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(54) Title: CURABLE FLUOROELASTOMER COMPOSITION AND HOT AIR HOSE MADE THEREFROM

(57) Abstract: This invention is a curable fluoroelastomer composition comprising a peroxide curable fluoroelastomer, 8 to 25 parts by weight, per hundred parts by weight fluoroelastomer, of carbon black having a nitrogen adsorption specific surface area (N2SA) of 25-130 m²/g and a dibutyl phthalate (DBP) absorption of 50-140 ml/100g, and 0.1 to 8 parts by weight, per hundred parts by weight fluoroelastomer, of a plasticizer having at least one carbon-carbon double bond and at least one ester group.



WO 2013/032571 A1

TITLE OF INVENTION

CURABLE FLUOROELASTOMER COMPOSITION AND HOT AIR HOSE
MADE THEREFROM

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FIELD OF THE INVENTION

This invention pertains to a curable fluoroelastomer composition comprising a peroxide curable fluoroelastomer; carbon black having a nitrogen adsorption specific surface area (N₂SA) of 25-130 m²/g and a
10 dibutyl phthalate (DBP) absorption of 50-140 ml/100g; and a plasticizer having at least one carbon-carbon double bond and at least one ester group.

BACKGROUND OF THE INVENTION

15 Due to tightening emission regulations the proportion of vehicles having turbocharged engines is increasing. Also the temperature to which air ducts are exposed in turbocharged engines is increasing. Fluoroelastomer is typically employed for high temperature air ducts.

Turbocharger hose is subject to repetitive vibration at high
20 temperature during operation. Therefore, the rubber employed in the hose should have sufficient resistance to dynamic fatigue and high temperature. Dynamic fatigue performance is typically estimated by the elongation at break (Eb) at both room temperature and at high temperature. The larger the Eb, the better the fatigue resistance. Eb tends to decrease during
25 static heat aging. Thus, a high initial Eb at room temperature is advantageous in order to ensure adequate performance at high temperatures.

It is possible to make a fluororubber having a high Eb at room temperature of at least 350% by employing a relatively low crosslink
30 density and/or relatively low filler reinforcement. However, it is difficult to obtain the necessary Eb at elevated temperatures by conventional means. Physical properties of rubber at high temperatures are usually governed

by a component of internal energy (i.e. energy elasticity), rather than entropy elasticity. Internal energy is mostly attributable to the filler component.

- 5 Carbon black is the typical reinforcing filler employed in rubber formulations. Relatively low surface area carbon black (e.g. MT, N990) is typically used in fluoroelastomer formulations and the reinforcement effect is typically low. This results in poor Eb performance at high temperatures for fluoroelastomer compounds. Highly reinforcing carbon black (e.g.
10 HAF, N330) improves the high temperature elongation at break. However, the Mooney viscosity of a fluoroelastomer composition containing highly reinforcing black is often too high to easily extrude into a hose.

- Plasticizers are known to decrease the Mooney viscosity of elastomer compositions. However, most plasticizers employed in the
15 rubber industry are fugitive at fluoroelastomer curing temperatures and at the temperatures where turbocharger hoses are employed.

- It would be desirable to have a curable fluoroelastomer composition that yields cured articles having good high temperature Eb and that has a sufficiently low Mooney viscosity to readily process the composition into
20 hose.

SUMMARY OF THE INVENTION

One aspect of the present invention provides a curable fluoroelastomer composition comprising:

- 25 A) peroxide curable fluoroelastomer;
B) 8 to 25 parts by weight, per hundred parts by weight fluoroelastomer, of carbon black having a nitrogen adsorption specific surface area of 25-130 m²/g and a dibutyl phthalate absorption of 50-140 ml/100g;
30 C) 0.1 to 8 parts by weight, per hundred parts by weight fluoroelastomer, of a plasticizer having at least one carbon-carbon double bond and at least one ester group;

D) 0.25 to 2 parts by weight, per hundred parts by weight
fluoroelastomer, of organic peroxide; and

E) 0.3 to 1.3 parts by weight, per hundred parts by weight
5 fluoroelastomer, of a multifunctional coagent.

