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(54) Titre : COMPOSITIONS D'HYDROCARBURES THERMOPLASTIQUES EXTRUDABLES  
(54) Title: EXTRUDABLE THERMOPLASTIC HYDROCARBON COMPOSITIONS

(57) Abrégé/Abstract:

Briefly, in one aspect, this invention provides 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. The fluoropolymer process aid contains at least about 50 weight percent of fluorine and comprises one or more fluoropolymers which are essentially completely ethylenically saturated and consist essentially of interpolymers derived from the following monomers: (a) one or more fluorinated olefin monomers having the following general formula:  $\text{CF}_2=\text{CXR}^1$  wherein X is a hydrogen or a halogen atom; and  $\text{R}^1$  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 2 carbon atoms;  $\text{R}^1$  groups may contain one or more heteroatoms such as nitrogen or oxygen and may be partially-, fully- or non-halogenated, provided, however, that whenever X is a hydrogen atom,  $\text{R}^1$  contains an allylic carbon atom relative to the  $\alpha$ -unsaturation and that allylic carbon atom is not perfluorinated; (b) one or more olefin monomers of the general formula:  $\text{CH}_2=\text{CXR}^2$  wherein X is a hydrogen or a halogen atom; and  $\text{R}^2$  is a hydrogen or a halogen atom with the proviso that  $\text{R}^2$  and X are not both fluorine;  $\text{R}^2$  may also be an alkyl, cyclic alkyl, or aryl group having from 1 to 10 carbon atoms, and preferably is a hydrogen atom or a group having 1 to 2 carbon atoms; and  $\text{R}^2$  may be partially-, fully- or non-halogenated and may contain one or more heteroatoms such as oxygen or nitrogen; and (c) 0 to 15 weight percent, of the total weight of the fluoropolymer, of one or more monomers that produce an acidic hydrogen on the backbone of the resulting fluoropolymer after polymerization. Component (2) has a Carreau-Yasuda Equation m1 parameter of about 0.7 or less, and the ratio of the melt viscosity of component (2) to the melt viscosity of component (1) is between about 0.01 and 100 at the melt processing conditions of the composition. The above-described admixture of components (1 and 2) may also be admixed with other conventional additives and adjuvants, such as fluorinated and non-fluorinated process additives, light stabilizers, antioxidants, fillers, antiblocking agents, and pigments. In another aspect, the present invention provides compositions such as those described above that further comprise one or more poly(oxyalkylene) polymers. Methods using these compositions to improve the processability of a melt-processable thermoplastic hydrocarbon polymer are also disclosed.

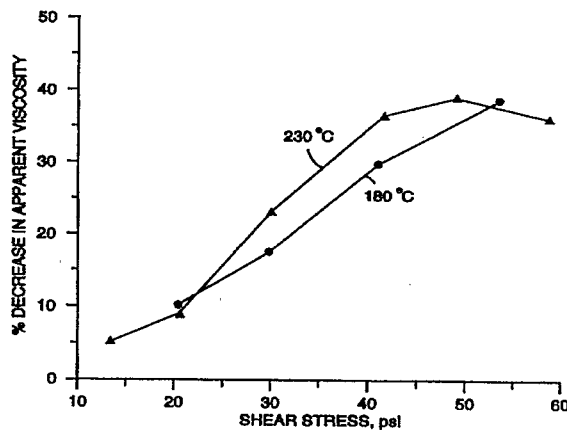
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US96/13149 <b>(22) International Filing Date:</b> 13 August 1996 (13.08.96) <b>(30) Priority Data:</b> 60/003,811 15 September 1995 (15.09.95) US <b>(71) Applicant:</b> MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). <b>(72) Inventors:</b> BLONG, Thomas, J.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). GREUEL, Michael, P.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). LAVALLEE, Claude; P.O. Box 5757, London, Ontario N5V 1H4 (CA). <b>(74) Agents:</b> BURTIS, John, A. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		<b>(81) Designated States:</b> CA, CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

**(54) Title:** EXTRUDABLE THERMOPLASTIC HYDROCARBON COMPOSITIONS**(57) Abstract**

Briefly, in one aspect, this invention provides 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. The fluoropolymer process aid contains at least about 50 weight percent of fluorine and comprises one or more fluoropolymers which are essentially completely ethylenically saturated and consist essentially of interpolymerized units derived from the following monomers: (a) one or more fluorinated olefin monomers having the following general formula:  $\text{CF}_2=\text{CXR}^1$  wherein X is a hydrogen or a halogen atom; and  $\text{R}^1$  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 2 carbon atoms;  $\text{R}^1$  groups may contain one or more heteroatoms such as nitrogen or oxygen and may be partially-, fully- or non-halogenated, provided, however, that whenever X is a hydrogen atom,  $\text{R}^1$  contains an allylic carbon atom relative to the  $\alpha$ -unsaturation and that allylic carbon atom is not perfluorinated; (b) one or more olefin monomers of the general formula:  $\text{CH}_2=\text{CXR}^2$  wherein X is a hydrogen or a halogen atom; and  $\text{R}^2$  is a hydrogen or a halogen atom with the proviso that  $\text{R}^2$  and X are not both fluorine;  $\text{R}^2$  may also be an alkyl, cyclic alkyl, or aryl group having from 1 to 10 carbon atoms, and preferably is a hydrogen atom or a group having 1 to 2 carbon atoms; and  $\text{R}^2$  may be partially-, fully- or non-halogenated and may contain one or more heteroatoms such as oxygen or nitrogen; and (c) 0 to 15 weight percent, of the total weight of the fluoropolymer, of one or more monomers that produce an acidic hydrogen on the backbone of the resulting fluoropolymer after polymerization. Component (2) has a Carreau-Yasuda Equation m1 parameter of about 0.7 or less, and the ratio of the melt viscosity of component (2) to the melt viscosity of component (1) is between about 0.01 and 100 at the melt processing conditions of the composition. The above-described admixture of components (1 and 2) may also be admixed with other conventional additives and adjuvants, such as fluorinated and non-fluorinated process additives, light stabilizers, antioxidants, fillers, antiblocking agents, and pigments. In another aspect, the present invention provides compositions such as those described above that further comprise one or more poly(oxyalkylene) polymers. Methods using these compositions to improve the processability of a melt-processable thermoplastic hydrocarbon polymer are also disclosed.



## Extrudable Thermoplastic Hydrocarbon Compositions

### FIELD OF THE INVENTION

5           This invention relates to thermoplastic hydrocarbon polymers, such as polyolefins, having improved extrusion characteristics. In another aspect, it relates to the use of fluorocarbon polymers to improve the extrusion characteristics of such thermoplastic hydrocarbon polymers. In a further aspect, it relates to a polymer processing aid composition.

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### BACKGROUND

          For any extrudable 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*, 8  
15   Encyclopedia of Polymer Science and Technology 573-81 (John Wiley & Sons 1968). The desire 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  
20   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  
25   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 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  
30   can also 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 can affect film  
5 orientation.

Certain fluorocarbon elastomer 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  
10 hydrocarbon polymers wherein the fluorinated polymers 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  
15 processing aid for use with a difficultly melt-processable polymer comprising (1) a fluorocarbon copolymer 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  
20 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 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.

25 U.S. Pat. Nos. 5,064,594 (Priester et al.) and 5,132,368 (Chapman, Jr. et al. describe the use of certain fluoropolymer process aids containing functional polymer chain end groups including  $\text{—COF}$ ,  $\text{—SO}_2\text{F}$ ,  $\text{—SO}_2\text{Cl}$ ,  $\text{SO}_3\text{M}$ ,  $\text{—OSO}_3\text{M}$ , and  $\text{—COOM}$ , wherein is M hydrogen, a metal cation, or a quaternary ammonium cation for use with a difficultly melt-processable polymer.

30 While these known fluoropolymer process aids may provide improved extrusion characteristics over extrudable compositions formulated in their absence,

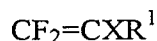
enabling substantially faster extrusion rates and yielding extrudates with smoother surfaces, many of the fluoropolymers within the compositions are themselves susceptible to chemical attack by basic or amine-containing extrudate additives, particularly to light stabilizers. As a result, these fluoropolymer process aids readily  
 5 degrade within the extrudable composition and lose their effectiveness. Also as a result of chemical activity, these fluoropolymers can severely discolor, often resulting in discoloration or loss of transparency of the final extrudate even if present in the extrudable composition at relatively low concentrations.

10

**SUMMARY**

Briefly, in one aspect, this invention provides 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  
 15 amount of a chemically-resistant, fluoropolymer process aid to improve the processability of the composition. The fluoropolymer process aid contains at least about 50 weight percent of fluorine and comprises one or more fluoropolymers which are essentially completely ethylenically saturated and consist essentially of interpolymerized units derived from the following monomers:

20 (a) one or more fluorinated olefin monomers having the following general formula:



wherein:

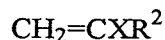
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X is a hydrogen or a halogen atom; and

R<sup>1</sup> 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 2 carbon atoms; R<sup>1</sup> groups may contain one or more heteroatoms such as nitrogen or oxygen and may be partially-, fully- or  
 30 non-halogenated, provided, however, that whenever X is a hydrogen

atom,  $R^1$  contains an allylic carbon atom relative to the  $\alpha$ -unsaturation and that allylic carbon atom is not perfluorinated;

(b) one or more olefin monomers of the general formula:



5 wherein:

X is a hydrogen or a halogen atom; and

$R^2$  is a hydrogen or a halogen atom with the proviso that  $R^2$  and X are not both fluorine;  $R^2$  may also be an alkyl, cyclic alkyl, or aryl group having from 1 to 10 carbon atoms, and preferably is a hydrogen atom or a  
10 group having 1 to 2 carbon atoms; and  $R^2$  may be partially-, fully- or non-halogenated and may contain one or more heteroatoms such as oxygen or nitrogen; and

(c) 0 to 15 weight percent, of the total weight of the fluoropolymer, of one or more monomers that produce an acidic hydrogen on the backbone of the  
15 resulting fluoropolymer after polymerization.

Component (2) has a Carreau-Yasuda Equation m1 parameter of about 0.7 or less, and the ratio of the melt viscosity of component (2) to the melt viscosity of component (1) is between about 0.01 and 100 at the melt processing conditions of the composition. The above-described admixture of components (1) and (2)  
20 may also be admixed with other conventional additives and adjuvants, such as fluorinated and non-fluorinated process additives, light stabilizers, antioxidants, fillers, antiblocking agents, and pigments.

In a particularly preferred embodiment of the melt-processable composition described above, the fluoropolymer process aid contains at least 65 weight percent  
25 fluorine and consists essentially of one or more of the fluoropolymers described above. However, in this embodiment, the fluoropolymers consist essentially of interpolymerized units derived from: (a) one or more monomers selected from the group consisting of tetrafluoroethylene and hexafluoropropylene, (b) one or more monomers selected from the group consisting of propylene and ethylene, and (c)  
30 from 0 to 10 wt.% of one or more monomers selected from the group consisting of

76950-10

vinylidene fluoride, trifluoroethylene, 1-hydropentafluoropropene and 2-hydropentafluoropropene.

In another aspect, the present invention provides a melt-processable composition that further comprises a small amount (i.e., less than 20 percent by weight and preferably less than 2 percent by weight of the melt-processable composition) of a poly(oxyalkylene) polymer component dispersed in the hydrocarbon polymer. In a particularly preferred embodiment of this invention, the poly(oxyalkylene) polymer component consists essentially of one or more poly(oxyalkylene) polymers.

In yet another aspect, this invention provides a method of improving the extrusion characteristics of melt-processable thermoplastic hydrocarbon polymers by using an effective amount of any of the fluoropolymer process aids described above, and optionally, a small but effective amount of the poly(oxyalkylene) polymer components described above.

In yet another aspect, this invention provides a processing aid composition useful for improving the extrusion characteristics of thermoplastic, melt-processable hydrocarbon polymers comprising, in admixture, any of the poly(oxyalkylene) polymer components described above and any of the fluoropolymer process aids described above. A preferred embodiment of the processing aid composition comprises, and preferably consists essentially of, about 5 to 95 weight percent of the poly(oxyalkylene) polymer component and about 95 to 5 weight percent of the fluoropolymer process aid.

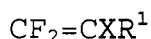
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According to one aspect of the present invention, there is provided a melt-processable composition having essentially no sites of ethylenic unsaturation and comprising a blend of:

5 (1) one or more melt-processable thermoplastic hydrocarbon polymers;

(2) an amount of a process aid to improve the processability of the melt-processable composition, wherein the process aid comprises one or more fluoropolymers having  
10 essentially no sites of ethylenic unsaturation, and wherein the process aid contains at least 50 weight % fluorine and the at least one fluoropolymer consists essentially of interpolymerized units of:

(a) one or more fluorinated olefin monomers of the  
15 general formula:



wherein:

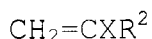
X is a hydrogen or a halogen atom; and

R<sup>1</sup> is a halogen atom or is a C<sub>1-10</sub>-alkyl, a  
20 C<sub>3-10</sub>-cyclic alkyl, or a C<sub>6-10</sub>-aryl group, wherein the alkyl, cyclic alkyl or aryl group optionally contains one or more heteroatoms selected from oxygen and nitrogen and is partially-, fully-, or non-halogenated provided, however, that when X is a hydrogen atom, R<sup>1</sup> contains an allylic carbon  
25 atom relative to the α-unsaturation and that allylic carbon atom is not perfluorinated; and

(b) one or more olefin monomers of the general formula:



76950-10



wherein:

X is a hydrogen or a halogen atom; and

R<sup>2</sup> is a hydrogen or is a halogen atom with the  
 5 proviso that R<sup>2</sup> and X are not both fluorine; or  
 R<sup>2</sup> is a C<sub>1-10</sub>-alkyl, a C<sub>3-10</sub>-cyclic alkyl, or a C<sub>6-10</sub>-aryl group,  
 wherein the alkyl, cyclic alkyl or aryl group is partially-,  
 fully-, or non-halogenated and optionally contains one or  
 more heteroatoms selected from oxygen and nitrogen; and

10 (c) 0 to 15 weight percent, of the total weight of  
 the fluoropolymer, of one or more monomers that produce an  
 acidic hydrogen on the backbone of the resulting  
 fluoropolymer after polymerization, and

(3) optionally less than 20 percent by weight of  
 15 the melt-processable composition of: a poly(oxyalkylene)  
 polymer component comprising one or more poly(oxyalkylene)  
 polymers;

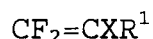
wherein the fluoropolymer or fluoropolymers  
 constituting component (2) either have a polydispersity  
 20 greater than or equal to 2.0 or have a Carreau-Yasuda  
 Equation m1 parameter of 0.7 or less and wherein the ratio  
 of the melt viscosity of the fluoropolymer or fluoropolymers  
 constituting component (2) to the melt viscosity of the  
 thermoplastic hydrocarbon polymer or polymers constituting  
 25 component (1) is between 0.01 and 100 at the melt processing  
 conditions of the composition.

