a) 20% to 70% by weight of at least one hindered phenol-based antioxidant agent;

b) 0% to 40% by weight of at least one phosphite-based antioxidant agent; and

d) 20% to 40% by weight of at least one solvent having boiling point higher than 185°C and freezing point lower than -10°C under 101.325KPa, wherein said solvent is one or more selected from linear or branched alkane having C_9 to C_{30}, cyclane having C_{10} to $C_{30,}$ linear saturated carboxylic acid having C_8 to C_{18}, branched saturated carboxylic acid having C_8 to C_{12}, linear saturated alcohol having C_8 to C_{18} and branched saturated alcohol having C_8 to C_{12}, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, hexyl benzoate, diethyl phthalate, dipropyl phthalate, dibutyl phthalate, dipentyl phthalate, dihexyl phthalate, diheptyl phthalate, dioctyl phthalate, diisooctyl phthalate, dinonyl phthalate, diisononyl phthalate, didecyl phthalate, diisodecyl phthalate, trimethyl orthobenzoate , ethyl oleate, butyl oleate octyl acetate, decyl acetate, isononyl acetate, nonyl acetate, n-octyl propanoate, decyl propanoate, isononyl propanoate, nonyl propanoate, pentyl butanoate, hexyl butyrate, heptyl butanoate, n-octyl butanoate, butyl valerate, amyl valerate, hexyl valerate, butyl caproate, amyl caproate, hexyl hexanoate, ethyl heptanoate, propyl heptanoate, butyl heptoate, pentyl heptanoate, methyl octanoate, etheyl octanoate, propyl octanoate, butyl octanoate, amyl octanoate, hexyl octanoate, heptyl octanoate, octyl octanoate, nonyl octanoate, methyl nonanoate, ethyl nonanoate, isoamyl nonanoate, isononyl isononanoate, methyl caprate, ethyl caprate, propyl decanoate, butyl caprate, isoamyl decanoate, lauricacidisoamylester, ethylene glycol diacetate, ethylene glycol di-n-butyrate, dibutyl malonate, diethyl malonate, dihexyl malonate, diethyl succinate, dibutyl succinate, dipentyl succinate, dimethyl glutarate, diethyl glutarate, diethyl adipate, diisopropyl adipate, diisobutyl adipate, di(2-ethylhexyl)adipate, dihexyl adipate, diisononyl adipate, diisodecyl adipate, dibutyl sebacate, bishexyl sebacate, bis(2-ethylhexyl) sebacate, dioctyl sebacate, diisooctyl sebacate, glyceryl triacetate, glyceryl tripropionate, glyceryl tributyrate, triisobutyl phosphate, triamyl phosphate, trihexyl phosphate and trioctyl phosphate.

The present disclosure provides a liquid antioxidant composition used for raw rubbers, comprising

a) 5% to 20% by weight of solid aromatic amine-based antioxidant agent;

b) 20% to 50% by weight of solid hindered phenol-based antioxidant agent;

c) 0% to 30% by weight of solid phosphite-based antioxidant agent; and

d) 30% to 40% by weight of solvent having boiling point higher than 185°C and freezing point lower than -10°C under 101.325KPa, the weight percentage of component a), b) , c) or d) is based on the total weight of antioxidant composition.

In another aspect, there is provided a liquid antioxidant composition used for raw rubbers, comprising

a) 5% to 20% by weight of solid aromatic amine-based antioxidant agent;

b) 20% to 50% by weight of solid hindered phenol-based antioxidant agent;

