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(71) Applicants (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19899 (US). **DOSHI, Shailesh Ratilal** [CA/CA]; 866 Old Colony Road, Kingston, Ontario K7P1S5 (CA).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **NOZAKI, Masahiro** [JP/JP]; B-305 East Suzumi342-1 Hiramatsu, Honchoutsu-nomiya, Tochigi 321-0932 (JP).

(74) Agent: **HAMBY, William H.**; 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: POLYAMIDE COMPOSITIONS FOR THE INNER LAYER OF A MULTI-LAYER TUBULAR ARTICLE AND ARTICLES INCORPORATING SAME

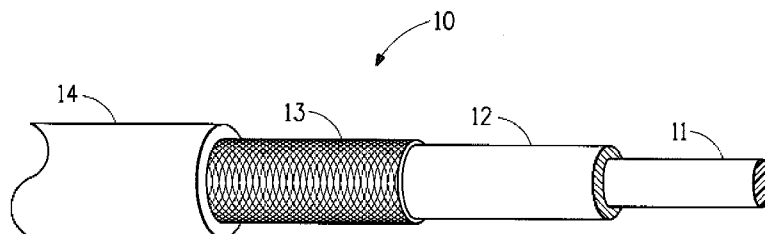


FIG. 1

(57) Abstract: Polyamide compositions suitable for the inner layer of multi-layer tubular articles for circulating a heat transfer fluid composition within a refrigeration or air conditioning system are provided and including articles prepared from these compositions. Such compositions are particularly suitable in air conditioning and refrigeration applications and systems in which new, low global warming potential refrigerant alternatives are used.

POLYAMIDE COMPOSITIONS FOR THE INNER LAYER OF A MULTI-LAYER TUBULAR ARTICLE AND ARTICLES INCORPORATING SAME

Field of the Invention

The present invention relates to polyamide compositions suitable for the
5 inner layer of a multi-layer tubular article for circulating a heat transfer fluid
composition within a refrigeration or air conditioning system and to articles
prepared from these compositions. More particularly, the present invention
relates to constructing hoses in multi layers of which the inner layer is exposed
to a heat transfer fluid composition circulated within said system, made from
10 these compositions.

Background of the Invention

As is widely understood by those having skill in the field, in a typical
refrigeration or air conditioning system heat transfer fluids are circulated within a
closed loop including a compressor, a condenser and an evaporator. Hoses are
15 typically connected between the outlet of the compressor and the inlet of the
condenser; between the outlet of the condenser and the inlet of the evaporator;
and between the outlet of the evaporator and the inlet of the compressor. Such
hoses must be able to withstand the higher pressure of the fluids which are
circulated through such system.

20 Hoses used for these purposes need to be flexible for ease of installation
and use, and often must be shaped into curves and bends for connecting
components already installed into fixed positions. They must also be able to
contain the fluid pressure. These hoses are often made of elastomeric materials

such as natural or synthetic rubber or thermoplastic elastomers, and are typically reinforced with braiding to impart high pressure capability.

Moreover, it is essential that the hoses of such systems offer superior barrier resistance to permeation of the contained fluid through the wall of the hose construction. In addition, the hose wall must provide high barrier resistance to the ingress of external fluids, such as air or moisture, into the contained fluid.⁴

In order to meet barrier requirements, hoses are often provided with a suitable thermoplastic barrier layer on the inside. A typical high pressure barrier hose may thus consist of multiple layers—an inner thermoplastic barrier layer made of a polyamide, an over-layer of an elastomeric material to provide flexibility; and a braid layer over the elastomeric layer to provide pressure capability and an outer protective cover layer of an elastomeric material.

