ , and the like, wherein  $n=1-3$ , such as disclosed in U.S. Pat. No. 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-(vinyl)oxy ethane; 2-iodo-1(perfluorovinyl)oxy-1,1,2,2-tetrafluoroethylene; 1,1,2,3,3,3-hexafluoro-2-iodo-1-(perfluorovinyl)oxy propane; 2-iodoethyl vinyl ether; 3,3,4,5,5,5-hexafluoro-4-iodopentene; and iodotrifluoroethylene are disclosed in U.S. Pat. No. 4,694,045. Allyl iodide and 2-iodo-perfluoroethyl perfluorovinyl ether are also useful cure site monomers.

[0025] Units of cure site monomer, when present in the fluoroelastomers employed in this invention, are typically present at a level of 0.05-10 wt. % (based on the total weight of fluoroelastomer), preferably 0.05-5 wt. % and most preferably between 0.05 and 3 wt. %.

[0026] Additionally, 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. %.

[0027] Examples of chain transfer agents include iodine-containing compounds that result in incorporation of bound iodine at one or both ends of the polymer molecules. Methylene iodide; 1,4-diiodoperfluoro- $n$ -butane; and 1,6-diiodo-



TABLE I-continued

	Ex. 1	Ex. 2	Comp. Ex. A	Comp. Ex. B	Comp. Ex. C	Comp. Ex. D	Comp. Ex. E
Triallyl iso- cyanurate <sup>2</sup>	2.5	2.5	0	2.5	2.5	2.5	2.5
Peroxide <sup>3</sup>	1.5	1.5	0	1.5	1.5	1.5	1.5
MgO <sup>4</sup>	0	0	3	0	3	0	0
Ca(OH) <sub>2</sub>	0	0	6	0	0	3	0
ZnO	0	0	0	3	0	0	3
Tensile Properties:							
Hardness, Shore A	68	71	74	69	69	69	72
M100, MPa	3.4	5.2	5.6	3.6	4.2	4.0	5.1
Tb, MPa	17.9	18.1	13.9	18.3	17.8	19.3	18.4
Eb, %	349	259	226	356	292	337	281
Volume Swell							
B20 Fuel, %	6	5	56	18	14	39	15
B100 Fuel, %	5	4	99	17	21	27	17

<sup>1</sup>parts by weight per hundred parts rubber (i.e. fluoroelastomer)

<sup>2</sup>Diak 7 (available from DuPont Performance Elastomers)

<sup>3</sup>Elastomag ® 170 (available from Rohm and Haas)

<sup>4</sup>Varox ® DBPH-50 (available from R. T. Vanderbilt)

## Examples 3-4

## Comparative Examples F-I

**[0044]** Cured slabs were prepared and cured as described in Example 1 from the formulations shown in Table 2 except that post cure was for 16 hours. Tensile properties are shown in Table 2. Coupons were exposed to rapeseed oil methyl ester (B100 RME) and to blends of 5 vol. % RME and 20 vol. % RME in petroleum diesel fuel (B5 and B20, respectively) for 1008 hours at 125° C. The fuels contained 0.5 wt. % water. Results are shown in Table 2. Comparative examples (containing inorganic acid acceptors) all showed higher volume swell than Examples 3-4 (no inorganic acid acceptor), even in fuel containing only 5 vol. % biodiesel (B5).