c) 0% to 30% by weight of solid phosphite-based antioxidant agent; and

d) 30% to 40% by weight of solvent having boiling point higher than 185°C and freezing point lower than -10°C under 101.325KPa, wherein said solvent is one or more selected from linear or branched alkane having C_9 to C_{30}, cyclane having C_{10} to C_{30}, linear saturated carboxylic acid having C_8 to C_{18}, branched saturated carboxylic acid having C_8 to C_{12}, linear saturated alcohol having C_8 to C_{18} and branched saturated alcohol having C_8 to C_{12}, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, hexyl benzoate, diethyl phthalate, dipropyl phthalate, dibutyl phthalate, dipentyl phthalate, dihexyl phthalate, diheptyl phthalate, dioctyl phthalate, diisooctyl phthalate, dinonyl phthalate, diisononyl phthalate, didecyl phthalate, diisodecyl phthalate, trimethyl orthobenzoate , ethyl oleate, butyl oleate octyl acetate, decyl acetate, isononyl acetate, nonyl acetate, n-octyl propanoate, decyl propanoate, isononyl propanoate, nonyl propanoate, pentyl butanoate, hexyl butyrate, heptyl butanoate, n-octyl butanoate, butyl valerate, amyl valerate, hexyl valerate, butyl caproate, amyl caproate, hexyl hexanoate, ethyl heptanoate, propyl heptanoate, butyl heptoate, pentyl heptanoate, methyl octanoate, etheyl octanoate, propyl octanoate, butyl octanoate, amyl octanoate, hexyl octanoate, heptyl octanoate, octyl octanoate, nonyl octanoate, methyl nonanoate, ethyl nonanoate, isoamyl nonanoate, isononyl isononanoate, methyl caprate, ethyl caprate, propyl decanoate, butyl caprate, isoamyl decanoate, lauricacidisoamylester, ethylene glycol diacetate, ethylene glycol di-n-butyrate, dibutyl malonate, diethyl malonate, dihexyl malonate, diethyl succinate, dibutyl succinate, dipentyl succinate, dimethyl

glutarate, diethyl glutarate, diethyl adipate, diisopropyl adipate, diisobutyl adipate, di(2-ethylhexyl)adipate, dihexyl adipate, diisononyl adipate, diisodecyl adipate, dibutyl sebacate, bishexyl sebacate, bis(2-ethylhexyl) sebacate, dioctyl sebacate, diisooctyl sebacate, glyceryl triacetate, glyceryl tripropionate, glyceryl tributyrate, triisobutyl phosphate, triamyl phosphate, trihexyl phosphate and trioctyl phosphate.

In another aspect, the present disclosure provides a use of said antioxidant composition in raw rubbers synthesized via solution polymerization or in natural rubbers.

In another aspect, there is provided a process of using antioxidant composition as defined above in raw rubbers synthesized via solution polymerization comprising steps of i) dissolving component a), b) and c) into d); ii) diluting liquid antioxidant composition by solvent for solution polymerization of raw rubbers; iii) adding diluted liquid antioxidant composition into raw rubbers synthesized via solution polymerization.

In another aspect, the present disclosure provides a raw rubber product comprising said antioxidant composition.

In a an embodiment, the present disclosure provides a process of using the invented antioxidant composition in raw rubbers synthesized via solution polymerization or natural rubbers comprising steps of i) dissolving component a), b) and c) into d); ii) diluting liquid antioxidant composition by solvent for solution polymerization of raw rubbers; iii) adding diluted liquid antioxidant composition into raw rubbers synthesized via solution polymerization or natural rubbers.

Detailed Description of Invention

Technical Problems

For rubber resins synthesized via solution polymerization, one significant step of process is to remove solvent and monomer residues from raw rubber solution by hot water or steam. During this step, antioxidant agents are prone to separate from rubber resins and dissolve into water, which in one side, leads to a loss of antioxidant agents in rubber resins and in another side contaminates water. The contaminated water needs to be treated to prevent environmental damages.

Part of antioxidant agents are liquid while the others are solid at around 25°C. The term “liquid” means the upper limit of melting range or melting point of an antioxidant agent without dissolving into any solvent is no more than 25°C under 101.325KPa. The term “solid” means the lower limit of melting range or melting point of an antioxidant agent without dissolving into any solvent is more than 25°C under 101.325KPa. The liquid antioxidant agents turn to freeze at temperature like 5°C,