Further environmental regulations may ultimately cause global phase out of certain HFC refrigerants. Currently, the automobile industry is facing regulations relating to global warming potential (GWP) for refrigerants used in mobile air-conditioning. Therefore, there is a great current need to identify new refrigerants with reduced global warming potential for the automobile air-conditioning market. Should the regulations be more broadly applied in the future, an even greater need will be felt for refrigerants that can be used in all areas of the refrigeration and air-conditioning industry. The inner barrier layer has commonly used polyamide 6 based resin containing elastomeric material and copper compounds as a nylon heat stabilizer to obtain higher refrigerant barrier, flexural properties and long term durability of the layer.

However because of development of low GWP refrigerants, conventional polyamide layer materials do not sustain over the expected whole automotive life due to crack generation on the surface by degradation of the nylon polymer. A need exists for polyamides which are suitable for use with new, low GWP refrigerants without cracking and degradation even when exposed to low GWP.

The introduction of hindered-phenol type anti-oxidants into the conventional polyamide inner layer material surprisingly improves the durability of the polyamide inner layer.

Brief description of the Drawing

FIG 1 a perspective view in partial cross-section of one of the multi-layer tubular articles of the invention for circulating a heat transfer fluid composition within a refrigeration or air conditioning system

Summary of the Invention

There is disclosed and claimed herein a polyamide composition for an inner layer of a multi-layer tubular article useful for circulating a heat transfer fluid composition within a refrigeration or air conditioning system, comprising : a) 50 to 90 weight percent of one or more polyamides; b) 10 to 50 weight percent of toughener polymerized from alpha olefin monomers, diene monomers, or mixtures thereof; c) 0.05 to 8 weight percent of one or more hindered phenol antioxidants; d) 0 to 15 weight percent of plastizer, said weight percentages based on total weight of composition, and e) a copper-based heat stabilizer with a content of copper in the range of 40 to 1500 ppm, wherein said heat transfer

fluid composition comprises a compound selected from the group consisting of :
R32, R152a, Cf3I, 1234yf, 1225ye and trans-1234ze.

Weight percentages are based on the total weight of the composition.

Moreover component (b) in a preferred embodiment may be selected from the
5 group consisting of rubber polyethylene, and ionomeric copolymer.

Detailed Description of the Invention

Having reference to Figure 1, there is shown a perspective cut-away view
of a hose for circulating a heat transfer fluid composition within a refrigeration or
10 air conditioning system. A typical high pressure barrier hose 10 is comprised of
an inner thermoplastic barrier layer 11 surrounded by an over-layer 12 of
elastomeric material to provide flexible, that is surrounded by a braid layer 13 to
provide pressure capability, that is in turn surrounded by an outer protective
cover layer 14.

15 An aspect of the present invention provides a polyamide composition for
an inner layer of a multi-layer tubular article useful for circulating a heat transfer
fluid composition within a refrigeration or air conditioning systems which is
suitable for use with HFC refrigerants, having a global warming potential of less
than 1000.

20 A further aspect of the present invention relates to a hose for circulating a
heat transfer fluid composition within the refrigeration or air conditioning system,
which comprises a) an inner thermoplastic barrier layer; b) an over-layer which is
positioned over the inner thermoplastic barrier layer; c) a braid layer that is

positioned over the over-layer; and d) an outer layer that is positioned over the braid layer.

Further this hose would not require the use of aggressive chemicals such as bonding techniques which was conventionally used to fabricate high pressure barrier hoses using a metallic tube, would be economical to make, and would meet stringent barrier requirements. The HFC refrigerants are available commercially or may be prepared by processes known in the art as described in U.S. Patent 7,914,698, incorporated by reference.

So long as they do not affect the advantageous performances of the ingredients (a) – (d) above, other ingredients may be present in the compositions of the invention. The other ingredients include but are not limited to, lubricants, plasticizer, anti oxidants, UV stabilizers, impact modifiers, inorganic filler, and fiberform reinforcement agent other than glass fiber.

