

METHOD FOR PREPARING POLYETHYLENE WITH HIGH MELT STRENGTHCross-Reference to Related Applications

This application claims priority from U.S. patent application serial number 12/685,148, filed January 11, 2010, the disclosure of which is incorporated herein by reference for purposes of U.S. practice.

5 Background and Summary of the Invention

Polyethylene has desirable properties that have helped to make it the highest volume polymer manufactured. Polyethylene can be made in different processes in order to give different properties. Known families of polyethylene include high density polyethylene (HDPE), linear low density polyethylene (LLDPE), and low density polyethylene made
10 using high pressure reactors (LDPE). Within these broad classes many variations exist resulting from different types of polyolefin process technologies (for example, solution, slurry or gas phase) or from the use of different catalysts (for example, Ziegler-Natta or constrained geometry catalysts). The desired application requires a careful balance of rheological properties which will lead a person of skill in the art to select one type of
15 polyethylene over another. In many applications, such as blow-molding and blown film applications, melt strength of the polyethylene is a key parameter, frequently measured as elongational viscosity of the polymer.

The melt strength is a practical measurement that can predict material performance when submitted at elongational deformations. In melt processing good
20 elongational viscosity is important to maintain stability during processes such as coating, blow film production, fiber spinning and foamed parts. The melt strength is related with a number of molecular entanglements on molten polymers and relaxation times of each molecular structure, which is basically dependant on overall molecular weight and number of branches over critical molecular weight.

25 Melt strength directly effects several processing parameters such as bubble stability and therefore thickness variation during blow film production; parison formation during blow molding process; sagging during profile extrusion; cells formation during foaming process; more stable thickness distribution during sheet / film thermoforming.

This property can be enhanced by using resins with higher molecular weight, but such resins will generally require more robust equipment and more energy use because they tend to generate higher extrusion pressure during the extrusion process. Therefore, properties must be balanced to provide an acceptable combination of physical properties and processability.

In thick film applications blends of LDPE and LLDPE are used in order to obtain a balance of processability (extruder amps and pressure) and film mechanical properties. In this blend the LDPE component is the processability component whereas the LLDPE is the mechanical end component. Therefore, the ability to decrease the LDPE portion of the blend should increase the mechanical properties of the blend. Through this invention, the ability to increase the melt strength of the LLDPE component allows the use of a higher percentage of LLDPE blend, thus increasing the mechanical properties without sacrificing processability or the creation of unacceptable levels of insoluble material.

The present invention is a new process for increasing the melt strength of polyethylene involving reacting molten polyethylene with an alkoxyamine derivative through regular extrusion processing. Accordingly, one aspect of the invention is a method for increasing the melt strength of a polyethylene resin comprising first selecting a polyethylene resin having a density, as determined according to ASTM D792, in the range of from 0.865 g/cm³ to 0.962 g/cm³, and a melt index, as determined according to ASTM D1238 (2.16 kg, 190°C), in the range of from 0.01 g/10min to 100 g/10 min and then reacting an alkoxy amine derivative with the polyethylene resin in an amount and under conditions sufficient to increase the melt strength of the polyethylene resin.

The present invention is a new process for increasing the elongational viscosity of polyethylene involving reacting molten polyethylene with an alkoxyamine derivative through regular extrusion processing. Accordingly, one aspect of the invention is a method for increasing the melt strength of a polyethylene resin comprising first selecting a polyethylene resin having a density, as determined according to ASTM D792, in the range of from 0.865 g/cm³ to 0.962 g/cm³, and a melt index, as determined according to ASTM D1238 (2.16 kg, 190°C), in the range of from 0.01 g/10min to 100 g/10 min and then reacting an alkoxy amine derivative with the polyethylene resin in an amount and under conditions sufficient to increase the elongational viscosity of the polyethylene resin.

The present invention is a new process that increases the elongational viscosity at low (0.1 s^{-1}) shear rates while maintaining the viscosity at higher shear rates ($> 100 \text{ s}^{-1}$) such that the ease of processing of the material is maintained at typical extrusion conditions. One aspect of the invention is that the extruder pressure does not increase more than 10% of the comparative resin upon processing the inventive resin at the same operating conditions.

Brief Description of the Drawings:

Figure 1 is a plot of melt strength versus stretching velocity with increasing additive concentration.

Figure 2 is a plot of viscosity versus shear rate with increasing additive concentration.

Figure 3 is a plot of melt strength at the plateau region versus melt index (I_2 , g/10 min).

Figure 4 is a plot of phase angle ($^\circ$) versus the complex modulus (G^*) measured using a constant temperature of 190°C at a frequency sweep in a TA Instruments “Advanced Rheometric Expansion System (ARES)”

Figure 5 is a plot of phase angle ($^\circ$) versus the complex modulus (G^*) measured using a constant temperature of 190°C at a frequency sweep in a TA Instruments “Advanced Rheometric Expansion System (ARES)”

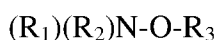
Detailed Description of the Invention

In its broadest sense, the present invention is a method for increasing the melt strength of a polyethylene resin. Polyethylene resin includes all polymers or polymer blends which are derived at least 50% by weight from ethylene monomer units. This includes materials known in the art as high density polyethylene (HDPE), linear low density polyethylene (LLDPE), and low density polyethylene made using high pressure reactors (LDPE).

The target polyethylene resin selected should have a density, as determined according to ASTM D792, in the range of from 0.865 g/cm^3 to 0.970 g/cm^3 , more preferably from 0.905 g/cm^3 to 0.957 g/cm^3 and a melt index, as determined according to ASTM

D1238 (2.16 kg, 190°C), in the range of from 0.01 g/10min to 100 g/10 min, more preferably 0.1 g/10min to 15 g/10min. Suitable target polyethylene resins can be produced with conventional Ziegler Natta or Chromium catalysts but also with metallocene or single site catalysts. Such resins may have monomodal or multimodal molecular weight distributions.

