



Office de la Propriété

Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2360169 A1 2000/08/03

(21) **2 360 169**

(12) **DEMANDE DE BREVET CANADIEN**
CANADIAN PATENT APPLICATION

(13) **A1**

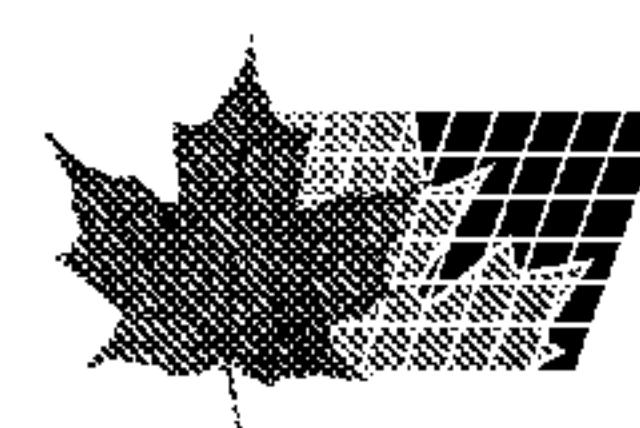
(86) Date de dépôt PCT/PCT Filing Date: 1999/06/03
(87) Date publication PCT/PCT Publication Date: 2000/08/03
(85) Entrée phase nationale/National Entry: 2001/07/11
(86) N° demande PCT/PCT Application No.: US 99/12359
(87) N° publication PCT/PCT Publication No.: WO 00/44829
(30) Priorité/Priority: 1999/01/29 (09/240,450) US

(51) Cl.Int.⁷/Int.Cl.⁷ C08L 23/02, C08L 27/12, C08L 71/02
(71) Demandeur/Applicant:
DYNEON LLC, US
(72) Inventeur/Inventor:
WOODS, SUSAN S., US
(74) Agent: SMART & BIGGAR

(54) Titre : POLYMER THERMOPLASTIQUE A ADDITIF DE TRAITEMENT FLUOROTHERMOPLASTIQUE
(54) Title: THERMOPLASTIC POLYMER WITH A FLUOROTHERMOPLASTIC PROCESSING ADDITIVE

(57) Abrégé/Abstract:

A polymer processing aid composition, a melt processable thermoplastic hydrocarbon polymer composition that uses the polymer processing aid, and a method of improving the melt processability of a thermoplastic hydrocarbon polymer are provided. The polymer processing aid composition comprises a major amount of a fluorothermoplastic polymer that comprises interpolymerized units derived from vinylidene fluoride, at least one ethylenically unsaturated copolymerizable fluorinated monomer, and, optionally, at least one low molecular weight non-fluorinated olefin monomer.





PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08L 23/02 // (C08L 23/02, 71:02, 27:12)		A1	(11) International Publication Number: WO 00/44829
			(43) International Publication Date: 3 August 2000 (03.08.00)
(21) International Application Number:	PCT/US99/12359	(81) Designated States:	AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(22) International Filing Date:	3 June 1999 (03.06.99)		
(30) Priority Data:	09/240,450 29 January 1999 (29.01.99)	US	
(71) Applicant:	DYNEON LLC [US/US]; 6744 33rd Street North, Oakdale, MN 55128-3624 (US).		
(72) Inventor:	WOODS, Susan, S.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		
(74) Agent:	LILLY, James, V.; Chief Intellectual Property Counsel, Dyneon LLC, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).		

(54) Title: THERMOPLASTIC POLYMER WITH A FLUOROTHERMOPLASTIC PROCESSING ADDITIVE

(57) Abstract

A polymer processing aid composition, a melt processable thermoplastic hydrocarbon polymer composition that uses the polymer processing aid, and a method of improving the melt processability of a thermoplastic hydrocarbon polymer are provided. The polymer processing aid composition comprises a major amount of a fluorothermoplastic polymer that comprises interpolymerized units derived from vinylidene fluoride, at least one ethylenically unsaturated copolymerizable fluorinated monomer, and, optionally, at least one low molecular weight non-fluorinated olefin monomer.

THERMOPLASTIC POLYMER WITH A FLUOROTHERMOPLASTIC PROCESSING ADDITIVE

5

FIELD OF THE INVENTION

10 This invention relates to a polymer processing additive that employs a tetrafluoroethylene copolymer and a poly(oxyalkylene) polymer, melt processable thermoplastic compositions that utilize this polymer processing additive, and methods of improving the melt processability of thermoplastic hydrocarbon polymers.

15 **BACKGROUND**

For any melt processable thermoplastic polymer composition, there exists a critical shear rate above which the surface of the extrudate becomes rough and below which the extrudate will be smooth. See, for example, R. F. Westover, *Melt Extrusion*, Encyclopedia of Polymer Science and Technology, Vol. 8, pp 573-81 (John Wiley & Sons 1968). The desire 20 for a smooth extrudate surface competes, and must be optimized with respect to, the economic advantages of extruding a polymer composition at the fastest possible speed (i.e. at high shear rates).