The compositions of the present invention are melt-mixed blends. Any melt-blending method may be used to prepare the compositions. For example, the polymeric components and non-polymeric ingredients may be added to a melt mixer, such as, for example, a single or twin-screw extruder; a blender; a kneader; or a Banbury mixer, either all at once through a single step addition, or in a stepwise fashion, and then melt-mixed. When adding the polymeric components and non-polymeric ingredients in a stepwise fashion, part of the polymeric components and/or non-polymeric ingredients are first added and melt-mixed with the remaining polymeric components and then with the non-polymeric ingredients being subsequently added and further melt-mixed until a well-mixed composition is obtained.

Polyamides used in the composition of the present invention are well known to those skilled in the art. Polyamide can be semicrystalline polyamide, which is well known to one skilled in the art such as those produced from lactams or amino acids or from condensation of diamines such as
5 hexamethylene diamine with dibasic acids such as sebacic acid. Copolymers and terpolymers of these polyamides are also included. Examples include, but are not limited to, polyepsilon-caprolactam (nylon-6), polyhexamethylene adipamide (nylon-66), nylon-11, nylon-12, nylon-12,12, nylon-6/66, nylon-6/610, nylon-6/12, nylon-66/12, nylon-6/66/610, nylon-6/6T, and combinations of two or
10 more thereof. Frequently used polyamides are nylon 6,.

The composition of the present invention incorporates from 15 wt % percent to 50 wt% of toughener, more preferably from 20 wt% to 40 wt%, based on the total weight of the composition. If the amount of toughener is within this range, the composition can be easily processed as a film into a variety of article
15 with an acceptable level of toughness. As toughener (also referred to as impact modifier), in general, elastomers can be used. Useful elastomers include an elastomer consisting of ethylene- α -olefin, an elastomer consisting of ethylene-propylene-diene. an elastomer consisting of ethylene-unsaturated carboxylic acid, an elastomer consisting of ethylene-unsaturated carboxylic acid
20 ester, an elastomer consisting of ethylene-unsaturated carboxylic acid-unsaturated carboxylic acid ester, an elastomer consisting of α -olefin-unsaturated carboxylic acid, an elastomer consisting of cc-olefin-unsaturated carboxylic acid ester, an elastomer consisting of α -olefin-unsaturated carboxylic acid-unsaturated carboxylic acid ester, an

elastomer consisting of α -olefin-unsaturated carboxylic acid-unsaturated carboxylic acid ester; and graft modified materials of the above-mentioned elastomers. Two or more of unmodified elastomers or modified elastomers may also be blended. At least one of the above-mentioned unmodified elastomers and at least one of the above-mentioned modified elastomers may also be blended. Preferably, an elastomer consisting essentially of ethylene-propylene-diene modified with carboxylic acid-carboxylic acid anhydride can be used. The elastomer consisting essentially of ethylene-propylene-dienes modified with carboxylic acid-carboxylic acid anhydride, may be, for example, a mixture of ethylene/propylene/1,4-hexadiene-g-maleic anhydride/ethylene/propylene/1,4-hexadiene and ethylene/maleic anhydride; a mixture of ethylene/propylene/1,4-hexadiene and ethylene/propylene/1,4-hexadiene-g-maleic anhydride; ethylene/propylene/1,4-hexadiene/norbomadiene-g-maleic anhydride fumaric acid; ethylene/1,4-hexadiene/norbomadiene-g-maleic anhydride monoethyl ester; ethylene/propylene/1,4-hexadiene/norbomadiene-g-fumaric acid; a mixture of ethylene/propylene/1,4-hexadiene and ethylene/monoethyl ester of maleic anhydride; a mixture of ethylene/propylene/1,4-hexadiene and ethylene/maleic acid monobutyl ester; a mixture of ethylene/propylene/1,4-hexadiene and ethylene/maleic anhydride, etc. Furthermore, polyethylene, polypropylene and other polyolefins and their copolymers, and styrene-type elastomers can also be appropriately used as impact modifiers.

The polyamide composition of this invention may contain up to 15 weight percent (and preferably about 6 weight percent) of plastizer, based on total weight of the composition.