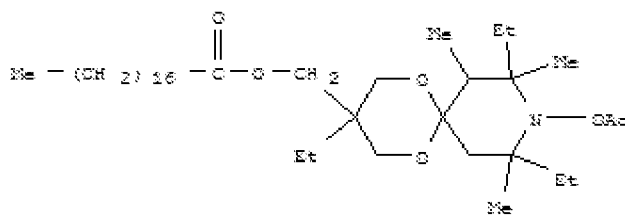
Once the target polyethylene resin is selected, it is reacted with an alkoxy amine derivative. For purposes of the present invention "alkoxy amine derivatives" includes nitroxide derivatives. The alkoxy amine derivative is added in an amount and under conditions sufficient to increase the melt strength of the polyethylene resin. The alkoxy amine derivatives correspond to the formula:



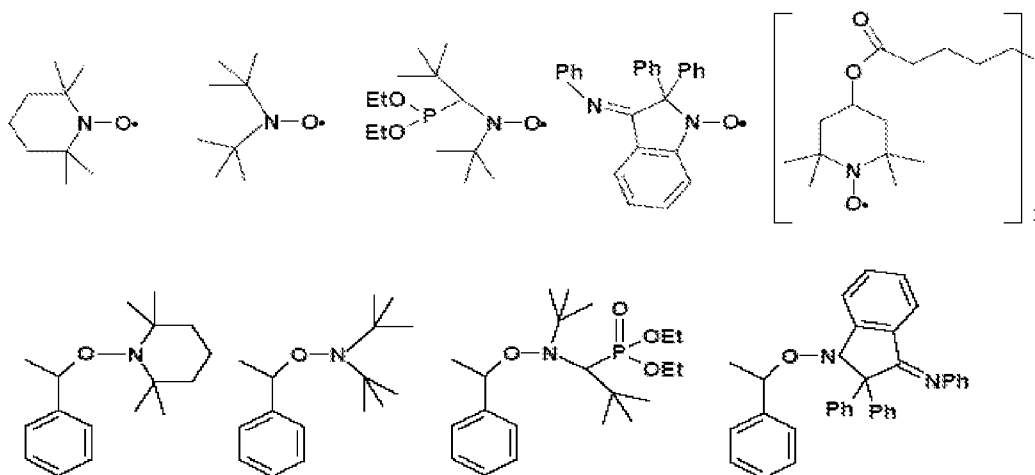
where R_1 and R_2 are each independently of one another, hydrogen, C_4 - C_{42} alkyl or C_4 - C_{42} aryl or substituted hydrocarbon groups comprising O and/or N, and where R_1 and R_2 may form a ring structure together; and where R_3 is hydrogen, a hydrocarbon or a substituted hydrocarbon group comprising O and/or N. Preferred groups for R_3 include - C_1 - C_{19} alkyl; - C_6 - C_{10} aryl; - C_2 - C_{19} akenyl; -O- C_1 - C_{19} alkyl; -O- C_6 - C_{10} aryl; -NH- C_1 - C_{19} alkyl; -NH- C_6 - C_{10} aryl; -N-(C_1 - C_{19} alkyl)₂. R_3 most preferably contains an acyl group.

The preferred compound may form nitroxylradical $(R_1)(R_2)N-O^*$ or aminylradical $(R_1)(R_2)N^*$ after decomposition or thermolysis.

A particularly preferred species of alkoxy amine derivative is 9-(acetyloxy)-3,8,10-triethyl-7,8,10-trimethyl-1,5-dioxo-9-azaspiro[5.5]undec-3-yl)methyl octadecanoate which has the following chemical structure:



Examples of some preferred species for use in the present invention include the following:



In general hydroxyl amine esters are more preferred with one particularly favored hydroxyl amine ester being 9-(acetyloxy)-3,8,10-triethyl-7,8,10-trimethyl-1,5-dioxo-9-azaspiro[5.5]undec-3-yl]methyl octadecanoate.

5 The alkoxy amine derivatives are added in an amount sufficient to increase the melt strength and/or increase the elongational viscosity to the desired level. Preferably, the melt strength is increased by at least 10%, 20%, 25%, 35% or even 50% compared to a similar resin which has not been reacted with an alkoxy amine derivative. In general the alkoxy amine derivatives are added in an amount of from 1 to 900 ppm of the total amount
10 of polyethylene polymer by weight (that is from 1 to 900 parts alkoxy amine derivative per million parts of target resin plus carrier resin, if any), preferably from 15 to 600 ppm, more preferably from 25 to 400 ppm and still more preferably from 30 to 200 ppm.

The addition to the polyethylene polymer can be carried out in all customary mixing machines in which the polymer is melted and mixed with the additives. Suitable
15 machines are known to those skilled in the art. They are predominantly mixers, kneaders and extruders.

The process is preferably carried out in an extruder by introducing the additive during processing. Particularly preferred processing machines are single-screw extruders, contra rotating and co rotating twin-screw extruders, planetary-gear extruders,
20 ring extruders or cokneaders. It is also possible to use processing machines provided with at least one gas removal compartment to which a vacuum can be applied. Suitable extruders and kneaders are described, for example, in Handbuch der Kunststoffextrusion, Vol. 1 Grundlagen, Editors F. Hensen, W. Knappe, H. Potente, 1989, pp. 3-7, ISBN.3-446-14339-4

(VoL 2 Extrusionsanlagen 1986, ISBN 3-446-14329-7). For example, the screw length can be 1-60 times the screw diameter, preferably 35-48 times the screw diameters. The rotational speed of the screw is preferably 10-600 rotations per minute (rpm), more preferably 25-300 rpm. It is also possible to first prepare a concentrated mixture of the additive in a carrier polyethylene resin, preferably at 1000 to 10000 ppm, and then introduce this concentrate, or "masterbatch", via an extruder into a melted polyethylene using a static mixer to blend the two materials, preferably at 1 to 20 wt% of the concentrate in the melted resin. The concentrate could be processed in an extruder, preferably at temperatures from 180 to 220°C. The temperatures in the static mixer could range from 200 to 250°C, with a residence time in the mixer ranging from 1 to 10 minutes.

The maximum throughput is dependent on the screw diameter, the rotational speed and the driving force. The process of the present invention can also be carried out at a level lower than maximum throughput by varying the parameters mentioned or employing weighing machines delivering dosage amounts.

If a plurality of components is added, these can be premixed or added individually.

The polymers need to be subjected to an elevated temperature for a sufficient period of time, so that the desired changes occur. The temperature is generally above the softening point of the polymers. In a preferred embodiment of the process of the present invention, a temperature range lower than 280°C, particularly from about 160°C to 280°C is employed. In a particularly preferred process variant, the temperature range from about 200°C to 270°C is employed.

The period of time necessary for reaction can vary as a function of the temperature, the amount of material to be reacted and the type of, for example, extruder used. It is usually from about 10 seconds to 30 minutes, in particular from 20 seconds to 20 minutes.

The alkoxy amine derivative can advantageously be added to the mixing device by use of a masterbatch. As will be appreciated by those of ordinary skill in the art, the carrier resin for the masterbatch should be chosen to be compatible with the resin to be modified. LDPE high pressure low density polyethylene polymers (referred to in the industry as "LDPE") were unexpectedly found to be the preferred carrier due to the lower

reactivity as evidenced by little variation of the extrusion pressure during masterbatch production. HDPE may be a better carrier as it will react even less because it does not have tertiary carbons and very low trisubstituted unsaturation units per 1,000,000 carbons.