According to another aspect of the present  
 invention, there is provided a process aid for improving the  
 processability of melt-processable thermoplastic hydrocarbon  
 30 polymers, wherein the process aid comprises one or more

76950-10

fluoropolymers having essentially no sites of ethylenic unsaturation, wherein the process aid contains at least 50 weight % fluorine and the at least one fluoropolymer consists essentially of interpolymerized units of:

- 5 (a) one or more fluorinated olefin monomers of the general formula:



wherein:

X is a hydrogen or a halogen atom; and

- 10  $\text{R}^1$  is a halogen atom or is a  $\text{C}_{1-10}$ -alkyl, a  $\text{C}_{3-10}$ -cyclic alkyl, or a  $\text{C}_{6-10}$ -aryl group, wherein the alkyl, cyclic alkyl or aryl group optionally contains one or more heteroatoms selected from oxygen and nitrogen and is partially-, fully-, or non-halogenated provided, however,  
 15 that when X is a hydrogen atom  $\text{R}^1$  contains an allylic carbon atom relative to the  $\alpha$ -unsaturation and that allylic carbon atom is not perfluorinated; and

(b) one or more olefin monomers of the general formula:



wherein:

X is a hydrogen or a halogen atom; and

- $\text{R}^2$  is a hydrogen or is a halogen atom with the proviso that  $\text{R}^2$  and X are not both fluorine or  
 25  $\text{R}^2$  is a  $\text{C}_{1-10}$ -alkyl, a  $\text{C}_{3-10}$ -cyclic alkyl, or a  $\text{C}_{6-10}$ -aryl group, wherein the alkyl, cyclic alkyl or aryl group is partially-, fully-, or non-halogenated and optionally contains one or more heteroatoms selected from oxygen and nitrogen; and

76950-10

(c) 0 to 15 weight percent, of the total weight of the fluoropolymer, of one or more monomers that produce an acidic hydrogen on the backbone of the resulting fluoropolymer after polymerization; and

5 optionally a poly(oxyalkylene) polymer component comprising one or more poly(oxyalkylene) polymers;

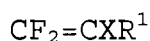
wherein the fluoropolymer or fluoropolymers have a Carreau-Yasuda Equation m1 parameter of 0.7 or less and wherein the fluoropolymer or fluoropolymers have a maximum  
10 zero shear viscosity ( $\eta_0$ ) of less than  $32 \times 10^6$  Pa-s ( $32 \times 10^6$  poise) at a reference temperature of 190°C.

According to yet another aspect of the present invention, there is provided a method of improving the extrusion characteristics of a melt-processable  
15 thermoplastic hydrocarbon polymer comprising blending:

(1) one or more melt-processable thermoplastic hydrocarbon polymers;

(2) an amount of a process aid to improve the processability of the melt-processable composition, wherein  
20 the process aid comprises one or more fluoropolymers having essentially no sites of ethylenic unsaturation, and wherein the process aid contains at least 50 weight % fluorine and the at least one fluoropolymer consists essentially of interpolymerized units of:

25 (a) one or more fluorinated olefin monomers of the general formula:



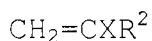
wherein:

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X is a hydrogen or a halogen atom; and

R<sup>1</sup> is a halogen atom or is a C<sub>1-10</sub>-alkyl, a C<sub>3-10</sub>-cyclic alkyl, or a C<sub>6-10</sub>-aryl group wherein the alkyl, cyclic alkyl or aryl group optionally contains one or more  
5 heteroatoms selected from oxygen and nitrogen and is partially-, fully-, or non-halogenated provided, however, that when X is a hydrogen atom, R<sup>1</sup> contains an allylic carbon atom relative to the α-unsaturation and that allylic carbon atom is not perfluorinated; and

10 (b) one or more olefin monomers of the general formula:



wherein:

X is a hydrogen or a halogen atom; and

15 R<sup>2</sup> is a hydrogen or is a halogen atom with the proviso that R<sup>2</sup> and X are not both fluorine or R<sup>2</sup> is a C<sub>1-10</sub>-alkyl, a C<sub>3-10</sub>-cyclic alkyl, or a C<sub>6-10</sub>-aryl group wherein the alkyl, cyclic alkyl or aryl group is partially-, fully-, or non-halogenated and optionally contains one or  
20 more heteroatoms selected from oxygen and nitrogen; and

(c) 0 to 15 weight percent, of the total weight of the fluoropolymer, of one or more monomers that produce an acidic hydrogen on the backbone of the resulting fluoropolymer after polymerization, and

25 (3) optionally less than 20 percent by weight of the melt-processable composition of: a poly(oxyalkylene) polymer component comprising one or more poly(oxyalkylene) polymers;

76950-10

wherein the fluoropolymer or fluoropolymers constituting component (2) either have a polydispersity greater than or equal to 2.0 or have a Carreau-Yasuda Equation m1 parameter of about 0.7 or less and wherein the  
5 ratio of the melt viscosity of the fluoropolymer or fluoropolymers constituting component (2) to the melt viscosity of the thermoplastic hydrocarbon polymer or polymers constituting component (1) is between 0.01 and 100 at the melt processing conditions of the composition, and  
10 extruding the blend.

According to still another aspect of the present invention, there is provided an extrudate comprising the blend described herein.

#### BRIEF DESCRIPTION OF THE FIGURE

15 **FIG. 1** is a plot of the percent decrease in apparent viscosity vs. shear stress of base resin at 190°C and at 230°C of a fluoropolymer in a thermoplastic hydrocarbon resin in accordance with the invention.

#### DETAILED DESCRIPTION

20 The compositions of the present invention are effective in reducing melt defects in thermoplastic hydrocarbon polymers, e.g. polyolefins, or in postponing

these defects to higher extrusion rates than can be achieved without such processing aids. The fluoropolymer process aids of this invention furthermore reduce or eliminate the existence of melt defects such as sharkskin in extruded thermoplastic hydrocarbon polymers without alteration of the chemical structure of the thermoplastic polymer and without the need for resorting to conventional methods of reducing melt defecting such as raising the melt-processing temperature or extruding at slower line speeds and lower shear rates. The fluoropolymer process aids of this invention are chemically stable in the presence of other additives, e.g., hindered amine light stabilizers, both under processing conditions and within the finished plastic article, yet they possess viscosities which permit efficient and easy incorporation into the thermoplastic hydrocarbon polymer melt. They also possess polydispersities or molecular weight distributions which permit the fluoropolymer process aid to function more efficiently over a range of processing or extrusion temperatures. Additionally, the fluoropolymer process aids retain most their efficiency even in extrudable compositions in which antioxidant consumption takes place (e.g., compositions containing minimal levels of antioxidant). As a result, less fluoropolymer can be used to achieve a melt-defect-free extrudate at a particular set of operating conditions, extrusion efficiencies can be retained even when processing temperature varies somewhat and the extrudate will retain its initial color better over time. The fluoropolymer process aids are also effective in reducing die buildup within an extruder. The compositions of the invention find particular utility in extrusion applications such as film, pipe, sheet, rod, fiber, and blow molding.

The amount of the fluoropolymer process aid necessary to provide a desired reduction in sharkskin and other melt defect phenomena 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 fluoropolymer process aid 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 fluoropolymer process aid is present in the melt-

5 processable composition at a concentration of about 0.005 and 50 weight percent. If the melt-processable composition is a masterbatch, the amount of fluoropolymer process aid in the composition may vary between about 2 to 50 weight percent of the composition. If the melt-processable composition is to be extruded into final form and is not further diluted by the addition of thermoplastic hydrocarbon

10 polymer, the melt-processable composition typically contains a lower concentration of fluoropolymer process aid, 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 fluoropolymer process aid in the melt-processable composition generally is determined by economic

15 limitations rather than by any adverse physical effect of the concentration of the processing aid.

The thermoplastic hydrocarbon polymers to which the fluoropolymer process aids of the present invention are added comprise polymers obtained by the homopolymerization or copolymerization of olefins, as well as copolymers of one or

20 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

25 atoms, preferably from one to six carbon atoms. Representative olefins are ethylene, 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

30 monomers and their alkyl esters, amides, and nitriles such as acrylic acid, methacrylic acid, ethacrylic acid, methyl acrylate, ethyl acrylate, N,N-dimethyl

acrylamide, methacrylamide, and acrylonitrile; vinyl aryl monomers such as styrene, *o*-methoxystyrene, *p*-methoxystyrene, and vinyl naphthalene; vinyl and vinylidene halide monomers such as vinyl chloride, vinylidene chloride, and vinylidene bromide; alkyl ester monomers of maleic and fumaric acid and anhydrides thereof  
5 such as dimethyl maleate, diethyl maleate, and maleic anhydride; vinyl alkyl ether monomers such as vinyl methyl 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  
10 free carboxylic acid groups. Illustrative of the metals that can be used to provide the salts of said carboxylic acids polymers are the one, 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  
15 thermoplastic hydrocarbon polymers or blends thereof containing conventional adjuvants such as antioxidants, light stabilizers, fillers, antiblocking agents, and pigments.

Representative examples of thermoplastic hydrocarbon polymers useful in the present invention are polyethylene, polypropylene, poly(1-butene), poly(3-  
20 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.

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  
25 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.

30 Typically, melt defect phenomena are most pronounced in those thermoplastic hydrocarbon polymers that have an ASTM D 1238 melt flow index of

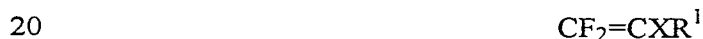


less than 2 g/10 min. measured at 190 °C with a loading of 2.16 kg. The fluoropolymer process aid and the process aids of this invention are therefore most useful in eliminating melt defects in these thermoplastic hydrocarbon polymers. The fluoropolymer process aids and the processing aids described herein may also be  
 5 used in thermoplastic hydrocarbon polymers with a higher melt index, e.g., for reducing or eliminating die buildup.

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  
 10 and propylene or copolymers of ethylene and 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, propylene, vinyl acetate and methyl acrylate.

The fluoropolymer process aids admixed with the thermoplastic hydrocarbon polymers of this invention are generally copolymers of: (a) one or more fluorinated olefin monomers with (b) one or more substantially  
 15 nonfluorinated hydrocarbon olefin monomers, and optionally with (c) a limited amount of vinylidene fluoride or one or more other monomers that yield acidic hydrogen on the backbone of the resulting fluoropolymer.

The fluorinated olefin (a) monomers may be characterized according to the general structure:

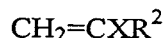


wherein:

X is a hydrogen or a halogen atom; and

R<sup>1</sup> 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  
 25 having 1 to 2 carbon atoms; R<sup>1</sup> groups may contain one or more heteroatoms such as oxygen or nitrogen and may be partially-, fully- or non-halogenated, for example with fluorine atoms, provided, however, that when X is a hydrogen atom, R<sup>1</sup> contains an allylic carbon atom relative to the α-unsaturation and that allylic carbon atom is not  
 30 perfluorinated (i.e. the allylic carbon atom is not saturated with fluorine atoms).

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



5 wherein:

X is a hydrogen or a halogen atom; and

$\text{R}^2$  is a hydrogen or a halogen atom with the proviso that  $\text{R}^2$  and X are not both fluorine;  $\text{R}^2$  may also be an alkyl, cyclic alkyl, or aryl group having from 1 to 10 carbon atoms; preferably  $\text{R}^2$  is a hydrogen atom or a group having 1 to 2 carbon atoms;  $\text{R}^2$  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.  $\text{R}^2$  preferably is nonfluorinated but may be fluorinated.

Representative fluorinated olefin (a) monomers are tetrafluoroethylene, hexafluoropropene, chlorotrifluoroethylene, 2-chloropentafluoropropene, perfluoroalkyl vinyl ethers, e.g.  $\text{CF}_3\text{OCF}=\text{CF}_2$  or  $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ , 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). Tetrafluoroethylene or hexafluoropropylene are preferred for use as the fluoroolefin (a) monomer and tetrafluoroethylene is particularly preferred. Representative examples of the nonfluorinated (b) monomers include ethylene, propylene, butylene, isobutylene and higher order  $\alpha$ -olefins. Ethylene and propylene are preferred. Preferably, also, one of the above-described (a) or (b) monomers contain at least 3 carbon atoms. The most preferred fluoropolymer of this invention are copolymers of tetrafluoroethylene and propylene.

The above-described (a) and (b) monomers may also optionally be copolymerized with a small amount of (c) one or more monomers that produce an acidic hydrogen on the backbone of the resulting fluoropolymer. To preserve the chemical resistance of the fluoropolymer process aid, monomers that yield an acidic

hydrogen within the structure of the fluoropolymer backbone are disfavored, and their presence must be minimized. Generally, monomers in which one vinyl carbon atom is perfluorinated (i.e. is saturated with fluorine atoms) and in which the other vinyl carbon atom contains at least one hydrogen atom will yield acidic hydrogen  
5 atoms on the backbone of a fluoropolymer into which they are polymerized, leaving the fluoropolymer susceptible to chemical attack by a base. This monomer class includes vinylidene fluoride, trifluoroethylene, 1-hydropentafluoropropene, and 2-hydropentafluoropropene. Monomers of this class are preferably not present in the fluoropolymer. If present, however, these monomers should not comprise greater  
10 than approximately 15 weight percent of the fluoropolymer, preferably comprising not more than 10 weight percent, even more preferably comprising less than 5 weight percent of the composition.

The fluoropolymer process aids of this invention are formed by copolymerizing one or more of the above-described fluorinated olefinic (a)  
15 monomers with one or more of the above-described (b) monomers, and optionally with a limited amount of one or of the above-described (c) monomer, such that the resulting process aid contains greater than 50 weight percent fluorine, preferably greater than 60 weight percent, even more preferably greater than 65 weight percent.

20 The fluoropolymers made in this manner from these constituent olefin monomers may be either semicrystalline or amorphous in nature, though the preferred fluoropolymer process aids are semicrystalline and can be easily pelleted.

The fluoropolymers should also contain essentially no ethylenic unsaturations because ethylenic unsaturations in the fluoropolymer may be sites for  
25 chemical attack by additives or other components present in the melt-processable composition. This means that the fluoropolymers will contain very little ethylenic unsaturation (e.g., carbon-carbon double bonds) along their backbone or in their pendant chains or groups. While very low levels of ethylenic unsaturation in the fluoropolymer process aid may be tolerated without substantial effect in this  
30 invention, higher levels cannot be tolerated without risking the chemical stability of its fluoropolymer process aid.

Fluoropolymers used in the invention should readily flow under the processing conditions of the thermoplastic hydrocarbon polymer into which it is admixed. In matching the fluoropolymer process aid with a thermoplastic hydrocarbon polymer, the fluoropolymer preferably should be chosen such that its melt viscosity matches or is about the same as the melt viscosity of the hydrocarbon polymer. For such matching, the fluoropolymer process aid can be selected such that the ratio of its melt viscosity to the melt viscosity of the thermoplastic hydrocarbon polymer is in the range of ratios from 0.01 to 100, more preferably in the range from 0.02 to 20, most preferably in the range between 0.05 and 5.

The fluorocarbon polymers used in accordance with this invention also preferably have an average molecular weight greater than about 10,000 and have a broad molecular weight distribution, and a polydispersity index (ratio of weight average molecular weight to number average molecular weight) of greater than about 1.5. These values generally correlate to fluoropolymer process aid Carreau-Yasuda Equation  $m_1$  values, as determined by the Dynamic Mechanical Analysis Evaluation described in Section I (C) of the Examples, of less than approximately 0.7. Preferably the polydispersity index of the fluoropolymer process aid is about 2 or more. This polydispersity index generally correlates to an  $m_1$  value of about 0.6 or less.

Preferred fluoropolymer process aids consist essentially of one or more fluoropolymers which consist essentially of interpolymerized units derived from: (a) one or more monomers selected from the group consisting of tetrafluoroethylene and hexafluoropropylene, (b) one or more monomers selected from the group consisting of propylene and ethylene, and (c) from 0 to 10 wt.% of one or more monomers selected from the group consisting of vinylidene fluoride, trifluoroethylene, 1-hydropentafluoropropene and 2-hydropentafluoropropene. The weight percentages of tetrafluoroethylene, hexafluoropropylene, propylene, ethylene and monomer (c) used to make the fluoropolymers are selected such that the resulting weight percent of fluorine in the resulting fluoropolymer process aid is at least 50, and preferably is at least 65, weight percent of the process aid and the

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ratio of the melt viscosity of the fluoropolymer process aid to the melt viscosity of the thermoplastic hydrocarbon polymer or polymers is between 0.01 and 100.

