operation is involved because the elevated temperatures can accelerate polymerization.

[0005] The manufacture of ethylenically unsaturated monomers typically comprises three stages: reaction, recovery, and purification. Distillation operations at elevated temperatures are often involved in the recovery and the purification stages. Polymerization of the ethylenically unsaturated monomer during manufacture is generally unwanted because the resulting polymer can precipitate out of the process stream, deposit on the process equipment surfaces, and impair the proper functioning of the equipment. Thus, polymerization inhibitors have conventionally been used when carrying out the monomer manufacturing processes.

[0006] Phenolic and phenylenediamine antioxidants, nitroxide stable free radicals, and phenothiazine derivatives are commonly used reagents for polymerization inhibition in the industry. Hydroquinone (HQ), phenothiazine (PTZ), phenylenediamine (PDA), and 4-hydroxy-2,2,6,6-tetramethyl piperidinyl oxy (HTMPO) are examples of some of the most commonly used polymerization inhibitors in the industry. However, a conventional inhibitor treatment often does not provide adequate protection from the polymerization-induced fouling. Furthermore, use of the conventional inhibitors often poses logistic, economic, and safety concerns.

BRIEF SUMMARY

[0007] Compositions are provided for inhibiting polymerization of monomers. In ~~one aspect~~an embodiment, a composition for inhibiting polymerization of monomers comprises at least one hydroxylamine of a nitroxide and at least one phenylenediamine.

[0008] Methods of inhibiting the polymerization of monomers are also provided herein. In one aspect, there is provided a method of inhibiting polymerization of an ethylenically unsaturated monomer comprising: providing a fluid comprising an ethylenically unsaturated monomer; adding an effective amount of a polymerization inhibitor composition to the fluid, wherein the polymerization inhibitor composition comprises an effective

amount of 2,2,6,6-tetramethyl piperidinol and an effective amount of at least one phenylenediamine; and inhibiting polymerization of the ethylenically unsaturated monomer. In an embodiment, the present disclosure relates to a method of inhibiting polymerization of a monomer comprises providing a fluid comprising an ethylenically unsaturated monomer and adding an effective amount of a polymerization inhibitor composition to the fluid. The polymerization inhibitor composition comprises an effective amount of at least one hydroxylamine of a nitroxide

CLAIMS

What is claimed is:

1. A method of inhibiting polymerization of an ethylenically unsaturated monomer comprising:

providing a fluid comprising an ethylenically unsaturated monomer;

adding an effective amount of a polymerization inhibitor composition to the fluid, wherein the polymerization inhibitor composition comprises an effective amount of 2,2,6,6-tetramethyl piperidinol and an effective amount of at least one phenylenediamine; and

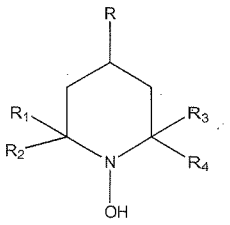
inhibiting polymerization of the ethylenically unsaturated monomer.

2. The method of claim 1, wherein the effective amount of the 2,2,6,6-tetramethyl piperidinol and the effective amount of the at least one phenylenediamine is from about 1 ppm to about 2,000 ppm by weight of monomer.

3. The method of claim 1, wherein the ethylenically unsaturated monomer is selected from the group consisting of acrylic acid, methacrylic acid, acrylonitrile, methacrylonitrile, acrolein, methacrolein, acrylate, methacrylate, acrylamide, methacrylamide, vinyl acetate, butadiene, styrene, ethylene, propylene, and any combination thereof.

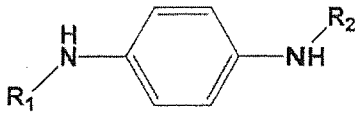
4. The method of claim 1, wherein the polymerization inhibitor composition is added continuously or intermittently to the fluid.

5. The method of claim 1, wherein the 2,2,6,6-tetramethyl piperidinol comprises the following structure:



wherein each R_1, R_2, R_3 and R_4 ismethyl and R is selected from the group consisting of hydrogen, oxygen, alkyl, hydroxyl, alkoxyl, amino, N-alkylamino, amido, N-alkylamido, carboxylate and carboxyl.

6. The method of claim 1, wherein the at least one phenylenediamine comprises the following structure:



wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, alkylaryl, hydroxyl-containing alkyl groups, ethoxylate-containing alkyl groups, and amino-containing alkyl groups.

