A DIISOCYANATE STABILIZER, USE THEREOF, AND DIISOCYANATE COMPOSITION

TECHNICAL FIELD

The present disclosure relates to a diisocyanate stabilizer, use of the diisocyanate stabilizer for stabilizing diisocyanate, and a diisocyanate composition comprising said stabilizer.

BACKGROUND

Diisocyanates are important intermediates in organic synthesis, for example, in the preparation of polyurethane resins. However, due to the high reactivity of isocyanate groups, diisocyanates tend to turn yellow and/or become turbid due to self-polymerization during storage which thereby affects its application in downstream industries. In order to prevent diisocyanates from turning yellow and/or becoming turbid, skilled person in the art usually adds a certain amount of antioxidants to the diisocyanates.

For example, US3555072 discloses a process for inhibiting discolouration and turbidity formation in toluene diisocyanate (TDI) which comprises adding thereto a stabilizing amount of thioether compounds.

However, the long-term thermal stability of the TDI solution obtained according to US3555072 is poor. In order to prolong the thermal stability, skilled person in the art may increase the amount of the thioether but this in turn will cause an odor issue to TDI which is also unacceptable.

Therefore, there is still a need in the art to provide a stabilizer for stabilizing diisocyanates, which enables diisocyanates to maintain clolorless and transparent after a long storage period.

SUMMARY OF THE INVENTION

The present disclosure provides a diisocyanate stabilizer which solves or at least partly solves above problems or other potential problems for stabilizing diisocyanates that exist in prior art.

In specific, in a first asepct, the present disclosure provides a diisocyanate stabilizer, comprising a sterically hindered phenol other than butylated hydroxytoluene, a thioether and a phosphite other than triphenyl phosphite.

The term “transmission intensity” used herein means the percentage of light travelling through an object. For example, in embodiments of the present disclosure, it refers to the percentage of light travelling through a glass vial containing the diisocyanate composition.

As mentioned above, diisocyanates are important intermediates in many organic synthesis, for example, for preparing polyurethane resins. However, diisocyanates have very reactive groups which make it easily get self-polymerized and thereby become turbid during storage. These problems exist in various diisocyanates including aliphatic, cycloaliphatic and aromatic diisocyanates.

I. Diisocyanate stabilizer

In view of the existing difficulties in stabilizing diisocyanates in prior art, in a first aspect, the present disclosure provides a diisocyanate stabilizer, comprising a sterically hindered phenol other than butylated hydroxytoluene, a thioether and a phosphite other than triphenyl phosphite.

Inventors of the present disclosure surprisingly found that sterically hindered phenol, thioether and phosphite can work synergistically to effectively prevent diisocyanate from self-polymerization. By combining sterically hindered phenol, thioether and phosphite together, the present disclosure provides a stabilizer, which can prevent diisocyanate from turning yellow and/or becoming turbid during long-term storage and heating condition (e.g. melting process having a temperature of around 100°C). The stabilizer of the present disclosure has effectively solved the problems that the diisocyanates are easy to turn yellow and become turbid during long-term storage and heating condition.

Sterically hindered phenol

The sterically hindered phenol includes phenols that have one or more phenolic hydroxyl groups on the aromatic ring, and preferably those that have a substituent, preferably an alkyl group, in the ortho positions, most preferably in the ortho and para positions, to the phenolic hydroxyl group(s).

It should be understood that above description is not intended to limit the scope of sterically hindered phenols that are suitable for the present disclosure. ~~The present disclosure has no limitation on the sterically hindered phenols as long as they have antioxidant properties.~~

Examples of suitable phenols include alkylphenols, for example, o-, m- or p-cresol (methylphenol), 2-tert-butyl-4–methylphenol, 6-tert-butyl-2,4-dimethylphenol, 2,6-di-tert-butyl-4-methylphenol, 2-tert-butylphenol, 4-tert-butylphenol, 2,4-di-tert-butylphenol, 2-methyl-4-tert-

thiodipropionate (DSTDP), dimyristyl thiodipropionate (DMTDP) and 2,2-bis[[3-(dodecylthio)-1-oxopropoxy]methyl]propane-1,3-diyl bis[3-(dodecylthio)propionate] (e.g., Seenox 412S).