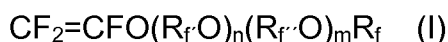
Another aspect of the invention is a hot air hose made from the
above fluoroelastomer composition.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a curable fluoroelastomer
10 composition and to hot air hose made therefrom. By "fluoroelastomer" is
meant an amorphous elastomeric fluoropolymer. The fluoropolymer
contains at least 53 percent by weight fluorine, preferably 63 to 72 wt.%
fluorine. Fluoroelastomers that may be employed in the compositions of
this invention contain between 25 and 70 weight percent, based on the
15 weight of the fluoroelastomer, of copolymerized units of vinylidene fluoride
(VF₂). The remaining units in the fluoroelastomers are comprised of one
or more additional copolymerized monomers, different from said VF₂,
selected from the group consisting of fluorine-containing olefins, fluorine-
containing vinyl ethers, hydrocarbon olefins and mixtures thereof.

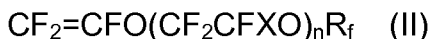
20 Fluorine-containing olefins copolymerizable with the VF₂ include,
but are not limited to, hexafluoropropylene (HFP), tetrafluoroethylene
(TFE), 1,2,3,3,3-pentafluoropropene (1-HPFP), chlorotrifluoroethylene
(CTFE) and vinyl fluoride.

Fluorine-containing vinyl ethers copolymerizable with VF₂ include,
25 but are not limited to perfluoro(alkyl vinyl) ethers. Perfluoro(alkyl vinyl)
ethers (PAVE) suitable for use as monomers include those of the formula



where R_f and R_{f'} are different linear or branched perfluoroalkylene groups
of 2-6 carbon atoms, m and n are independently 0-10, and R_f is a
30 perfluoroalkyl group of 1-6 carbon atoms.

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



where X is F or CF₃, n is 0-5, and R_f is a perfluoroalkyl group of 1-6 carbon atoms.

5 A most preferred class of perfluoro(alkyl vinyl) ethers includes those ethers wherein n is 0 or 1 and 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 R_f is a perfluoroalkyl group having 1-6 carbon atoms, m = 0 or 1, n = 0-5, and Z = F or CF₃. Preferred members of this class are those in which R_f is C₃F₇, m = 0, and n = 1.

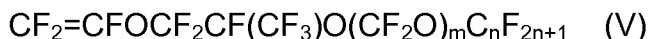
Additional perfluoro(alkyl vinyl) ether monomers include those of
15 the formula



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.

20 Other examples of useful perfluoro(alkyl vinyl) ethers include



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

If copolymerized units of PAVE are present in fluoroelastomers employed in this invention, the PAVE content generally ranges from 25 to
25 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.

Other fluoroelastomers that may be employed in the compositions of the invention comprise copolymers of tetrafluoroethylene and a
30 perfluoro(alkyl vinyl) ether, preferably PMVE. Such fluoroelastomers typically contain between 30 and 55 wt.% copolymerized PMVE units.

The fluoroelastomers employed in the compositions of the present invention are peroxide curable, meaning that they contain iodine and/or bromine cure sites. The source of these cure sites may be a

5 copolymerized cure site monomer and/or the result of polymerization of the fluoroelastomer in the presence of a cure site-containing chain transfer agent.

Examples of suitable cure site monomers include: i) bromine - containing olefins; ii) iodine-containing olefins; iii) bromine-containing vinyl

10 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 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{Br}$; bromotrifluoroethylene; 4-bromo-3,3,4,4-tetrafluorobutene-1 (BTfB); and others such as vinyl bromide, 1-

15 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-

20 perfluoroethyl perfluorovinyl ether and fluorinated compounds of the class $\text{CF}_2\text{Br}-\text{R}_f-\text{O}-\text{CF}=\text{CF}_2$ (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 $\text{ROCFBr}=\text{CF}_2$ (where R is a lower alkyl group or fluoroalkyl group) such as $\text{CH}_3\text{OCF}=\text{CFBr}$ or $\text{CF}_3\text{CH}_2\text{OCF}=\text{CFBr}$.