7. The method of claim 10, wherein the at least one phenylenediamine is selected from the group consisting of 1,2-phenylenediamine, 1,4-phenylenediamine, N,N'-di-methyl-p-phenylenediamine, N,N'-di-sec-butyl-1,4-phenylenediamine, N,N'-di-1,4-dimethylpentyl-1,4-phenylenediamine, N,N'-di-acetyl-1,4-phenylenediamine, N-tert-butyl-N'-phenyl-1,4-phenylenediamine, N,N'-di-phenyl-1,4-phenylenediamine, and any combination thereof.

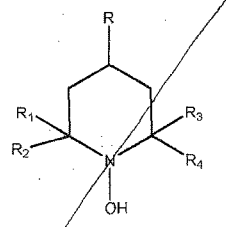
8. The method of claim 1, wherein the 2,2,6,6-tetramethyl piperidinol is 4-hydroxy-2,2,6,6-tetramethyl piperidinol and the at least one phenylenediamine comprises N,N'-di-sec-butyl-1,4-phenylenediamine.

CLAIMS

What is claimed is:

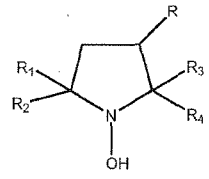
1. A composition for inhibiting polymerization of a monomer, the composition comprising at least one hydroxylamine of a nitroxide and at least one phenylenediamine.

2. The composition of claim 1, wherein the at least one hydroxylamine of a nitroxide comprises the following structure:



wherein each R_1, R_2, R_3 and R_4 is independently selected from an alkyl group and R is selected from the group consisting of hydrogen, oxygen, alkyl, hydroxyl, alkoxyl, amino, N-alkylamino, amido, N-alkylamido, carboxylate and carboxyl.

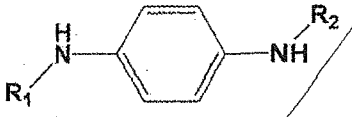
3. The composition of claim 1, wherein the at least one hydroxylamine of a nitroxide comprises the following structure:



wherein each R_1, R_2, R_3 and R_4 is independently selected from an alkyl group and R is selected from the group consisting of hydrogen, oxygen, alkyl, hydroxyl, alkoxyl, amino, N-alkylamino, amido, N-alkylamido, carboxylate and carboxyl.

4. The composition of claim 1, wherein the at least one hydroxylamine of a nitroxide is selected from the group consisting of 4-hydroxy-2,2,6,6-tetramethyl piperidinol, 4-oxo-2,2,6,6-tetramethyl piperidinol, 4-methoxy-2,2,6,6-tetramethyl piperidinol, 4-acetate-2,2,6,6-tetramethyl piperidinol, 4-amino-2,2,6,6-tertrmethyl piperidinol, 4-acetamido-2,2,6,6-tetramethyl piepridinol, 1,2,3,6-tetrahydro-2,2,6,6-tetramethyl piperidinol, bis(2,2,6,6-tetramethylpiperidinol) sebacate, and any combination thereof.

5. The composition of claim 1, wherein the at least one phenylenediamine comprises the following structure:



wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, alkylaryl, aryl, and arylalkyl, and further wherein R_1 and R_2 optionally comprise heteroatoms, hydroxyl groups, and/or amino groups.

6. The composition of claim 1, wherein the at least one phenylenediamine is selected from the group consisting of 1,2-phenylenediamine, 1,4-phenylenediamine, N,N'-di-methyl-p-phenylenediamine, N,N'-di-sec-butyl-1,4-phenylenediamine, N,N'-di-1,4-dimethylpentyl-1,4-phenylenediamine, N,N'-di-acetyl-1,4-phenylenediamine, N-tert-butyl-N'-phenyl-1,4-phenylenediamine, N,N'-di-phenyl-1,4-phenylenediamine, and any combination thereof.

7. The composition of claim 1, wherein the at least one hydroxylamine of a nitroxide is 4-hydroxy-2,2,6,6-tetramethyl piperidinol and the at least one phenylenediamine is selected from the group consisting of N,N'-di-sec-butyl-1,4-phenylenediamine and N,N'-di-1,4-dimethylpentyl-1,4-phenylenediamine.