Some of the various types of extrudate roughness and distortion observed in high and low density polyethylenes are described by A. Rudin, et al., *Fluorocarbon Elastomer Aids Polyolefin Extrusion*, Plastics Engineering, March 1986, at 63-66. The authors state that for a given set of processing conditions and die geometry, a critical shear stress exists above which polyolefins such as linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and polypropylene suffer melt defects. At low shear rates, defects may take the form of "sharkskin", a loss of surface gloss, that in more serious manifestations appears as 25 ridges running more or less transverse to the extrusion direction. At higher rates, the extrudate can undergo "continuous melt fracture" becoming grossly distorted. At rates lower than those at which continuous melt fracture is first observed, LLDPE and HDPE can also 30 suffer from "cyclic melt fracture", in which the extrudate surface varies from smooth to

rough. The authors state further that lowering the shear stress by adjusting the processing conditions or changing the die configuration can avoid these defects to a limited extent, but not without creating an entirely new set of problems. For example, extrusion at a higher temperature can result in weaker bubble walls in tubular film extrusion, and a wider die gap 5 can affect film orientation.

Certain fluorocarbon processing aids are known to partially alleviate melt defects in extrudable thermoplastic hydrocarbon polymers and allow for faster, more efficient extrusion. U.S. Pat. No. 3,125,547 to Blatz, for example, first described the use of fluorocarbon polymer process aids with melt-extrudable hydrocarbon polymers wherein the fluorinated polymers 10 are homopolymers and copolymers of fluorinated olefins having an atomic fluorine to carbon ratio of at least 1:2 and wherein the fluorocarbon polymers have melt flow characteristics similar to that of the hydrocarbon polymers.

U.S. Pat. No. 4,904,735 (Chapman, Jr. et al.) describes a fluorinated processing aid for use with a difficultly melt-processable polymer comprising (1) a fluorocarbon copolymer 15 which at the melt-processing temperature of the difficultly melt-processable polymer is either in a melted form if crystalline, or is above its glass transition temperature if amorphous, and (2) at least one tetrafluoroethylene homopolymer or copolymer of tetrafluoroethylene and at least one monomer copolymerizable therewith wherein the mole ratio is at least 1:1, and which is solid at the melt-processable temperature of the difficultly melt-processable 20 polymer.

U.S. Pat. No. 5,397,897 to Morgan et al. Describes the use of copolymers of tetrafluoroethylene and hexafluoropropylene having high hexafluoropropylene content as processing aids in polyolefins.

U.S. Pat. Nos. 5,064,594 to Priester et al., and 5,132,368 to Chapman, Jr. et al. 25 describe the use of certain fluoropolymer process aids containing functional polymer chain end groups including -COF, -SO₂F, -SO₂Cl, SO₃M, -OSO₃M, and -COOM, wherein M is hydrogen, a metal cation, or a quaternary ammonium cation for use with a difficultly melt-processable polymer.

U.S. Pat. No. 5,464,904 to Chapman et al. discloses the use of a copolymer of 30 tetrafluoroethylene and hexafluoropropylene with a polyolefin. The copolymer is partially crystalline, contains no more than 2% by weight hydrogen, has a melt viscosity of from

06. April 2001

0.1x10³ to 20x10³ Pa.s, and has an end of crystalline melting (T_m (end)) of from 170° C to 265° C. The only enhancement of melt-processability described in this patent is shown in Example 25 where a concentration of 1000 ppm of the fluoropolymer in linear low density polyethylene is said to reduce the extrusion pressure of the extrudable composition. There is no showing of a reduction in melt defects.

U.S. Pat. Nos. 5,015,693 and 4,855,013 to Duchesne and Johnson disclose the use of a combination of a poly(oxyalkylene) polymer and a fluorocarbon polymer as a processing additive for thermoplastic hydrocarbon polymers. The poly(oxyalkylene) polymer and the fluorocarbon polymer are used at such relative concentrations and proportions as to reduce the occurrence of melt defects during extrusion. Generally the concentration of the fluoropolymer is present at a level of from 0.005 to 0.2 weight percent of the final extrudate and the poly(oxyalkylene) polymer is present at a level of from 0.01 to 0.8 weight percent of the final extrudate. Preferably, the weight of the fluorocarbon polymer in the extrudate and the weight of the poly(oxyalkylene) polymer in the extrudate are in a ratio of 1:1 to 1:10.