In more preferable embodiments, the thioether is at least one selected from a group consisting of didodecyl 3,3'-thiodipropionate (DLTDP) and ditridecyl 3,3′-thiodipropionate (DTDTP). These more preferable thioethers are liquid or solid having a low melting point which enables the stabilizer being liquid at typical operational temperature (e.g., 45°C to 50°C).

Phosphite

~~The present disclosure has no limitation on phosphite.~~ Suitable phosphites according to the present disclosure include but not limited to mono phosphites and polymeric phosphites.

Examples of suitable mono phosphites according to the present disclosure include compounds having a structure of formula (IV)

$$P(OR^6)\,(OR^7)\,(OR^8) \qquad (IV)$$

wherein

R^6, R^7 and R^8 can each be, independently of one another, C_1-C_{18}-alkyl, C_6-C_{12}-aryl or C_5-C_{12}-cycloalkyl, wherein the radicals mentioned are optionally substituted by hydroxy, amino, aryl, alkyl, aryloxy, alkyloxy, alkylthio, alkoxycarbonyl, nitro, acyl, carbocycles, heteroatoms and/or heterocycles.

Here, R^6, R^7 and R^8 can each be, independently of one another, selected from a group consisting of the following groups:

methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, 2,4,4-trimethylpentyl, n-decyl, n-dodecyl, n-tetradecyl, n-hetadecyl, n-octadecyl, 1,1-dimethylpropyl, 1,1-dimethylbutyl, 1,1,3,3-tetramethylbutyl, benzyl, 1-phenylethyl, 2-phenylethyl, α,α-dimethylbenzyl, benzhydryl, p-tolylmethyl,1-(p-butylphenyl)ethyl, p-chlorobenzyl, 2,4-dichlorobenzyl, p-methoxybenzyl, m-ethoxybenzyl, 2-cyanoethyl, 2-cyanopropyl, 2-methoxycarbonethyl, 2-ethoxycarbonylethyl, 2-butoxycarbonylpropyl, 1,2-di(methoxycarbonyl)ethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-butoxyethyl, diethoxymethyl, diethoxyethyl, 1,3-dioxolan-2-yl, 1,3-dioxan-2-yl, 2-methyl-1,3-dioxolan-2-yl, 4-methyl-1,3-dioxolan-2-yl, 2-isopropoxyethyl, 2-butoxypropyl, 2-octyloxyethyl, chloromethyl, 2-chloroethyl, trichloromethyl, trifluoromethyl, 1,1-dimethyl-2-chloroethyl, 2-methoxyisopropyl, butylthiomethyl, 2-

CLAIMS

1. A diisocyanate stabilizer, comprising a sterically hindered phenol other than butylated hydroxytoluene, a thioether, and a phosphite other than triphenyl phosphite.

2. The diisocyanate stabilizer according to claim 1, wherein the sterically hindered phenol is present in an amount of 10 to 90 wt%, the thioether is present in an amount of 5 to 80 wt%, and the phosphite is present in an amount of 5 to 80 wt%, based on the total weight of the diisocyanate stabilizer.

3. The diisocyanate stabilizer according to claim 1 or 2, consisting of a sterically hindered phenol, a thioether and a phosphite.

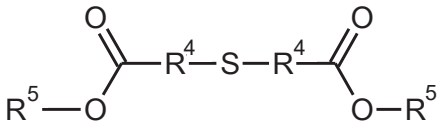
4. The diisocyanate stabilizer according to claim 1 or 2, wherein the diisocyanate stabilizer has a melting point of lower than 50°C, preferably lower than 20°C.