Claim

1. A liquid antioxidant composition used for raw rubbers, comprising
    a) 5% to 30% by weight of at least one aromatic amine-based antioxidant agent;
    b) 20% to 70% by weight of at least one hindered phenol-based antioxidant agent;
    c) 0% to 40% by weight of at least one phosphite-based antioxidant agent; and
    d) 20% to 40% by weight of at least one solvent having boiling point higher than 185°C and freezing point lower than -10°C under 101.325KPa, wherein said solvent is one or more selected from linear or branched alkane having C_9 to C_{30}, cyclane having C_{10} to $C_{30,}$ linear saturated carboxylic acid having C_8 to C_{18}, branched saturated carboxylic acid having C_8 to C_{12}, linear saturated alcohol having C_8 to C_{18} and branched saturated alcohol having C_8 to C_{12},methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, hexyl benzoate, diethyl phthalate, dipropyl phthalate, dibutyl phthalate, dipentyl phthalate, dihexyl phthalate, diheptyl phthalate, dioctyl phthalate, diisooctyl phthalate, dinonyl phthalate, diisononyl phthalate, didecyl phthalate, diisodecyl phthalate, trimethyl orthobenzoate , ethyl oleate, butyl oleate octyl acetate, decyl acetate, isononyl acetate, nonyl acetate, n-octyl propanoate, decyl propanoate, isononyl propanoate, nonyl propanoate, pentyl butanoate, hexyl butyrate, heptyl butanoate, n-octyl butanoate, butyl valerate, amyl valerate, hexyl valerate, butyl caproate, amyl caproate, hexyl hexanoate, ethyl heptanoate, propyl heptanoate, butyl heptoate, pentyl heptanoate, methyl octanoate, etheyl octanoate, propyl octanoate, butyl octanoate, amyl octanoate, hexyl octanoate, heptyl octanoate, octyl octanoate, nonyl octanoate, methyl nonanoate, ethyl nonanoate, isoamyl nonanoate, isononyl isononanoate, methyl caprate, ethyl caprate, propyl decanoate, butyl caprate, isoamyl decanoate, lauricacidisoamylester, ethylene glycol diacetate, ethylene glycol di-n-butyrate, dibutyl malonate, diethyl malonate, dihexyl malonate, diethyl succinate, dibutyl succinate, dipentyl succinate, dimethyl glutarate, diethyl glutarate, diethyl adipate, diisopropyl adipate, diisobutyl adipate, di(2-ethylhexyl)adipate, dihexyl

adipate, diisononyl adipate, diisodecyl adipate, dibutyl sebacate, bishexyl sebacate, bis(2-ethylhexyl) sebacate, dioctyl sebacate, diisooctyl sebacate, glyceryl triacetate, glyceryl tripropionate, glyceryl tributyrate, triisobutyl phosphate, triamyl phosphate, trihexyl phosphate and trioctyl phosphate.

2. The antioxidant composition according to Claim 1, wherein said aromatic amine-based antioxidant agent is one or more selected from N,N'-di-sec-butyl-1,4-phenylenediamine, N-phenylbenzenamine reaction products with 2,4,4-trimethylpentene, bis(4-octylphenyl)amine, 4,4'-bis(α,α-dimethylbenzyl)diphenylamine, N,N'-di-2-naphthyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N-phenyl-N'-isopropyl-p-phenylenediamine, N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine, N-phenyl-N'-(3-methacryloyloxy-2-hydroxypropyl)-p-phenylenediamine, N,N'-bis(methyl-phenyl)-1,4-benzendiamine.

3. The antioxidant composition according to Claim 1 or 2, wherein said hindered phenol-based antioxidant agent is one or more selected from poly(oxy-1,2-ethanediyl)-alpha-[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]-omega-[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy], 2,4-bis[(octylthio)methyl]-o-cresol, 2,4-bis[(dodecylthio)methyl]-o-cresol, octyl-3,5-di-tert-butyl-4-hydroxy-hydrocinnamate, 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid C7-C9-branched alkyl ester, 4,4'-butylidene bis-(3-methyl-6-tert-butylphenol), 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid octadecyl ester, pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate], 2,4-bis(n-octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3,5-triazine, tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate, 2,2-thio-diethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate].

4. The antioxidant composition according to any one of Claims 1 to 3, wherein said phosphite-based antioxidant agent is one or more selected from diphenyl-mono(2-ethylhexyl)phosphite, diphenyl-monotridecyl-phosphite, diphenyl-isodecylphosphite, diphenyl-isooctyl-phosphite, diphenyl-nonylphenyl-phosphite, triphenyl phosphite, triisodecyl phosphite, tris(2-ethylhexyl)phosphite, tetraphenyltetra(tridecyl)pentaerythritol tetraphosphite, 1,1,3-tris(2-methyl-

4-di-tridecylphosphite-5-tert-butylphenyl)butane, 4,4'-butylidene bis(3-methyl-6-tert-butyl-di-tridecyl phosphite), 2,2'-ethylidene bis(4,6-di-tert-butyl-phenol)fluorophosphite, 4,4'-isopropylidene-diphenyl alkyl (C_{12} to C_{15}) phosphites, bis(nonylphenyl)pentaerythritol diphosphite, hydrogenated bisphenol A-pentaerythritol phosphite polymers, 3,9-bis(octadecyloxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane, tetra-C12-15-alkyl(propane-2,2-diylbis(4,1-phenylene))bis(phosphite), 2-entylhexyldiphenyl phosphite, tris((mono and di)-nonylphenyl)phosphite, tri-(2,4-di-tert-butylphenyl)phosphite, tetraphenyl dipropylene glycol diphosphite, distearylpentaerythritoldiphosphite.