The polyamide composition of this invention contains an essential
5 copper based thermal stabilizer. The copper based thermal stabilizer will preferably be present in the range of from 15 wt% to 50 wt%, based on the total weight of the composition. Examples of such thermal stabilizers are those containing copper in which the copper content is preferably 40 to 1500 ppm, more preferably 70 to 800ppm. If the content of copper is not greater than 40
10 ppm, the durability of the formed film can be lower, resulting into raising crack problem. If the content of copper is greater than 1500 ppm, the formed film can be brittle, resulting into not being of acceptable durability.

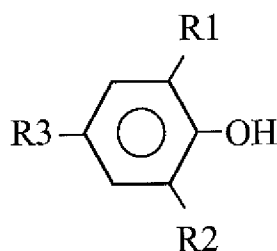
The polyamide composition of this invention comprises copper-based heat stabilizer (e.g., in a form of copper salt or copper salt derivatives such as for
15 example copper iodide, copper bromide or copper halides or derivatives thereof, or mixtures thereof). Copper(I) salts are preferred. Examples of the heat stabilizer include without limitation copper iodide, copper bromide, copper chloride, copper fluoride; copper thiocyanate, copper nitrate, copper acetate, copper naphthenate, copper caprate, copper laurate, copper stearate, copper
20 acetylacetonate; copper oxide. Preferably, the heat stabilizer is copper halide being selected from the group consisting of copper iodide, copper bromide, copper chloride, and copper fluoride, and still preferably, is copper iodide, and more preferably copper (I) iodide.

A copper halide such as copper iodide such as CuI-KI stabilizer or copper bromide is particularly desirable. An alkyl halogen compound is ordinarily added as an auxiliary thermal stabilizer.

In another embodiment the polyamide composition of this invention may further comprise 0.004 to 5.0 weight % of an metal halide salt in combination with LiI, NaI, KI, MgI₂, KBr, or CaI₂ as the heat stabilizer, the weight percent being based on the total weight of the polyamide composition. When present, the metal halide is preferably KI or KBr.

In order to provide such level of copper content in the polyamide composition of the invention, the stabilizer is present in the range of from about 0.1 weight % to about 4%.

Hindered phenol anti oxidants (also referred to as hindered phenol stabilizer) comprised in the polyamide composition of this invention, to hinder thermally induced oxidation of polyamide where high temperature applications are used, are chemical compounds containing the following functionality groups in the chemical structure.



R1 and R3 are composed of hydrocarbon group, such as methyl, ethyl, propyl, butyl, t-butyl and others. R2 is either hydrogen or other organic compounds. Examples materials are di-butyl hydroxyl benzene (BHT), Irganox® 1010,

Irganox® 1098, Irganox ®245 (commercially available from Chiba under the trademark Irganox®), Adekastab AO-80 (commercially available from Asahi Denka Kogyo) or other hindered phenol antioxidants.

The hindered phenol stabilizer content is preferably in an amount from 5 0.05 weight % to 8 weight % and preferably from 0.1 to 5 weight percent, the weight percent being based on the total weight of the polyamide composition. If the content of the hindered phenol stabilizer is not greater than 0.05 weight %, the durability of the formed film can be insufficient because of loss of Mw. If the content of the hindered phenol stabilizer is greater than 8 weight % , it is difficult 10 to produce a compounded resin due to sever surging and strand breakage.

Any conventional method can be used for making the hoses of the invention including the inner thermoplastic barrier layer, the over-layer of elastomeric materials and the braid layer. For instance, one common technique 15 involves disposing the inner thermoplastic barrier layer, the over-layer of elastomeric materials and the braid layer on a mandrel in this order and curing and adhering these layers by press vulcanization, steam vulcanization, oven vulcanization (hot air vulcanization) or hot water vulcanization under the condition of 130 to 180 degree C and 30 to 120 minutes.