TABLE II

	Ex. 3	Comp. Ex. F	Come. Ex. G	Comp. Ex. H	Comp. Ex. I	Ex. 4
Ingredient, phr <sup>1</sup>						
FKM1	0	0	100	0	0	0
FKM2	100	100	0	100	0	0
FKM3	0	0	0	0	0	100
FKM4	0	0	0	0	100	0
N990 Carbon Black	30	30	30	30	30	30
Triallyl isocyanurate <sup>2</sup>	2.5	2.5	0	2.5	0	2.5
Peroxide <sup>3</sup>	1.5	1.5	0	1.5	0	1.5
MgO <sup>4</sup>	0	0	3	0	3	0
Ca(OH) <sub>2</sub>	0	3	6	1.5	6	0
Tensile Properties:						
Hardness, Shore A	72	73	78	72	79	76
M100, MPa	3.5	4.5	6.0	4.3	5.2	5.5

TABLE II-continued

	Ex. 3	Comp. Ex. F	Come. Ex. G	Comp. Ex. H	Comp. Ex. I	Ex. 4
Tb, MPa	19.8	21.4	14.7	22.1	13.8	20
Eb, %	309	295	212	327	278	275
Volume Swell						
B100 Fuel, %	5	26	90	19	48	3
B20 Fuel, %	5	14	37	8	75	4
B5 Fuel, %	5	10	10	8	10	5

## Examples 5-8

**[0045]** Cured slabs were prepared and cured as described in Example 1 from the formulations shown in Table 3 except that post cure was for 16 hours. Tensile properties are shown in Table 3. Coupons were exposed to rapeseed oil methyl ester (B100 RME) for 3024 hours at 125° C. Results are shown in Table 3. Even after 3024 hours of exposure to biodiesel fuel, the coupons of the invention (contained no inorganic acid acceptors) exhibited low volume swell.

TABLE 3

	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Ingredient, phr <sup>1</sup>				
FKM2	100	0	0	0
FKM3	0	100	0	0
FKM5	0	0	100	0
FKM6	0	0	0	100
N990 Carbon Black	30	30	30	30
Triallyl isocyanurate <sup>2</sup>	2.5	2.5	2.5	2.5
Peroxide <sup>3</sup>	1.5	1.5	1.5	1.5
Tensile Properties:				
Hardness, Shore A	71	76	72	68
M100, MPa	3.3	6.0	5.0	3.4
Tb, MPa	20.9	20.0	15.9	19.0
Eb, %	359	279	200	285
Volume Swell				
B100 Fuel, %	5	4	5	6

What is claimed is:

1. In a fuel management system having at least one fluororubber component in contact with biodiesel fuel, the improvement wherein said fluororubber component comprises i) a peroxide cured fluoroelastomer comprising copolymerized units of vinylidene fluoride and at least one other fluoromonomer, said fluoroelastomer having cure sites selected from the group consisting of iodine and bromine atoms, and ii) 0 to 5000 parts by weight of an inorganic acid acceptor per million parts fluoroelastomer.

2. A fuel management system of claim 1 wherein said biodiesel fuel comprises a fatty acid alkyl ester of biological origin.

3. A fuel management system of claim 2 wherein said fatty acid alkyl ester of biological origin is selected from the group consisting of rape seed oil methyl ester, soybean oil methyl ester, and palm kernel oil methyl ester.

4. A fuel management system of claim 1 wherein said biodiesel fuel comprises a blend of a fatty acid alkyl ester of biological origin and petroleum diesel fuel.

5. A fuel management system of claim 1 wherein said fuel management system is in a motor vehicle.

6. A fuel management system of claim 1 wherein said fuel management system is in a stationary diesel powered device.

7. A fuel management system of claim 1 wherein said fuel management system is in a biodiesel supply system.

8. A fuel management system of claim 1 wherein said fuel management system is in a biodiesel manufacturing plant.

9. A fuel management system of claim 1 wherein said peroxide cured fluoroelastomer comprises copolymerized units of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene.

10. A fuel management system of claim 1 wherein said peroxide cured fluoroelastomer comprises copolymerized units of vinylidene fluoride, perfluoro(methyl vinyl ether) and tetrafluoroethylene.

11. A fuel management system of claim 1 comprising 0 to 1000 parts by weight of an inorganic acid acceptor per million parts fluoroelastomer.

12. A fuel management system of claim 11 comprising 0 to 500 parts by weight of an inorganic acid acceptor per million parts fluoroelastomer.

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