5. The diisocyanate stabilizer according to claim 1 or 2, wherein the sterically hindered phenol is at least one selected from a group consisting of alkylphenols, bisphenol A, bisphenol F, bisphenol B, bisphenol C, bisphenol S, 3,3',5,5'-tetrabromobisphenol A, methyl 3,5-di-tert-butyl-4-hydroxybenzoate, 4-tert-butylpyrocatechol, 2-hydroxybenzyl alcohol, 2-methoxy-4-methylphenol, n-octadecyl β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 1,1,3-tris-(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5,-tris-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxyethyl isocyanurate, 1,3,5-tris-(2,6-dimethyl-3-hydroxy-4-tert-butylbenzyl) isocyanurate or pentaerythritol tetrakis[β-(3,5,-di-tert-butyl-4-hydroxyphenyl)propionate], 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 6-isobutyl-2,4-dinitrophenol, 6-sec-butyl-2,4-dinitrophenol, 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol, octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, hexadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, octyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, thiodiethylenebis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate], 4,8-dioxa-1,11-undecanediol bis[(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate], 4,8-dioxa-1,11-undecanediol bis[(3'-tert-butyl-4'-hydroxy-5'-methylphenyl)propionate], 1,9-nonanediol bis[(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate], 1,7-heptanediaminebis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionamide], 1,1-methanediaminebis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionamide], 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionoic hydrazide, 3-(3',5'-dimethyl-4'-hydroxyphenyl)propionoic hydrazide, bis(3-tert-butyl-5-ethyl-2-hydroxyphen-1-yl)methane, bis(3,5-di-tert-butyl-4-hydroxyphen-1-yl)methane, bis[3-(1'-methylcyclohex-1'-yl)-5-

methyl-2-hydroxyphen-1-yl]methane, bis(3-tert-butyl-2-hydroxy-5-methylphen-1-yl)methane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphen-1-yl)ethane, bis(5-tert-butyl-4-hydroxy-2-methylphen-1-yl) sulfide, bis(3-tert-butyl-2-hydroxy-5-methylphen-1-yl) sulfide, 1,1-bis(3,4-dimethyl-2-hydroxyphen-1-yl)-2-methylpropane, 1,1-bis(5-tert-butyl-3-methyl-2-hydroxyphen-1-yl)butane, 1,3,5-tris[1'-(3'',5''-di-tert-butyl-4''-hydroxyphen-1''-yl)-meth-1'-yl]-2,4,6-trimethylbenzene, 1,1,4-tris(5'-tert-butyl-4'-hydroxy-2'-methylphen-1'-yl)butane, aminophenols, nitrosophenols, alkoxyphenols, eugenol, dihydroeugenol, isoeugenol, tocopherols, tocol, α-tocopherolhydroquinone, 4-methylpyrocatechol, 3-methylpyrocatechol, hydroquinone monobenzyl ether, p-phenoxyphenol, hydroquinone, tert-butylhydroquinone, 2,5-di-tert-butylhydroquinone, 2-methyl-p-hydroquinone, 2,3-dimethylhydroquinone, trimethylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,3-dihydro-2,2-dimethyl-7-hydroxybenzofuran (2,2-dimethyl-7-hydroxycoumaran), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, and derivatives thereof.

6. The diisocyanate stabilizer according to claim 1 or 2, wherein the sterically hindered phenol is at least one selected from a group consisting of 3,5-bis(1,1-dimethylethyl)-4-benzenepropanoic acid, branched C_7-C_9-alkyl ester, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid, branched C_{13}-C_{15}-alkyl esters, esters of polyglycol ether terminated with phenol derivatives, 2,4-dimethyl-6-(1-methylpentadecyl)-phenol and 4,6-bis(octylthiomethyl)-o-cresol.

7. The diisocyanate stabilizer according to claim 1 or 2, wherein the thioether is at least one selected from formula (III)



(III)

wherein

R^4 is selected from C_1-C_{20}-alkylene or C_3-C_{12}-cycloalkylene, optionally substituted by hydroxy, amino, aryl, alkyl, aryloxy, alkyloxy, alkylthio, alkoxycarbonyl, nitro, acyl, carbocycles, heteroatoms and/or heterocycles, and

R^5 is selected from C_1-C_{18}-alkyl, C_2-C_{18}-alkyl, which is interrupted by one or more oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups, C_6-C_{12}-aryl or C_5-C_{12}-cycloalkyl, which are optionally substituted by hydroxy, amino, aryl, alkyl, aryloxy, alkyloxy, alkylthio, alkoxycarbonyl, nitro, acyl, carbocycles, heteroatoms and/or heterocycles.