20 It is readily apparent to those having skill in the art to which this invention pertains that in addition to the materials mentioned herein, a variety of other materials are suitable for each layer as is well known and understood. Likewise, representative thicknesses of each layer and techniques for braiding are already

well appreciated by those having skill in the field, and are selected according to the intended application.

In accordance with the method of the present invention, the heat transfer fluid composition comprises a compound selected from the group consisting of:

5 R32, R152a, CF₃I, 1234yf, 1225ye and trans-1234ze.

Examples

The invention will become better understood upon having reference to the Examples herein. These examples and the comparative example to the
10 invention are given below by way of illustration, and not by way of limitation.

Example 1 to 3 and Comparative Example 1

The components shown in Table 1 were blended at a ratio (parts by weight) shown in Table 1 to prepare polyamide compositions for the inner layer
15 of a multi-layer tubular article suitable for circulating a heat transfer fluid composition within a refrigeration or air conditioning system.

Each composition was inject-molded into 5mm(w) x 50mm (h) x 1mm (t) test bars. The molded test bars were put in the glass tube with approximately 10mm diameter and 100mm height capable to be pulled vacuum and heat
20 sealed.

Measurement of Weight Average Molecular Weight (Mw)

The weigh average molecular weight (Mw) was determined by gel permeation chromatography (GPC) method using the following apparatus and the conditions specified below.

Measure Mw of Polyamide 6 by GPC (Shodex, manufactured by Showa Denko Co.) dissolved in HFIP (hexafluoroisopropyl alcohol) (0.1% polyamide solution) with Shodex GPC HFIP 606Mx2 column (as isolation column) for analysis.

- 5 The shield aging test was made to measure the retention of Mw of the composition of the present invention before and after being subjected to the test . The results are shown in Tables 1 and 2.

a) Shield aging test

Test bars : Injection molded test bar with 5mm(w) x 50mm (h) x 1mm

(t)

Put the bar in the glass tube with approxi. 10mm diameter and 100mm high. capb be pulled vacuum and heat sealed.

Load 3.5 grams oil (Apollo PS-46 PAG oil) in each tube.

Load 1.75 g refrigerant (1234yf) after the tube is pulled vacuum.

Further load 760mm Hg air in the tube, and then sealed the tube.

Aged at 150C x 6 days in an oven

- 10 In addition, the properties of the polyamide compositions of the present invention corresponding to basic requirements from constructing hoses described herein are measured by the following procedures.

- b) Melt viscosity measured on Kayness viscometer at 280C and 1000 sec⁻¹ shear rate after 5min. hold-up at 280C.
 - c) Notched charpy impact strength measured based on ISO 179.
 - d) Elongation and elongation after air oven aging (AOA). Elongation is
- 5 measured based on ISO 527. The bars are aged in a dry oven at 150 °C for 250
500 hours and the elongation is subsequently measured.
- All properties' are summarized on the Tables 1 and 2.

Table 1

	Exp.1	Exp.2	Exp.3	Comp.1
PA6 (RV 90)	70.7	70.7	70.7	71.7
MHA-EPDM rubber	28	28	28	28
Cu heat stabilizer	0.3	0.3	0.3	0.3
Cu in the stabilizer (ppm)	120	120	120	120
AO-80	1.0			
Irganox 245		1.0		
Irganox 1010			1.0	
PA6 Mw Initial	72000	74000	72000	74000
PA6 Mw after shield aging test	19000	16000	19000	12000
% retention of Mw	26	22	26	16
Melt viscosity (Pa.sec)	210	200	210	230
N-Charpy impact strength (kJ/m ²)	88	87	85	86
Elongation (%)	>200	>200	>200	>200
Elongation after air oven aging (%)	32	30	32	35