25 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 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

30 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 $\text{ICH}_2\text{CF}_2\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}=\text{CF}_2$, 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-(vinylloxy)ethane; 2-iodo-1-(perfluorovinylloxy)-1,1,2,2-tetrafluoroethylene; 1,1,2,3,3,3-hexafluoro-2-iodo-1-(perfluorovinylloxy)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.

10 Units of cure site monomer, when present in the fluoroelastomers employed in the 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.%.

 Additionally or alternatively to copolymerized cure site monomers, 15 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 20 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 bound iodine at one or both ends of the polymer molecules. Methylene iodide; 1,4-diiodoperfluoro-n-butane; 25 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; moniodoperfluoroethane; moniodoperfluorobutane; 2-iodo-1- 30 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.

5 Specific fluoroelastomers which may be employed in this invention include, but are not limited to those having at least 53 wt.% fluorine and comprising copolymerized units of i) vinylidene fluoride and hexafluoropropylene; ii) vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, iii) vinylidene fluoride, perfluoro(methyl vinyl) ether and
10 tetrafluoroethylene and iv) tetrafluoroethylene and perfluoro(methyl vinyl) ether. For simplicity, iodine and/or bromine –containing cures sites are not shown on these copolymers. However, it is understood that these fluoroelastomers are peroxide curable so they contain iodine and/or bromine cure sites as described above.

15 The carbon black filler employed in this invention has a specific range of nitrogen adsorption specific surface area (ASTM D-6556) of 25-130 (preferably 25-80) m²/g and a dibutylphthalate absorption (ASTM D-2414) of 50-140 (preferably 90-125) ml/100 g. Examples of such types of carbon black include, but are not limited to HAF (ASTM N330), ISAF
20 (ASTM N220), SAF (ASTM N110), SRF-HS-HM (N774) and FEF (N550). FEF is preferred. Mixtures of various carbon blacks may be employed.

The amount of carbon black employed in the curable compositions of this invention is 8 to 25 (preferably 15 to 20) parts by weight per hundred parts by weight fluoroelastomer.

25 Plasticizers that may be employed in the present invention are those that comprise at least one carbon-carbon double bond and at least one ester group. Typically the plasticizer contains at least one acrylate, methacrylate or ethacrylate group. Specific examples of such plasticizers include, but are not limited to trimethylolpropane trimethacrylate,
30 polyhydric alcohol ethacrylate, polyhydric alcohol methacrylate and polyhydric alcohol acrylate. The amount of plasticizer employed is 0.1 to 8

(preferably 1 to 4) parts by weight plasticizer per hundred parts by weight fluoroelastomer.

Fluoroelastomer, carbon black and plasticizer are combined in an
5 internal mixer (e.g. Banbury®, Kneader or Intermix®). Other ingredients (except for organic peroxide) may also be combined at this time.

The level of curative employed to crosslink the fluoroelastomer compositions employed in this invention is set to balance properties such as elongation at break and compression set. The lower the level of
10 curative, the higher the elongation at break, but low levels of curative cause undesirably high compression set at elevated temperatures.

The level of multifunctional coagent (e.g. triallyl isocyanurate, triallyl cyanurate or trimethallyl isocyanurate) is 0.3-1.3, preferably 0.5-1.0, parts by weight, per hundred parts by weight fluoroelastomer.

15 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-dihydroperoxide; di-t-butyl
20 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.
25 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 level of organic peroxide is 0.25-2, preferably 0.7-1.5, parts by weight, per hundred parts by weight fluoroelastomer.

