LUBRICANT TREATMENTS FOR FREE-RADICAL POLYMERIZATIONS

REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of U.S. Provisional Application 62/471077, filed March 14, 2017, and U.S. Provisional Application 62/400815, filed September 28, 2016.

BACKGROUND OF THE INVENTION

In high pressure, free-radical polymerizations, compressors are used to pressurize the ethylene, and any comonomer, to the desired reaction pressures, and the pressurization step is often followed by a preheating step, to heat the ethylene up to the desired reaction temperatures. Typically, some form of mineral oil based lubricating oil is added to the cylinders of the compressor, to prevent erosion. It is often found that fouling or plugging can occur in either the compressor's cylinders and/or the preheater, leading to a downtime period to replace cylinders, and/or clean the preheater, which, in turn, leads to decreased production rates. This fouling is caused by undesired ethylene and/or comonomer polymerization in these areas. There is need for new polymerization processes that result in a reduction of such fouling and/or plugging.

Lubricating oils, have been made using a polyalkylene glycol base oil. However, these polyalkylene glycol oils often have their own problems, such as reactions with different comonomers or poor electrical properties. Inhibitors have also been used, as mineral oil additives, to reduce plugging or fouling; however these inhibitors can have solubility issues or may require oxygen to be active**.** Lubrication oils, inhibitors, and/or polymerization using the same, are disclosed in the following references: 1) IP.com Journal, (2011), 11(9A), 13; 2) Lubrication Engineering, Volume 54, Issue 11, Pages 12-18, 1998; 3) International Publication No. WO 2010071669; 4) International Publication No. WO 2016077512; and 5) International Publication No. WO 2013149698. However, as discussed above, there remains a need for new polymerization processes that result in reduced fouling and/or plugging. These needs have been met by the following invention.

SUMMARY

A process to prepare an ethylene-based polymer, said process comprising polymerizing a mixture comprising ethylene, at a pressure greater than, or equal to, 100 MPa, in the presence of at least one free-radical initiator; and in a reactor system comprising at

least one reactor and at least one Hyper-compressor, and

wherein at least one oil formulation, optionally comprising one or more lubrication agents, is added to the Hyper-compressor; and wherein at least one of the following steps takes place:

A) thermally treating the one or more lubrication agents, in an oxygen-free atmosphere, to achieve a peroxide level ≤ 10 ppm, based on the weight of the lubrication agent(s), and then adding said agent(s) to the oil formulation, prior to adding the oil formulation to the Hyper-compressor; or

B) thermally treating the oil formulation, in an oxygen-free atmosphere, to achieve a peroxide level ≤ 10 ppm, based on the weight of the oil formulation, prior to adding the oil formulation to the Hyper-compressor;

C) a combination of A and B.

In one aspect, there is provided a process to prepare an ethylene-based polymer, said process comprising polymerizing a mixture comprising ethylene, at a pressure greater than, or equal to, 100 MPa, in the presence of at least one free-radical initiator; and in a reactor system comprising at least one reactor and at least one Hyper-compressor, and

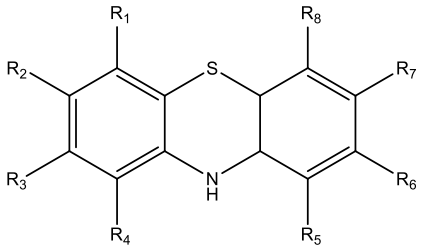
wherein at least one oil formulation, optionally comprising one or more lubrication agents, is added to the Hyper-compressor; and wherein at least one of the following steps takes place:

A) thermally treating the one or more lubrication agents, in an oxygen-free atmosphere, at from 50 °C to 200 °C for from 1 hour to 24 hours, to achieve a peroxide level ≤ 10 ppm, based on the weight of the lubrication agent(s), and then adding the lubrication agent(s) to the at least one oil formulation, prior to adding the at least one oil formulation to the Hyper-compressor;

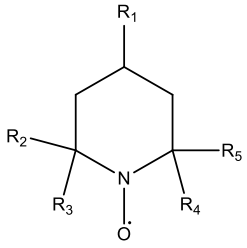
B) thermally treating the at least one oil formulation, in an oxygen-free atmosphere, at from 50 °C to 200 °C for from 1 hour to 24 hours, to achieve a peroxide level ≤ 10 ppm, based on the weight of the at least one oil formulation, prior to adding the at least one oil formulation to the Hyper-compressor; or

C) a combination of A and B; and

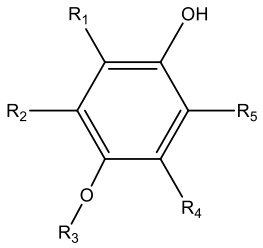
wherein the one or more oil formulation contains a compound selected from the following compounds i) through iv):

i)  (Compound 1),

wherein, for Compound 1, R1, R2, R3, R4, R5, R6, R7 and R8 are each independently selected from H, an alkyl, or an alkoxy;

ii)  (Compound 2),

wherein, for Compound 2, R1 is selected from OH or O-R, wherein R is alkyl; and R2, R3, R4 and R5 are each independently selected from H, an alkyl, or an alkoxy;

iii)  (Compound 3),

wherein, for Compound 3, R1, R2, R4 and R5 are each independently selected from H, an alkyl, or an alkoxy; and R3 is selected from H or an alkyl; or

iv) a combination of two or more of Compounds 1 through 3.