These fluoropolymer process aids exhibit superior chemical resistance, particularly in the presence of a base. When exposed to an organic or inorganic  
5 base, the fluoropolymer process aids will not significantly degrade and will not suffer substantial diminution of their original properties. In comparison, fluoropolymers that chemically degrade in the presence of a base may notably change in appearance and may discolor when extruded in thermoplastic hydrocarbon polymers. The degree of chemical resistance of the fluoropolymer  
10 process aids of the invention may be measured, for example, by thermogravimetric analysis (TGA) techniques. Comparison of the weight loss obtained by TGA individually for a given fluoropolymer process aid and an organic basic additive with the weight loss obtained from the mixture of the two provides an indication of the degree of chemical reactivity of those components. Otherwise stated, a predicted  
15 weight loss for the component blend may be calculated from the average weight loss of the components measured individually (e.g., a simple arithmetic average of the two individual weight losses for equal weight blending of the two components). If no chemical activity occurs between the fluoropolymer process aid and the additive, the measured weight loss of their blend should equal their predicted weight  
20 loss, and the ratio of the measured to the predicted weight loss (hereinafter the "weight loss ratio") will be equal to 1. Significant chemical activity between the two components may release a measurable amount of gaseous product and the measured weight loss of the blend will be greater than that predicted for no chemical activity. In such a case, the weight loss ratio will be significantly greater  
25 than one. Using this measure of chemical resistance, the fluoropolymer process aids of the invention will have a weight loss ratio less than 1.75, preferably less than 1.25, when measured according to the method described above using TGA analysis at 275 °C for 30 minutes for a blend, in equal proportion by weight, of the fluoropolymer process aid with a hindered-amine light stabilizer (HALS).

30 The fluorinated polymers used in this invention may be made according to the method disclosed by U.S. Pat. No. 5,285,002 (Grootaert),

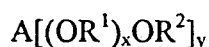
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wherein the polymerization reaction is carried out  
 at about 50 °C or higher under free-radical conditions in an aqueous emulsion or  
 suspension of a polymerizable mixture comprising the component (a) and (b)  
 monomers, a fluoroaliphatic-radical containing sulfinate, and a suitable oxidizing  
 5 agent.

The fluorocarbon process aids of this invention may also be combined with a  
 poly(oxyalkylene) polymer component to further improve the extrusion  
 characteristics of the thermoplastic hydrocarbon polymer. The poly(oxyalkylene)  
 polymer component may comprise one or more poly(oxyalkylene) polymers, and a  
 10 useful processing aid composition comprises, and preferably consists essentially of,  
 between about 5 and 95 weight percent of the poly(oxyalkylene) polymer  
 component and 95 and 5 weight percent of the fluoropolymer process aid.  
 Typically, the ratio of the fluoropolymer process aid to the poly(oxyalkylene)  
 polymer component in the processing aid will be from 1/2 to 2/1.

15 The poly(oxyalkylene) polymer component generally may comprise between  
 about 0.005 and 20 weight percent of the overall melt-processable composition,  
 more preferably between about 0.01 and 5 weight percent, and most preferably  
 between about 0.02 and 1 weight percent.

Generally, poly(oxyalkylene) polymers useful in this invention include  
 20 poly(oxyalkylene) polyols and their derivatives. A class of such poly(oxyalkylene)  
 polymers may be represented by the general formula:



wherein:

25 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-trimethylol propane, and poly(oxypropylene)  
 glycol;

30 y is 2 or 3;

(OR<sup>1</sup>)<sub>x</sub> is a poly(oxyalkylene) chain having a plurality of oxyalkylene groups, (OR<sup>1</sup>), wherein the R<sup>1</sup> moieties can be the same or different and are selected from the group consisting of C<sub>1</sub> to C<sub>5</sub> alkylene radicals and, preferably, C<sub>2</sub> or C<sub>3</sub> alkylene radicals, and x is the number of oxyalkylene units in said chain. Said 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 —OC<sub>2</sub>H<sub>4</sub>— and —OC<sub>3</sub>H<sub>6</sub>— units, or can be a chain having alternating blocks or backbone segments of repeating oxyalkylene groups, e.g., a polymer comprising —(OC<sub>2</sub>H<sub>4</sub>)<sub>a</sub> and —(OC<sub>3</sub>H<sub>6</sub>)<sub>b</sub> blocks, wherein a+b = 5 to 5000 or higher, and preferably 10 to 500.

R<sup>2</sup> 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, R<sup>2</sup> can be methyl, butyl, phenyl, benzyl, and acyl groups such as acetyl (CH<sub>3</sub>CO—), benzoyl (C<sub>6</sub>H<sub>5</sub>CO—) and stearyl (C<sub>17</sub>H<sub>35</sub>CO—).

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, (C<sub>17</sub>H<sub>35</sub>COO—). 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, (OR<sup>1</sup>).

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(OC<sub>2</sub>H<sub>4</sub>)<sub>n</sub>OH, where n is about 15 to 3000, such as those sold under the Carbowax trademark, such as Carbowax™ PEG 8000, where

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n is about 181, and those sold under the trade name Polyox, such as Polyox™ WSR N-10 where n is about 2272.

The blends of fluoropolymer and hydrocarbon polymer components (2) and (1), along with the poly(oxyalkylene) polymer component if present in the melt-processable composition, can be prepared 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 fluoropolymer process aid and poly(oxyalkylene) polymer component are uniformly distributed throughout the hydrocarbon polymer. The fluoropolymer process aid 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 hydrocarbon polymer, though it is also feasible to dry-blend the component 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.).

Blends of the thermoplastic hydrocarbon and fluoropolymer process aid, along with the poly(oxyalkylene) polymer component, if present, may be compounded as a masterbatch in a hydrocarbon resin. The masterbatch subsequently may be diluted prior to melt-processing to effect a desired concentration of fluoropolymer process aid and poly(oxyalkylene) polymer



component in the composition to be melt-processed. The fluoropolymer process aid and/or poly(oxyalkylene)polymer component alternatively may be fed to an extruder directly as a fine powder, therein combining with the thermoplastic hydrocarbon. The fluoropolymer process aid and/or 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. Such a slurring technique may be particularly useful if the fluoropolymer or fluoropolymers employed are semicrystalline.

The blended composition can contain conventional adjuvants such as antioxidants, pigments, and fillers, e.g. titanium dioxide, carbon black, and silica.

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.

## EXAMPLES

### I. FLUOROPOLYMER SYNTHESIS AND POLYMER PROPERTY EVALUATION

Thermal analysis of the polymers by differential scanning calorimetry (DSC) was performed on the following polymers using a TA Instruments DSC-2910 with a 2000 series controller and a LNCA-II controlled cooling accessory. Samples were heated to 350 °C and held isothermally for 1 min. to erase thermal history. Samples were then equilibrated at -100 °C. Next, samples were heated at 10 °C/min. from -100 °C to 350 °C. Data was analyzed using TA Instruments DSC Analysis V4.0 software.

#### A. FLUOROPOLYMER SYNTHESIS AND PROPERTY EVALUATION Fluoropolymer F1

A 19-liter vertically-stirred polymerization reactor was charged with 14,000 g deionized water, 9 g KOH, 81 g ammonium perfluoro octanoate (available from 3M as Fluorad™ FC-143 Surfactant), 50 g K<sub>2</sub>HPO<sub>4</sub>, and 324 g of a 20 wt%

solution of  $C_6F_{13}SO_2Na$  in deionized water. The reactor was then alternately evacuated and purged with  $N_2$  until the  $O_2$  level was less than 50 ppm. The reactor was then evacuated, the temperature raised to 71 °C, and the agitation set at 445 rpm. Next, the reactor was charged with 578.4 g of tetrafluoroethylene (TFE) and 30.54 g of propylene to give a pressure of 2.02 MPa (293 psig). The polymerization was initiated by feeding a 10 wt% solution of  $(NH_4)_2S_2O_8$  in deionized water to the reactor by means of a metering pump at approximately 3 g/min until 389 g of solution was fed. Upon the observation of a pressure drop, the running feed, which consisted of 75% TFE and 25% propylene, was started and continuously adjusted by the reactor's control system in order to maintain the desired pressure. The polymerization was halted by slowing the agitation after 2,998 g of TFE and 992 g of propylene had been fed. The reactor was then vented, cooled, and drained to isolate the latex. The resulting polymer was isolated by dripping the latex into a solution of magnesium chloride in water, followed by washing and drying, to yield a rubbery polymer.

#### Fluoropolymer F2

A 150-liter vertically-stirred polymerization reactor was charged with 120,000 g deionized water, 78 g KOH, 694 g ammonium perfluoro octanoate, 430 g  $K_2HPO_4$ , and 1,025 g of a 20% solution of  $C_4F_9SO_2Na$  in deionized water. The reactor was then alternately evacuated and purged with  $N_2$  until the  $O_2$  level was less than 50 ppm. The reactor was then evacuated, the temperature raised to 71 °C, and the agitation set at 210 rpm. Next, the reactor was charged with 3,549 g of TFE and 63.95 g of propylene to give a pressure of 1.52 MPa (220 psig). The polymerization was initiated by feeding a 5% solution of  $(NH_4)_2S_2O_8$  in deionized water to the reactor by means of a metering pump at approximately 25 g/min until one equivalent of  $(NH_4)_2S_2O_8$  was fed (approximately 3,200 g of solution). Upon the observation of a pressure drop, the running feed, which consisted of 92% TFE and 8% propylene, was started and continuously adjusted by the reactor's control system in order to maintain the desired pressure. The polymerization was halted by

slowing the agitation after 31,096 g of TFE and 2,704 g of propylene had been fed. The reactor was then vented, cooled, and drained to isolate the latex. The resulting polymer was coagulated by adding HCl to the latex, granulated, washed six times with deionized water, and dried overnight in an oven at 120 °C to yield a thermoplastic polymer in a white granular form. The polymer exhibited a melting endotherm with a peak melting temperature ( $T_m$ ) of 193 °C, when analyzed using differential scanning calorimetry (DSC).

#### Fluoropolymer F3

10 A 150-liter vertically-stirred polymerization reactor was charged with 105,000 g deionized water, 68 g KOH, 607 g ammonium perfluoro octanoate, 376 g  $K_2HPO_4$ , and 1,790 g of a 20% solution of  $C_4F_9SO_2Na$  in deionized water. The reactor was then alternately evacuated and purged with  $N_2$  until the  $O_2$  level was less than 50 ppm. The reactor was then evacuated, the temperature raised to 71 °C, 15 and the agitation set at 210 rpm. Next, the reactor was charged with 3,386 g of TFE, 886g of vinylidene fluoride ( $VF_2$ ), and 88 g of propylene to give a pressure of 1.60 MPa (232 psig). The polymerization was initiated by feeding a 10% solution of  $(NH_4)_2S_2O_8$  in deionized water to the reactor by means of a metering pump at approximately 25 g/min until 2,800 g of  $(NH_4)_2S_2O_8$  solution was fed. Upon the 20 observation of a pressure drop, the running feed, which consisted of 70% TFE, 10% vinylidene fluoride, and 20% propylene, was started and continuously adjusted by the reactor's control system in order to maintain the desired pressure. The polymerization was halted by slowing the agitation after 21,000 g of TFE, 3,000 g of vinylidene fluoride, and 6,000 g of propylene had been fed. The reactor was then 25 vented, cooled, and drained to isolate the latex. The resulting polymer was isolated by dripping the latex into a solution of magnesium chloride in water, followed by washing and drying, to yield a rubbery polymer.

#### Fluoropolymer F4

30 An 86-liter vertically-stirred polymerization reactor was charged with 52,000 g deionized water, 140 g KOH, 300 g ammonium perfluoro octanoate, 55.2

g  $\text{Na}_2\text{SO}_3$ , 2 g  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , and 1,000 g of a 20% solution of  $\text{C}_6\text{F}_{13}\text{SO}_2\text{Na}$  in deionized water. The reactor was then alternately evacuated and purged with  $\text{N}_2$  until the  $\text{O}_2$  level was less than 50 ppm. The reactor was then evacuated, the temperature raised to 54 °C, and the agitation set at 150 rpm. Next, the reactor was charged with 1,256 g of TFE and 37.18 g of propylene to give a pressure of 0.83 MPa (120 psig). The polymerization was initiated by feeding a 10% solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in deionized water to the reactor by means of a metering pump at approximately 3 g/min until 778 g of solution was fed. Upon the observation of a pressure drop, the running feed, which consisted of 88% TFE and 12% propylene, was started and continuously adjusted by the reactor's control system in order to maintain the desired pressure. The polymerization was halted by slowing the agitation to 30 rpm after 7,824 g of TFE and 1,080 g of propylene had been fed. The reactor was then vented, cooled, and drained to isolate the latex. The resulting polymer was isolated by freeze coagulation, washed six times with hot deionized water, and dried overnight in an oven at 100 °C to yield a thermoplastic polymer in a white granular form. The polymer exhibited a melting endotherm with a peak melting temperature ( $T_m$ ) of 103 °C, when analyzed using differential scanning calorimetry (DSC).

#### 20 Fluoropolymer F5

A 150-liter vertically-stirred polymerization reactor was charged with 120,000 g deionized water, 78 g KOH, 694 g ammonium perfluoro octanoate, 430 g  $\text{K}_2\text{HPO}_4$ , and 1,025 g of a 20% solution of  $\text{C}_4\text{F}_9\text{SO}_2\text{Na}$  in deionized water. The reactor was then alternately evacuated and purged with  $\text{N}_2$  until the  $\text{O}_2$  level was less than 50 ppm. The reactor was then evacuated, the temperature raised to 71 °C, and the agitation set at 210 rpm. Next, the reactor was charged with 3,730 g of TFE and 76.14 g of propylene to give a pressure of 1.52 MPa (220 psig). The polymerization was initiated by feeding a 5% solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in deionized water to the reactor by means of a metering pump at approximately 25 g/min until one equivalent of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was fed (approximately 3,200 g of solution). Upon

the observation of a pressure drop, the running feed, which consisted of 88% TFE and 12% propylene, was started and continuously adjusted by the reactor's control system in order to maintain the desired pressure. The polymerization was halted by slowing the agitation after 28,424 g of TFE and 3,876 g of propylene had been fed.

5 The reactor was then vented, cooled, and drained to isolate the latex. The resulting polymer was coagulated by adding HCl to the latex, granulated, washed six times with deionized water, and dried overnight in an oven at 120 °C to yield a thermoplastic polymer in a white granular form. The polymer exhibited a melting endotherm with a peak melting temperature ( $T_m$ ) of 116 °C and an end of melting

10 temperature of 175 °C, when analyzed using differential scanning calorimetry (DSC).

#### Fluoropolymer F6

An 86-liter vertically-stirred polymerization reactor was charged with

15 45,000 g deionized water, 29 g KOH, 260 g ammonium perfluoro octanoate, 161 g  $K_2HPO_4$ , and 1,300 g of a 20% solution of  $C_6F_{13}SO_2Na$  in deionized water. The reactor was then alternately evacuated and purged with  $N_2$  until the  $O_2$  level was less than 50 ppm. The reactor was then evacuated, the temperature raised to 71 °C, and the agitation set at 150 rpm. Next, the reactor was charged with 2,246 g of

20 TFE and 47.41 g of propylene to give a pressure of 1.38 MPa (200 psig). The polymerization was initiated by feeding a 10% solution of  $(NH_4)_2S_2O_8$  in deionized water to the reactor by means of a metering pump at approximately 7 g/min until 1,200 g of solution was fed. Upon the observation of a pressure drop, the running feed, which consisted of 91% TFE and 9% propylene, was started and

25 continuously adjusted by the reactor's control system in order to maintain the desired pressure. The polymerization was halted by slowing the agitation after 18,266 g of TFE and 1,824 g of propylene had been fed. The reactor was then vented, cooled, and drained to isolate the latex. The resulting polymer was isolated by freeze coagulation, washed six times with hot deionized water, and dried

30 overnight in an oven at 100 °C to yield a thermoplastic polymer in a white granular

form. The polymer exhibited a melting endotherm with a peak melting temperature ( $T_m$ ) of 130 °C, when analyzed using differential scanning calorimetry (DSC).

