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United States Patent [19][11] **Patent Number:** **5,902,857****Wlassics et al.**[45] **Date of Patent:** **May 11, 1999**[54] **FLUOROELASTOMERIC COMPOSITIONS**

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[75] Inventors: **Ivan Wlassics**, Rapallo; **Vito Tortelli**, Milan; **Walter Navarrini**, Boffalora Ticino; **Margherita Albano**, Milan, all of Italy

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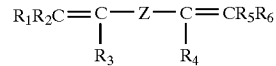
[73] Assignee: **Ausimont S.p.A.**, Milan, Italy*Primary Examiner*—Bernard Lipman[21] Appl. No.: **08/733,938***Attorney, Agent, or Firm*—Finnegan, Henderson, Farabow Garrett & Dunner[22] Filed: **Oct. 18, 1996**[30] **Foreign Application Priority Data**[57] **ABSTRACT**

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[51] **Int. Cl.**⁶ **C08F 8/00**[52] **U.S. Cl.** **525/248; 525/276; 525/326.3; 525/370**[58] **Field of Search** **525/326.3, 370, 525/248, 276**

Curing systems for fluoroelastomers curable by peroxidic route which comprise bromine, optionally iodine, the bromine always being higher than iodine, comprising as essential elements:

(I) a curing agent comprising a bis-olefin having general formula:



(I)

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,810,874	5/1974	Mitsch et al.	260/75
4,035,565	7/1977	Apotheker et al.	526/249
4,214,060	7/1980	Apotheker et al.	525/387
4,243,770	1/1981	Tatemoto et al.	525/331
4,501,869	2/1985	Tatemoto et al.	526/249
4,564,662	1/1986	Albin	526/247
4,694,045	9/1987	Moore	525/276
4,745,165	5/1988	Arcella et al.	526/247
4,789,717	12/1988	Giannetti et al.	526/209
4,831,085	5/1989	Okabe et al.	525/387
4,864,006	9/1989	Giannetti et al.	526/209
4,943,622	7/1990	Naraki et al.	526/206
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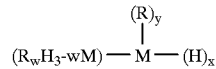
FOREIGN PATENT DOCUMENTS

0 136 596	4/1985	European Pat. Off. .
0 199 138	10/1986	European Pat. Off. .
0 407 937 A1	1/1991	European Pat. Off. .
0 410 351 A1	1/1991	European Pat. Off. .
0 661 304 A1	7/1995	European Pat. Off. .
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WO 95/28442	10/1995	WIPO .

wherein:

R₁, R₂, R₃, R₄, R₅, R₆, equal to or different from each other, are H or alkyl C₁-C₅; Z is a linear or branched alkylene or cycloalkylene radical C₁-C₁₈, optionally containing oxygen atoms, or a (per) fluoropolyoxyalkylene radical.

(II) a metallorganic hydride of formula:



(III)

wherein: M is selected from Sn, Si, Ge, Pb; x is an integer from 1 to 3; y, z are zero or integers from 1 to 3, with the proviso y+z=4-x; w is an integer from 1 to 3; the R groups, equal to or different from each other, are selected from: alkyls C₁-C₄, aryls C₆-C₁₂, arylalkyls and alkylaryls C₇-C₁₄, optionally containing nitrile and/or hydroxyl groups.**10 Claims, No Drawings**

preferred, for instance: tri(n-butyl)-tin-hydride, tri(ethyl)-silyl-hydride, di(trimethylsilyl)-silylmethyl-hydride, tri(trimethylsilyl)-silylhydride, and the like, or mixtures thereof.

The fluoroelastomers containing bromine, as already said, are known products. They contain bromine in amounts generally comprised between 0.001 and 5% by weight, preferably between 0.01 and 2.5% by weight with respect to the total weight of the polymer. The bromine atoms can be present along the chain and/or in terminal position.