30 Organic peroxide curative is added to the fluoroelastomer, carbon black, plasticizer mixture at a temperature below 120°C in order to prevent premature vulcanization. Typically, peroxide is added on a roll mill, rather

than in the internal mixer. The resulting curable composition has a Mooney viscosity, ML(1+4) at 100°C, of 80 or less. Mooney viscosity is measured according to JIS K6300.

5 The curable composition is then shaped (e.g. extruded) and cured in order to manufacture the cured hot air hose of the invention. The fluoroelastomer may form the entire hose, or more likely, the inner layer of a multilayer hose. Typical curing conditions are 10 minutes at 180°C in a press, followed by 4 hours at 200°C in an air oven.

10 Optionally, the cured hot air hoses of the invention may contain further ingredients commonly employed in the rubber industry such as process aids, colorants, acid acceptors, etc.

Cured (i.e. crosslinked) hot air hoses of this invention (e.g. turbocharger hoses) have a remarkable balance of heat resistance and mechanical performance. Cured rubber made from the compositions of the invention exhibits elongation at break (Eb) greater than or equal to 120% (preferably $\geq 130\%$) at 230°C. Hardness (Duro A, JIS K6253) at 23°C is 73 to 85 points. The change in hardness after oven heat aging at 230°C for 168 hours (measured according to JIS K6257) is 8 points or less. Compression set after 25% compression at 230°C for 70 hours (large specimen, measured according to JIS K6262) is less than or equal to 70%.

25 The fluoroelastomer compounds described above are also useful in other applications requiring dynamic fatigue resistance at high temperature, e.g. diaphragms.

EXAMPLES

TEST METHODS

30	Mooney viscosity	JIS K6300
	Duro A hardness	JIS K6253
	Tensile properties	JIS K 6251

Compression set

JIS K6262

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

Example 1

Curable compositions of the invention (Samples 1-4) and
comparative compositions (Samples A-F) were made in a 1.0 L Kneader
10 internal mixer. First, fluoroelastomer was added to the mixing chamber
and mixing was begun. After polymer temperature was at least 90°C, the
other ingredients, except for the organic peroxide, were added. Mixing
was at a rotor speed of 40-60 rpm for several minutes. If the temperature
of the composition increased above 130°C, mixing was slowed. The
15 composition was dumped. A band of the composition was then made on a
roll mill and the organic peroxide was added to form a curable
composition.

Formulations are shown in Table I. Mooney viscosities and
physical properties of cured slab sheets are shown in Table II. Slab
20 sheets were press cured at 180°C for 10 minutes, followed by a post cure
in an oven at 200°C for 4 hours.

TABLE I

Formulation, phr ¹	Sample A	Sample 1	Sample 2	Sample 3	Sample 4	Sample B	Sample C	Sample D	Sample E	Sample F
Fluoroelastomer ²	100	100	100	100	100	100	100	100	100	100
MgO	6	6	6	6	6	6	6	6	6	6
MT (N990) ³	20	0	0	0	0	0	0	0	0	0
SRF (N774) ⁴	0	20	0	0	0	0	0	0	0	0
FEF (N550) ⁵	0	0	20	15	0	5	30	15	15	15
HAF (N330) ⁶	0	0	0	0	10	0	0	0	0	0
Process aid ⁷	1	1	1	1	1	1	1	1	1	1
Organic peroxide ⁸	1	1	1	1	1	1	1	1	1	1
Coagent ⁹	1	0.8	0.5	0.8	0.6	1	0.5	0.8	0.8	0.8
Placticizer ¹⁰	3	3	3	3	3	3	3	0	10	0
Placticizer ¹¹	0	0	0	0	0	0	0	0	0	3

¹ parts by weight ingredient per 100 parts by weight rubber, i.e. fluoroelastomer

² Viton® GBL200S available from DuPont

³ Thermax N990 available from Cancarb Ltd.