U.S. Patent No. 5,527,858 to Blong and Lavallée discloses a melt processable fluoroplastic composition that comprises a melt processable fluoroplastic polymer and a minor amount (i.e., less than 20% by weight) of a poly(oxyalkylene) polymer. The fluoroplastic polymer comprises interpolymerized units derived from vinylidene fluoride and at least one ethylenically unsaturated copolymerizable, fluorinated monomer. By combining the poly(oxyalkylene) polymer with the fluoroplastic polymer, the fluoroplastic polymer can be melt processed at relatively low melt temperatures to form extrudates such as fuel line hoses or tubing. This is achieved without the need to modify the chemical structure of the fluoropolymer, to raise the melt-processing temperature, or to extrude at lower line speeds or shear rates. [page 3a]

It has been discovered that mixing a composition comprising a fluorothermoplastic polymer and a poly(oxyalkylene) polymer with a melt processable thermoplastic hydrocarbon polymer is surprisingly effective in reducing melt defects such as sharkskin in thermoplastic hydrocarbon polymers, especially polyolefins, or in postponing these defects to higher extrusion rates than can be typically achieved without the use of such a composition. These results are achieved without alteration of the chemical structure of the thermoplastic polymer and without the need for resorting to conventional methods of reducing melt defecting such

US-A-5,830,947

relates to a melt-processable composition comprising, in admixture: (1) one or more melt-processable thermoplastic hydrocarbon polymers as the major component of the composition by weight, and, as a minor component of the composition by weight, (2) an effective amount of a chemically-resistant, fluoropolymer process aid to improve the processability of the composition and (3) one or more poly(oxyalkylene) polymers.

US-A-4,855,360

relates to an extrudable composition comprising thermoplastic hydrocarbon polymers, poly(oxyalkylene) polymers and fluorocarbon polymers. The poly(oxyalkylene) polymer and the fluorocarbon polymer are present in the composition in such relative proportions and concentrations as to reduce the occurrence of melt defects during the extrusion of said hydrocarbon polymer composition.

3a

AMENDED SHEET

as raising the melt-processing temperature or extruding at slower line speeds and lower shear rates. The use of this composition is also effective in reducing die buildup within an extruder.

5 SUMMARY

Briefly, in one aspect, the present invention provides a melt-processable composition that comprises a major amount (i.e., at least 50% by weight) of a melt processable thermoplastic hydrocarbon polymer and a minor, but effective, amount of a processing additive that comprises (a) a fluorothermoplastic polymer containing interpolymerized units derived from (i) vinylidene fluoride, and (ii) at least two separate ethylenically unsaturated, copolymerizable fluorinated comonomers, and (iii) optionally at least one low molecular weight non-fluorinated alpha olefin comonomer, (i.e. ethylene or propylene), and (b) a poly(oxyalkylene) polymer.

In another aspect, the present invention provides a novel processing additive composition that comprises from about 50 to 80% by weight of the fluorothermoplastic polymer, and correspondingly from about 50 to 20 weight percent of the poly(oxyalkylene) polymer.

In yet another aspect, the present invention provides a method for improving the melt processability of a melt processable thermoplastic hydrocarbon resin by combining the thermoplastic hydrocarbon resin with an effective amount of the processing additive, blending the materials until there is preferably a uniform distribution of the processing additive in the thermoplastic hydrocarbon polymer, and melt processing the resulting blend.

DETAILED DESCRIPTION

The thermoplastic hydrocarbon polymers useful in the present invention include, but are not limited to, polyamides, polyimides, polyurethanes, polyolefins, polystyrenes, polyesters, polycarbonates, polyketones, polyureas, polyvinyl resins, polyacrylates and polymethylacrylates. A particularly useful class of thermoplastic hydrocarbon polymers are polyolefins. Such polymers may be obtained by the homopolymerization or copolymerization of olefins, as well as copolymers of one or more olefins and up to about 30 weight percent or more, but preferably 20 weight percent or less, of one or more monomers

that are copolymerizable with such olefins, e.g. vinyl ester compounds such as vinyl acetate. The olefins may be characterized by the general structure $\text{CH}_2=\text{CHR}$, wherein R is a hydrogen or an alkyl radical, and generally, the alkyl radical contains not more than 10 carbon atoms, preferably from one to six carbon atoms. Representative olefins are ethylene, 5 propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Representative monomers that are copolymerizable with the olefins include: vinyl ester monomers such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl chloroacetate, and vinyl chloropropionate; acrylic and alpha-alkyl acrylic acid monomers and their alkyl esters, amides, and nitriles such as acrylic acid, methacrylic acid, ethacrylic acid, methyl acrylate, ethyl acrylate, N,N-10 dimethyl acrylamide, methacrylamide, and acrylonitrile; vinyl aryl monomers such as styrene, o-methoxystyrene, p-methoxystyrene, and vinyl naphthalene; vinyl and vinylidene halidemonomers such as vinyl chloride, vinylidene chloride, and vinylidene bromide; alkyl ester monomers of maleic and fumaric acid and anhydrides thereof such as dimethyl maleate, diethyl maleate, and maleic anhydride; vinyl alkyl ether monomers such as vinyl methyl 15 ether, vinyl ethyl ether, vinyl isobutyl ether, and 2-chloroethyl vinyl ether; vinyl pyridine monomers; N-vinyl carbazole monomers; and N-vinyl pyrrolidine monomers.