To introduce bromine atoms along the chain, the copolymerization of the basic monomers of the fluoroelastomer is carried out with a suitable fluorinated comonomer containing bromine, cure-site monomer, see for instance U.S. Pat. No. 4,745,165, U.S. Pat. No. 4,831,085, and U.S. Pat. No. 4,214,060. Such a comonomer can be selected from instance from:

(a) bromo(per)fluoroalkyl-perfluorovinylethers of formula:



wherein R_f is a (per)fluoroalkylene C_1-C_{12} , optionally containing chlorine atoms and/or ethereal oxygen; for instance: $\text{BrCF}_2-\text{O}-\text{CF}=\text{CF}_2$, $\text{BrCF}_2\text{CF}_2-\text{O}-\text{CF}=\text{CF}_2$, $\text{BrCF}_2\text{CF}_2\text{CF}-\text{O}-\text{CF}=\text{CF}_2$, $\text{CF}_3\text{CFBrCF}_2-\text{O}-\text{CF}=\text{CF}_2$, and the like;

(b) bromo-(per)fluoroolefins of formula:



wherein R'_f is a (per)fluoroalkylene C_1-C_{12} , optionally containing chlorine atoms; for instance: bromotrifluoroethylene, 1-bromo-2,2-difluoroethylene, bromo-3,3,4,4-tetrafluorobutene-1, 4-bromoperfluorobutene-1, and the like.

The units of brominated comonomer in the final polymer are present in amounts generally comprised between 0.01 and 3% by moles, preferably between 0.1 and 1% by moles.

In alternative or in addition to the brominated comonomer, the fluoroelastomer can contain bromine atoms in terminal position, deriving from a suitable brominated chain transfer agent introduced in the reaction medium during the preparation of the polymer, as described in U.S. Pat. No. 4,501,869. Such transfer agents have the formula $R_{f0}(\text{Br})_{x0}$, wherein R_{f0} is a (per)fluoroalkylic or chlorofluoroalkylic radical C_1-C_{12} , optionally containing chlorine atoms, while $x0$ is 1 or 2. They can be selected for instance from: CF_2Br_2 , $\text{Br}(\text{CF}_2)_2\text{Br}$, $\text{Br}(\text{CF}_2)_4\text{Br}$, CF_2ClBr , $\text{CF}_3\text{CFBrCF}_2\text{Br}$, and the like. The bromine amount in terminal position is generally comprised between 0.001 and 1%, preferably between 0.01 and 0.5%, by weight with respect to the fluoroelastomer weight.

The fluoroelastomer can also contain optionally in addition to bromine also iodine atoms, iodine is generally comprised between 0.01 and 1% by weight with respect to the fluoroelastomer, preferably between 0.05 and 0.5% by weight.

The amount of curing agent (i) must be such as to involve bromine in the curing. Therefore the amount of iodine is generally lower than that of bromine and such that bromine takes part in the curing to obtain a polymer with good properties of the cured product.

The introduction of such iodine atoms can be carried out by addition of iodinated cure-site comonomers such as iodine olefins having from 2 to 10 C atoms, see for instance U.S. Pat. No. 4,035,565 and U.S. Pat. No. 4,694,045, iodofluoroalkylvinylethers, see U.S. Pat. No. 4,745,165 and

U.S. Pat. No. 4,564,662, EP 95107005.1. Also iodine can be introduced as chain end by addition of iodinated chain transfer agents, such as $R_f(\text{I})_{x'}(\text{Br})_{y'}$, wherein R_f has the meaning indicated above, x' and y' are integers comprised between 0 and 2, with $1 \leq x'+y' \leq 2$; x' being higher than 0, see for instance patents U.S. Pat. No. 4,243,770 and U.S. Pat. No. 4,943,622.

It is also possible to introduce iodine as chain end by using alkaline or alkaline-earth metals iodides and/or bromides according to EP patent application 407,937.

In combination with or in alternative to the chain transfer agents containing bromine, optionally iodine, other chain transfer agents known in the art, such as ethyl acetate, diethylmalonate, etc., can be used.