8. The composition of claim 1, wherein the monomer is an ethylenically unsaturated monomer.

9. The composition of claim 1, wherein the composition includes the at least one hydroxylamine of a nitroxide and the at least one phenylenediamine in a ratio from about 10:1 to about 1:10 by weight of the monomer.

10. A method of inhibiting polymerization of an ethylenically unsaturated monomer comprising:

providing a fluid comprising an ethylenically unsaturated monomer;

adding an effective amount of a polymerization inhibitor composition to the fluid, wherein the polymerization inhibitor composition comprises an effective amount of at least one hydroxylamine of a nitroxide and an effective amount of at least one phenylenediamine; and

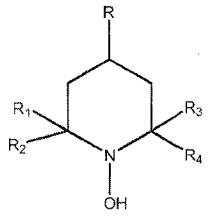
inhibiting polymerization of the ethylenically unsaturated monomer.

11. The method of claim 10, wherein the effective amount of the at least one hydroxylamine of a nitroxide and the effective amount of the at least one phenylenediamine is from about 1 ppm to about 2,000 ppm by weight of monomer.

12. The method of claim 10, wherein the ethylenically unsaturated monomer is selected from the group consisting of acrylic acid, methacrylic acid, acrylonitrile, methacrylonitrile, acrolein, methacrolein, acrylate, methacrylate, acrylamide, methacrylamide, vinyl acetate, butadiene, styrene, ethylene, propylene, and any combination thereof.

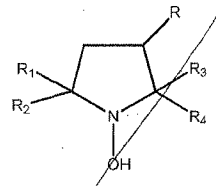
13. The method of claim 10, wherein the polymerization inhibitor composition is added continuously or intermittently to the fluid.

14. The method of claim 10, wherein the at least one hydroxylamine of a nitroxide comprises the following structure:



wherein each R_1, R_2, R_3 and R_4 is independently selected from an alkyl group and R is selected from the group consisting of hydrogen, oxygen, alkyl, hydroxyl, alkoxyl, amino, N-alkylamino, amido, N-alkylamido, carboxylate and carboxyl.

15. The method of claim 10, wherein the at least one hydroxylamine of a nitroxide comprises the following structure:



wherein each R_1, R_2, R_3 and R_4 is independently selected from an alkyl group and R is selected from the group consisting of hydrogen, oxygen, alkyl, hydroxyl, alkoxyl, amino, N-alkylamino, amido, N-alkylamido, carboxylate and carboxyl.

16. The method of claim 10, wherein the at least one hydroxylamine of a nitroxide is selected from the group consisting of 4-hydroxy-2,2,6,6-tetramethyl piperidinol, 4-oxo-2,2,6,6-tetramethyl piperidinol, 4-methoxy-2,2,6,6-tetramethyl piperidinol, 4-acetate-2,2,6,6-tetramethyl piperidinol, 4-amino-2,2,6,6-tertrmethyl piperidinol, 4-acetamido-2,2,6,6-tetramethyl piepridinol, 1,2,3,6-tetrahydro-2,2,6,6-tetramethyl piperidinol, bis(2,2,6,6-tetramethylpiperidinol) sebacate, and any combination thereof.

17. The method of claim 10, wherein the at least one phenylenediamine comprises the following structure:



wherein R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, alkylaryl, hydroxyl-containing alkyl groups, ethoxylate-containing alkyl groups, and amino-containing alkyl groups.

18. The method of claim 10, wherein the at least one phenylenediamine is selected from the group consisting of 1,2-phenylenediamine, 1,4-phenylenediamine, N,N'-di-methyl-p-phenylenediamine, N,N'-di-sec-butyl-1,4-phenylenediamine, N,N'-di-1,4-dimethylpentyl-1,4-phenylenediamine, N,N'-di-acetyl-1,4-phenylenediamine, N-tert-butyl-N'-phenyl-1,4-phenylenediamine, N,N'-di-phenyl-1,4-phenylenediamine, and any combination thereof.

19. The method of claim 10, wherein the at least one hydroxylamine of a nitroxide is 4-hydroxy-2,2,6,6-tetramethyl piperidinol and the at least one phenylenediamine is selected from the group consisting of N,N'-di-sec-butyl-1,4-phenylenediamine and N,N'-di-1,4-dimethylpentyl)-1,4-phenylenediamine.