The thermoplastic hydrocarbon polymers also include the metallic salts of said olefin copolymers, or blends thereof, that contain free carboxylic acid groups. Illustrative of the metals that can be used to provide the salts of said carboxylic acids polymers are the one, 20 two, and three valence metals such as sodium, lithium, potassium, calcium, magnesium, aluminum, barium, zinc, zirconium, beryllium, iron, nickel, and cobalt. The thermoplastic hydrocarbon polymers also include blends of thermoplastic hydrocarbon polymers with other thermoplastic hydrocarbon polymers or blends thereof containing conventional adjuvants such as antioxidants, light stabilizers, fillers, antiblocking agents, and pigments.

25 Representative examples of thermoplastic hydrocarbon polymers useful in the present invention are polyethylene, polypropylene, poly(1-butene), poly(3-methylbutene), poly(4-methylpentene) and copolymers of ethylene with propylene, 1-butene, 1-hexene, 1-octene, 1-decene, 4-methyl-1-pentene, and 1-octadecene.

30 Representative blends of thermoplastic hydrocarbon polymers useful in the invention are blends of polyethylene and polypropylene, linear or branched low-density polyethylenes, high-density polyethylenes, and polyethylene and olefin copolymers containing said

copolymerizable monomers, some of which are described above, e.g., ethylene and acrylic acid copolymers; ethylene and methyl acrylate copolymers; ethylene and ethyl acrylate copolymers; ethylene and vinyl acetate copolymers; ethylene, acrylic acid, and ethyl acrylate copolymers; and ethylene, acrylic acid, and vinyl acetate copolymers.

5 The thermoplastic hydrocarbon polymers may be used in the form of powders, pellets, granules, or in any other extrudable form. The preferred thermoplastic hydrocarbon polymers of the invention are homopolymers of ethylene and propylene or copolymers of ethylene and 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, propylene, vinyl acetate and methyl acrylate.

10 The fluorothermoplastic polymers employed in the process additives of this invention are semi-crystalline and have a peak melting temperature in the range of 80°C to 350°C. They are polymers containing interpolymerized units derived from (i) vinylidene fluoride, and (ii) at least two separate ethylenically unsaturated, copolymerizable fluorinated comonomers, and (iii) optionally, at least one low molecular weight non-fluorinated alpha 15 olefin monomer.

at least two separate
15 The ~~ethylenically unsaturated~~ copolymerizable fluorinated comonomer may be characterized according to the general structure:



wherein:

20 X is a hydrogen or a halogen atom; and

R¹ is a halogen atom or is an alkyl, cyclic alkyl, or aryl group having from 1 to 10 carbon atoms, and preferably it is either a halogen atom or a group having 1 to 3 carbon atoms; R¹ groups may contain one or more heteroatoms such as oxygen or nitrogen and may be partially-, fully- or non-halogenated, for example with 25 fluorine atoms, provided, however, that when X is a hydrogen atom, R¹ contains an allylic carbon atom relative to the α -unsaturation and that allylic carbon atom is not perfluorinated (i.e. the allylic carbon atom is not saturated with fluorine atoms).

*[See
Claim 13]*

*[Says 7, 8, 9
optional
claim 1]*

The substantially nonfluorinated olefin (b) monomers copolymerized with the fluorinated (a) monomer of monomers may be characterized according to the general structure:



5 wherein:

X is a hydrogen or a halogen atom; and

R² is a hydrogen or a halogen atom with the proviso that R² and X are not both fluorine; R² may also be an alkyl, cyclic alkyl, or aryl group having from 1 to 10 carbon atoms; preferably R² is a hydrogen atom or a group having 1 to

10

3 carbon atoms; R² group may be partially-, fully- or non-halogenated, for example with fluorine atoms, and may contain one or more heteroatoms such as oxygen or nitrogen. R² preferably is nonfluorinated but may be fluorinated.

Representative fluorinated copolymerizable fluorinated comonomers are
15 tetrafluoroethylene, hexafluoropropene, chlorotrifluoroethylene, 2-chloropentafluoropropene, perfluoroalkyl vinyl ethers, e.g. CF₃OCF=CF₂ or CF₃CF₂CF₂OCF=CF₂, dichlorodifluoroethylene, 1,1-dichlorofluoroethylene, and mixtures thereof. Perfluoro-1,3-dioxoles may also be used. The perfluoro-1,3-dioxole monomers and their copolymers are described, for example, in U.S. Pat. No. 4,558,141 (Squire).