The fluoroelastomers are TFE or vinylidene fluoride (VDF) copolymers and at least a fluorinated olefin having a terminal unsaturation, containing at least a fluorine atom on each carbon atom of the double bond, the other atoms can be fluorine, hydrogen, fluoroalkyl or fluoroalkoxy from 1 to 10 carbon atoms, preferably 1-4 carbon atoms; or copolymers of fluorinated olefins as defined above; in both types a vinyl ether and/or non fluorinated olefins can be present. In particular the basic structure of the fluoroelastomer can be selected from:

(1) copolymers based on VDF, wherein the latter is copolymerized with at least a comonomer selected from: perfluoroolefins C_2-C_8 , such as tetrafluoroethylene (TFE), hexafluoropropene (HFP); chloro- and/or bromo- and/or iodo-fluoroolefins C_2-C_8 , such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)fluoroalkylvinylethers (PAVE) $\text{CF}_2=\text{CFOR}_{f0}$ wherein R_{f0} is a (per)fluoroalkyl C_1-C_6 , for instance trifluoromethyl, bromodifluoromethyl, pentafluoropropyl; perfluoro-oxyalkylvinylethers $\text{CF}_2=\text{CFOX}_1$, wherein X_1 is a perfluoro-oxyalkyl C_1-C_{12} having one or more ethereal groups, for instance perfluoro-2-propoxy-propyl; non fluorinated olefins (OI) C_2-C_8 , for instance ethylene and propylene;

(2) copolymers based on TFE, wherein the latter is copolymerized with at least a comonomer selected from: (per)fluoroalkylvinylethers (PAVE) $\text{CF}_2=\text{CFOR}_{f2}$, wherein R_{f2} has the same meaning of R_{f0} ; perfluoro-oxyalkylvinylethers $\text{CF}_2=\text{CFOX}_0$, wherein X_0 has the same meaning of X_1 ; fluoroolefins C_2-C_8 containing hydrogen and/or chlorine and/or bromine and/or iodine atoms; non fluorinated olefins (OI) C_2-C_8 , preferably ethylene.

Inside the classes defined above, preferred basic monomer compositions are the following (% by moles):

(a) VDF 45-85%, HFP 15-45%, 0-30% TFE; (b) VDF 50-80%, PAVE 5-50%, TFE 0-20%; (c) VDF 20-30%, OI 10-30%, HFP and/or PAVE 18-27%, TFE 10-30%; (d) TFE 50-80%, PAVE 20-50%; (e) TFE 45-65%, OI 20-55%, 0-30% VDF; (f) TFE 32-60%, OI 10-40%, PAVE 20-40%.

The fluoroelastomers can contain also monomeric units in the chain deriving from small amounts of a bis-olefin (i) as described in European patent application No. 94120504.9, generally 0.01-1% by moles with respect to the polymer.

Other fluoroelastomers which can be used are those having a high content of fluorine, which have for instance the following composition:

33-75% by moles of tetrafluoroethylene (TFE), preferably 40-60%;
15-45% by moles of a perfluorovinylether (PVE), preferably 20-40%;

10–22% by moles of vinylidene fluoride (VDF), preferably 15–20%.

The PVE have the formula: $\text{CF}_2=\text{CFO}-\text{R}_n$, with R_n equal to perfluoroalkyl C_1-C_6 , preferably C_1-C_4 , or containing one or more ethereal groups C_2-C_9 .

Of the polymers indicated above, the following ones based on VdF are for instance commercially known: VITON® GF, GBL 200, GBL 900 by Du Pont; TECNOFLON® P2, P819, PFR 91 by AUSIMONT.

The curing by peroxidic route is carried out, according to known techniques, by addition of peroxides capable of generating radicals by heating. Among the most commonly used peroxides we can cite: dialkylperoxides, such as for instance di-terbutyl-peroxide and 2,5-dimethyl-2,5-di-(terbutylperoxy)-hexane; dicumyl peroxide; dibenzoyl peroxide; diterbutyl perbenzoate; di[1,3-dimethyl-3-(terbutylperoxy)butyl]-carbonate. Other peroxidic systems are described, for instance, in European patent applications EP 136,596 and EP 410,351.

Other products are then added to the curing blend, such as:

- (a) optionally other curing coagents, besides the essential ones for the present invention, in amounts generally comprised between 0.01 and 5% by weight, preferably between 0.1 and 1%, by weight with respect to the polymer; among them those commonly used are: triallyl-cyanurate; triallyl-isocyanurate (TAIC); tris(diallylamine)-s-triazine; triallylphosphite; N,N-diallyl-acrylamide, N,N,N',N'-tetraallyl-malonamide; trivinyl-isocyanurate; 2,4,6-trivinyl-methyltrisiloxane, etc.; TAIC is particularly preferred;
- (b) a metal compound, in amounts comprised between 1 and 15%, preferably between 2 and 10%, by weight with respect to the polymer, selected from oxides or hydroxides of divalent metals, such as for instance Mg, Zn, Ca or Pb, optionally combined with a salt of a weak acid, such as for instance stearates, benzoates, carbonates, oxalates or Ba, Na, K, Pb, Ca phosphites;
- (c) other conventional additives, such as reinforcing fillers, pigments, antioxidants, stabilizers and the like.