#### Fluoropolymer F7

5           An 86-liter vertically-stirred polymerization reactor was charged with  
45,000 g deionized water, 29 g KOH, 260 g ammonium perfluoro octanoate, 161 g  
K<sub>2</sub>HPO<sub>4</sub>, and 1,300 g of a 20% solution of C<sub>6</sub>F<sub>13</sub>SO<sub>2</sub>Na in deionized water. The  
reactor was then alternately evacuated and purged with N<sub>2</sub> until the O<sub>2</sub> level was  
less than 50 ppm. The reactor was then evacuated, the temperature raised to 71 °C,  
10   and the agitation set at 150 rpm. Next, the reactor was charged with 869.2 g of  
TFE and 019.32 g of propylene to give a pressure of 0.55 MPa (80 psig). The  
polymerization was initiated by feeding a 10% solution of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in  
deionized water to the reactor by means of a metering pump at approximately 7  
g/min until 1,200 g of solution was fed. Upon the observation of a pressure drop,  
15   the running feed, which consisted of 91% TFE and 9% propylene, was started and  
continuously adjusted by the reactor's control system in order to maintain the  
desired pressure. The polymerization was halted by slowing the agitation after  
7,459 g of TFE and 754.3 g of propylene had been fed. The reactor was then  
vented, cooled, and drained to isolate the latex. The resulting polymer was isolated  
20   by freeze coagulation, washed six times with hot deionized water, and dried  
overnight in an oven at 100 °C to yield a thermoplastic polymer in a white granular  
form. The polymer exhibited a melting endotherm with a peak melting temperature  
( $T_m$ ) of 68 °C, when analyzed using differential scanning calorimetry (DSC).

#### 25   Fluoropolymer F8

An 86-liter vertically-stirred polymerization reactor was charged with  
45,000 g deionized water, 29 g KOH, 260 g ammonium perfluoro octanoate, 161 g  
K<sub>2</sub>HPO<sub>4</sub>, and 1,300 g of a 20% solution of C<sub>6</sub>F<sub>13</sub>SO<sub>2</sub>Na in deionized water. The  
reactor was then alternately evacuated and purged with N<sub>2</sub> until the O<sub>2</sub> level was  
30   less than 50 ppm. The reactor was then evacuated, after which 100 g of hexamethyl

disilane was added by injection. The temperature was then raised to 71 °C, and the agitation set at 150 rpm. Next, the reactor was charged with 2,006 g of TFE and 42.73 g of propylene to give a pressure of 1.24 MPa (180 psig). The polymerization was initiated by feeding a 20% solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in

5 deionized water to the reactor by means of a metering pump at approximately 7 g/min until 644 g of solution was fed. Upon the observation of a pressure drop, the running feed, which consisted of 91% TFE and 9% propylene, was started and continuously adjusted by the reactor's control system in order to maintain the desired pressure. The polymerization was halted by slowing the agitation after

10 18,330 g of TFE and 1,833 g of propylene had been fed. The reactor was then vented, cooled, and drained to isolate the latex. The resulting polymer was isolated by freeze coagulation, washed six times with hot deionized water, and dried overnight in an oven at 100 °C to yield a thermoplastic polymer in a white granular form. The polymer exhibited a melting endotherm with a peak melting temperature

15 ( $T_m$ ) of 123 °C, when analyzed using differential scanning calorimetry (DSC).

#### Comparative Fluoropolymer V10

A 4-liter vertically-stirred polymerization reactor was charged with 2,600 g deionized water, 7 g KOH, 15 g ammonium perfluoro octanoate, 5.6 g  $\text{Na}_2\text{SO}_3$ ,

20 0.1 g  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , and 68 g of a 20% solution of  $\text{C}_6\text{F}_{13}\text{SO}_2\text{Na}$  in deionized water. The reactor was then alternately evacuated and purged with  $\text{N}_2$  until the  $\text{O}_2$  level was less than 50 ppm. The reactor was then evacuated, the temperature raised to 54 °C, and the agitation set at 550 rpm. Next, the reactor was charged with 138.2 g of TFE and 7.17 g of propylene to give a pressure of 1.87 MPa

25 (270 psig). The polymerization was initiated by feeding a 5% solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in deionized water to the reactor by means of a metering pump at approximately 0.5 g/min until 130 g of solution was fed. Upon the observation of a pressure drop, the running feed, which consisted of 75% TFE and 25% propylene, was started and continuously adjusted by the reactor's control system in order to

30 maintain the desired pressure. The polymerization was halted by slowing the agitation to 60 rpm after 652.3 g of TFE and 220.4 g of propylene had been fed.

The reactor was then vented, cooled, and drained to isolate the latex. The resulting polymer was isolated by dripping the latex into a solution of magnesium chloride in water, followed by washing and drying, to yield a rubbery polymer.

5     Comparative Fluoropolymer V11

          An 86-liter vertically-stirred polymerization reactor was charged with 52,000 g deionized water, 300 g NaOH, 300 g ammonium perfluoro octanoate, 55.2 g Na<sub>2</sub>SO<sub>3</sub>, 2 g CuSO<sub>4</sub> • 5 H<sub>2</sub>O, and 191 g of a 70% solution of C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>Na in deionized water. The reactor was then alternately evacuated and purged with N<sub>2</sub>

10    until the O<sub>2</sub> level was less than 50 ppm. The reactor was then evacuated, the temperature raised to 52 °C, and the agitation set at 150 rpm. Next, the reactor was charged with 2,298 g of TFE and 65.71 g of propylene to give a pressure of 1.52 MPa (220 psig). The polymerization was initiated by feeding a 10% solution of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in deionized water to the reactor by means of a metering pump at

15    approximately 8 g/min until 1,000 g of solution was fed. Upon the observation of a pressure drop, the running feed, which consisted of 88% TFE and 12% propylene, was started and continuously adjusted by the reactor's control system in order to maintain the desired pressure. The polymerization was halted by slowing the agitation to 30 rpm after 5,130 g of TFE and 715.2 g of propylene had been fed.

20    The reactor was then vented, cooled, and drained to isolate the latex. The resulting polymer was isolated by freeze coagulation, washed five times with hot deionized water, and dried overnight in an oven at 100 °C to yield a thermoplastic polymer in a white granular form. The polymer exhibited a melting endotherm with a peak melting temperature (T<sub>m</sub>) of 80 °C, when analyzed using differential scanning

25    calorimetry (DSC).



Table 1

Fluoropolymer		Monomer Composition (wt%)				Polymer Composition (wt%)	
		TFE	P	VF <sub>2</sub>	HFP	H	F
V1	Fluorel™ FC-2145	--	--	60	40	1.88	66.0
V2	Dynamar™ FX-9613	--	--	60	40	1.88	66.0
V3	experimental	--	--	60	40	1.88	66.0
V4	THV-500G	60	--	20	20	0.63	72.7
V5	Fluorel™ FX-11705	54	15	32	--	3.14	60.0
V6	Aflas™ 100N	75	25	--	--	3.57	57.0
V7	experimental	75	25	--	--	3.57	57.0
V8	Aflas™ 150C	75	25	--	--	3.57	57.0
V9	Aflas™ 150L	75	25	--	--	*	*
V10	experimental	75	25	--	--	3.57	57.0
V11	experimental	88	12	--	--	1.71	66.9
F1	experimental	75	25	--	--	3.57	57.0
F2	experimental	92	8	--	--	1.14	69.9
F3	experimental	70	20	10	--	3.17	59.1
F4	experimental	88	12	--	--	1.71	66.9
F5	experimental	88	12	--	--	1.71	66.9
F6	experimental	91	9	--	--	1.29	69.2
F7	experimental	91	9	--	--	1.29	69.2
F8	experimental	91	9	--	--	1.29	69.2
F9	experimental	not measured					

\* Aflas™ 150L is produced by a thermal treatment of Aflas™ 150C. The thermal treatment removes hydrogen and fluorine from polymer backbone to yield carbon to carbon double bonds. The resultant polymer is black in color. The thermal treatment is believed to reduce the Mooney viscosity through chain scission.

WO 97/10294

PCT/US96/13149

Sources\*

- V1: 3M Company  
 V2: 3M Company, 90% fluoroelastomer, 6% talc, 2% CaCO<sub>3</sub> and 2% SiO<sub>2</sub>  
 V3: Same composition as V1, but polymerized according to method described in  
 5 Example 3 of U.S. Patent 5,285,002 (Grootaert).  
 V4: 3M Company, formerly available from Hoechst as Hostaflon™ TFBX-7100.  
 V5: Distributed by 3M Company  
 V6: Asahi Glass Company  
 V7: Sample polymerized according to method described in Example 5 of U.S.  
 10 Patent 4,463,144.  
 V8: Asahi Glass Company, lowest known viscosity of commercially available  
 TFE/P polymers.  
 V9: Asahi Glass Company  
 F9: Experimental product from Hoechst, ET 6810, polymer containing  
 15 Ethylene, TFE & HFP, with a T<sub>m</sub> peak of 160 °C.

\* V10, V11 and F1-F8 made as previously described

Monomers

- 20 TFE: Tetrafluoroethylene  
 P: Propylene  
 VF<sub>2</sub>: Vinylidene fluoride  
 HFP: Hexafluoropropylene  
  
 25 H: Hydrogen  
 F: Fluorine

**B. DESCRIPTION OF THE POLYETHYLENES USED IN THE  
EXAMPLES.**

30

Table 2

Commercial Polyethylenes						
Resin	Product Code	Company	MI	Comonomer	Density	Form
A	LL-1001.32	Exxon Chem.	1.0	1-Butene	0.917	pellets
B	LL-1001.09	Exxon Chem.	1.0	1-Butene	0.917	powder
C	LL-3201.00	Exxon Chem.	0.8	1-Hexene	0.925	powder
D	TFY826F	Novacor Chem., Ltd.	0.8	1-Hexene	0.926	pellets
E	DMDA-6147	Petromont, Inc.	8*	1-Hexene	0.945	pellets

MI: Determined in accordance with ASTM D-1238, melt index at 190 °C with a load of 2.16 kg.

\* HLMI, high load melt index at 190 °C with a load of 21.6 kg

Density: grams/cm<sup>3</sup>

### C. DYNAMIC MECHANICAL ANALYSIS EVALUATION OF FLUOROPOLYMER PROPERTIES

A Rheometrics Mechanical Spectrometer (RMS) model RDA II was used to  
 5 conduct Dynamic Mechanical Analysis (DMA) and determine various viscoelastic  
 properties of the polymers listed in Tables 1 and 2. Samples for testing were first  
 molded into a 1 mm thick plaque, using a Carver press. Samples were pressed at a  
 minimum temperature of 150 °C for about a minute and at a pressure sufficient to  
 produce a uniform plaque thickness. Higher temperatures and longer press times  
 10 were used if the sample did not flow sufficiently. A 25.4 mm circular sample was  
 then cut from the plaque using a circular punch.

Measurements were conducted in the molten state, using parallel plates with  
 a radius of 12.5 mm and a gap of about 0.75 mm. For each sample, isothermal  
 frequency sweeps were run at four to six different test temperatures between the  
 15 range of 170 °C and 340 °C. The validity of the results was verified using a Cole-  
 Cole plot and unreliable data were rejected. For each sample, the results from at  
 least four temperatures were used for further calculations.

The viscosity data were fitted to the Carreau-Yasuda (ref. 1,2,3) Equation  
 (Equation 1), using the Marquardt-Levenberg Algorithm (ref. 4), as obtained from  
 20 Jandel Scientific. Since the voltage output of the torque transducer of the RMS  
 instrument is proportional to the logarithm of the torque, and in order to give an  
 equivalent statistical weight to lower and higher viscosities, the logarithmic form in  
 Equation 1 was used:

$$25 \quad 1) \quad \log (\eta) = \log (\eta_0) - (((1-n)/m1) \log (1+(\omega\tau)^{m1}))$$

Where:  $(\eta)$  is the viscosity of the molten polymer,  $(\eta_0)$  is the zero shear  
 viscosity,  $(\tau)$  is the relaxation time and  $(\omega)$  is the frequency. In this  
 equation,  $n$  is the power law exponent and is an indicator of the slope of  
 30 the curve in the pseudoplastic region; while  $m1$  is a relative scale of the  
 molecular weight distribution (MWD), with large values of  $m1$   
 corresponding to narrower molecular weight distributions.

The time-temperature superposition principle was applied here by combining Equation 1 with Equations 2, 3 and 4. The time-temperature superposition principle allows measurements made at a given temperature to be shifted to a reference temperature using a shift factor (at), which is described below:

5

$$2) \quad \log (at) = (\Delta H_a / 2.3R)(1/T - 1/T_r)$$

Where  $\Delta H_a$  is the activation energy of the polymer flow, R is the gas constant, T is the temperature and  $T_r$  is the reference temperature, in Kelvin.

10

This Equation is considered valid at the testing temperatures considered here (ref. 5). Although  $T_g$ , the glass transition temperature, is often used as the reference temperature, Equation 2 remains valid with any reference temperature. Also, the activation energy,  $\Delta H_a$ , is considered constant over the temperature ranges considered here.

15

The zero shear viscosity and relaxation time at a specific temperature can be obtained from Equations 3 and 4:

$$3) \quad \log (\eta_o) = \log (\eta_r) + \log (at)$$

20

$$4) \quad \log (\tau) = \log (\tau_r) + \log (at)$$

Where  $\eta_r$  and  $\tau_r$  are the zero shear viscosity and the relaxation time respectively at the reference temperature.

In some cases it was not always possible to obtain a measurement at the reference temperature of 190 °C, particularly if the sample was not fully molten, or if the viscosity was near the limit of the transducer accuracy. However, the  $\log (\eta_o)$  and  $\log (\tau)$  can be extrapolated to the reference temperature for comparison purposes. Equations 2 through 4 can be used to convert the results from one reference temperature to another.

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This set of equations, 1 through 4, was fitted simultaneously to the  $\eta'$  and  $\eta^*$  curves obtained from the DMA measurements. The Carreau-Yasuda Equation was used to fit the true and complex viscosity data, where  $\eta'$  is the true viscosity and  $\eta^*$  is the complex viscosity. The  $n'$  parameter for the  $\eta'$  curve will be different  
 5 from the  $n^*$  parameter for the  $\eta^*$  curve. However, in the equations used here, the values of  $\eta_0$ ,  $\tau$  and  $m_1$  are equivalent for both curves, these variables are characteristics of the molecular weight and molecular weight distribution.

The polymers listed in Tables 1 and 2 were tested as described, and the measured experimental data was fitted to Equations 1 through 4 using a reference  
 10 temperature of 190 °C in each case. The six constants:  $m_1$ ,  $n'$ ,  $n^*$ ,  $\log(\eta_r)$ ,  $\log(\tau_r)$  and  $\Delta H_a$  were used as the fitting parameters. A value of  $n^* \geq 0$  was used as a constraint in the calculations, since a value smaller than zero is unrealistic. The parameters are listed in Table 3.