Table 2

	Exp.4	Exp.5	Exp.6	Exp.7
PA6 (RV 90)	83.7	78.7	58.7	48.7
MHA-EPDM rubber (%)	15	20	40	50
Cu heat stabilizer (%)	0.3	0.3	0.3	0.3
Cu in the stabilizer (ppm)	120	120	120	120
AO-80 (%)	1	1	1	1
PA6 Mw Initial	73000	74000	72000	74000
PA6 Mw after shield aging test	19000	22000	25000	22000
Retention of Mw (%)	26	30	35	30
Melt viscosity (Pa.sec)	206	221	268	302
N-Charpy impact strength (kJ/m ²)	70	71	109	68
Elongation (%)	>200	>200	>200	>200
Elongation after air oven aging (%)	29	27	62	27

	Comp. 2	Comp. 3	Exp. 8	Exp. 9
PA6 (RV 90)	88.7	43.7	70.9	70.83
MHA-EPDM rubber (%)	10	55	28	28

Cu heat stabilizer (%)	0.3	0.3	0.1	0.17
Cu in the stabilizer (ppm)	120	120	39	67
AO-80 (%)	1	1	1	1
PA6 Mw Initial	72000		73000	73000
PA6 Mw after shield aging test	18000		23000	22000
Retention of Mw (%)	25		32	30
Melt viscosity (Pa.sec)	130		202	257
N-Charpy impact strength (kJ/m ²)	28		87	82
Elongation (%)	>200		>200	>200
Elongation after air oven aging (%)	26		25	30

	Exp. 10	Exp. 11	Comp. 4	Comp. 5
PA6 (RV 90)	69	68.3	70.95	66
MHA-EPDM rubber (%)	28	28	28	28
Cu heat stabilizer (%)	2	2.7	0.05	5
Cu in the stabilizer (ppm)	800	1100	20	1960
AO-80 (%)	1	1	1	1

PA6 Mw Initial	72000	74000	74000	73000
PA6 Mw after shield aging test	22000	21000	20000	16000
Retention oif Mw (%)	31	28	27	22
Melt viscosity (Pa.sec)	231	227	206	160
N-Charpy impact strength (kJ/m2)	90	92	87	79
Elongation (%)	>200	>200	>200	>200
Elongation after air oven aging (%)	43	33	14	19

	Exp.12	Exp.13	Exp.14	Exp.15	Comp. 6
PA6 (RV 90)	71.65	71.6	66.7	64.7	62.7
MHA-EPDM rubber (%)	28	28	28	28	28
Cu heat stabilizer (%)	0.3	0.3	0.3	0.3	0.3
Cu in the stabilizer (ppm)	120	120	120	120	120
AO-80 (%)	0.05	0.1	5	7	9
PA6 Mw Initial	72000	74000	72000	74000	

PA6 Mw after shield aging test	19000	20000	20000	23000	
Retention of Mw (%)	26	27	28	31	
Melt viscosity (Pa.sec)	225	216	200	200	
N-Charpy impact strength (kJ/m ²)	87	85	75	88	
Elongation (%)	>200	>200	>200	> 200	
Elongation after air oven aging (%)	49	38	29	31	

The various components of

Tables 1 and 2 are as follows:

Ingredients

PA6 (RV90) : Unextracted Polyamide 6 with RV 90 measured in formic acid (ASTM D1

MHA-EPDM rubber : maleic anhydride modified EPDM

Cu stabilizer : Mixture of CuI/ KI

AO-80 : Hindered phenolic antioxidant supplied by

ADEKA

Irganox 245 : Hindered phenol antioxidant supplied by BASF

Irganox 1010EP: Hindered phenol antioxidant supplied by BASF

As shown in Tables 1 and 2, the samples comprising toughener and copper based heat stabilizer within the ranges meet with the requirements from constructing hoses for the applications, i.e. melt viscosity, n-charpy impact strength, and retention of elongation after air oven aging, respectively, as
5 compared with the comparative examples.