Also, a process to reduce the peroxide content in an oil formulation, optionally comprising one or more lubrication agents; said process comprising at least one of the following steps:

A) thermally treating the one or more lubrication agents, in an oxygen-free atmosphere, to achieve a peroxide level ≤ 10 ppm, based on the weight of the lubrication agent(s), and then adding said agent(s) to the oil formulation; or

B) thermally treating the oil formulation, in an oxygen-free atmosphere, to achieve a peroxide level ≤ 10 ppm, based on the weight of the oil formulation;

C) a combination of A and B.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts the polymerization fouling in an agitator and the inside of a reactor tank; which fouling occurred during polymerization run in the presence of a mineral oil containing untreated oleic acid (CE#1, far left), or oleic acid thermally treated under nitrogen (IE#1, middle), or oleic acid thermally treated under air (CE#2, far right).

Figure 2 depicts a schematic of a general flow diagram showing a reactor system for a high pressure polymerization process.

Figure 3 depicts a simplified schematic of a high pressure polymerization, showing the Hyper-compressor and preheater areas (tubular reactor) which are prone to undesired polymerization and fouling.

CLAIMS

1. A process to prepare an ethylene-based polymer, said process comprising polymerizing a mixture comprising ethylene, at a pressure greater than, or equal to, 100 MPa, in the presence of at least one free-radical initiator; and in a reactor system comprising at least one reactor and at least one Hyper-compressor, and

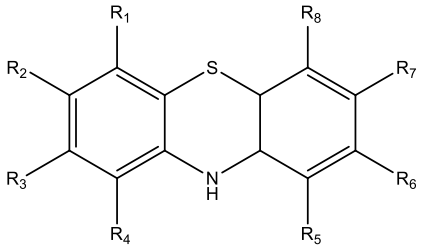
wherein at least one oil formulation, optionally comprising one or more lubrication agents, is added to the Hyper-compressor; and wherein at least one of the following steps takes place:

A) thermally treating the one or more lubrication agents, in an oxygen-free atmosphere, at from 50 °C to 200 °C for from 1 hour to 24 hours, to achieve a peroxide level ≤ 10 ppm, based on the weight of the lubrication agent(s), and then adding the lubrication agent(s) to the at least one oil formulation, prior to adding the at least one oil formulation to the Hyper-compressor;

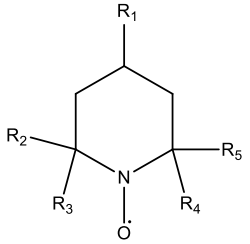
B) thermally treating the at least one oil formulation, in an oxygen-free atmosphere, at from 50 °C to 200 °C for from 1 hour to 24 hours, to achieve a peroxide level ≤ 10 ppm, based on the weight of the at least one oil formulation, prior to adding the at least one oil formulation to the Hyper-compressor; or

C) a combination of A and B; and

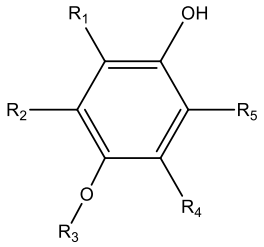
wherein the one or more oil formulation contains a compound selected from the following compounds i) through iv):

i)  (Compound 1),

wherein, for Compound 1, R1, R2, R3, R4, R5, R6, R7 and R8 are each independently selected from H, an alkyl, or an alkoxy;

ii)  (Compound 2),

wherein, for Compound 2, R1 is selected from OH or O-R, wherein R is alkyl; and R2, R3, R4 and R5 are each independently selected from H, an alkyl, or an alkoxy;

iii)  (Compound 3),

wherein, for Compound 3, R1, R2, R4 and R5 are each independently selected from H, an alkyl, or an alkoxy; and R3 is selected from H or an alkyl; or

iv) a combination of two or more of Compounds 1 through 3.

2. The process of claim 1, wherein the at least one reactor is a tubular reactor.

3. The process of claim 1 or claim 2, wherein the at least one oil formulation comprises greater than, or equal to, 70.0 wt% oil, based on the weight of the at least one oil formulation.

4. The process of any one of the previous claims, wherein the at least one oil formulation is injected at one or more injection points into the Hyper-compressor.

5. The process of any one of the previous claims, wherein the ethylene-based polymer is an ethylene homopolymer.