The polydispersity of the samples were assessed from the curve-fitting  
 15 parameters. The curvature of the viscosity curve with shear rate or angular frequency can be associated with polydispersity (ref. 6). The  $m_1$  parameter is a measurement of the curvature of the viscosity curve and can be associated with polydispersity (ref. 7). Therefore, the parameter  $m_1$  was used as a scale of polydispersity. Values of  $m_1$  of about 0.7 or more are taken here to correspond to  
 20 relatively narrow molecular weight distributions (an  $m_1$  value of about 0.6 is believed to correspond to a polydispersity of roughly 2), while  $m_1$  values around 0.35 are representative of broader molecular weight distribution samples.

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Table 3

Viscoelastic Properties						
Material	ML	$\log(\eta_0)$	$\log(\tau)$	m1	$\Delta H_a$	n
A	----	5.13	-1.67	0.49	27	0.15
D	----	5.28	-1.52	0.43	24	0.14
E	----	7.35	1.18	0.21	15.2	0.21
V1	32	5.44	-0.17	0.37	61	0.29
V2	32	**	----	----	----	----
V3	32	**	----	----	----	----
V4	----	5.54	-1.40	0.59	52	0.09
V5	46	7.5*	1.3	0.20	50	0.16
V6	150+	9.97*	4.13	0.17	66	0.17
V7	121	10**	----	----	----	----
V8	100+	10.37*	4.74	0.15	78	0.20
V9	25	5.77	-0.87	0.19	56	0.13
V10	68	7.76	2.29	0.35	29	0.22
V11	----	6.19	2.40	1.22	86	0.56
F1	25	5.42	0.33	0.39	44	0.37
F2	----	7.27	1.52	0.41	132	0.32
F3	50	7.16	1.94	0.37	91	0.28
F4	----	4.62	-1.04	0.68	128	0.27
F5	----	6.89	1.10	0.31	96	0.30
F6	----	6.19	0.14	0.37	98	0.14
F7	----	4.16	-1.21	0.61	102	0.36
F8	----	4.60	-2.01	0.32	29	0
F9	----	7.38	2.14	0.43	83	0.45

ML: Mooney viscosity, ASTM D1646, condition ML 1 + 10 minutes, measured at 121 °C. Not tested on semi-crystalline materials.

$\log(\eta_0)$ : log of the zero shear viscosity at 190 °C, in poise.

5  $\log(\tau)$ : log of the relaxation time of the polymer at 190 °C, in seconds

m1: measurement of the curvature of the viscosity curve; m1 is inversely proportional to polydispersity.

$\Delta H_a$ : activation energy of flow in kJ/mol

n: power law index

\* Results are near the upper torque and accuracy limit of the DMA viscometer  
\*\* Estimated value, not measured. The viscoelastic properties of V7 is taken to  
5 be within the range of properties of V6 and V8 given its measured Mooney  
viscosity is within this range. The viscoelastic properties of V2 and V3  
were not measured, but are taken to be similar to that of V1 given they have  
the same Mooney viscosity.

10 **D. ANALYSIS OF MELT-PROCESSABLE COMPOSITIONS AND  
THEIR COMPONENTS USING THERMOGRAVIMETRIC  
ANALYSIS**

**COMPARATIVE EXAMPLE C1**

Step A: A sample of Chimassorb™ 944, hindered amine light stabilizer  
15 (HALS, from Ciba-Geigy) was placed in a Perkin Elmer TGA (thermo-gravimetric  
analyzer) and evaluated in air. The temperature was ramped from 30 °C to 275 °C  
at 200 °C/minute and then held at 275 °C for 30 minutes. After 30 minutes, the  
sample had lost 5.012 % of its weight and was brown in color throughout.

Step B: A sample of fluoropolymer V1, described in Table 1, was tested  
20 under the same conditions as the HALS in Step A. The sample lost 0.479 % of its  
weight after 30 minutes.

Step C: 25 grams of V1 was blended at ambient conditions with an equal  
amount of the HALS used in Step A using a Thropp™ 7.62 cm (3 inch) two-roll  
mill. A portion of this blend was tested in the TGA under the same conditions as  
25 the HALS in Step A. The sample was removed after testing and examined for  
discoloration both on its surface and interior by cutting it in half. The weight losses  
of the HALS measured in Step A and V1 in Step B were averaged to predict a  
weight loss value for the milled two component blend. The results are listed in  
Table 4.

30 **EXAMPLE 1**

Step A: A sample of fluoropolymer F1 was tested in the TGA under the  
same conditions as fluoropolymer V1 in Step B of Comparative Example C1 and  
lost 0.539 % of its weight after 30 minutes.

Step B: A blend was prepared and evaluated according to the procedure described in Step C of Comparative Example C1 except that fluoropolymer F1 was used in place of V1. The results are listed in Table 4.

Table 4

TGA results, 30 minutes at 275 °C, in air				
Example	50/50 Blend	Measured % Wt loss	Predicted* % Wt loss	Weight Loss Ratio **
C1	V1 & HALS	6.106	2.746	2.22
1	F1 & HALS	2.384	2.776	0.86

5

Example	50/50 Blend	Color before TGA***		Color after TGA	
		initial	10 months	outside	inside
C1	V1 & HALS	white	tan	black	black
1	F1 & HALS	white	white	brown	white

Size of TGA test samples ranged from 8 to 12 mg.

\*Predicted weight loss based on average weight loss of the individual components used to make the 50/50 milled blend.

10 \*\* Ratio is the actual measured loss divided by the predicted weight loss. A weight loss ratio of 1.0 indicates the sample is losing the predicted amount. A ratio greater than 1.0 indicates a decrease in thermal stability, most probably due to chemical reaction between blend components. A ratio of less than 1.0 is interpreted as non-reactive, this may occur if the volatiles from either individual component become trapped within the blend matrix.

15 \*\*\* Color of milled blend when initially made, and after 10 months at ambient conditions. Comparative Example C1 showed discoloration after 10 days at ambient.

20 The results show that fluoropolymer F1 has better chemical resistance than V1 in the presence of reactive additives such as HALS. The TGA measured weight loss of Comparative Example C1 was greater than the predicted weight loss, which indicates a decrease in thermal stability. Also, the color of Comparative Example C1 changed from white to black throughout, a further indication of chemical interaction between the two components. Finally, Comparative Example C1 also

25 showed discoloration at ambient conditions over time, this is taken to indicate chemical interaction with the HALS. This demonstrates that polymers of the V1-type are susceptible to chemical reaction even while at ambient conditions.



In contrast, Example 1 had a weight loss less than what was predicted, indicating no loss in stability with temperature. Likewise, it retained its original white color on the inside. The brown outer surface is believed to be due to HALS on the outer surface of the blend discoloring to the same brown color that the HALS exhibits when tested alone. Even though fluoropolymer F1 contains nearly twice the weight % hydrogen as fluoropolymer V1 (Table 1), it is non-reactive in comparison. The blend of fluoropolymer F1 and HALS showed no change in color over time at ambient conditions.

#### COMPARATIVE EXAMPLE C2

Step A: A sample of HALS was placed in a TGA and evaluated under the same conditions as the HALS evaluated in Step A of Comparative Example C1. The sample lost 3.817 % of its weight after 30 minutes and was brown in color throughout.

Step B: A sample of fluoropolymer V3 was evaluated in the TGA under the same conditions as the fluoropolymer evaluated in Step B of Comparative Example C1 and lost 0.394 % of its weight.

Step C: 25 grams of fluoropolymer V3 was blended at ambient conditions with an equal amount of the HALS used in Step A using a Thropp™ 7.62 cm two-roll mill. A portion of this blend was tested in the TGA under the same conditions as the blend evaluated in Step C of Comparative Example C1. The weight losses measured for the individual components in Steps A and B of this Example were averaged to predict a weight loss value for the milled two component blend. The results are listed in Table 5.

#### COMPARATIVE EXAMPLE C3

Step A: A sample of fluoropolymer V5 was evaluated in the TGA under the same conditions as the fluoropolymer evaluated in Step B of Comparative Example C1, the sample lost 0.502 % of its weight after 30 minutes.

Step B: A blend was prepared and evaluated using the procedures described in Comparative Example C2 except that fluoropolymer V5 was used in place of fluoropolymer V3. The results are listed in Table 5.

EXAMPLE 2

Step A: A sample of HALS was placed in a TGA and evaluated under the same conditions as the HALS evaluated in Step A of Comparative Example C1. The sample lost 2.595 % of its weight after 30 minutes and was brown in color throughout.

Step B: A sample of fluoropolymer F3 was evaluated in the TGA under the same conditions as the fluoropolymer evaluated in Step B or Comparative Example C1, the sample lost 0.362 % of its weight after 30 minutes.

Step C: 25 grams of fluoropolymer F3 was blended at ambient conditions with an equal amount of the HALS used in Step B using a Thropp™ 3 inch two-roll mill. A portion of this blend was tested in the TGA under the same conditions as the blend evaluated in Step C of Comparative Example C1. The weight losses measured for the individual components in Steps A and B of this example were averaged to predict a weight loss value for the milled two component blend. The results are listed in Table 5.

Table 5

TGA results, 30 minutes at 275 °C, in air				
Example	50/50 Blend	Measured % Wt loss	Predicted* % Wt loss	Weight Loss Ratio **
C2	V3 & HALS	7.469	2.106	3.55
C3	V5 & HALS	3.876	2.160	1.79
2	F3 & HALS	2.429	1.479	1.64

Example	50/50 Blend	Color before TGA***		Color after TGA	
		initial	1 month	outside	inside
C2	V3 & HALS	white	tan	black	black
C3	V5 & HALS	white	white	brown	tan
2	F3 & HALS	white	white	brown	tan

\* Predicted weight loss based on average weight loss of the individual components used to make the 50/50 milled blend.

\*\* Ratio is of the actual measured loss divided by the predicted weight loss.

\*\*\* Color of milled blend when initially made, and after one month at ambient conditions. Comparative Example C2 began to show discoloration after 4 days at ambient.

5 Comparative Example C2 showed a weight loss greater than that predicted from the average of the individual components used to make the blend. Also, its color changed from white to black throughout, a further indication of reaction. Finally, the color of Comparative Example C2 changed overtime, even while at ambient conditions. Comparative Example C3 had a weight loss greater than that  
10 predicted. The surface of this sample was brown, as was the pure HALS, and its interior changed from white to tan. Example 2 also had a weight loss greater than predicted, but its loss ratio was smaller than that of sample C3. The surface of Example 2 was brown like the pure HALS, and the interior changed from white to tan. This again indicates that the inclusion of  $\text{VF}_2$  increases the reactivity of the  
15 fluoropolymer, and demonstrates a relation between reactivity and the amount of this (c) monomer in a fluoropolymer. The sample of Example 2 showed no change in color at ambient conditions. While the change in color and increased weight loss indicated a reaction with the HALS, the inclusion of a smaller amount of  $\text{VF}_2$  in fluoropolymer F3 in Example 2 was not as reactive as the fluoropolymer V5 in  
20 Comparative Example C3.

The reactivity and weight loss ratios of the fluoropolymers blended with HALS in these examples is inversely related to the % hydrogen in the fluoropolymer (as listed in Table 1). This indicates that the amount of hydrogen contained in a fluoropolymer is not as important as the type of monomers used.

25 COMPARATIVE EXAMPLE C4

Step A: A sample of fluoropolymer V4 was tested in the TGA under the same conditions as the fluoropolymer evaluated in Step B of Comparative Example C1. The sample lost 0.090 % of its weight after 30 minutes.

Step B: 64 grams of fluoropolymer V4 and 16 grams of the HALS used in  
30 Step A of Comparative Example C1 were melt mixed in a Haake Rheocord™ System 90 using a Rheomix™ 600 bowl fitted with roller blades. The mixing sequence lasted for five minutes at a constant temperature of 220 °C. The rotors

were programmed in the following sequence; 15 rpm for the first two minutes, then increased to 50 rpm during the third minute and held at 50 rpm for the duration. A portion of the blend was tested in the TGA under the same conditions as the blend evaluated in Step C of Comparative Example C1. The HALS TGA weight loss  
5 measured in Step A of Comparative Example C1 and the fluoropolymer TGA weight loss measured in Step A were averaged to predict a weight loss for the melt mixed blend. The results are listed in Table 6.

#### EXAMPLE 3

Step A: A sample of fluoropolymer F5 was tested in the TGA under the  
10 same conditions as the fluoropolymer evaluated in Step B of Comparative Example C1. The sample lost 0.102 % of its weight after 30 minutes.

Step B: A blend of fluoropolymer F5 and HALS was prepared and evaluated using the procedure described in Step B of Comparative Example C4. The HALS TGA weight loss measured in Step A of Comparative Example C1 and  
15 the TGA weight loss for F5 measured in Step A were averaged to predict a weight loss for the melt mixed blend. The results are listed in Table 6.

#### EXAMPLE 4

Step A: A sample of fluoropolymer F9 was tested under the same conditions as the fluoropolymer evaluated in Step B of Comparative Example 1.  
20 The sample lost 0.214 % of its weight after 30 minutes.

Step B: A blend of fluoropolymer F9 and HALS was prepared and evaluated using the procedure described in Comparative Example C4. The HALS TGA weight loss measured in Step A of Comparative Example C1 and the TGA weight loss for F9 measured in Step A were averaged to predict a weight loss for  
25 the melt mixed blend. The results are listed in Table 6.

Table 6

TGA results, 30 minutes at 275 °C, in air				
Example	80/20 Blend	Measured % Wt loss	Predicted* % Wt loss	Weight Loss Ratio **
C4	V4 & HALS	5.589	1.074	5.20
3	F5 & HALS	1.056	1.084	0.96
4	F9 & HALS	1.060	1.174	0.90

\* Predicted weight loss based on average weight loss of the individual components used to make the 80/20 melt mixed blend.

\*\* Ratio is the actual measured loss divided by the predicted.

5 Size of TGA test samples ranged from 33 to 38 mg.

The data in Table 6 shows that semi-crystalline fluoroplastics containing a significant amount of VF<sub>2</sub> are susceptible to chemical attack by bases. Comparative Example C4 shows a weight loss greater than that predicted from the sum of its individual components. In contrast, the semi-crystalline fluoropolymers of the invention, fluoropolymers F5 and F9, as illustrated by Examples 3 and 4, that contain monomers that do not produce acidic hydrogens in the backbone of the fluoropolymer, do not exhibit this reactive behavior. Although the fluoroplastics used in Examples 3 and 4 contain considerably more hydrogen than that used in Comparative Example C4, they do not exhibit the same reactivity as the fluoropolymer used in Comparative Example C4. Fluoropolymer F5 contains 5.5 times more hydrogen than fluoropolymer V4.

#### COMPARATIVE EXAMPLE C5

A 3.8 gram sample of the 50/50 milled blend of V1 and HALS produced in Step C of Comparative Example C1 was melt mixed in resin A using the described SP1 method (described below) to produce a combined concentrate containing 1% each of the fluoropolymer V1 and HALS. The resultant mixture was beige in color indicating that the reaction between bases such as HALS and V1 can occur even when the HALS and the fluoropolymer are mixed and diluted in polyethylene.

#### EXAMPLE 5

A 3.8 gram sample of the 50/50 milled blend of fluoropolymer F1 and HALS produced in Example 2 was melt mixed into resin A according to the same

SP1 method, the resultant mixture contained 1% each of fluoropolymer F1 and HALS, and was white in color. This indicates that polymers of the invention are not prone to discoloration in the presence of bases when admixed into polyolefins.