Claims

What is claimed is:

1. A polyamide composition for an inner thermoplastic barrier layer of a
5 multi-layer tubular article for circulating a heat transfer fluid composition within a
refrigeration or air conditioning system comprising, a) 30 to 90 weight percent of
one or more polyamides; b) 10 to 50 weight percent of toughener polymerized
from alpha olefin monomers, diene monomers, or mixtures thereof; c) 0.05 to 8
weight percent of one or more hindered phenol antioxidants; d) 0 to 15 weight
10 percent of plastizer, said weight percentages based on total weight of
composition; and e) a copper-based heat stabilizer with a content of copper in
the range of 40 to 1500 ppm, wherein said heat transfer fluid composition
comprises a compound selected from the group consisting of: R32, R152a, Cf3I,
1234yf, 1225ye and trans-1234ze.
- 15 2. The polyamide composition to claim 1, where the polyamide is
polyepsiloncaprolactam (nylon 6)
3. A hose for circulating a heat transfer fluid composition within a refrigeration or
air conditioning system, comprising a) an inner thermoplastic barrier layer; b) an
over-layer which is positioned over the inner thermoplastic barrier layer; c) a
20 braid layer that is positioned over the over-layer; d) an outer layer that is
positioned over the braid layer, wherein the inner thermoplastic barrier layer is
formed from the composition of claim 1 or 2, and said heat transfer fluid
composition comprises a compound selected from the group consisting of: R32,
R152a, Cf3I, 1234yf, 1225ye and trans-1234ze.

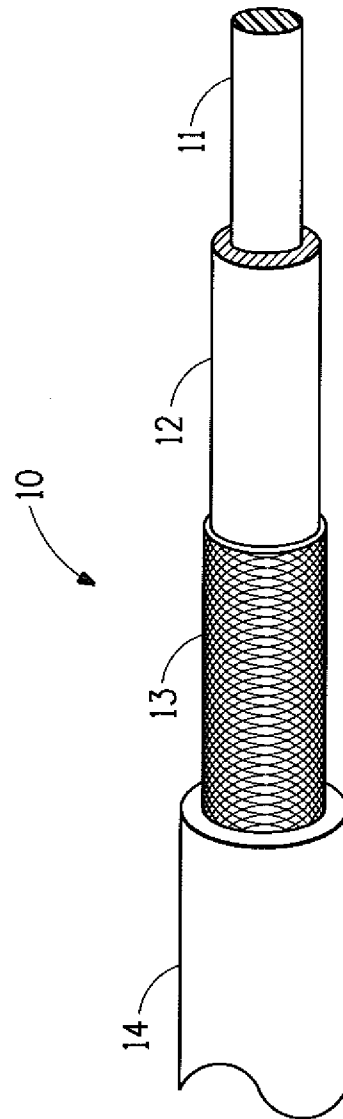


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/036432

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08L77/00 C08L77/02 C08L23/16 F16L11/04 B32B27/34
B32B27/32 B60H1/00

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)

C08L F16L B32B B60H

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	US 2010/028580 A1 (PALMER ROBERT J [FR] ET AL) 4 February 2010 (2010-02-04)	1,2
Y	example 2 page 8, paragraphs 117,134	3
X	JP 61 296079 A (UBE INDUSTRIES) 26 December 1986 (1986-12-26)	1,2
Y	page 623; example 8; table 1	3
X	US 6 518 341 B1 (HURLEY JAMES M [US] ET AL) 11 February 2003 (2003-02-11)	1,2
Y	column 15; example 3; table 2 column 13, line 26 - line 62	3
X	US 4 880 036 A (KITAMI TETSU [JP] ET AL) 14 November 1989 (1989-11-14)	3
Y	claim 1	3
A	example 1; table 3	1,2
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Barrère, Matthieu

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/036432

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 264 262 A (IGARASHI ICHIRO [JP]) 23 November 1993 (1993-11-23)	3
Y	example 1	3
A		1,2

X	WO 2010/110419 A1 (BRIDGESTONE CORP [JP]; KAWAI ATSUSHI [JP]; TSUNODA KATSUHIKO [JP]; AOK) 30 September 2010 (2010-09-30)	3
Y	claim 8	3
A	page 25; example 5	1,2