20

A preferred subclass of fluorothermoplastic polymers useful in the invention comprises fluoropolymers having interpolymerized units derived solely from (i) vinylidene fluoride, (ii) more than 25 weight percent of the ethylenically unsaturated copolymerizable fluorinated monomer having the general structure



25 wherein R_f is H, F, Cl, or a perfluoroalkyl of 1 to 8, preferably 1 to 3, carbon atoms, and, (iii), optionally, minor amounts (i.e., less than 50% by weight of said fluoropolymer) of perfluoro(alkyl vinyl ether) having, for example, 1 to 4 carbon atoms, e.g., perfluoro(methyl vinyl ether).

A preferred class of the fluoropolymers used in this invention is derived by
30 copolymerizing 30 to 70 wt %, preferably 35 to 65 wt % tetrafluoroethylene, 10 to 30 wt %,

preferably 15 to 25 wt % hexafluoropropylene, and 5 to 50 wt %, preferably 15 to 45 wt % vinylidene fluoride. A subclass of the fluoropolymer useful in making blends of this invention are fluoroplastics which contain interpolymerized units derived from copolymerization of a monomer charge of 45 to 65 wt % tetrafluoroethylene, 10 to 20 wt % 5 hexafluoropropylene, and 15 to 35 wt % vinylidene fluoride.

Commercial fluoropolymers which can be used in the invention are the THV Fluoroplastics, which are described in product bulletins 98 0211-7703-9(103.02)R1, 98 0211-7010-9, -7011-7, -7012-6, -7013-3, -7014-1, and -8100-7 of Dyneon LLC. Grades THV 200, THV 400, and THV 500 of these fluoroplastics have ASTM D 3418 melting ranges of 115°-10 125° C., 150°-160° C., and 165°-180° C., respectively, and ASTM D 1238 melt flow indices of 20, 10, and 10, respectively, at 265° C. and 5 kg.

The poly(oxyalkylene) polymer employed in the process additives of this invention include poly(oxyalkylene) polyols and their derivatives. A class of such poly(oxyalkylene) polymers may be represented by the general formula:



wherein:

A is an active hydrogen-free residue of a low molecular weight, initiator organic compound having a plurality of active hydrogen atoms (e.g., 2 or 3), such as a polyhydroxyalkane or a polyether polyol, e.g., ethylene glycol, glycerol, 1,1,1-20 trimethylol propane, and poly(oxypropylene) glycol;

y is 2 or 3;

(OR¹)_x is a poly(oxyalkylene) chain having a plurality of oxyalkylene groups, (OR¹), wherein the R¹ moieties can be the same or different and are selected from the group consisting of C₁ to C₅ alkylene radicals and, preferably, C₂ or C₃ alkylene radicals, and x is the number of oxyalkylene units in said chain. Said 25 poly(oxyalkylene) chain can be a homopolymer chain, e.g., poly(oxyethylene) or poly(oxypropylene), or can be a chain of randomly distributed (i.e., a heteric mixture) oxyalkylene groups, e.g., a copolymer of -OC₂H₄- and -OC₃H₆- units, or can be a chain having alternating blocks or backbone segments of repeating

oxyalkylene groups, e.g., a polymer comprising $-\text{OC}_2\text{H}_4-$ _a and $-\text{OC}_3\text{H}_6-$ _b blocks, wherein a+b=5 to 5000 or higher, and preferably 10 to 500.

R² is H or an organic radical, such as alkyl, aryl, or a combination thereof such as aralkyl or alkaryl, and may contain oxygen or nitrogen heteroatoms. For example, R² can be methyl, butyl, phenyl, benzyl, and acyl groups such as acetyl (CH₃CO—), benzoyl (C₆H₅CO—) and stearyl (C₁₇H₃₅CO—).

Representative poly(oxyalkylene) polymer derivatives can include poly(oxyalkylene) polyol derivatives wherein the terminal hydroxy groups have been partly or fully converted to ether derivatives, e.g., methoxy groups, or ester derivatives, e.g., stearate groups, (C₁₇H₃₅COO—). Other useful poly(oxyalkylene) derivatives are polyesters, e.g., prepared from dicarboxylic acids and poly(oxyalkylene) glycols. Preferably, the major proportion of the poly(oxyalkylene) polymer derivative by weight will be the repeating oxyalkylene groups, (OR¹).

The poly(oxyalkylene) polyols and their derivatives can be those which are solid at room temperature and have a molecular weight of at least about 200 and preferably a molecular weight of about 400 to 20,000 or higher. Poly(oxyalkylene) polyols useful in this invention include polyethylene glycols which can be represented by the formula H(OC₂H₄)_nOH, where n is about 15 to 3000, such as those sold under the Carbowax trademark, such as CarbowaxTM PEG 8000, where n is about 181, and those sold under the trade name Polyox, such as PolyoxTM WSR N-10 where n is about 2272.

The amount of the processing additive employed in the melt processable composition is that which is effective to provide a desired reduction in the melt defect phenomena. The exact amount will depend upon a number of factors including the particular melt-processable thermoplastic hydrocarbon polymer used, the formulation of that thermoplastic hydrocarbon polymer (i.e., the amount and types of additives present), and the process conditions under which the composition is to be extruded.