Another advantage of this invention is the discovery that polypropylene is not a good carrier for this additive, as it tends to degrade at typical processing temperatures. Another discovery is that the carrier resin should be substantially free of any antioxidant additives, preferably having less than 1,000 ppm of antioxidant additives, as they tend to suppress the activity of the additive.

The preferred carrier resin should be compatible with the application at hand; it should have similar viscosity with the target polyethylene resin with which it is going to be blended. It should be preferably an LDPE or HDPE resin with minimal trisubstituted unsaturation units, preferably fewer than 70 per 1,000,000 carbons. The preferred carrier resin should have a molecular weight (Mn) that is less than 50,000 so that it is easy to process, as demonstrated by the pressure drop through the extruder. The carrier resin could incorporate other additives for processing aids but it should preferably be substantially free of antioxidant compounds, preferably containing less than 1,000 ppm of any antioxidant compound, preferably less than 500 ppm, more preferably less than 100 ppm by weight.

The target polyethylene resin could be a copolymer of ethylene with any alkene monomer containing 3 to 12 carbons. Preferably, the target polyethylene resin should have a level of trisubstituted unsaturation units per 1,000,000 carbons ranging from 200 to 450. It should have a molecular slightly slower than the carrier resin, as indicated by the melt index (g/10 min). Preferably, the melt index of the target polyethylene resin should be higher by 0.2-0.5 units (g/10 min) than the final desired resin. Preferably, the polyethylene resin should contain minimal or no antioxidant additives, and any additives should be well-dispersed in the resin prior to being blended with the carrier resin.

The amount of the alkoxy amine derivative material in the carrier resin should be in the range of 0.1 to 30% by weight, preferably from 0.1 to 5%, and more preferably in the range of 0.2 to 1%. The amount of the masterbatch is added so that the alkoxy amine derivative is added to the target product in the range of 1 to 900 ppm, preferably from 15 to 600 ppm, more preferably from 25 to 400 ppm and still more preferably from 30 to 200 ppm. It will readily be understood by one of skill in the art that

the amount of alkoxy amine derivative in the final product will be reduced from the added amounts as the compound reacts with the target and carrier polyethylene.

Preferably, the amount of the alkoxy amine derivative ingredient should be kept below 1000 ppm to minimize reaction in the carrier resin, reduce the potential for gels in the final product, and be substantially reacted out in the final product so that the final product remains stable with further processing. It should be understood that after the alkoxy amine derivative has been allowed to react with the target resin, it may be desirable to add one or more antioxidant additives, to protect the properties of the modified target resin. One way to accomplish this is to blend the resin after reaction with the alkoxy amine derivative with another resin that is rich in antioxidants.

Testing Methods

Melt Strength

Melt strength measurements were conducted on a Gottfert Rheotens 71.97 (Göettfert Inc.; Rock Hill, SC), attached to a Gottfert Rheotester 2000 capillary rheometer. The melted sample (about 25 to 30 grams) was fed with a Göettfert Rheotester 2000 capillary rheometer, equipped with a flat entrance angle (180 degrees) of length of 30 mm, diameter of 2.0 mm, and an aspect ratio (length/diameter) of 15. After equilibrating the samples at 190°C for 10 minutes, the piston was run at a constant piston speed of 0.265 mm/second. The standard test temperature was 190°C. The sample was drawn uniaxially to a set of accelerating nips located 100 mm below the die, with an acceleration of 2.4 mm/s². The tensile force was recorded as a function of the take-up speed of the nip rolls. Melt strength was reported as the plateau force (cN) before the strand broke. The following conditions were used in the melt strength measurements: plunger speed = 0.265 mm/second; wheel acceleration = 2.4 mm/s²; capillary diameter = 2.0 mm; capillary length = 30 mm; and barrel diameter = 12 mm.

Melt Index

The melt index is used as an indication of molecular weight. Melt index was determined using ASTM method D-1238 at 190°C using a Tinius-Olsen Extrusion Plastometer Model MP987, with orifices with capillary dimensions of 0.0825" diameter and 0.315" length; a piston of stainless steel with three scribe marks (4.17", 4.33", and 5.25")

above the foot of the piston; weights of such size that the combined masses of a weight and piston equal 2.16 and 10.00 kg; and a plug gauge for measuring the orifice capillary. The melt index identified as I2 refers to the measurement with 2.16 kg weight and the melt index identified as I10 refers to the measurement using a 10 kg weight.

5 Density

Samples for density measurements were prepared according to ASTM D 4703-10.

Dynamic Mechanical Spectroscopy

Resins were compression-molded into “3 mm thick x 1 inch” circular plaques at 350°F for five minutes, under 1500 psi pressure in air. The sample was then taken out of the
10 press, and placed on the counter to cool.

A constant temperature frequency sweep was performed using a TA Instruments “Advanced Rheometric Expansion System (ARES),” equipped with 25 mm (diameter) parallel plates, under a nitrogen purge. The sample was placed on the plate, and allowed to melt for five minutes at 190°C. The plates were then closed to a gap of 2 mm, the sample
15 trimmed (extra sample that extends beyond the circumference of the “25 mm diameter” plate is removed), and then the test was started. The method had an additional five minute delay built in, to allow for temperature equilibrium. The experiments were performed at 190°C over a frequency range of 0.1 to 100 rad/s. The strain amplitude was constant at 10%. The stress response was analyzed in terms of amplitude and phase, from which the
20 storage modulus (G'), loss modulus (G''), complex modulus (G^*), complex viscosity η^* , $\tan(\delta)$ or $\tan \delta$, viscosity at 0.1 rad/s ($V_{0.1}$), the viscosity at 100 rad/s (V_{100}), and the Viscosity Ratio ($V_{0.1}/V_{100}$) were calculated.

Gel Permeation Chromatography

The Triple Detector Gel Permeation Chromatography (3D-GPC or TD-GPC)
25 system consists of a Waters (Milford, Mass) 150°C high temperature chromatograph (other suitable high temperatures GPC instruments include Polymer Laboratories (Shropshire, UK) Model 210 and Model 220 equipped with an on-board differential refractometer (RI). Additional detectors can include an IR4 infra-red detector from Polymer ChAR (Valencia, Spain), Precision Detectors (Amherst, Mass.) 2-angle laser light scattering (LS) detector
30 Model 2040, and a Viscotek (Houston, Tex.) 150R 4-capillary solution viscometer. A GPC with these latter two independent detectors and at least one of the former detectors is

sometimes referred to as “3D-GPC or TD-GPC” while the term “GPC” alone generally refers to conventional GPC. Depending on the sample, either the 15° angle or the 90° angle of the light scattering detector is used for calculation purposes. Data collection is performed using Viscotek TriSEC software, Version 3, and a 4-channel Viscotek Data Manager

5 DM400. The system is also equipped with an on-line solvent degassing device from Polymer Laboratories (Shropshire, United Kingdom).