The preparation of the fluoroelastomers object of the present invention can be carried out by copolymerization of the monomers in aqueous emulsion according to well known methods in the art, in the presence of radicalic initiators (for instance persulphates, perphosphates, or alkaline or ammonium carbonates or percarbonates), optionally with ferrous or silver salts or of other easily oxidizable metals. Surfactants, such as for instance (per)fluoroalkylic carboxylates or sulphonates (for instance ammonium perfluorooctanoate) or (per)fluoropolyoxyalkylenic, or others known in the art, are also present in the reaction medium.

When the polymerization is over, the fluoroelastomer is isolated from the emulsion by conventional methods, such as coagulation by addition of electrolytes or by cooling.

Alternatively, the polymerization reaction can be carried out in mass or in suspension, in an organic liquid wherein a suitable radicalic initiator is present, according to well known techniques.

The polymerization reaction is generally carried out at temperatures comprised between 25° and 150° C. under pressure up to 10 MPa.

The preparation of the fluoroelastomers object of the present invention is preferably carried out in aqueous emulsion in the presence of an emulsion, dispersion or microemulsion of perfluoropolyoxyalkylenes, according to U.S. Pat. No. 4,789,717 and U.S. Pat. No. 4,864,006, which are incorporated herein by reference.

The following examples are given for illustrative purposes but are not limitative of the scope of the present invention.

EXAMPLES 1–3

A rubber TECNOFLON® P2 (53% moles VDF, 23% moles HFP, 24% moles TFE), containing 0.59 by weight of bromine deriving from the introduction as comonomer of 2-bromo-perfluoroethylperfluorovinylether (BVE), having number average molecular weight equal to 64,000 and weight average molecular weight equal to 250,000, was used for the preparation of the curable compositions of the present invention.

To 100 g of such rubber were added:

3 phr of peroxide LUPERCO® 101 XL (2,5-dimethyl-2,5-di(terbutylperoxy)hexane);

4.3 phr of bisolefin BO having the formula $\text{CH}_2=\text{CH}(\text{CF}_2)_6\text{CH}=\text{CH}_2$;

1.07 phr of TBSI (tri-n-butyl-tin hydride) having the formula $[\text{CH}_3(\text{CH}_2)_3]_3\text{S}_n-\text{H}$;

5 phr of ZnO;

30 phr of carbon black MT.

The mixing was carried out in an open mixer. The composition of the blend and its Mooney viscosity (ASTM D1646-82) are reported in Table 1.

The curing curve was determined on the composition thus obtained by Oscillating Disk Rheometer (ODR) by Monsanto (100S Model), according to ASTM D2084-81, by operating at 177° C. with an oscillation amplitude of 3°.

The data (ODR) are reported in Table 1:

M_L (minimum torque); M_H (maximum torque); t_{52} , (time required for an increase of the torque of 2 lb.in above M_L); $t'50$ and $t'90$ (time required for an increase of 50% and of 90%, respectively, of the torque).

On the cured product were determined and reported in Table:

the compression set on O-ring at 200° C. for 70 h after post-curing at 230° C. for (8 h+16 h) according to ASTM D395;

the mechanical properties after post-curing at 230° C. for 8 h+16 h according to ASTM D412-83.

Example 2

(Comparative)

Example 1 was repeated but the curing was carried out with triallyl isocyanurate (TAIC) (4 phr), conventional system known in the art instead of the curing system bisolefin BO and TBSI.

Example 2A

(Comparative)

Example 1 was repeated but by utilizing only the bisolefin without using TBSI.

Example 3

Example 1 was repeated but by using 2.15 phr of tributyl-tin hydride (TBSI).