5     **II.     EVALUATION OF EXTRUDABLE SAMPLES BY USING**  
          **CAPILLARY RHEOMETRY TESTING**

10     **A.     SAMPLE PREPARATION FOR CAPILLARY RHEOMETRY**  
          **TESTING (SP1)**

Formulations for capillary rheometry testing were prepared using a Haake Rheocord™ System 40 torque rheometer and Rheomix™ 3000E mixing bowl attachment fitted with roller blades. The mixing sequence began with a two minute material loading period at 15 rpm, during the third minute the rotor speed was  
15     increased to 50 rpm and held constant for the duration. The temperature of the bowl was initially programmed at 230 °C for one minute and then decreased to 180 °C for the duration. The entire mixing cycle lasted for eight minutes. Total batch size was 190 grams, final melt temperatures of the sample were in the range of 180 to 200 °C. Masterbatch concentrates of fluoropolymers were prepared at a 2%  
20     level with a total batch size of 190 grams in resin A, and the mixture was allowed to cool below its T<sub>m</sub>. The cooled mixture was chopped into small pieces with a hydraulic bale cutter.

Compositions containing lower fluoropolymer concentrations were prepared by diluting the above-described 2% fluoropolymer concentrate with more  
25     polyethylene resin using the procedure described above to mix the desired amounts of polyethylene and fluoropolymer concentrate. Typical fluoropolymer test levels were 500 ppm or in some cases 1000 ppm. The cooled mixtures were again chopped and then ground at ambient temperature in a No. 4 Wiley™ mill fitted with a screen with 1 cm openings.

30     The concentrates used in the following Examples were either produced using the above-described SP1 method, using twin screw method described in the Examples in Section III (A), or was a concentrate of 3% fluoropolymer V2, Dynamar™ FX-9613, commercially available from Ampacet, product #10925.

## B. CAPILLARY RHEOMETRY EVALUATIONS

Experiments were conducted using an Instron™ 4202 or 4204 mainframe  
5 fitted with a 3210 capillary rheometer barrel. The die had a flat entry with a 0.508  
mm diameter and a length to diameter ratio (L/D) of about 40/1. Test temperatures  
were at 190, 210, 230 or 250 °C. Ground samples prepared according to the SP1  
method were packed into the rheometer barrel and allowed to dwell for 10 minutes.  
This was done to ensure a uniform melt temperature before the testing was begun.

10 Samples were initially extruded at a shear rate of either 600 or 400s<sup>-1</sup>, a strip  
chart recorder displayed the pressure on the capillary piston versus time. As a  
sample containing a fluoropolymer was extruded, the pressure would decrease,  
indicating if the fluoropolymer was serving to reduce the required force of  
extrusion. When the pressure reached an equilibrium, the shear rate was decreased  
15 to the lowest test value, and again allowed to proceed until a new equilibrium was  
reached and the apparent viscosity was recorded. The shear rate was then increased  
in a stepwise manner, with the equilibrium viscosity recorded at each shear rate. If  
a sample had not reached an equilibrium by the end of the test, (before the capillary  
barrel had emptied), the barrel was reloaded and the test continued. Samples of the  
20 extrudate were collected at each shear rate, were allowed to air-cool and were then  
visually inspected for melt fracture under a optical microscope at 30X  
magnification. Strand surfaces were classified as either smooth (free of any visible  
surface defects), sharkskined, or cyclic melt fractured (CMF). The latter was also  
detectable by a saw-toothed pattern displayed on the strip chart recorder. The  
25 apparent viscosities recorded were not corrected for die entrance effects.

At the conclusion of each test, the capillary die was removed, and the barrel  
cleaned with a brush and cotton gauze. The die was reinserted and the barrel was  
loaded with a concentrate of 70% CaCO<sub>3</sub>, product HM-10 available from Heritage  
Plastics. This purge material was extruded at a shear rate of 2000s<sup>-1</sup>. When  
30 emptied, the barrel was again cleaned and then loaded with Resin A, approximately  
one-half of the barrel was extruded at 2000s<sup>-1</sup>, the rate was then decreased to

400s<sup>-1</sup> and then to 100s<sup>-1</sup>. The extruded filament was observed at both rates and the viscosities recorded. If the filament did not exhibit melt fracture on 100% of its circumference, or if the viscosities were not similar to previously established values, the entire purge procedure was repeated. This purging step was performed to  
5 insure that the entire rheometer was free of fluoropolymer from the previous test. If after repeating the purge procedure, the Resin A still did not exhibit the previous results, the capillary die was placed in a pyrolysis oven at 400 °C for 20 minutes to remove all polymer residues.

The base resins, without fluoropolymer additives, were tested in the same  
10 manner to establish base lines for comparison. Using these baselines, the percent decrease in apparent viscosity provided by the presence of a fluoropolymer can be determined as a function of shear rate. The percent decrease is defined here as the difference in apparent viscosity for a polymer without fluoropolymer (V) and with fluoropolymer (Vp), divided by the viscosity for the base polymer without the  
15 fluoropolymer (V), % decrease = (V-Vp)/V.

### C. EXAMPLES

#### COMPARATIVE C6

20 A sample of resin A was tested in the capillary rheometer at 190 °C and 210 °C by the described method to generate a viscosity shear rate profile. The results at 190 °C are presented in Table 7.

#### COMPARATIVE EXAMPLE C7

A sample containing 500 ppm fluoropolymer V1 in resin A was produced by  
25 the previously described SP1 method and tested in the capillary rheometer at 190 °C. The results are presented in Table 7.

#### EXAMPLE 6

A melt mixed sample containing 1000 ppm of fluoropolymer F1 in resin A was prepared by the SP1 method and tested in the capillary rheometer at 190 °C.  
30 The results are presented in Table 7.



COMPARATIVE EXAMPLE C8

19 grams of the concentrate produced in Comparative Example C5 was diluted into resin A according to the SP1 method to produce a sample containing 1000 ppm each of fluoropolymer V1 and HALS. The sample was evaluated in the capillary rheometer at 190 °C as described. The results are presented in Table 7.

EXAMPLE 7

19 grams of the concentrate produced in Example 5 was diluted into resin A according to the SP1 method to produce a sample containing 1000 ppm each of the fluoropolymer F1 and HALS. It was tested in the capillary rheometer at 190 °C. The results are presented in Table 7.

**Table 7**

Capillary rheometer data, 190 °C, in Resin A

Examples	Additives	Viscosity (P) and Surface Characteristics at Shear Rate (s <sup>-1</sup> )			Shear Rate at CMF Onset (s <sup>-1</sup> )
		200	400	1000	
C6	-----	14050 SS	9040 SS	----- CMF	600
C7	V1	5610 Sm	4520 Sm	3460 Sm	>1400
6	F1	10110 Sm	6270 Sm	3690 Sm	>1400
C8	V1 & HALS	14360 SS	9150 SS	----- CMF	600
7	F1 & HALS	13750 Sm	7510 Sm	3930 Sm	1400

Surface characteristics

Sm: Smooth  
SS: Sharkskin  
CMF: Cyclic Melt Fracture

The data in Table 7 shows that although the fluoropolymer V1 in Comparative Example C7 functioned as a process aid in the absence of non-reactive additives, the addition of HALS, as illustrated by Comparative Example C8, completely eliminated the effectiveness of fluoropolymer V1. Comparative Example C8 gave the same extrusion behavior as the base resin A in Comparative Example C6 which contained no fluoropolymer. In contrast, the same level of fluoropolymer F1 with HALS in Example 7, eliminated the sharkskin, postponed

the onset of cyclic melt fracture, and provided a decrease in the apparent viscosity. Surprisingly, the hydrogen content of the fluoropolymer F1 is nearly twice that of the fluoropolymer V1 (see Table 1). Thus, in the selection of a fluoropolymer process aid that is chemically-resistant at thermoplastic polymer processing  
5 conditions, the amount of hydrogen in a fluoropolymer is not as important as the type of monomers used.

A more precise selection of the properties of fluoropolymer F1 would allow it to provide further reductions in apparent viscosity at lower use levels.

Examples 6 and 7 and Comparative Examples C6-C8 were designed to  
10 simulate the interactions between fluoropolymer process aids and commonly used light stabilizing additives that occur during commercial polyolefin extrusion production. Such interactions may be worse in commercial-scale extrusion equipment because commercial extrusions runs occur over long periods of time, there is a greater degree of mixing in commercial extrusion equipment, and  
15 extrudable compositions have longer residence times in commercial-scale extruders.

#### COMPARATIVE EXAMPLE C9

A sample with 500 ppm fluoropolymer V2 in resin A was prepared according to the SP1 method and evaluated in the capillary rheometer at 190 °C.  
20 The percent reduction in apparent viscosity provided by fluoropolymer V2 was calculated and is listed in Table 8.

#### COMPARATIVE EXAMPLE C10

Same as Comparative Example C9, but resin B was substituted for resin A. The results are in Table 8. Resins A and B have the same specifications for melt  
25 index, density and co-monomer (see Table 2), but resin B contains a smaller amount of thermal stabilizer than resin A.

#### EXAMPLE 8

A sample containing 500 ppm fluoropolymer F5 in resin A was prepared according to the SP1 method and tested in the capillary rheometer at 190 °C. The  
30 results are listed in Table 8.

EXAMPLE 9

A sample similar to that of Example 8, except that resin B was substituted for resin A, was prepared and evaluated according to the procedure described in Example 8. The results are listed in Table 8.

5

**Table 8**

Capillary rheometer data, 190 °C

Example	Add	Resin	Apparent Viscosity Reduction, (%), at Particular Shear Rates (sec-1)			
			50	100	400	
C9	V2	A	43.0	58.5	52.6	Average
C10	V2	B	4.9	15.6	34.5	
Retention of Viscosity Reduction (%)			11.4	26.7	65.6	35.65
8	F5	A	19.9	30.8	43.7	Average
9	F5	B	17.5	26.5	40.0	
Retention of Viscosity Reduction (%)			87.9	86.0	91.5	88.6

\*All examples were free of melt fracture at the shear rates tested.

10 Although the viscoelastic properties of fluoropolymer F5 are not optimally matched to base resins A and B, F5 still eliminated melt fracture and reduced the apparent viscosity. When fluoropolymer F5 was tested in the less stabilized resin B, as illustrated by Example 9, it provided a larger decrease in apparent viscosity than that achieved by polymer V2 tested under the same conditions (see Comparative

15 Example C10). Fluoropolymer F5 was less affected by under-stabilized polyethylene than fluoropolymer V2, because fluoropolymer F5 retained a larger percentage of its ability to reduce apparent viscosity.

Examples 8 and 9 and Comparative Examples C9 and C10 were designed to simulate the "consumption" of anti-oxidants that can occur in larger commercial

20 extruders. Consumption, which may not always be demonstrated in studies involving the capillary rheometer, is more common in commercial extruders possibly because of the greater shearing and mixing, longer residence times, and/or higher melt temperatures achieved in commercial extruders. The data indicates that some of the fluoropolymer process aids of the invention are particularly efficient

because they continue to function as process aids even under conditions of anti-oxidant consumption.

#### COMPARATIVE EXAMPLE C11

The sample produced in Comparative Example C9 was tested in the  
5 capillary rheometer at 210 °C as previously described. The extrudate was smooth, and the results are presented in Table 9. The data from Comparative Example C6 was used to calculate the percent decrease in apparent viscosity.

#### COMPARATIVE EXAMPLE C12

A commercial concentrate containing 10% of HALS Chimassorb™ 944,  
10 Ampacet product #100438, was diluted into resin A along with a concentrate of fluoropolymer V2 to produce a sample containing 1000 ppm HALS and 500 ppm of fluoropolymer V2 according to the previously described SP1 method. The resultant mixture was evaluated in the capillary rheometer at 210 °C. The extrudate was smooth, and the results are presented in Table 9. The data from Comparative  
15 Example C6 was used to calculate the percent decrease in apparent viscosity.

#### COMPARATIVE EXAMPLE C13

A sample containing 1000 ppm of the HALS in resin B was mixed using the SP1 method. The resultant mixture was evaluated in the capillary rheometer at 210 °C. The surface of the extrudate had sharkskin melt fracture and exhibited CMF at  
20 1400 s<sup>-1</sup>.

#### COMPARATIVE EXAMPLE C14

A sample containing 1000 ppm of HALS and 500 ppm fluoropolymer V2 in resin B was mixed using the previously described SP1 method. The resultant mixture was evaluated in the capillary rheometer at 210 °C, the extrudate displayed  
25 sharkskin melt fracture at all shear rates tested below the onset of CMF. The data from Comparative Example C13 was used to calculate the percent decrease in apparent viscosity. The results are presented in Table 9.

#### EXAMPLE 10

A sample containing 1000 ppm of HALS and 500 ppm fluoropolymer F5 in  
30 resin B was mixed according to the SP1 method. The resultant mixture was evaluated in the capillary rheometer at 210 °C, the extrudate was smooth at all

shear rates tested. The data from Comparative Example C13 was used to calculate the percent decrease in apparent viscosity. The results are reported in Table 9.

**Table 9**

5 Capillary rheometer data, 210 °C

Ex.	Additives	Resin	% Apparent Viscosity Decrease at Shear Rate ( $s^{-1}$ )					Shear Rate at CMF Onset ( $s^{-1}$ )
			100	200	400	600	1000	
C11	V2	A	47.2	55.2	51.4	45.2	-----	>1400*
C12	V2 & HALS	A	15.2	20.3	24.9	23.6	-----	>1400*
C14	V2 & HALS	B	0	0	0	0	CMF	1000
10	F5 & HALS	B	21.8	33.7	39.8	39.2	34.0	>1400*

CMF: Cyclic Melt Fracture

\* test was terminated at  $1400s^{-1}$ .

The data in Table 9 shows that the addition of HALS to resin A which  
 10 contained V2 impaired the ability of this fluoropolymer to function. As illustrated  
 by Comparative Examples C12 and C11, the % decrease in apparent viscosity  
 provided by V2 was about half of what it was in the absence of HALS. As  
 illustrated by Comparative Example C14, the addition of fluoropolymer V2 and to  
 resin HALS B (which contained a minimal level of antioxidant) had no apparent  
 15 effect on the apparent viscosity. V2 was also unable to eliminate sharkskin and  
 unable to postpone the onset of CMF. The fluoropolymer of the invention, F5, was  
 able to eliminate the melt defects, postpone CMF, and provide a reduction in  
 apparent viscosity even in the presence of HALS. Both the prior art fluoropolymer  
 V2 and fluoropolymer F5 have about the same weight percent hydrogen in their  
 20 structure, see Table 1.

Example 10 and Comparative Examples C11-C14 were designed to  
 demonstrate what can occur in an industrial setting when multiple factors, such as  
 anti-oxidant consumption and interfering additives, are simultaneously impacting the  
 performance of a fluoropolymer process aid.

COMPARATIVE EXAMPLE C15

Resin A was tested in the capillary rheometer at 190, 210, & 230 °C. The extrudate exhibited sharkskin melt fracture below the onset of CMF.

COMPARATIVE EXAMPLE C16

- 5 A sample containing 500 ppm of fluoropolymer V11 in Resin A was prepared according to the previously described SP1 method and tested in the capillary rheometer at 190 and 210 °C. The data from Comparative Example C15 was used to calculate the percent decrease in apparent viscosity. The results are listed in Table 10.

10 COMPARATIVE EXAMPLE C17

A sample containing 1000 ppm of fluoropolymer V11 in Resin A was prepared by the SP1 method and tested in the capillary rheometer at 210 °C. The data from Comparative Example C15 was used to calculate the percent decrease in apparent viscosity. The results are listed in Table 10.

15 EXAMPLE 11

A sample containing 500 ppm of fluoropolymer F5 in Resin A was prepared according to the SP1 method and tested in the capillary rheometer at 190, 210, and 230 °C. The data from Comparative Example C15 was used to calculate the percent decrease in apparent viscosity. The results are listed in Table 10.