Suitable high temperature GPC columns can be used such as four 30 cm long Shodex HT803 13 micron columns or four 30 cm Polymer Labs columns of 20-micron mixed-pore-size packing (MixA LS, Polymer Labs). The sample carousel compartment is
10 operated at 140 °C and the column compartment is operated at 150 °C. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent. The chromatographic solvent and the sample preparation solvent contain 200 ppm of butylated hydroxytoluene (BHT) in trichloro benzene (TCB). Both solvents are sparged with nitrogen. The polyethylene samples are gently stirred at 160 °C for four hours. The
15 injection volume is 200 microliters. The flow rate through the GPC is set at 1 ml/minute.

The GPC column set is calibrated by running 21 narrow molecular weight distribution polystyrene standards. The molecular weight (MW) of the standards ranges from 580 to 8,400,000, and the standards are contained in 6 “cocktail” mixtures. Each standard mixture has at least a decade of separation between individual molecular weights.
20 The standard mixtures are purchased from Polymer Laboratories. The polystyrene standards are prepared at 0.025 g in 50 mL of solvent for molecular weights equal to or greater than 1,000,000 and 0.05 g in 50 mL of solvent for molecular weights less than 1,000,000. The polystyrene standards were dissolved at 80 °C with gentle agitation for 30 minutes. The narrow standard mixtures are run first and in order of decreasing amount of the highest
25 molecular weight component to minimize degradation.

The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)):

$$M_{\text{polyethylene}} = A(M_{\text{polystyrene}})^B \quad (1)$$

30 Here B has a value of 1.0, and the experimentally determined value of A is 0.38.

A first order polynomial was used to fit the respective polyethylene-equivalent calibration points obtained from equation (1) to their observed elution volumes. The actual polynomial fit was obtained so as to relate the logarithm of polyethylene equivalent molecular weights to the observed elution volumes (and associated powers) for each polystyrene standard.

Number, weight, and z-average molecular weights were calculated according to the following equations:

$$\overline{Mn} = \frac{\sum_i Wf_i}{\sum_i \left(\frac{Wf_i}{M_i} \right)} \quad (2)$$

$$\overline{Mw} = \frac{\sum_i (Wf_i * M_i)}{\sum_i Wf_i} \quad (3)$$

$$\overline{Mz} = \frac{\sum_i (Wf_i * M_i^2)}{\sum_i (Wf_i * M_i)} \quad (4)$$

Where, Wfi is the weight fraction of the i-th component and Mi is the molecular weight of the i-th component.

The MWD was expressed as the ratio of the weight average molecular weight (Mw) to the number average molecular weight (Mn).

The A value was determined by adjusting A value in equation (1) until Mw, the weight average molecular weight calculated using equation (3) and the corresponding retention volume polynomial, agreed with the independently determined value of Mw obtained in accordance with the linear homopolymer reference with known weight average molecular weight of 115,000 g/mol.

Trisubstituted Unsaturation Group Determination Method (FTIR)

Pellets are pressed first to make a thick film of 0.25 mm and then pressed again to make a thin film of 0.125 mm. The film is then secured on a scan card and then sanded on both sides before being loaded on a Nicolet 6700 FTIR instrument. The area under the peak at 909 cm⁻¹ is integrated to obtain the value of number of trisubstituted unsaturation units per 1,000,000 carbons using 64 scans with resolution of 2 cm⁻¹. This technique has been calibrated using a known absorbance and concentration and corrects for film thickness in order to determine the concentration of the sample.

Using the above measurements, the ratio of the elongational viscosities at 0.1 to 100 shear rates (s^{-1}) provides an indication of branching in the polymer and an indication of the effect of the additive. In this invention, resins with the additive showed a 10 to 60% increase in the viscosity ratio, preferably an increase of 20 to 40% when compared with the same resin with no additive.

Resins modified with the additive show a decrease in I_2 of 5% to 25% and a decrease in I_{10} of 4 to 20%. Therefore, the ratio of I_{10} to I_2 for the resins increases with increasing amount of additive, indicating extent of change in the polymer.

Resins modified according to the methods of the present invention will exhibit an increase in melt strength of at least 10%, preferably in the range of from 20 to 50% as compared to the same resin which has not been reacted with the alkoxy amine derivative. Similar performance improvement will also be seen with respect to elongational viscosity. For the inventive resins, improvement in melt strength and viscosity performance is better than anticipated with the changes observed in the melt index measurements.

With the increase in melt strength and/or elongational viscosity, resins made according to the present invention are particularly well suited for fabricated articles such as films, sheets, pipes or blow molded articles.

Films made using the additive and processing conditions in this invention retain the mechanical properties of the polyethylene resins that were the base resins without the addition of the alkoxy amine derivative.

Examples

The four examples (two resins with two different amounts of additive each) described below have a similar molecular weight, with different concentrations of an alkoxy amine derivative additive. The specific additive used is 9-(acetyloxy)-3,8,10-triethyl-7,8,10-trimethyl-1,5-dioxo-9-azaspiro[5.5]undec-3-yl)methyl octadecanoate, which is added as an LDPE masterbatch having less than 1% of the additive (Note that the ppm levels reported below refer to the amount of alkoxy amine derivative added and not the amount of the entire masterbatch added).

The masterbatch is prepared as follows: The alkoxy amine derivative additive is compounded with a homopolymer ethylene resin made in a high-pressure tubular reactor (that is, an LDPE resin) having a melt index of 0.7 g/10 min (at 190°C, 2.16kg ASTM D-1238) and a density of 0.925 g/cm³ (ASTM D792). This LDPE resin is the same as Resin D described below and the additive concentration in the LDPE resin is at 5,600 parts per million weight to create a masterbatch.

The LDPE and derivative are compounded in a 30mm co-rotating, intermeshing Coperion Werner-Pfleiderer ZSK-30 (ZSK-30) twin screw extruder to form a masterbatch. The ZSK-30 has ten barrel sections with an overall length of 960 mm and a 32 length to diameter ratio (L/D). A two hole strand die is used without a breaker plate or screen pack. The extruder consist of a DC motor, connected to a gear box by V-belts. The 15HP motor is powered by a GE adjustable speed drive located in a control cabinet. The control range of the screw shaft speed is 1:10. The maximum screw shaft speed is 500 RPM. A pressure transducer is positioned in front of the die to measure die pressure.