Generally, the process additive is present in the melt-processable composition at a low concentration. However, this may vary depending upon whether the melt-processable composition is to be extruded into its final form (e.g., a film) or whether the melt-processable composition is to be used as a masterbatch and is to be further diluted with thermoplastic

polymer before it is extruded into its final form. Generally, the process additive is present in the melt-processable composition at a concentration of from about 0.005 to about 50 weight percent. If the melt-processable composition is a masterbatch, the amount of process additive in the composition may vary between about 2 to 50 weight percent of the composition. If the 5 melt processable composition is to be extruded into final form and is not further diluted by the addition of thermoplastic hydrocarbon polymer, the melt-processable composition typically contains a lower concentration of process additive, e.g., about 0.005 to 2 weight percent, and preferably about 0.01 and 0.2 weight percent of the melt-processable composition. In any event, the upper concentration of the process additive in the melt- 10 processable composition generally is determined by economic limitations rather than by any adverse physical effect of the concentration of the processing aid.

The processing additive composition employed in the melt processable composition of the invention comprises at least 50 percent by weight of the fluorothermoplastic polymer and up to 50 percent by weight of the polyoxyalkylene polymer. That is, the weight ratio of 15 the fluorothermoplastic polymer to the poly(oxyalkylene) polymer in the processing additive composition is at least 1:1. Generally, the processing additive composition comprises from 50 to 99.5 percent by weight fluorothermoplastic and correspondingly from 50 to 0.5 percent by weight poly(oxyalkylene). Preferably the processing additive composition comprises from 50 to 80 percent by weight fluorothermoplastic and correspondingly from 50 to 20 percent by weight poly(oxyalkylene). This composition represents a novel processing 20 additive composition. Even more preferably, the processing additive composition comprises from 50 to 70 weight percent fluorothermoplastic and correspondingly from 50 to 30 percent by weight poly(oxyalkylene). A list of useful processing additive compositions is set out in Table 1. In the Table, and throughout the remainder of this description, FT means 25 "fluorothermoplastic polymer" and PEO means "poly(oxyalkylene) polymer".

Table 1

FT (Wgt %)	PEON (Wgt %)	Weight Ratio FT:PEO
50	50	1:1
60	40	1:0.67
70	30	1:0.43
80	20	1:0.25
90	10	1:0.11
95	5	1:0.05
95.5	0.5	1:0.005

The melt processable composition of the invention can be prepared by any of a variety of ways. For example, the thermoplastic hydrocarbon polymer and the processing additive can be combined by any of the blending means usually employed in the plastics industry, such as with a compounding mill, a Banbury mixer, or a mixing extruder in which the processing additive are uniformly distributed throughout the hydrocarbon polymer. The processing additive and the hydrocarbon polymers may be used in the form, for example, of powders, pellets, or granules. The mixing operation is most conveniently carried out at a temperature above the melting point of the fluorothermoplastic polymer, though it is also feasible to dry-blend the components in the solid state as particulates and then cause uniform distribution of the components by feeding the dry blend to a twin-screw melt extruder.

The resulting melt-blended mixture can be pelleted or otherwise comminuted into a desired particulate size or size distribution and fed to an extruder, which typically will be a single-screw extruder, that melt-processes the blended mixture. Melt-processing typically is performed at a temperature from 180° to 280° C., although optimum operating temperatures are selected depending upon the melting point, melt viscosity, and thermal stability of the blend. Different types of extruders that may be used to extrude the compositions of this invention are described, for example, by Rauwendaal, C., "Polymer Extrusion," Hansen Publishers, p. 23-48, 1986. The die design of an extruder can vary, depending on the desired extrudate to be fabricated. For example, an annular die can be used to extrude tubing, useful in making fuel line hose, such as that described in U.S. Pat. No. 5,284,184 (Noone et al.), which description is incorporated herein by reference.

Blends of the fluorothermoplastic polymer and the poly(oxyalkylene) polymer component, may be compounded as a masterbatch in the thermoplastic hydrocarbon resin.

The masterbatch subsequently may be diluted prior to melt-processing to effect a desired concentration of the processing additive in the composition to be melt-processed. The fluorothermoplastic polymer and/or the poly(oxyalkylene) polymer may alternatively be fed to an extruder directly as a fine powder, therein combining with the thermoplastic hydrocarbon. The fluorothermoplastic polymer and/or the poly(oxyalkylene) polymer component may be slurried or dissolved in a liquid and the resulting mixture may be blended with the hydrocarbon polymer to create a melt-processable composition.

The blended composition can contain conventional adjuvants such as antioxidants, antiblocks, pigments, and fillers, e.g. titanium dioxide, carbon black, and silica. Antiblocks, when used, may be coated or uncoated materials.