8. The diisocyanate stabilizer according to claim 1 or 2, wherein the thioether is at least one selected from a group consisting of didodecyl 3,3'-thiodipropionate, dioctadecyl 3,3'-thiodipropionate, ditridecyl 3,3′-thiodipropionate, dimyristyl thiodipropionate and 2,2-bis[[3-(dodecylthio)-1-oxopropoxy]methyl]propane-1,3-diyl bis[3-(dodecylthio)propionate].

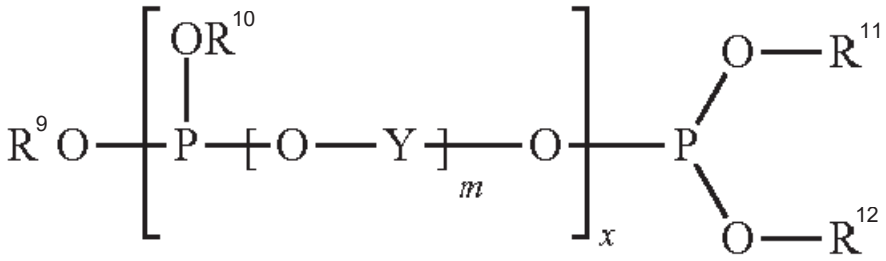
9. The diisocyanate stabilizer according to claim 1 or 2, wherein the phosphite is at least one selected from formula (IV)

$$P(OR^6)\,(OR^7)\,(OR^8) \qquad (IV)$$

wherein

R^6, R^7 and R^8 are each independently selected from C_1-C_{18}-alkyl, C_6-C_{12}-aryl or C_5-C_{12}-cycloalkyl, which are optionally substituted by hydroxy, amino, aryl, alkyl, aryloxy, alkyloxy, alkylthio, alkoxycarbonyl, nitro, acyl, carbocycles, heteroatoms and/or heterocycles.

10. The diisocyanate stabilizer according to claim 1 or 2, wherein the phosphite is polymeric phosphites having a structure of formula (V)



wherein

each R^9, R^{10}, R^{11} and R^{12} can be the same or different and independently selected from the group consisting of C1-20 alkyl, C3-22 alkenyl, C6-40 cycloalkyl, C7-40 cycloalkylene, C1-20 methoxy alkyl glycol ethers, C1-20 alkyl glycol ethers, and/ or Y—OH (serving as an end capping moiety);

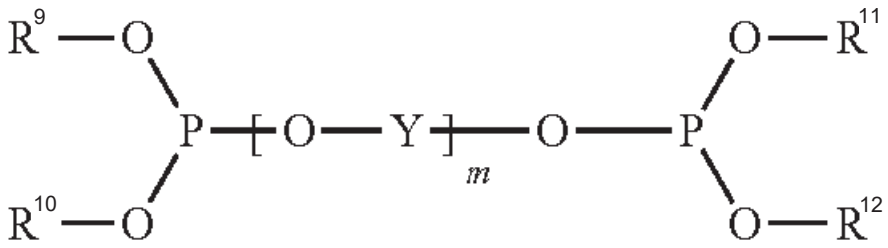
Y is selected from the group consisting of C2-40 alkylene, C2-40 alkyl lactone, (e.g., ethylene, propylene, caprylactone), —R^{13} —N(R^{14})—R^{15} — (e.g., C2-40 alkyl diamines and C2-40 alkyl triamines),

wherein R^{13}, R^{14} and R^{15} are independently selected from the group previously defined for R^9, R^{10}, R^{11} and R^{12}, now further including H;

m is an integral value ranging from 2 to 100; and

x is an integral value ranging from 1 to 1,000.