20

**Table 10**

Capillary rheometer data

Ex.	Conc. (ppm)	Temp (°C)	% Apparent Viscosity Decrease at Shear Rate (s <sup>-1</sup> )				
			100	200	400	600	1000
C16	500	190	29.2	41.9	41.9	--*	--*
	500	210	1.2	29.8	29.8	35.5	--*
C17	1000	210	3.6	35.6	35.6	37.9	--*
11	500	190	17.1	38.1	38.1	--*	--*
	500	210	15.2	33.7	33.7	34.9	--*
	500	230	8.9	36.2	36.2	38.6	35.7

\* Resin A enters CMF at 600s-1 at 190 °C and 1000s-1 at 210 °C, hence the viscosity and shear stress can not be measured. Therefore, the % decrease from the process aid can not be calculated.

5           Resin A in Comparative Example C15 exhibited sharkskin melt fracture at shear rates below the cyclic melt fracture onset (CMF). Example 11 containing fluoropolymer process aid according to the invention gave smooth and glossy extrudates, and postponed the onset of cyclic melt fracture.

10           The data of Table 10 also shows that fluoropolymer processing additives of the invention, with their broader molecular weight distributions (MWD), give better performance over a range of extrusion temperatures than fluoropolymers having a narrower molecular weight distribution (i.e., V11). This is true even though fluoropolymer V11 has a closer viscosity match to the resin than fluoropolymer F5. 500 ppm of fluoropolymer F5 provided a larger decrease in apparent viscosity at  
15           210 °C than twice the level of V11.

#### EXAMPLE 12

          The percent decrease in apparent viscosity provided by fluoropolymer F5 in Example 11 was plotted against the shear stress measured for the base resin in Comparative Example C15. The results at 190 and 230 °C are in shown FIG. 1.

20           The shear rate for cyclic melt fracture onset (CMF) in an unmodified LLDPE is known to increase with temperature. However, the shear stress for CMF is a constant regardless of the processing temperature (Tp). Thus, plotting decrease in apparent viscosity as a function of shear stress rather than shear rate, will correct the plot for viscosity changes in the base LLDPE resin due to  
25           temperature changes. FIG. 1 shows that the performance of fluoropolymer F5 increased with increasing extrusion processing temperature (Tp). Surprisingly, it also shows that the performance of the fluoropolymer process aid F5 improved as the Tp diverged from the end of melt point ( $T_{m, end}$ ) of the fluoropolymer F5. The Tp of 230 °C is 55 °C greater than the  $T_{m, end}$  for the fluoropolymer F5 (175 °C).  
30           This is surprising in view of the teaching of U.S. Pat. No. 5,266,639 (Chapman, Jr. et al.) which teaches that the performance of certain semi-crystalline, low melting, fluoropolymer process aids will improve as the Tp and  $T_{m, end}$  converge. Proper

selection of the viscoelastic properties of the fluoropolymers, as taught by the present invention, will provide processing improvements over a broader range of extrusion .

#### COMPARATIVE EXAMPLE C18

- 5 A sample containing 500 ppm fluoropolymer V2 in resin A was prepared according to the previously described SP1 method was tested in the capillary rheometer at 190 and 230 °C. The extrudate surface was smooth, results are listed in Table 11.

#### EXAMPLE 13

- 10 A sample containing 500ppm fluoropolymer F4 in resin A was prepared by the SP1 method and tested at 190 °C and 230 °C. The extrudate surface was smooth, results are listed in Table 11.

**Table 11**

Example	Temp (°C)	% Viscosity Reduction, Measured at the Specified Shear Rates (sec-1)				
		100	200	400	600	
C18	190	58.5	60.2	52.6	--*	Average
	230	5.5	16.1	24.4	26.0	
Retention of Viscosity Reduction (%)		9.4	26.7	46.4	--	27.5
13	190	46.1	51.4	47.4	--*	Average
	230	20.0	38.0	39.9	39.1	
Retention of Viscosity Reduction (%)		43.4	73.9	83.7	--	76.0

- 15 \* At 190 °C, resin A enters CMF at  $600\text{s}^{-1}$ , hence the viscosity and shear stress can't be measured and therefore, the % decrease from the process aid can not be calculated.

- 20 At 190 °C, fluoropolymer F4 in Example 13 exhibited comparable performance to fluoropolymer V2 in Comparative Example C18. At higher temperatures it substantially outperformed fluoropolymer V2 and retained a higher percentage of its ability to reduce the apparent viscosity. The ability of the fluoropolymers of this invention to perform over a broad range of extrusion temperatures is a function of their viscoelastic properties as taught in this invention.



This, coupled with their improved chemical and thermal resistance, makes the fluoropolymers of the invention optimal process aids for higher temperature applications such as cast film extrusion for die build-up prevention.

#### COMPARATIVE EXAMPLE C19

5 A sample containing 500 ppm fluoropolymer V2 was made in resin A using the SP1 method and tested in the capillary rheometer at 190 °C, results are listed in Table 12.

#### COMPARATIVE EXAMPLE C20

10 Comparative Example C19 was repeated using fluoropolymer V7 instead of V2. The extrudate was smooth and free of melt fracture. The results are listed in Table 12.

#### EXAMPLES 14-18

Using the SP1 method, a series of samples were produced each containing 500 ppm of a fluoropolymer additive in resin A. All were tested in the capillary  
15 rheometer at 190 °C. The extrudate surfaces from all the examples was smooth and glossy, results are listed in Table 12.

**Table 12**

Capillary rheometer results, 190 °C

			% Apparent Viscosity Reduction at Shear Rate (sec <sup>-1</sup> )			
Example	Additive	$\eta_0$ Ratio*	50	100	200	400
C19	V2	2.04	43.0	58.5	60.2	52.6
C20	V7	74,131	5.6	16.1	32.1	34.7
14	F5	57.5	19.8	30.8	38.6	43.7
15	F6	11.5	20.7	33.4	43.9	45.0
16	F4	0.309	34.4	47.8	51.8	47.5
17	F8	0.295	47.1	54.5	56.0	50.3
18	F7	0.107	34.4	47.4	51.0	47.1

20 \* $\eta_0$  ratio is the ratio of the zero shear viscosity of the fluoropolymer divided by the zero shear viscosity of the base resin A (see Table 3).

The data of Table 12 demonstrate that careful selection of the viscoelastic properties of the fluoropolymer such as  $\eta_0$  and  $m_1$  and their relative relationship to the same properties of the host polymer permits maximization of the process aid's performance in the host resin. The data of Table 12 demonstrates that the performance of fluoropolymers F4 to F8 improved as the viscosity ratio approaches the center of the preferred range. The ability of fluoropolymers F4 to F8 to lower apparent viscosity was most noticeable at lower shear rates. While fluoropolymer V7 of Comparative Example C20 provided a decrease in apparent viscosity in the capillary rheometer, its viscosity ratio is far outside the range taught by this invention, as such it is believed that it will not perform nearly as well as those fluoropolymers within the scope of the invention in when used as a processing aid in commercial extrusion equipment.

#### COMPARATIVE EXAMPLE C21

Resin A was extruded in the capillary rheometer at 250 °C. The surface of the extrudate was smooth at shear rates below  $200\text{s}^{-1}$ , and displayed sharkskin from  $400\text{s}^{-1}$  until  $1800\text{s}^{-1}$  when it entered CMF. Resin A has a calculated log zero shear viscosity of 4.78 at 250 °C.

#### EXAMPLE 19

A sample containing 500 ppm of fluoropolymer F4 in resin A was prepared according to the SP1 method and was extruded at 250 °C. The sample was smooth and glossy up to  $2000\text{s}^{-1}$ , it did not display CMF. The data in Comparative Example C21 was used to calculate the percent apparent viscosity decrease listed in Table 13. Fluoropolymer F4 has a calculated log zero shear viscosity of 2.97 at 250 °C.

**Table 13**

Capillary rheometer results, 250 °C

			% Apparent Viscosity Reduction at Shear Rate ( $\text{sec}^{-1}$ )					
Example	Additive	$\eta_0$ Ratio*	200	400	600	1000	1400	1600
19	F4	0.015	0	8.3	10.5	15.5	17.8	17.0

\* $\eta_0$  ratio is the ratio of the zero shear viscosity of the fluoropolymer divided by the zero shear viscosity of the base resin A.

The data of Table 13 shows that fluoropolymers with viscosities much lower than that of the host polymer, but still within the ranges taught by this invention, can provided processing improvements.

#### 5 COMPARATIVE EXAMPLE C22

A sample containing 500 ppm of fluoropolymer V9 in resin A was prepared according to the SP1 method and tested in the capillary rheometer at 190 °C, results are listed in Table 14.

#### EXAMPLE 20

10 A sample containing 500 ppm fluoropolymer F1 in resin A was prepared according to the SP1 method and tested at 190 °C and 230°C, results are listed in Table 14.

**Table 14**

			% Apparent Viscosity Reduction at Shear Rate (sec <sup>-1</sup> )			
Example	Additive	Temp (°C)	50	100	200	400
C22	V9	190	5.0	8.1	23.6	32.0
20	F1	190	7.8	20.2	29.9	32.4
	F1	230	0	0.3	0.8	3.9

15 The data of Table 14 show that although fluoropolymers V9 and F1 have the same Mooney viscosity and same monomer composition and similar log ( $\eta_0$ ), the fluoropolymer F1 outperformed fluoropolymer V9. It is believed that V9 contains ethylenic unsaturations which provide a site for attack, for example by peroxide. This process for unsaturation also turns the V9 black in color which

20 makes it undesirable for use as a polyolefin processing aid. Fluoropolymers with unsaturation are also less desirable in a polymer formulation in resins that are insufficiently stabilized because peroxides that form within the polyolefin during extrusion may react with the ethylenic unsaturations present in the fluoropolymer.

#### EXAMPLE 21

25 A sample with 1000 ppm fluoropolymer F9 in resin E was blended according to the previously described SP1 method and was tested in the capillary

rheometer at 230 °C. The ratio of zero shear viscosities of F9 and resin E at 230 °C is 0.27. Capillary rheometer results are listed in Table 15.

#### COMPARATIVE EXAMPLE C23

A sample containing 2.5% of resin A in resin E was mixed using the SP1 method and was tested in the capillary rheometer at 230 °C. The results are listed in Table 15.

**Table 15**

Capillary rheometer data, 230 °C

Shear Rate (sec <sup>-1</sup> )	Comp. Ex. C23		Example 21	
	Poise	CMF, psi oscillation	Poise	CMF, psi oscillation
50	23510	-----	18350	-----
100	15190	-----	11200	-----
200	9930	-----	7050	-----
400	6310	-----	4420	-----
600	CMF	220	CMF	20
800	CMF	220	CMF	20
1000	CMF	220	1900	-----
1200	CMF	220	1660	-----
1400	1580	-----	1495	-----

\* Value determined from strip chart recorder when extrudate exhibits cyclic melt fracture.

The filaments for both the Comparative Example C23 and Example 21 that were extruded below 400s<sup>-1</sup> had a surface appearance often characterized in HDPE as "orange-peel". This surface is thought to be related to the crystallization of the polyethylene and not due to melt fracture. The data of Table 15 show that fluoropolymer F9 provided a significant reduction in apparent viscosity and substantially reduced and/or eliminated CMF at the various shear rates tested.

### III. EVALUATION OF EXTRUDABLE COMPOSITIONS ON A BLOWN FILM LINE

#### A. DESCRIPTION OF THE BLOWN FILM EVALUATION METHOD

5

Concentrates of fluoropolymers for evaluation in a blown film line were prepared at a level of 2% in resin C (see Table 2), which was stabilized with 1000 ppm Irganox™ 1076 and 1000 ppm Irgafos™ 168 (both available from Ciba-Geigy). The concentrates were compounded using a Haake Rheomix™ TW-100 counter-rotating, intermeshing, conical twin screw extruder. Prior to compounding, the resin, antioxidants and fluoropolymer additive were dry-blended in a pail tumbler. This powder blend was starve-fed to the compounder at a nominal rate of 4.5 kg/hr. The extruder was operating at 200 rpm, with an extrusion profile of 140/200/220 °C and die temp of 220 °C. The extrudate was water quenched and strand pelleted. The resulting pellets were collected in a plastic one gallon container, hand mixed by shaking, and passed through the extruder a second time to ensure adequate dispersion and distribution of the fluoropolymer within resin C.

Films were produced using a Kiefel blown film line with a 40 mm, 24/1:L/D, grooved feed extruder. The die was of spiral design, with a diameter of 40 mm and a die gap of 0.6 mm. An adjustable single lip air ring with chilled air was used for cooling. An iris and sizing cage provided further bubble stability. Film was produced with a nominal gauge of 25 microns.

The Kiefel extruder and die zones were set at 200 °C and the die adapter zone was adjusted in the range of 210 to 220 °C to maintain a target melt temperature of 205 °C. The screw was maintained at about 45 rpm to deliver an output of about 13.6 kg/hr corresponding to a shear rate of about  $660\text{s}^{-1}$ . The film winder was set at 12.2 m/min.

Prior to each evaluation it was necessary to ensure that the blown film line was free of residual fluoropolymer from the previous evaluation. This was accomplished by extruding approximately 9 kg of a 70% calcium carbonate masterbatch (product #HM-10, Heritage Plastics) followed by 4.5 kg of Dowlex™

30

685 polystyrene and 4.5 kg of the resin being tested. All three materials were extruded at the maximum allowable rpm below the pressure limit of the extruder. The base resin was then extruded into film, under the original conditions for a minimum of one hour, until the previously determined extrusion pressure was  
5 achieved and the resultant film was fully melt fractured.

Samples for extrusion were prepared by weighing the required amount of fluoropolymer additive concentrate, pelleted resin and other additive concentrates into a 5 gallon pail and mixing on a pail tumbler for a minimum of 10 minutes. The fluoropolymer additive concentrates used in the following examples were produced  
10 as described above using the Haake twin screw extruder or was a commercially available concentrate of 3% FX-9613 (Ampacet product #10925).

The percent melt fracture was determined by taking a section of the film lay flat, opening it along the edge, measuring the individual bands (regions) of melt fracture in the transverse direction of the film, summing their total, and then  
15 dividing by the total width of the opened lay flat film.

## B. EXAMPLES

### COMPARATIVE EXAMPLES C24

20 A sample containing 500 ppm of fluoropolymer V10 in resin D was extruded using the described blown film method. The results are listed in Table 16.

### EXAMPLES 22-23

Two samples containing 500 ppm of a fluoropolymer additive in resin D were extruded using the described blown film method. The results are listed in  
25 Table 16.

Table 16

Blown film Data, Resin D

Ex.	Add.	$\eta_0$ ratio @ 205 °C	% Melt Fracture as a Function of Time (min.)							
			MF	0	10	20	30	40	50	60
C24	V10	288	H	100	--	--	--	--	--	29
			L	0	--	--	--	--	--	71
			C	0	--	--	--	--	--	0
22	F4	0.093	H	100	--	--	--	--	--	15
			L	0	--	--	--	--	--	52
			C	0	--	--	--	--	--	33
23	F1	1.15	H	88	80	29	25	10	10.5	8
			L	12	20	49	10	4	2	2
			C	0	0	22	65	86	87.5	90

MF: Melt Fracture

H: Heavy melt fracture

5 L: Light melt fracture, reduced severity, but still not acceptable

C: Clear, free of melt fracture

The data in Table 16 shows that fluoropolymer V10, which had a viscosity ratio that was greater than 100 did not eliminate melt fracture in a blown film line.

10 The blown film line is representative of commercial scale extrusion. However, fluoropolymers F1 and F4 were much more effective in eliminating melt defects under the same conditions. Whether or not melt fracture is eliminated or when it is eliminated by a given concentration of a fluoropolymer will depend in part upon the viscoelastic properties of the fluoropolymer and whether those properties are

15 properly matched to the viscoelastic properties of the base or host polymer. The presence and concentrations of other additives or adjuvants in the base polymer (e.g., hindered amine light stabilizers and the concentration of antioxidants) may also effect how easy it is for the fluoropolymer process aid to eliminate melt defects.