The extruder has 8 heated/cooled barrel sections along with a 30 mm spacer, which makes up five temperature controlled zones. It has a cooled only feed section and a heated only die section, which is held together by tie-rods and supported on the machine frame. Each section can be heated electrically with angular half-shell heaters and cooled by a special system of cooling channels.

The screws consist of continuous shafts on which screw-flighted components and special kneading elements are installed in any required order. The elements are held together radially by keys and keyways and axially by a screwed-in screw tip. The screw shafts are connected to the gear-shafts by couplings and can easily be pulled out of the screw barrel for dismantling.

A Conair pelletizer is used to pelletize the blends. It is a 220 volt variable speed, solid cutter unit. The variable speed motor drives a solid machined cutting wheel, which in turn drives a fixed metal roller. A movable rubber roller presses against the fixed roller and helps pull the strands by friction into the cutting wheel. The tension on the movable roller may be adjusted as necessary.

The temperatures are set in the feed zone, 4 zones in the extruder, and the die as:

	Feed:	80°C
	Zone 1:	160°C
	Zone 2:	180°C
	Zone 3:	185°C
5	Zone 4:	190°C
	Die:	210°C

The screw shaft speed is set at 276 revolutions per minute (RPM), resulting in an output rate of approximately 52 lb/hr.

The masterbatch defined above is dry-blended with additional amounts of the
 10 LDPE resin D in order to bring the concentration of the alkoxyamine derivative to a desired level such that when added in an amount of 3% by weight compared to the target polyethylene, the additive will be added in the amounts shown in the Table. The masterbatch or the dry-blended material thereof is blended with LLDPE resins B or C using the following setup: the masterbatch or the dry-blended material is fed through a hopper into
 15 a Sterling 2 ½ inch single screw extruder which is used as the side arm conveyer with a rupture disc of 3200 psig. The four heating zones in the single screw extruder are set at 220°C.

The LLDPE resins B or C are fed through another hopper into a Century- ZSK-40 extruder (37.13 length-to-diameter ratio extruder, a co-rotating, intermeshing, 40 mm twin
 20 screw extruder with 150 Hp drive, 244 Armature amps (maximum), and 1200 screw rpm (maximum)). The nine heating zones in the extruder are set as follows: the first at 25°C, the second at 100°C, and the rest at 200°C.

The polymer melt pump is a Maag 100 cc/revolution pump that helps convey the molten polymer from the extruder, and through the downstream equipment. It is powered
 25 by a 15 hp motor with a 20.55/1 reduction gear. The pump is equipped with a pressure transmitter and a 5200 psi rupture disc on the inlet and outlet transition piece. There are heater zones on the melt pump and the inlet and outlet transition pieces which are set at 220°C.

The melt pump is attached to the extruder and the single screw extruder's flow
 30 enters the polymer stream through an injector from the single screw side arm extruder. The

injector is a $\frac{3}{4}$ of an inch tubing protruding into the centerline of a pipe with 3.1 inch internal diameter.

The polymer coming from the extruder is blended with the single screw extruder resin as it flows through a static mixer with 18 Kenics mixing element mixer of 3.1 inch
5 internal diameter. The mixing elements have 1.3 length-to-diameter ratio. There are seven heating zones in the static mixer and are all set to 220°C.

The combined flow then flows through a Gala pelletizer system. The Gala is equipped with a 12 hole (2.36 mm hole diameter) Gala die with 4 of the holes plugged. The cutter has a 4 blade hub and operates at approximately 800 ppm. The water temperature in
10 the pelletizer is kept at 30°C.

The amount of the masterbatch or dry-blended masterbatch and resin D is approximately 3 wt% of the total resin amount. The residence time of the masterbatch in the side arm extruder is approximately 20 minutes and the residence time of the polymer in the static mixer is approximately 3 minutes.

15

The melt strength of each of these examples is measured using Göttfert Rheotester 2000 at 190°C. The viscosity is measured using a constant temperature of 190°C at a frequency sweep in a TA Instruments “Advanced Rheometric Expansion System (ARES)”. The melt indices are measured using ASTM method D-1238 at 190°C using a Tinius-Olsen
20 Extrusion Plastometer Model MP987. The molecular weights are determined using the method described under Testing Methods above.

Figure 1 shows the melt strength curve versus stretching velocity with increasing additive concentration. The incorporation of the additive changes the behavior of resins B and C, increasing the force needed to stretch the molten polymer. The melt strength of resin
25 B with 60 ppm additive is approximately the same as comparative resin E with the same amount of resin D but no additive, even though resin E has much lower melt index than resin B. All resins in this figure contain 3 wt% of resin D.

Figure 2 shows the elongational viscosity versus the shear rate frequency measured using a constant temperature of 190°C at a frequency sweep in a TA Instruments
30 “Advanced Rheometric Expansion System (ARES)”. The incorporation of the additive

changes the behavior of Resins B and C at low shear rates as compared to resins A and E. All resins in this figure contain 3 wt% of resin D.

Figure 3 shows the melt strength at the plateau versus the melt index (ASTM method D-1238 at 190°C with 2.16 kg, in g/10 minutes) for four Ziegler-Natta catalyzed polyethylene resins with no additive (resins A, B, C, and E) and inventive resins B, C with different amounts of the additive and resin E with 60 ppm additive. Inventive resins B, C and E have higher melt strength at the plateau when compared with resins that have similar melt index and no additive. All resins contain 3 wt% of resin D.

Figure 4 shows the phase angle (°) versus the complex modulus (G^*) measured using a constant temperature of 190°C at a frequency sweep in a TA Instruments “Advanced Rheometric Expansion System (ARES)”. Inventive resin B with different amounts of the additive is compared with comparative resin A, a resin that does not contain long chain branches. All resins contain 3 wt% of resin D.

Figure 5 shows the phase angle (°) versus the complex modulus (G^*) measured using a constant temperature of 190°C at a frequency sweep in a TA Instruments “Advanced Rheometric Expansion System (ARES)”. Inventive resin C with different amounts of the additive is compared with comparative resin E, a resin that does not contain long chain branches. All resins contain 3 wt% of resin D.

Resin description:

Resin A (Dowlex 61528.20) is a Ziegler-Natta catalyzed polyethylene resin made in a solution process having melt index of 0.5 g/10 min (at 190°C, 2.16kg ASTM D-1238) and a density 0.921 g/cm³ (ASTM D792).