5. A liquid antioxidant composition used for raw rubbers, comprising
    a) 5% to 20% by weight of solid aromatic amine-based antioxidant agent;
    b) 20% to 50% by weight of solid hindered phenol-based antioxidant agent;
    c) 0% to 30% by weight of solid phosphite-based antioxidant agent; and
    d) 30% to 40% by weight of solvent having boiling point higher than 185°C and freezing point lower than -10°C under 101.325KPa, wherein said solvent is one or more selected from linear or branched alkane having C_9 to C_{30}, cyclane having C_{10} to $C_{30,}$ linear saturated carboxylic acid having C_8 to C_{18}, branched saturated carboxylic acid having C_8 to C_{12}, linear saturated alcohol having C_8 to C_{18} and branched saturated alcohol having C_8 to C_{12}, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, hexyl benzoate, diethyl phthalate, dipropyl phthalate, dibutyl phthalate, dipentyl phthalate, dihexyl phthalate, diheptyl phthalate, dioctyl phthalate, diisooctyl phthalate, dinonyl phthalate, diisononyl phthalate, didecyl phthalate, diisodecyl phthalate, trimethyl orthobenzoate , ethyl oleate, butyl oleate octyl acetate, decyl acetate, isononyl acetate, nonyl acetate, n-octyl propanoate, decyl propanoate, isononyl propanoate, nonyl propanoate, pentyl butanoate, hexyl butyrate, heptyl butanoate, n-octyl butanoate, butyl valerate, amyl valerate, hexyl valerate, butyl caproate, amyl caproate, hexyl hexanoate, ethyl heptanoate, propyl heptanoate, butyl heptoate, pentyl heptanoate, methyl octanoate, etheyl octanoate, propyl octanoate, butyl octanoate, amyl octanoate,

hexyl octanoate, heptyl octanoate, octyl octanoate, nonyl octanoate, methyl nonanoate, ethyl nonanoate, isoamyl nonanoate, isononyl isononanoate, methyl caprate, ethyl caprate, propyl decanoate, butyl caprate, isoamyl decanoate, lauricacidisoamylester, ethylene glycol diacetate, ethylene glycol di-n-butyrate, dibutyl malonate, diethyl malonate, dihexyl malonate, diethyl succinate, dibutyl succinate, dipentyl succinate, dimethyl glutarate, diethyl glutarate, diethyl adipate, diisopropyl adipate, diisobutyl adipate, di(2-ethylhexyl)adipate, dihexyl adipate, diisononyl adipate, diisodecyl adipate, dibutyl sebacate, bishexyl sebacate, bis(2-ethylhexyl) sebacate, dioctyl sebacate, diisooctyl sebacate, glyceryl triacetate, glyceryl tripropionate, glyceryl tributyrate, triisobutyl phosphate, triamyl phosphate, trihexyl phosphate and trioctyl phosphate.

6. The antioxidant composition according to Claim 5, wherein said solid aromatic amine-based antioxidant agent is one or more selected from bis(4-octylphenyl)amine, 4,4'-bis(α,α-dimethylbenzyl)diphenylamine, N,N'-di-2-naphthyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N-phenyl-N'-isopropyl-p-phenylenediamine, N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine and N-phenyl-N'-(3-methacryloyloxy-2-hydroxypropyl)-p-phenylenediamine, N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine, N,N'-bis(methyl-phenyl)-1,4-benzendiamine.

7. The antioxidant composition according to any one of Claims 5 or 6, wherein said solid hindered phenol-based antioxidant agent is one or more selected from 2,4-bis[(dodecylthio)methyl]-o-cresol, 4,4'-butylidene bis-(3-methyl-6-tert-butylphenol), 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid octadecyl ester, pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydrophenyl)propionate], 2,4-bis(n-octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3,5-triazine, tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate, 2,2-thio-diethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate].

8. The antioxidant composition according to any one of Claims 5 to 7, wherein said solid phosphite-based antioxidant agent is one or more selected from tri-(2,4-di-tert-butylphenyl)phosphite, tetraphenyl dipropylene glycol diphosphite, distearylpentaerythritoldiphosphite and

3,9-bis(octadecyloxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane.