#### COMPARATIVE EXAMPLE C25

20 Using the SP1 method, a 220 gram combined concentrate of 20% talc and 2% fluoropolymer V8 in resin B, stabilized with 1000 ppm Irganox™ 1010 (Ciba-Geigy), was prepared. A portion of this blend was diluted into resin A to produce a

sample containing 5000 ppm talc and 500 ppm of fluoropolymer V8. This sample was tested in the capillary rheometer at 190 °C. The results of the evaluation are listed in Table 17.

#### EXAMPLE 24

- 5           Using the SP1 method, a 220 gram combined concentrate of 20% talc and 2% of fluoropolymer F5 in resin B, stabilized with 1000 ppm Irganox™ 1010 was prepared. A portion of this blend was diluted into resin A to produce a sample containing 5000 ppm talc and 500 ppm of fluoropolymer F5. This sample was tested in the capillary rheometer at 190 °C. The results of the evaluation are  
10           presented in Table 17.

**Table 17**

Capillary rheometer data, 190 °C

		% Apparent Viscosity Reduction at Shear Rate (sec <sup>-1</sup> )			
Example	Additives	50	100	200	400
C25	V8 & talc	1.2	2.2	5.2	20.6
24	F5 & talc	1.9	5.6	24.6	35.4

- 15           The data of Table 17 shows that a decrease in the viscosity of the fluoropolymer (F5 has a lower viscosity than V8--see Table 3) provided improved performance in the presence of abrasive additives such as talc anti-blocking agent. This is a surprising result in view of the teaching of U.S. Pat. No. 5,010,130 that increasing the viscosity of the molten portion of the fluoropolymer process aid  
20           minimizes the retarding effect of abrasive inorganic fillers on the ability of a process aid to eliminate melt defects. Preferably, the fluoropolymer process aid is somewhat less viscous than the base polymer, and typically a ratio of fluoropolymer process aid viscosity to thermoplastic hydrocarbon polymer viscosity of 0.3 is very effective.



EXAMPLES 25-28

Using the SP1 method, a series of samples in resin B, which had been stabilized with 1000 ppm Irganox™ 1010, were prepared. Each sample contained 500 ppm fluoropolymer F5 & 5000 ppm diatomaceous earth anti-blocking agent (available from Ampacet as product #10063). The samples also contained varying levels of various molecular weight polyethylene glycol (PEG). The PEG 8000 was added via a 3% concentrate prepared using a Haake twin screw extruder, PEG 1450 was added via a 2% concentrate prepared by the SP1 method. Each sample was tested in the capillary rheometer at 190 °C. The extrudates from all examples were smooth and glossy below the onset of CMF. Results are listed in Table 18.

**Table 18**

Capillary rheometer data, 190 °C

Ex.	PEG MW	PEG Conc (ppm)	Apparent Viscosity, poise, at Shear Rate (sec <sup>-1</sup> ) x 10 <sup>-2</sup>							CMF Onset (sec <sup>-1</sup> )
			50	100	200	400	600	1000	1400	
25	---	---	294	200	128	71.5	53.1	34.7	CMF	1400
26	8000	250	267	171	102	57.8	46.4	33.9	CMF	1400
27	8000	1000	200	115	73.2	48.6	40.0	31.4	26.3	1800
28	1450	1000	265	144	72.3	43.1	33.7	25.0	21.0	>2000

15

The data of Table 18 show that the molecular weight (MW) of a polyethylene glycol (PEG) added to the extrudable compositions of this invention will effect the tendency of the composition to melt defect. The data also suggest a relationship between shear rate and performance for differing molecular weight polyethylene glycols.

20

Various modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention and this invention should not be restricted to that set forth herein for illustrative purposes.

76950-10

CLAIMS:

1. A melt-processable composition having essentially no sites of ethylenic unsaturation and comprising a blend of:

(1) one or more melt-processable thermoplastic  
5 hydrocarbon polymers;

(2) an amount of a process aid to improve the processability of the melt-processable composition, wherein the process aid comprises one or more fluoropolymers having essentially no sites of ethylenic unsaturation, and wherein  
10 the process aid contains at least 50 weight % fluorine and the at least one fluoropolymer consists essentially of interpolymerized units of:

(a) one or more fluorinated olefin monomers of the general formula:

15  $\text{CF}_2=\text{CXR}^1$

wherein:

X is a hydrogen or a halogen atom; and

$\text{R}^1$  is a halogen atom or is a  $\text{C}_{1-10}$ -alkyl, a  $\text{C}_{3-10}$ -cyclic alkyl, or a  $\text{C}_{6-10}$ -aryl group, wherein the alkyl, cyclic alkyl or aryl group optionally contains one or more  
20 heteroatoms selected from oxygen and nitrogen and is partially-, fully-, or non-halogenated provided, however, that when X is a hydrogen atom,  $\text{R}^1$  contains an allylic carbon atom relative to the  $\alpha$ -unsaturation and that allylic carbon  
25 atom is not perfluorinated; and

(b) one or more olefin monomers of the general formula:

$\text{CH}_2=\text{CXR}^2$

76950-10

wherein:

X is a hydrogen or a halogen atom; and

R<sup>2</sup> is a hydrogen or is a halogen atom with the proviso that R<sup>2</sup> and X are not both fluorine; or

5 R<sup>2</sup> is a C<sub>1-10</sub>-alkyl, a C<sub>3-10</sub>-cyclic alkyl, or a C<sub>6-10</sub>-aryl group, wherein the alkyl, cyclic alkyl or aryl group is partially-, fully-, or non-halogenated and optionally contains one or more heteroatoms selected from oxygen and nitrogen; and

(c) 0 to 15 weight percent, of the total weight of  
10 the fluoropolymer, of one or more monomers that produce an acidic hydrogen on the backbone of the resulting fluoropolymer after polymerization, and

(3) optionally less than 20 percent by weight of the melt-processable composition of: a poly(oxyalkylene)  
15 polymer component comprising one or more poly(oxyalkylene) polymers;

wherein the fluoropolymer or fluoropolymers constituting component (2) either have a polydispersity greater than or equal to 2.0 or have a Carreau-Yasuda  
20 Equation m1 parameter of 0.7 or less and wherein the ratio of the melt viscosity of the fluoropolymer or fluoropolymers constituting component (2) to the melt viscosity of the thermoplastic hydrocarbon polymer or polymers constituting component (1) is between 0.01 and 100 at the melt processing  
25 conditions of the composition.

2. The composition of claim 1 wherein one or more of the fluoropolymers comprise interpolymerised units of tetrafluoroethylene and propylene.

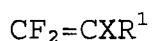
3. A process aid for improving the processability of  
30 melt-processable thermoplastic hydrocarbon polymers, wherein

76950-10

the process aid comprises one or more fluoropolymers having essentially no sites of ethylenic unsaturation, wherein the process aid contains at least 50 weight % fluorine and the at least one fluoropolymer consists essentially of

5 interpolymerized units of:

(a) one or more fluorinated olefin monomers of the general formula:

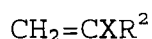


wherein:

10 X is a hydrogen or a halogen atom; and

R<sup>1</sup> is a halogen atom or is a C<sub>1-10</sub>-alkyl, a C<sub>3-10</sub>-cyclic alkyl, or a C<sub>6-10</sub>-aryl group, wherein the alkyl, cyclic alkyl or aryl group optionally contains one or more heteroatoms selected from oxygen and nitrogen and is  
 15 partially-, fully-, or non-halogenated provided, however, that when X is a hydrogen atom R<sup>1</sup> contains an allylic carbon atom relative to the α-unsaturation and that allylic carbon atom is not perfluorinated; and

(b) one or more olefin monomers of the general  
 20 formula:



wherein:

X is a hydrogen or a halogen atom; and

R<sup>2</sup> is a hydrogen or is a halogen atom with the  
 25 proviso that R<sup>2</sup> and X are not both fluorine or R<sup>2</sup> is a C<sub>1-10</sub>-alkyl, a C<sub>3-10</sub>-cyclic alkyl, or a C<sub>6-10</sub>-aryl group, wherein the alkyl, cyclic alkyl or aryl group is partially-,

76950-10

fully-, or non-halogenated and optionally contains one or more heteroatoms selected from oxygen and nitrogen; and

(c) 0 to 15 weight percent, of the total weight of the fluoropolymer, of one or more monomers that produce an  
5 acidic hydrogen on the backbone of the resulting fluoropolymer after polymerization;

wherein the fluoropolymer or fluoropolymers have a Carreau-Yasuda Equation m1 parameter of 0.7 or less and wherein the fluoropolymer or fluoropolymers have a maximum  
10 zero shear viscosity ( $\eta_0$ ) of less than  $32 \times 10^6$  Pa-s ( $32 \times 10^6$  poise) at a reference temperature of 190°C.

4. The process aid of claim 3 further comprising a poly(oxyalkylene) polymer component comprising one or more poly(oxyalkylene) polymers.

15 5. The process aid of claim 3 or 4, wherein one or more of the fluoropolymers comprise interpolymers of tetrafluoroethylene and propylene.

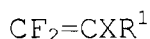
6. A method of improving the extrusion characteristics of a melt-processable thermoplastic  
20 hydrocarbon polymer comprising blending:

(1) one or more melt-processable thermoplastic hydrocarbon polymers;

(2) an amount of a process aid to improve the processability of the melt-processable composition, wherein  
25 the process aid comprises one or more fluoropolymers having essentially no sites of ethylenic unsaturation, and wherein the process aid contains at least 50 weight % fluorine and the at least one fluoropolymer consists essentially of interpolymers of:

76950-10

(a) one or more fluorinated olefin monomers of the general formula:

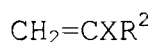


wherein:

5 X is a hydrogen or a halogen atom; and

R<sup>1</sup> is a halogen atom or is a C<sub>1-10</sub>-alkyl, a C<sub>3-10</sub>-cyclic alkyl, or a C<sub>6-10</sub>-aryl group wherein the alkyl, cyclic alkyl or aryl group optionally contains one or more heteroatoms selected from oxygen and nitrogen and is  
 10 partially-, fully-, or non-halogenated provided, however, that when X is a hydrogen atom, R<sup>1</sup> contains an allylic carbon atom relative to the α-unsaturation and that allylic carbon atom is not perfluorinated; and

(b) one or more olefin monomers of the general  
 15 formula:



wherein:

X is a hydrogen or a halogen atom; and

R<sup>2</sup> is a hydrogen or is a halogen atom with the  
 20 proviso that R<sup>2</sup> and X are not both fluorine or R<sup>2</sup> is a C<sub>1-10</sub>-alkyl, a C<sub>3-10</sub>-cyclic alkyl, or a C<sub>6-10</sub>-aryl group wherein the alkyl, cyclic alkyl or aryl group is partially-, fully-, or non-halogenated and optionally contains one or more heteroatoms selected from oxygen and nitrogen; and

25 (c) 0 to 15 weight percent, of the total weight of the fluoropolymer, of one or more monomers that produce an acidic hydrogen on the backbone of the resulting fluoropolymer after polymerization, and

76950-10

(3) optionally less than 20 percent by weight of the melt-processable composition of: a poly(oxyalkylene) polymer component comprising one or more poly(oxyalkylene) polymers;

5            wherein the fluoropolymer or fluoropolymers constituting component (2) either have a polydispersity greater than or equal to 2.0 or have a Carreau-Yasuda Equation m1 parameter of about 0.7 or less and wherein the ratio of the melt viscosity of the fluoropolymer or  
10 fluoropolymers constituting component (2) to the melt viscosity of the thermoplastic hydrocarbon polymer or polymers constituting component (1) is between 0.01 and 100 at the melt processing conditions of the composition, and extruding the blend.

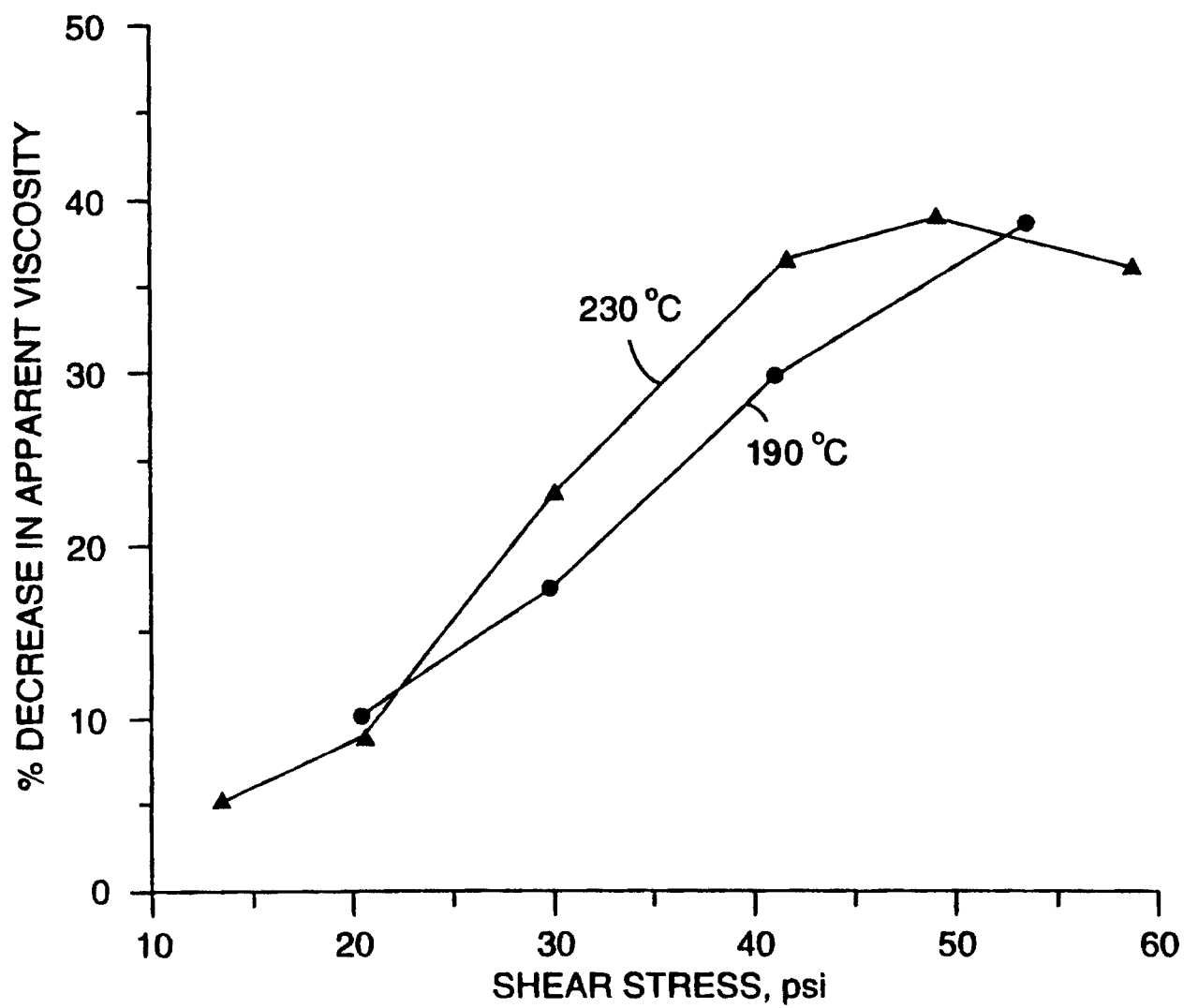
15 7.            The method of claim 6, wherein one or more of the fluoropolymers comprise interpolymerized units of tetrafluoroethylene and propylene.

8.            An extrudate comprising the blend defined in claim 1.

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PATENT AGENTS

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*Fig.1*