11. The diisocyanate stabilizer according to claim 10, wherein the polymeric phosphites are polymeric diphosphites having a structure of formula (VI)



wherein

each R^9, R^{10}, R^{11} and R^{12} can be the same or different and independently selected from the group consisting of C1-20 alkyl, C3-22 alkenyl, C6-40 cycloalkyl, C7-40 cycloalkylene, C1-20 methoxy alkyl glycol ethers, C1-20 alkyl glycol ethers, and/ or Y—OH (serving as an end capping moiety);

Y is selected from the group consisting of C2-40 alkylene, C2-40 alkyl lactone, (e.g., ethylene, propylene, caprylactone), —R^{13} —N(R^{14})—R^{15} — (e.g., C2-40 alkyl diamines and C2-40 alkyl triamines),

wherein R^{13}, R^{14} and R^{15} are independently selected from the group previously defined for R^9, R^{10}, R^{11} and R^{12}, now further including H; and

m is an integral value ranging from 2 to 100.

12. The diisocyanate stabilizer according to claim 1 or 2, wherein the phosphite is at least one selected from a group consisting of tridodecyl phosphite, phosphorous acid, mixed 2,4-bis(1,1-dimethylpropyl)phenyl and 4-(1,1-dimethylpropyl)phenyl triesters (CAS: 939402-02-5), 3,9-bis(isodecyloxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane, 4,4'-butylidene-bis(3-methyl6-tert-butylphenyl) alkyl(C_{13})-phosphite, and poly(dipropylene glycol) phenyl phosphite (CAS: 116265-68-0).

13. The diisocyanate stabilizer according to claim 1 or 2, wherein the sterically hindered phenol is at least one selected from a group consisting of 3,5-bis(1,1-dimethylethyl)-4-benzenepropanoic acid, branched C_7-C_9-alkyl ester, octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid, branched C_{13}-C_{15}-alkyl esters, esters of polyglycol ether terminated with phenol derivatives, 2,4-

dimethyl-6-(1-methylpentadecyl)-phenol and 4,6-bis(octylthiomethyl)-o-cresol; the thioether is at least one selected from a group consisting of didodecyl 3,3'-thiodipropionate, dioctadecyl 3,3'-thiodipropionate, ditridecyl 3,3′-thiodipropionate, dimyristyl thiodipropionate and 2,2-bis[[3-(dodecylthio)-1-oxopropoxy]methyl]propane-1,3-diyl bis[3-(dodecylthio)propionate]; and the phosphite is at least one selected from a group consisting of tridodecyl phosphite, phosphorous acid, mixed 2,4-bis(1,1-dimethylpropyl)phenyl and 4-(1,1-dimethylpropyl)phenyl triesters (CAS: 939402-02-5), 3,9-bis(isodecyloxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane, 4,4'-butylidene-bis(3-methyl6-tert-butylphenyl) alkyl(C_{13})-phosphite and poly(dipropylene glycol) phenyl phosphite.

14. Use of the diisocyanate stabilizer according to any one of claims 1 to 13 for stabilizing diisocyanate.

15. A diisocyanate composition comprising:
(A) a diisocyanate, and
(B) the diisocyanate stabilizer according to any one of claims 1 to 13.

16. The diisocyanate composition according to claim 15, wherein the diisocyanate stabilizer is present in an amount of 0.08 to 0.5 wt%, preferably 0.1 to 0.4 wt%, and more preferably 0.15 to 0.35 wt%, based on the total weight of the diisocyanate composition.

17. The diisocyanate composition according to claim 15 or 16, wherein the diisocyanate is aromatic diisocyanate.

18. The diisocyanate composition according to claim 17, wherein the aromatic diisocyanate is at least one selected from a group consisting of toluene 2,4- or 2,6-diisocyanate and the isomer mixtures thereof, m- or p xylylene diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenylmethane and the isomer mixtures thereof, phenylene 1,3- or 1,4-diisocyanate, 1-chlorophenylene 2,4 diisocyanate, naphthylene 1,5-diisocyanate, biphenylene 4,4'-diisocyanate, 4,4'-diisocyanato-3,3'-dimethylbiphenyl, 3-methyl-diphenylmethane 4,4'-diisocyanate, tetramethylxylylene diisocyanate, 1,4-diisocyanatobenzene or 4,4'-diisocyanatodiphenyl ether; preferably toluene 2,4- or 2,6-diisocyanate and the isomer mixtures thereof, m- or p-xylylene diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenylmethane and the isomer mixtures thereof.