A	JP 2010 091051 A (BRIDGESTONE CORP) 22 April 2010 (2010-04-22) page 11, line 1 - line 3	1-3

X,P	WO 2011/084421 A1 (DU PONT [US]; DOSHI SHAILESH [CA]) 14 July 2011 (2011-07-14)	1
A,P	page 22; example E1; table 1	2,3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/036432

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 2010028580	A1	04-02-2010	CA	2725384 A1		04-02-2010
			CA	2726010 A1		04-02-2010
			CN	102112525 A		29-06-2011
			CN	102112526 A		29-06-2011
			CN	102112527 A		29-06-2011
			CN	102112545 A		29-06-2011
			CN	102112549 A		29-06-2011
			CN	102112550 A		29-06-2011
			CN	102112551 A		29-06-2011
			EP	2307480 A1		13-04-2011
			EP	2307481 A1		13-04-2011
			EP	2307482 A1		13-04-2011
			EP	2307499 A2		13-04-2011
			EP	2307502 A1		13-04-2011
			EP	2307503 A1		13-04-2011
			EP	2307504 A1		13-04-2011
			JP	2011529986 A		15-12-2011
			JP	2011529987 A		15-12-2011
			JP	2011529988 A		15-12-2011
			JP	2011529989 A		15-12-2011
			JP	2011529990 A		15-12-2011
			JP	2011529991 A		15-12-2011
			JP	2011529993 A		15-12-2011
			KR	20110032001 A		29-03-2011
			KR	20110042091 A		22-04-2011
			US	2010028580 A1		04-02-2010
			US	2010028581 A1		04-02-2010
			US	2010029815 A1		04-02-2010
			US	2010029819 A1		04-02-2010
			US	2010029820 A1		04-02-2010
			US	2010029821 A1		04-02-2010
			US	2010029837 A1		04-02-2010
			WO	2010014785 A1		04-02-2010
			WO	2010014790 A1		04-02-2010
			WO	2010014791 A1		04-02-2010
			WO	2010014795 A1		04-02-2010
			WO	2010014796 A2		04-02-2010
			WO	2010014801 A1		04-02-2010
			WO	2010014810 A1		04-02-2010

JP 61296079	A	26-12-1986	JP	1622789 C		25-10-1991
			JP	2050150 B		01-11-1990
			JP	61296079 A		26-12-1986

US 6518341	B1	11-02-2003	AT	255619 T		15-12-2003
			AU	5612300 A		09-01-2001
			CA	2377494 A1		28-12-2000
			DE	60006968 D1		15-01-2004
			DE	60006968 T2		21-10-2004
			EP	1198520 A1		24-04-2002
			ES	2211563 T3		16-07-2004
			JP	4683802 B2		18-05-2011
			JP	2003503534 A		28-01-2003
			JP	2011012283 A		20-01-2011
			US	6518341 B1		11-02-2003
			WO	0078869 A1		28-12-2000

US 4880036	A	14-11-1989	DE	3739089 A1		26-05-1988

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/036432

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		JP 1863023 C	08-08-1994
		JP 5070759 B	05-10-1993
		JP 63125885 A	30-05-1988
		US 4880036 A	14-11-1989

US 5264262 A	23-11-1993	DE 69128081 D1	04-12-1997
		DE 69128081 T2	12-03-1998
		EP 0529136 A1	03-03-1993
		EP 0638750 A2	15-02-1995
		US 5264262 A	23-11-1993

WO 2010110419 A1	30-09-2010	CN 102365488 A	29-02-2012
		EP 2413010 A1	01-02-2012
		US 2012021157 A1	26-01-2012
		WO 2010110419 A1	30-09-2010

JP 2010091051 A	22-04-2010	NONE	

WO 2011084421 A1	14-07-2011	US 2011155359 A1	30-06-2011
		WO 2011084421 A1	14-07-2011