Resin B (Dowlex TG 2085B) is a Ziegler-Natta catalyzed polyethylene resin made in a solution process having a melt index of 0.95 g/10 min (at 190°C, 2.16kg ASTM D-1238_ and a density 0.919 g/cm³ (ASTM D792).

Resin C (Dowlex NG 5085B) is a Ziegler-Natta catalyzed polyethylene made in a slurry process having a melt index of 1.3 g/10 min (at 190°C, 2.16kg ASTM D-1238) and a density of 0.918 g/cm³ (ASTM D792).

Resin D (LDPE 208C/206M) is a homopolymer ethylene resin made in a high-pressure tubular reactor having a melt index of 0.7 g/10 min (at 190°C, 2.16kg ASTM D-1238) and a density of 0.925 g/cm³ (ASTM D792).

Resin E (Dowlex 2045) is a Ziegler-Natta catalyzed polyethylene resin made in a solution process having melt index of 1.0 g/10 min (at 190°C, 2.16kg ASTM D-1238) and a density 0.920 g/cm³ (ASTM D792).

Resins A, B, C, and E in the table below all additionally contain 3 wt% of resin D.

5

Samples	Density g/cm ³ (ASTM D792)	Conventional GPC				I ₂ (g/10 min)	I ₁₀ (g/10 min)	I ₁₀ /I ₂ (g/10 min)	Melt Strength (cN)	Viscosity at 0.1 rad/s (Pa- s)	Ratio viscosity at 0.1 to 100 shear rates
		Mn	Mw	Mz	Mw/Mn						
Resin A	0.921	31,322	150,495	582,495	4.80	0.50	3.96	7.92	6.8	16,356	7.6
Resin B (no additive)	0.919	25,380	110,400	321,500	4.35	0.90	7.23	8.03	4.8	9,700	5.8
Resin B + 30ppm additive	0.919	26,870	111,330	320,400	4.14	0.77	6.91	8.97	5.6	12,015	6.9
Resin B + 60ppm additive	0.918	26,100	111,920	331,200	4.29	0.69	6.4	9.28	6.4	14,480	8.2
Resin C (no additive)	0.918	23,830	100,000	291,800	4.20	1.25	10.46	8.37	3.5	6,760	4.8
Resin C + 60ppm additive	0.918	23,780	100,670	301,400	4.23	1.01	9.36	9.27	4.8	9,810	6.6
Resin C + 80ppm additive	0.918	25,470	117,120	359,600	4.60	0.92	8.58	9.29	5.8	12,040	7.7
Resin D	0.925	13,670	101,325	296,650	7.41	0.70	NS	NA	16	17,650	22.7
Resin E	0.920	26,031	115,576	360,140	4.44	1.00	7.96	7.96	4.6	8,395	5.5

From the above examples, it is demonstrated that addition of the additive results in changes to the molecular weight distribution and significantly increases melt strength, at levels compared to comparative resins A and E, without significantly increasing the molecular weight. For example, the molecular weight distribution is broadened as shown by a minimum of 10% increase in I₁₀I₂ over the comparative resin. The melt strength increases from 16 to 65 % over the comparative resin. It can also be seen that the addition of the additive results in resins having higher melt strength than resins with higher molecular weight that were made using same polymerization technology (Resins A and E). From the above examples it is demonstrated that the addition of the additive results in resins with higher ratio of elongational viscosities at 0.1 to 100 s⁻¹ shear rates, and this manifests in

lower pressure drop requirements in an extruder when these resins are processed further. The change over the comparative resins in the elongational viscosity ratio ranges from 19 to 60%, depending on the set of resins and amount of additive used.

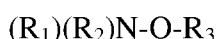
The following embodiments are expressly considered to be part of the present invention although each embodiment may not be separately claimed.

1) A method for increasing the melt strength of a target polyethylene resin comprising the steps of:

a) selecting a target polyethylene resin having a density, as determined according to ASTM D792, in the range of from 0.865 g/cm³ to 0.962 g/cm³, and a melt index, as determined according to ASTM D1238 (2.16 kg, 190°C), in the range of from 0.01 g/10min to 100 g/10 min;

b) reacting an alkoxy amine derivative in an amount less than 900 parts derivative per million parts of total polyethylene resin with the polyethylene resin under conditions sufficient to increase the melt strength of the polyethylene resin

2) The method of embodiment 1 wherein the alkoxy amine derivative corresponds to the formula:



where R₁ and R₂ are each independently of one another, hydrogen, C₄-C₄₂ alkyl or C₄-C₄₂ aryl or substituted hydrocarbon groups comprising O and/or N, and where R₁ and R₂ may form a ring structure together; and R₃ is hydrogen, a hydrocarbon or a substituted hydrocarbon group comprising O and/or N.

3) The method of embodiment 1 wherein the alkoxy amine derivative is a hydroxylamine ester.

4) The method of embodiment 3 wherein the hydroxyl amine ester is hydroxyl amine ester being 9-(acetyloxy)-3,8,10-triethyl-7,8,10-trimethyl-1,5-dioxo-9-azaspiro[5.5]undec-3-yl]methyl octadecanoate

5) The method of embodiment 1 wherein the alkoxy amine derivative is added to the target polyethylene resin as a masterbatch comprising the alkoxy amine derivative along with a carrier resin.

6) The method of embodiment 5 wherein the carrier resin is selected from the group consisting of HDPE, LLDPE, and LDPE.

- 7) The method of embodiment 6 wherein the carrier resin is LDPE and the LDPE resin has a vinyl concentration in the range of from 0 to 0.5 vinyls per 1,000 carbons.
- 8) The method of embodiment 7 wherein the carrier resin has a vinyl concentration less than 0.1 vinyls per 1,000 carbons.
- 5 9) The method of embodiment 6 wherein the carrier resin is HDPE and the HDPE resin has a vinyl concentration in the range of from 0 to 0.5 vinyls per 1,000 carbons.
- 10) The method of embodiment 9 wherein the carrier resin has a vinyl concentration less than 0.05 vinyls per 1000 carbons.
- 11) The method of embodiment 6 wherein the carrier resin is substantially free of
10 antioxidant compounds, in the range of 0 to 1,000 ppm.
- 12) The method of embodiment 11 wherein the carrier resin is free of primary antioxidant compounds.
- 13) The method of embodiment 1 wherein the alkoxy amine derivative is reacted with the polyethylene resin in a reactive extrusion process.
- 15 14) The method of embodiment 1 wherein the target resin comprises LLDPE resin derived from ethylene monomer and alpha-olefin comonomers having three to twelve carbons.
- 15) The method of embodiment 1 wherein the target polyethylene resin comprises LLDPE resin with vinyl content in the range of from 0 to 0.5 vinyls per 1,000 carbons.
- 16) The method of embodiment 1 wherein the target resin comprises blends of LDPE and
20 LLDPE resins.
- 17) The method of embodiment 1 wherein the target resin comprises blends of HDPE and LLDPE resins.
- 18) The method of embodiment 1 wherein the target resin comprises blends of HDPE and LDPE resins.
- 25 19) The method of embodiment 1 wherein the target polyethylene resin is substantially free of primary antioxidants, preferably in the range of 0 to 1,000 ppm.
- 20) The method of embodiment 1 wherein the alkoxy amine derivative is added in an amount of from 0.003 % to less than 0.09 % of the total amount of polyethylene polymer by weight.
- 30 21) The method of embodiment 5 wherein the masterbatch is produced by melt extruding a mixture of the carrier resin and the derivative at extruder temperatures below 250°C.