TABLE 1

		ex. 2 comp.	ex. 2A comp.	ex. 1	ex.3
Blend composition					
Polymer P2	(g)	100	100	100	100
Luperc 101XL	(phr)	3	3	3	3
TAIC drymix	(phr)	4	—	—	—
BO	(phr)	—	4.3	4.3	4.3
TBSI	(phr)	—	—	1.07	2.15
ZnO	(phr)	5	5	5	5
Carbon Black MT	(phr)	30	30	30	30
Viscosity ML (1-10) at 121° C.		91	100	66, 7	62
ASTM D1646					
Mooney (points)					
Blend characteristics ODR 177° C. arc 3° (ASTM D 2084-81)					
ML	(lb. in)	21.1	15.9	14	15.4
MH	(lb. in)	83.5	48.2	92	105.5
ts2	(sec)	78	203	116	103
t'50	"	150	363	230	216
t'90	"	394	600	425	341
Compression set at 200° C. x 70 h after post curing 230° C. x (8 + 16 h) (ASTM D395)					
O-ring	(%)	34	62	39	32
Mechanical properties after post curing 230° C. x (8 + 16 h) (ASTM D 412-83)					
Modulus at 100%	(MPa)	4.9	—	—	11.4
Stress at break	(MPa)	16.5	—	—	18.9
Elongation at break	(%)	219	—	—	148
Shore Hardness A	(points)	7.1	—	—	74

From the results of the examples in Table 1 it can be noticed that the processability of the curing system of the present invention is clearly improved compared with the conventional peroxidic curing system (TAIC) as it is evident from the (ODR) data: ML, and by the Mooney blend.

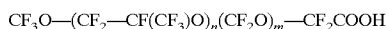
From example 2A it is noticed that the bisolefin alone is not capable of giving a sufficient curing.

EXAMPLES 4-5

Example 4

Preparation of the polymer TECNOFLON® PER91
Preparation of the perfluoropolyoxyalkylenes microemulsion

In a glass container equipped with stirrer 96.1 g of the compound having the formula:



having $n/m=10$ and average molecular weight of 570, with 14.5 g of 30% NH_4OH by volume, were mixed. 29 g of demineralized water were then added. 16 g of GALDEN® having the formula:



were added to the so obtained blend, having $n/m=20$ and average molecular weight of 450. At a temperature comprised between 18° and 50° C. the mixture is in the form of microemulsion and appears as a limpid, thermodynamically stable solution.

Polymerization reaction

In a 10 l reactor, equipped with stirrer working at 545 rpm, 6500 g of water and the microemulsion of perfluoropolyoxyalkylenes prepared as described above, were fed after evacuation. The reactor was brought under pressure with a monomeric mixture having the following molar composi-

tion: 4% of VDF, 64% of perfluoromethylvinylether (PMVE); 32% of TFE. The temperature was maintained for the duration of the reaction at 80° C., the pressure at 25 relative bar.

5 0.26 g of ammonium persulphate (APS), dissolved in water, were then added as polymerization initiator. 13.92 g of 1,4 diiodoperfluorohexane dissolved in 25.56 g of GALDEN® D02 and 3.24 g of bromovinylether (BVE) were then added to the reaction mixture.

10 During the reaction the pressure was kept constant by feeding the monomers with the following molar ratios: VDF 17%, PMVE 38%, TFE 45%. 3.24 g of BVE were fed at every 5% increase of the conversion.

15 After 130 minutes from the beginning of the reaction 2920 g of polymer were obtained. The emulsion was discharged from the reactor, cooled at room temperature, and the polymer was coagulated by addition of an aqueous solution of aluminium sulphate. The polymer, separated and washed with water, was dried in air-circulating stove at 60° C. for 24 hours.

The characteristics of the obtained polymer are reported in Table 2.

TABLE 2

EXAMPLE		4
Polymer composition		
TFE	(% by moles)	47
PMVE	"	33
VDF	"	20
Br	(% by weight)	0.4
I	"	0.23
Mooney viscosity ML ^{121° C.} (1 + 10) (ASTM D1646)		33

The polymer was then cured by peroxidic way: the blend composition and the characteristics of the cured product are reported in Table 3.

Example 5

The polymer of example 4 was formulated as indicated in Table 3 with the curing system of the invention by using the bisolefin of example 1.