The following examples are offered to aid in a better understanding of the present invention. These examples are not to be construed as an exhaustive compilation of all embodiments of the present invention and are not to be unnecessarily construed as limiting the scope of this invention.

15

EXAMPLES

The following examples illustrate the polymer processing additives of the invention and melt processable thermoplastics that utilize them. The composition of the polymer processing additive (PPA) compositions employed in the examples is set out in Table 2.

Table 2

Polymer Process Additive Compositions		
PPA1	FT	100% by weight
PPA2	FT Polyethylene glycol	70% by weight 30% by weight
PPA3	FT Polyethylene glycol	60% by weight 40% by weight
PPA4	FT Polyethylene glycol	50% by weight 50% by weight
PPA5	Fluoroelastomer Polyethylene glycol	30% by weight 70% by weight

The FT (fluorothermoplastic polymer) was derived from a monomer composition of about 60 weight % TFE, about 20 weight % VF₂, and about 20 weight % HFP.

The fluoroelastomer was derived from a monomer composition of about 60 weight % VF₂, and about 40 weight % HFP.

5 The polyethylene glycol used had a molecular of about 8000 and is represented by the formula H(OC₂H₄)_nOH where n is about 181.

PPA5 is commercially available as DynamarTM FX-5920A from Dyneon LLC, Oakdale, MN.

10 The melt processable thermoplastic hydrocarbon resin employed in the examples was an octane linear low density polyethylene resin having a melt index of 0.85 and a density of 0.92.

15 Masterbatch compositions comprising the PPA or polyethylene glycol and the thermoplastic hydrocarbon resin were prepared by weighing the appropriate amount of fluoropolymer or polyethylene glycol and polyethylene, tumble blending them together and then running them through a twin screw extruder at 190°C. The extruded blend was solidified by passing it through a water bath and then pelletized. The resulting pelletized masterbatch was then tumble blended and again run through the twin screw extruder, solidified and pelletized to ensure homogeneity.

20 The film compositions were made by tumble blending in the appropriate amount of a given fluoropolymer masterbatch (and polyethylene glycol masterbatch if appropriate) with the thermoplastic hydrocarbon resin. The resulting compositions were then run through a blown film line (182° C (360° F) feed, 221° C (430° F) flat temperature profile) at 600 sec⁻¹ shear rate. The initial concentration of PPA used was 400 parts per million (ppm). The concentration of PPA was increased by 200 ppm each hour until melt fracture was cleared. 25 At 60 minutes, the concentration was increased to 600ppm. At 120 minutes the concentration was increased to 800ppm. The time needed to clear melt fracture was recorded. The results are shown in Table 3. The numbers reported in Table 3 reflect the % melt fracture at the given time.

30 A commercially available purge composition comprising 50 weight % thermoplastic hydrocarbon resin and 50 weight % calcium carbonate was used to purge the equipment of

processing additives between each run. The base thermoplastic hydrocarbon resin was used to purge out the purge.

Table 3

Time (min)	PPA1	PPA2	PPA3	PPA4	PPA5
0	100	100	100	100	100
15	100	95	100	90	100
30	100	35	100	60	50
45	85	1	95	35	25
60	60	0	50	25	3
75	50		1	5	0
90	25		0	0	

5

These results show the following:

- A. PPA1 took 800 ppm and 150 minutes to clear melt fracture.
- B. PPA5 (a commercially available material) took 600 ppm and 75 minutes to clear melt fracture.
- 10 C. PPA2, 3 and 4 each took 600 ppm to clear melt fracture. PPA2 cleared melt fracture at 60 minutes; PPA3 and PPA4 cleared melt fracture at 90 minutes.
This data shows that improved extrusion characteristics^{are} achieved by the use of the polymer processing additives of the invention.

WHAT IS CLAIMED IS:

06. April 2001

1. A melt processable polymer composition comprising a major amount of a melt processable thermoplastic hydrocarbon polymer and a minor amount of a processing additive composition comprising (a) a fluorothermoplastic polymer containing units derived from (i) vinylidene fluoride and, (ii) at least two separate ethylenically unsaturated copolymerizable fluorinated comonomers, and (iii) optionally at least one low molecular weight non-fluorinated alpha olefin monomer, and (b) a poly(oxyalkylene) polymer wherein the weight ratio of said fluorothermoplastic polymer to said poly(oxyalkylene) polymer is ~~at least 1:1~~
10 ~~from 1:1 to about 1:0.005~~.

12. A melt processable polymer composition according to claim 1 wherein the weight ratio of the fluorothermoplastic polymer to the poly(oxyalkylene) polymer is in the range ~~of from about 1:0.005 to 1:1~~.

15 23. A melt processable polymer composition according to claim 1 wherein the fluorothermoplastic polymer contains only units derived from (i) vinylidene fluoride and (ii) the ethylenically unsaturated copolymerizable fluorinated comonomers.