9. The antioxidant composition according to any one of Claims 1 to 8, wherein said solvent is one or more selected from hendecane, n-dodecane, butylcyclohexane, pentylcyclohexane, hexylcyclohexane, heptylcyclohexane, octylcyclohexane, nonylcyclohexane, decylcyclohexane, undecylcyclohexane, dodecylcyclohexane, pentylcyclopentane, pentylcyclopentane, hexylcyclopentane, heptycyclopentane, octylcyclopentane, nonylcyclopentane, decylcyclopentane, undecylcyclopentane, dodecylclopentane, 2-ethylhexanoic acid, hexanoic acid, neo-decanoic acid, isononanoic acid, neodecanoic acid, n-octyl alcohol, n-nonanol, n-decyl alcohol, n-undecanol, isooctyl alcohol, isononyl alcohol, isodecyl alcohol, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, hexyl benzoate, diethyl phthalate, dipropyl phthalate, dibutyl phthalate, dipentyl phthalate, dihexyl phthalate, diheptyl phthalate, dioctyl phthalate, diisooctyl phthalate, dinonyl phthalate, diisononyl phthalate, didecyl phthalate, diisodecyl phthalate, trimethyl orthobenzoate , ethyl oleate, butyl oleate octyl acetate, decyl acetate, isononyl acetate, nonyl acetate, n-octyl propanoate, decyl propanoate, isononyl propanoate, nonyl propanoate, pentyl butanoate, hexyl butyrate, heptyl butanoate, n-octyl butanoate, butyl valerate, amyl valerate, hexyl valerate, butyl caproate, amyl caproate, hexyl hexanoate, ethyl heptanoate, propyl heptanoate, butyl heptoate, pentyl heptanoate, methyl octanoate, etheyl octanoate, propyl octanoate, butyl octanoate, amyl octanoate, hexyl octanoate, heptyl octanoate, octyl octanoate, nonyl octanoate, methyl nonanoate, ethyl nonanoate, isoamyl nonanoate, isononyl isononanoate, methyl caprate, ethyl caprate, propyl decanoate, butyl caprate, isoamyl decanoate, lauricacidisoamylester, ethylene glycol diacetate, ethylene glycol di-n-butyrate, dibutyl malonate, diethyl malonate, dihexyl malonate, diethyl succinate, dibutyl succinate, dipentyl succinate, dimethyl glutarate, diethyl glutarate, diethyl adipate, diisopropyl adipate, diisobutyl adipate, di(2-ethylhexyl)adipate, dihexyl adipate, diisononyl adipate, diisodecyl adipate, dibutyl sebacate, bishexyl sebacate, bis(2-ethylhexyl) sebacate, dioctyl sebacate, diisooctyl sebacate, glyceryl triacetate, glyceryl tripropionate, glyceryl tributyrate, triisobutyl phosphate, triamyl phosphate, trihexyl phosphate and trioctyl phosphate.

10. The antioxidant composition according to Claim 1 or 5, wherein said

solvent is one or more selected from paraffin oil, naphthenic oil, n-dodecane, hexanoic acid, heptanoic acid, 2-ethylhexanoic acid, isononanoic acid, neodecanoic acid, n-nonanol, isodecyl alcohol, isooctyl alcohol, ethyl oleate and butyl oleate.

11. The antioxidant composition according to any one of Claims 1 to 10, wherein the freezing point of the antioxidant composition is lower than 0°C under 101.325KPa.

12. Use of the antioxidant composition according to any one of Claims 1 to 11 in raw rubbers synthesized via solution polymerization or in natural rubber.

13. The use of the antioxidant composition according to Claim 12, wherein said raw rubbers synthesized via solution polymerization is selected from polybutadiene, polyisoprene, polybutene, poly(styrene-co-butadiene).

14. A process of using antioxidant composition according to any one of Claims 1 to 11 in raw rubbers synthesized via solution polymerization comprising steps of i) dissolving component a), b) and c) into d); ii) diluting liquid antioxidant composition by solvent for solution polymerization of raw rubbers; iii) adding diluted liquid antioxidant composition into raw rubbers synthesized via solution polymerization.

15. A raw rubber product comprising the antioxidant composition according to any one of Claims 1 to 11.

16. The raw rubber product according to Claim 15, wherein the yellowing index according to ASTM E313-1996 is less than 20.

17. The raw rubber product according to Claim 15, wherein the Mooney viscosity change from 0 to 72 hours is less than 10% and the Mooney viscosity is tested according to ISO 289-1:1994.