The blend composition and the characteristics of the cured product are reported in Table 3.

TABLE 3

		ex. 4 comp.	ex. 5
Blend composition			
PRF 91	(g)	100	100
Luperc 101XL	(phr)	1.5	4
TAIC drymix	"	2	—
BO	"	—	4
TBSI	"	—	1.38
ZnO	"	5	5
Carbon black MT	"	15	15
Blend characteristics ODR at 177° C., arc 3° (ASTM D2084-81)			
ML	(lb. in)	4	4
MH	"	102	119
ts2	(sec.)	60	57
t'50	"	78	162
t'90	"	111	258

TABLE 3-continued

		ex. 4 comp.	ex. 5
Mechanical properties after post curing at 200° C. × 8 h (ASTM D 412-83)			
Modulus at 100%	(MPa)	5.5	7.7
Stress at break	"	16.6	15.3
Elongation at break	(%)	172	185
Shore Hardness A	(points)	66	77
Mechanical properties after ageing at 275° C. × 70 h (ASTM D 573)			
Variation Modulus 100%	(%)	-58	-17
Variation stress at break	"	-58	-31
Variation elongation at break	"	187	6
Variation hardness	(points)	1	-2
Compression set at 200° C. × 70 h after post curing at 200° C. for 8 hours (ASTM D395)			
O-Ring	(%)	21	25

From the results of Table 3 it is clear that the thermal resistance of the cured product with the curing system of the present invention also at 275° C. results to be very high, in particular this can be noticed from the percent variations of the elongation at break.

On the contrary, the thermal resistance of the cured blend with the conventional systems of the art has resulted particularly worsened by passing from 200° C. to 275° C., see in particular the elongation data; this product therefore results unusable at the ageing temperature of 275° C.

We claim:

1. Curing systems for fluoroelastomers curable by peroxidic route which contain bromine, optionally iodine, the bromine always being higher than iodine, comprising as essential elements:

(i) a crosslinking agent comprising a bis-olefin having general formula:



wherein:

$R_1, R_2, R_3, R_4, R_5, R_6$, equal to or different from each other, are H or alkyl C_1-C_5 ;

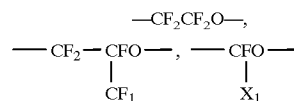
Z is a linear or branched alkylene or cycloalkylene radical C_1-C_{18} , optionally containing oxygen atoms, or a (per)fluoropolyoxyalkylene radical; and

(ii) a metallorganic hydride of formula:



wherein: M is selected from Sn, Si, Ge, Pb; x is an integer from 1 to 3; y, z are zero or integers from 1 to 3, with the proviso $y+z=4-x$; w is an integer from 1 to 3; the R groups, equal to or different from each other, are selected from: alkyls C_1-C_4 , aryls C_6-C_{12} , arylalkyls and alkylaryls C_7-C_{14} , optionally containing nitrile and/or hydroxyl groups; in amounts comprised between 0.2 and 10%.

2. Curing system for fluoroelastomers curable by peroxidic route which contain bromine, optionally iodine, the bromine always being higher than iodine, according to claim 1, wherein in the formula (I), Z is a perfluoroalkylene radical C_6-C_9 , or a (per)fluoropolyoxyalkylene radical comprising units selected from the following ones:



with $X_1=F, CF_3$; $-CF_2CF_2CF_2O-$, $-CF_2CF_2CH_2O-$; $R_1, R_2, R_3, R_4, R_5, R_6$ are hydrogen.

3. Curing system for fluoroelastomers curable by peroxidic route which contain bromine, optionally iodine, the bromine always being higher than iodine, according to claim 2, wherein Z is a (per)fluoropolyoxyalkylene radical of formula



wherein: Q is a alkylene or oxyalkylene radical C_1-C_{10} ; p is 0 or 1; m and n are such numbers that the m/n ratio is comprised between 0.2 and 5 and the molecular weight of said (per)fluoropolyoxyalkylene radical is comprised between 500 and 10,000.

4. Curing system for fluoroelastomers curable by peroxidic route which contain bromine, optionally iodine, the bromine always being higher than iodine, according to claims 1-3, wherein (i) ranges from 0.5-10% by weight with respect to the polymer, (ii) ranges from 0.5-2% by weight with respect to the polymer.