20 34. A melt processable polymer composition according to claim 23 wherein the ethylenically unsaturated copolymerizable fluorinated comonomers have the general structure



wherein

X is a hydrogen or a halogen atom; and

25 R¹ is a halogen atom or is an alkyl, cyclic alkyl, or aryl group having from 1 to 10 carbon atoms.

30 45. A melt processable polymer composition according to claim 44 wherein the comonomers of the formula $CF_2=CXR^1$ are selected from the group consisting of a perfluoroalkylvinyl ether, tetrafluoroethylene, hexafluoropropylene, chlorotrifluoroethylene and 2-chloropentafluoropropene.

5. ⁴ A melt processable polymer composition according to claim 5 wherein the perfluoroalkylvinyl ether has from 1 to 8 carbon atoms.

5. ³ 6. A melt processable polymer composition according to claim 4 wherein thermoplastic fluoropolymer comprises units derived from vinylidene fluoride, tetrafluoroethylene, and hexafluoropropylene.

7. ³ 8. A melt processable composition according to claim 1 wherein the hydrocarbon polymer comprises from about 50 to 99.995 weight % of the composition.

8. ³ 9. A melt processable composition according to claim 1 wherein the hydrocarbon polymer is a polyolefin.

15. ⁹ 10. A method for reducing melt defects in melt processable thermoplastic hydrocarbon polymer compositions which comprises admixing a melt processable thermoplastic hydrocarbon polymer with an effective amount of a polymer processing additive composition comprising (a) a fluorothermoplastic polymer containing units derived from (i) vinylidene fluoride, and (ii) at least two separate ethylenically unsaturated 20 copolymerizable fluorinated comonomers, and (iii) optionally at least one low molecular weight non-fluorinated alpha olefin monomer, and (b) a poly(oxyalkylene) polymer wherein the weight ratio of the fluorothermoplastic polymer to the poly(oxyalkylene) polymer is ~~at least 1:1~~ ^{to about 1:0.005,} mixing the polymer processing additive composition and the hydrocarbon polymer for a time sufficient to blend them together, and melt processing said admixture.

25. ⁹ 10. A method according to claim 10 wherein the poly(oxyalkylene) polymer is admixed with the melt processable thermoplastic hydrocarbon polymer prior to, simultaneously with, or subsequent to the admixture of the fluorothermoplastic polymer with the melt processable thermoplastic hydrocarbon polymer.

30

10
11.2. A method according to claim *11* wherein from 2 to 50 weight percent of the melt processable thermoplastic polymer composition comprises the polymer processing aid.

10
12.13. A method according to claim *11* wherein from 0.005 to 2 weight percent of the melt processable thermoplastic polymer composition comprises the polymer processing aid.

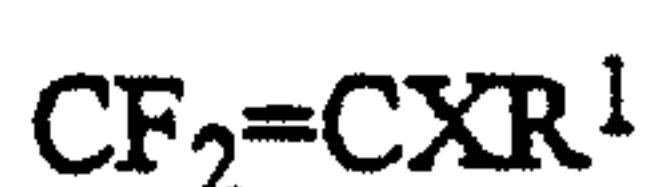
10
13.14. A method according to claim *11* wherein the hydrocarbon polymer comprises a polyolefin.

10
14.15. A method according to claim *11* wherein the fluorothermoplastic polymer is derived solely from vinylidene fluoride, tetrafluoroethylene and hexafluoropropylene.

15
15.16. A processing additive composition comprising (a) a fluorothermoplastic polymer containing units derived from (i) vinylidene fluoride and, (ii) at least two separate ethylenically unsaturated copolymerizable fluorinated comonomers, and (iii) optionally at least one low molecular weight non-fluorinated alpha olefin monomer, and (b) a poly(oxyalkylene) polymer wherein the weight ratio of said fluorothermoplastic polymer to said poly(oxyalkylene) polymer is in the range of from about 1:1 to 1:0.25.

15
16.17. A processing additive composition according to claim *16* wherein the fluorothermoplastic polymer contains only units derived from (i) vinylidene fluoride and (ii) *at least two separate* the ethylenically unsaturated copolymerizable fluorinated comonomers.

16
17.18. A processing additive composition according to claim *17* wherein the ethylenically unsaturated copolymerizable fluorinated comonomer has the general structure



wherein

X is a hydrogen or a halogen atom; and

R¹ is a halogen atom or is an alkyl, cyclic alkyl, or aryl group having from 30 1 to 10 carbon atoms.

[having a peak melting temperature from 80 to 350°C and]

18 19. A processing additive composition according to claim 18 wherein the thermoplastic fluoropolymer contains units derived from (i) the vinylidene fluoride, and (ii) two of the copolymerizable fluorinated comonomers of the formula $CF_2=CXR^1$.

5 19 20. A processing additive composition according to claim 19 wherein thermoplastic fluoropolymer comprises units derived solely from vinylidene fluoride, tetrafluoroethylene, and hexafluoropropylene.