- 22) The method of embodiment 1 wherein the melt strength is increased by at least 25% compared to a substantially similar polyethylene resin which has not been reacted with an alkoxy amine derivative.
- 23) The method of embodiment 1 further comprising the step of adding one or more
5 antioxidants to the target resin after the target resin has been reacted with the derivative.
- 24) A method for increasing the elongational viscosity of a target polyethylene resin at shear rates below 1 rad/s comprising the steps of:
- a) selecting a target polyethylene resin having a density, as determined according to ASTM D792, in the range of from 0.865 g/cm³ to 0.962 g/cm³, and a melt index, as
10 determined according to ASTM D1238 (2.16 kg, 190°C), in the range of from 0.01 g/10min to 100 g/10 min;
- b) reacting an alkoxy amine derivative with the target polyethylene resin in an amount and under conditions sufficient to increase the elongational viscosity of the target polyethylene resin.
- 15 25) The method of embodiment 23 wherein the elongational viscosity of the target polyethylene resin is increased by at least 25% compared to a substantially similar polyethylene resin which has not been reacted with an alkoxy amine derivative. The method of embodiment 23 wherein the elongational viscosity ratio of the target polyethylene resin at 0.1 to 100 rad/s is increased by at least 25% compared to a
20 substantially similar polyethylene resin which has not been reacted with an alkoxy amine derivative. The use of an alkoxy amine derivative to improve the melt strength and/or elongational viscosity of a target polyethylene resin wherein the alkoxy amine derivative is added to the target polyethylene resin in a reactive extrusion process.
- 28) A fabricated article made from a target polyethylene resin made according to the method
25 of embodiment 1.
- 29) A fabricated article according to embodiment 27 wherein the article is selected from the group consisting of films, sheets, pipes or blow molded articles.
- 30) A fabricated article according to embodiment 28 which is a film that retains the mechanical properties as the original resin with increased melt strength and good
30 processability when compared to films made of resins which have not been reacted with an alkoxy amine derivative. A fabricated article according to embodiment 27 that has

sufficient antioxidants added in the final processing step to completely stabilize the resin.

32) An ethylene-based polymer composition formed by reacting

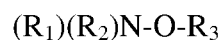
a) a target polyethylene resin having characterized by a resin having a density, as
 5 determined according to ASTM D792, in the range of from 0.865 g/cm³ to 0.962 g/cm³, and a melt index, as determined according to ASTM D1238 (2.16 kg, 190°C), in the range of from 0.01 g/10min to 100 g/10 min; with

b) an alkoxy amine derivative

in an amount less than 900 parts alkoxy amine derivative per million parts of total
 10 polyethylene resin in the composition, under conditions sufficient to increase the melt strength of the target polyethylene resin.

33) The ethylene-based polymer composition of embodiment 32 wherein the target polyethylene resin is further characterized by having more than 10 trisubstituted unsaturation units/1,000,000C.

15 34) The ethylene-based polymer composition of embodiment 32 wherein the alkoxy amine derivative corresponds to the formula:



where R₁ and R₂ are each independently of one another, hydrogen, C₄-C₄₂ alkyl or C₄-C₄₂ aryl or substituted hydrocarbon groups comprising O and/or N, and where R₁
 20 and R₂ may form a ring structure together; and R₃ is hydrogen, a hydrocarbon or a substituted hydrocarbon group comprising O and/or N.

35) The ethylene-based polymer composition of embodiment 32 wherein the alkoxy amine derivative is a hydroxylamine ester.

36) The ethylene-based polymer composition of embodiment 35 wherein the hydroxyl amine
 25 ester is hydroxyl amine ester being 9-(acetyloxy)-3,8,10-triethyl-7,8,10-trimethyl-1,5-dioxa-9-azaspiro[5.5]undec-3-yl)methyl octadecanoate.

37) The ethylene-based polymer composition of embodiment 32 wherein the alkoxy amine derivative is added to the polyethylene resin as a masterbatch comprising the alkoxy amine derivative along with a carrier resin.

30 38) The ethylene-based polymer composition of embodiment 37 wherein the carrier resin is selected from the group consisting of HDPE, LLDPE, and LDPE.

- 39) The ethylene-based polymer composition of embodiment 38 wherein the carrier resin is LDPE and the carrier LDPE resin has a trisubstituted unsaturation unit/1,000,000C in the range of from 0 to 500.
- 40) The ethylene-based polymer composition of embodiment 39 wherein the trisubstituted unsaturation unit/1,000,000C concentration is less than 100.
- 41) The ethylene-based polymer composition of embodiment 38 wherein the carrier resin is HDPE and the carrier HDPE resin has a trisubstituted unsaturation unit/1,000,000C in the range of from 0 to 500.
- 42) The ethylene-based polymer composition of embodiment 41 wherein the trisubstituted unsaturation unit/1,000,000C concentration is less than 50.
- 43) The ethylene-based polymer composition of embodiment 38 wherein the carrier resin is characterized by being substantially free of antioxidant compounds, in the range of from 0 to 1,000 parts antioxidant per million parts carrier resin.
- 44) The ethylene-based polymer composition of embodiment 43 wherein the carrier resin is free of primary antioxidant compounds.
- 45) The ethylene-based polymer composition of embodiment 32 wherein the alkoxy amine derivative is reacted with the polyethylene resin in a reactive extrusion process.
- 46) The ethylene-based polymer composition of embodiment 32 wherein the target polyethylene resin comprises LLDPE resin with trisubstituted unsaturation unit/1,000,000C in the range of from 0 to 500 ppm.
- 47) The ethylene-based polymer composition of embodiment 32 wherein the target polyethylene resin is substantially free of primary antioxidants, preferably in the range of from 0 to 1,000 ppm.
- 48) The ethylene-based polymer composition of embodiment 32 wherein the alkoxy amine derivative is added in an amount of from 0.003 % to less than 0.09 % of the total amount of polyethylene polymer by weight.
- 49) The ethylene-based polymer composition of embodiment 32 wherein the melt strength of the target polyethylene resin is increased by at least 15% compared to a substantially similar polyethylene resin which has not been reacted with an alkoxy amine derivative.
- 50) An ethylene-based polymer of increased elongational viscosity at shear rates below 1 rad/s comprising:

a polyethylene resin having a density, as determined according to ASTM D792, in the range of from 0.865 g/cm³ to 0.962 g/cm³, and a melt index, as determined according to ASTM D1238 (2.16 kg, 190°C), in the range of from 0.01 g/10min to 100 g/10 min; an alkoxy amine derivative with the polyethylene resin in an amount and under conditions sufficient to increase the elongational viscosity of the polyethylene resin at shear rates below 1 rad/s. The polymer of embodiment 50 wherein the elongational viscosity is increased by at least 20% compared to a substantially similar polyethylene resin which has not been reacted with an alkoxy amine derivative.

52) The polymer of embodiment 50 wherein the elongational viscosity ratio at 0.1 to 100 rad/s is increased by at least 20% compared to a substantially similar polyethylene resin which has not been reacted with an alkoxy amine derivative.

53) The use of an alkoxy amine derivative to improve the melt strength and/or elongational viscosity of a polyethylene resin wherein the alkoxy amine derivative is added to the polyethylene resin in a reactive extrusion process.

54) A fabricated article made from a polyethylene resin made according to embodiment 32.

55) A fabricated article according to embodiment 54 wherein the article is selected from the group consisting of films, sheets, pipes or blow molded articles.

56) A fabricated article according to embodiment 55 which is a film that retains the mechanical properties as the original resin with increased melt strength and good processability when compared to films made of resins which have not been reacted with an alkoxy amine derivative.

57) A film according to 56 which is a blend of LDPE and LLDPE resins.

58) A film according to 57 which is used in monolayer or multilayer films.

59) A film according to 58 which is used in thick film applications.

60) A fabricated article according to embodiment 54 that has sufficient antioxidants added in the final processing step to completely stabilize the resin.

Although the invention has been described in considerable detail through the preceding description and examples, this detail is for the purpose of illustration and is not to be construed as a limitation on the scope of the invention as it is described in the appended

claims. All United States patents, published patent applications and allowed patent applications identified above are incorporated herein by reference.

WHAT IS CLAIMED IS:

- 1) A method for increasing the melt strength of a target polyethylene resin comprising the steps of:
 - a) selecting a target polyethylene resin having a density, as determined according to ASTM D792, in the range of from 0.865 g/cm³ to 0.970 g/cm³, and a melt index, as determined according to ASTM D1238 (2.16 kg, 190°C), in the range of from 0.01 g/10min to 100 g/10 min;
 - b) reacting an alkoxy amine derivative in an amount less than 900 parts derivative per million parts of total polyethylene resin with the polyethylene resin under conditions sufficient to increase the melt strength of the polyethylene resin
- 2) The method of Claim 1 wherein the alkoxy amine derivative corresponds to the formula:

$$(R_1)(R_2)N-O-R_3$$
 where R₁ and R₂ are each independently of one another, hydrogen, C₄-C₄₂ alkyl or C₄-C₄₂ aryl or substituted hydrocarbon groups comprising O and/or N, and where R₁ and R₂ may form a ring structure together; and R₃ is hydrogen, a hydrocarbon or a substituted hydrocarbon group comprising O and/or N.
- 3) The method of claim 1 wherein the alkoxy amine derivative is a hydroxylamine ester.
- 4) The method of claim 3 wherein the hydroxyl amine ester is hydroxyl amine ester being 9-(acetyloxy)-3,8,10-triethyl-7,8,10-trimethyl-1,5-dioxo-9-azaspiro[5.5]undec-3-yl)methyl octadecanoate
- 5) The method of claim 1 wherein the alkoxy amine derivative is added to the target polyethylene resin as a masterbatch comprising the alkoxy amine derivative along with a carrier resin.
- 6) The method of claim 5 wherein the carrier resin is selected from the group consisting of HDPE, LLDPE, and LDPE.
- 7) The method of claim 6 wherein the carrier resin is LDPE and the LDPE resin has a trisubstituted unsaturation unit per 1,000,000 carbon atoms in the range of from 0 to 500.
- 8) The method of claim 7 wherein the carrier resin has a trisubstituted unsaturation unit per 1,000,000 carbon atoms of less than 100.

- 9) The method of claim 6 wherein the carrier resin is HDPE and the HDPE resin has a trisubstituted unsaturation unit per 1,000,000 carbon atoms in the range of from 0 to 500.
- 10) The method of claim 9 wherein the carrier resin has a trisubstituted unsaturation unit per
5 1,000,000 carbon atoms less than 50.
- 11) The method of claim 6 wherein the carrier resin is substantially free of antioxidant compounds, in the range of 0 to 1,000 ppm.
- 12) The method of claim 11 wherein the carrier resin is free of primary antioxidant compounds.
- 10 13) The method of claim 1 wherein the alkoxy amine derivative is reacted with the polyethylene resin in a reactive extrusion process.
- 14) The method of claim 1 wherein the target resin comprises LLDPE resin derived from ethylene monomer and alpha-olefin comonomers having three to twelve carbons.
- 15) The method of claim 1 wherein the target polyethylene resin comprises LLDPE resin
15 with trisubstituted unsaturation unit per 1,000,000 carbon atoms in the range of from 0 to 500.
- 16) The method of claim 1 wherein the target resin comprises a two or more resins selected from the group consisting of LDPE, LLDPE, and HDPE resins.
- 17) The method of claim 1 wherein the target polyethylene resin is substantially free of
20 primary antioxidants, preferably in the range of 0 to 1,000 ppm.
- 18) The method of claim 1 wherein the alkoxy amine derivative is added in an amount of from 0.003 % to less than 0.09 % of the total amount of polyethylene polymer by weight.
- 19) The method of claim 5 wherein the masterbatch is produced by melt extruding a mixture
25 of the carrier resin and the derivative at extruder temperatures below 250°C.
- 20) The method of claim 1 further comprising the step of adding one or more antioxidants to the target resin after the target resin has been reacted with the derivative.