5. Curing system for fluoroelastomers curable by peroxidic route which contain bromine, optionally iodine, the bromine always being higher than iodine, according to claims 1-4, wherein the fluoroelastomers are TFE or vinylidene fluoride (VDF) copolymers having at least a fluorinated olefin having a terminal unsaturation, containing at least a fluorine atom on each carbon atom of the double bond, the other atoms can be fluorine, hydrogen, fluoroalkyl or fluoroalkoxy from 1 to 10 carbon atoms, or copolymers of fluorinated olefins as defined above; in both types a vinyl ether and/or non fluorinated olefins can be present.

6. Curing system for fluoroelastomers curable by peroxidic route which contain bromine, optionally iodine, the bromine always being higher than iodine, according to claim 5, wherein the fluoroelastomers are selected from:

(1) copolymers based on VDF, wherein the latter is copolymerized with at least a comonomer selected from: perfluoroolefins C_2-C_8 , such as tetrafluoroethylene (TFE), hexafluoropropene (HFP); chloro- and/or bromo- and/or iodo-fluoroolefins C_2-C_8 , such as chlorotrifluoroethylene (CTFE) and bromotrifluoroethylene; (per)fluoroalkylvinylethers (PAVE) $CF_2=CFOR_{p0}$, wherein R_{p0} is a (per)fluoroalkyl C_1-C_6 , for instance trifluoromethyl, bromodifluoromethyl, pentafluoropropyl; perfluoro-oxyalkylvinylethers $CF_2=CFOX_1$, wherein X_1 is a perfluoro-oxyalkyl C_1-C_{12} having one or more ethereal groups, for instance perfluoro-2-propoxy-propyl; non fluorinated olefins (OI) C_2-C_8 , for instance ethylene and propylene;

(2) copolymers based on TFE, wherein the latter is copolymerized with at least a comonomer selected from: (per)fluoroalkylvinylethers (PAVE) $CF_2=CFOR_{f2}$, wherein R_{f2} is defined as above; perfluoro-

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oxyalkylvinylethers $CF_2=CFOX_0$, wherein X_0 is defined as above; fluoroolefins C_2-C_8 containing hydrogen and/or chlorine and/or bromine and/or iodine atoms; non fluorinated olefins (Ol) C_2-C_8 , preferably ethylene.

7. Curing system for fluoroelastomers curable by peroxidic route which contain bromine, optionally iodine, the bromine always being higher than iodine, according to claims 5 and 6, wherein the basic monomeric compositions are the following (% by moles):

- (a) VDF 45–85%, HFP 15–45%, 0–30% TFE; (b) VDF 50–80%, PAVE 5–50%, TFE 0–20%; (c) VDF 20–30%, Ol 10–30%, HFP and/or PAVE 18–27%, TFE 10–30%; (d) TFE 50–80%, PAVE 20–50%; (e) TFE 45–65%, Ol 20–55%, 0–30% VDF; (f) TFE 32–60%, Ol 10–40%, PAVE 20–40%;

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33–75% by moles of tetrafluoroethylene (TFE); 15–45% by moles of a perfluorovinylether (PVE); 10–22% by moles of vinylidene fluoride (VDF).

8. Fluoroelastomers curable by peroxidic route which contain bromine, optionally iodine, the bromine always being higher than iodine, comprising as curing system the one of claims from 1 to 7.

9. Fluoroelastomers cured by peroxidic route which contain bromine, optionally iodine, the bromine always being higher than iodine, comprising as curing system the one of claims from 1 to 7.

10. Cured fluoroelastomers according to claim 9, in which the fluoroelastomers are in the form of gaskets and sealing rings.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,902,857
DATED : May 11, 1999
INVENTOR(S) : Wlassics et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Claim 6, column 10, line 56, " $CF_2=CFOR_{fo}$ " should read $--CF_2=CFOR_{f'o}--$, and
" R_{fo} " should read $--R_{f'o}--$.

Signed and Sealed this

Twenty-sixth Day of October, 1999

Attest:



Q. TODD DICKINSON

Attesting Officer

Acting Commissioner of Patents and Trademarks