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- ⁴ Asahi #50 available from Asahi Carbon
⁵ Asahi #60 available from Asahi Carbon
⁶ Asahi #70 available from Asahi Carbon
⁷ HT-290 process aid available from Struktol
⁸ Perhexa 25B40 available from Akzo
⁹ triallyl isocyanurate available as Diak 7 from DuPont
¹⁰ SR350 trimethylolpropane methacrylate, available from Sartomer
¹¹ ADK Cizer RS-735 conventional plasticizer (polyether ester), available from Adeka

TABLE II

	Sample A	Sample 1	Sample 2	Sample 3	Sample 4	Sample B	Sample C	Sample D	Sample E	Sample F
Mooney viscosity, ML(1+4) @100°C	56.4	67.4	79.2	68.8	62.4	53.8	100.9	88.8	39	71.5
Duro A hardness @ 25°C, points	71	78	81	76	73	67	87	72	87	69
Eb @230°C, %	90	120	150	140	170	110	130	100	70	190
Change in hardness after 168 hours @ 230°C, points	+1	+3	+4	+4	+4	-1	+6	+5	-2	+11
Compression set, 70 hours, 230°C, 25% compression, %	37	48	63	48	57	31	77	42	46	98

CLAIMS**WHAT IS CLAIMED IS:**

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1. A curable fluoroelastomer composition comprising:

A) peroxide curable fluoroelastomer;

B) 8 to 25 parts by weight, per hundred parts by weight

fluoroelastomer, of carbon black having a nitrogen adsorption specific
10 surface area of 25-130 m²/g and a dibutyl phthalate absorption of 50-140
ml/100g;

C) 0.1 to 8 parts by weight, per hundred parts by weight
fluoroelastomer, of a plasticizer having at least one carbon-carbon double
bond and at least one ester group;

15 D) 0.25 to 2 parts by weight, per hundred parts by weight
fluoroelastomer, of organic peroxide; and

E) 0.3 to 1.3 parts by weight, per hundred parts by weight
fluoroelastomer, of a multifunctional coagent.

2. The curable composition of claim 1 wherein said plasticizer
20 comprises at least one acrylate selected from the group consisting of
acrylate, methacrylate and ethacrylate.

3. The curable composition of claim 2 wherein said plasticizer
is selected from the group consisting of trimethylolpropane trimethacrylate,
polyhydric alcohol ethacrylate, polyhydric alcohol methacrylate and
25 polyhydric alcohol acrylate.

4. The curable composition of claim 1 wherein said carbon
black is selected from the group consisting of HAF, ISAF SAF, SRF-HS-
HM and FEF.

5. The curable composition of claim 1 having a Mooney
30 viscosity measured according to JIS K6300, ML(1+4) at 100°C, of up to
80.

6. A cured high temperature air hose made from the composition of claim 1.

7. The high temperature air hose of claim 6 having an
5 elongation at break at 230°C, according to JIS K6251, of at least 120%.

8. The high temperature air hose of claim 6 having a Duro A hardness at 23°C, according to JIS K6253, of 73 to 85 points.

9. The high temperature air hose of claim 6 having a change in hardness after oven heat aging at 230°C for 168 hours, measured
10 according to JIS K6257, of 8 points or less.

10. The high temperature air hose of claim 6 having a compression set after 25% compression at 230°C for 70 hours (large specimen, measured according to JIS K6262) of 70% or less.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/044102

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K5/103 C08L15/02 C08L27/12
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.
X,P	US 2012/095151 A1 (TERADA JUNPEI [JP] ET AL) 19 April 2012 (2012-04-19) example 4 paragraph [0181] -----	1-5
A	US 2008/249240 A1 (BANDYOPADHYAY PRADIP K [US]) 9 October 2008 (2008-10-09) paragraphs [0032], [0037]; table 2 -----	1-10
A	EP 0 940 433 A1 (ROHM & HAAS [US]) 8 September 1999 (1999-09-08) paragraphs [0045], [0053]; example 9 -----	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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