Title: MODIFIED ISOCYANATE COMPOSITIONS AND METHODS OF PREPARING THE SAME

Abstract: Modified isocyanate compositions having improved properties are provided. The compositions may be formed from the reaction of an isocyanate component, which is a compound terminated with at least one isocyanate group, and an organic acid derivative having the formula (RO)n(M)(E)(EH)m, wherein M is nitrogen, phosphorus, arsenic, antimony, or bismuth, n is 1 or 2, each E is independently oxygen, sulfur, selenium, or tellurium, each R is independently hydrogen, an alkyl group, a cyclic aryl group, an acyclic aryl group, a halogen-substituted alkyl group, a halogen-substituted cyclic aryl group or a halogen-substituted acyclic aryl group and wherein the ratio of the weight of the isocyanate component to the combined weight of the organic acid derivative and the isocyanate component is from 0.7 to 0.95. The compositions can be utilized in a variety of applications and are adapted to prolonged storage and transportation. Methods of preparing such compositions are also provided.
MODIFIED ISOCYANATE COMPOSITIONS
AND METHODS OF PREPARING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of and priority to U.S. Provisional Patent Application No. 61/611,094, filed on March 15, 2012, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] The present invention generally relates to a modified isocyanate composition and a method of preparing the modified isocyanate composition. More particularly, the modified isocyanate composition includes the reaction product of an isocyanate component and a particular organic acid derivative. The isocyanate component is a compound terminated with at least one isocyanate group.

[0003] The use of compositions comprising the reaction products of organic phosphorus containing compounds and isocyanate or polyisocyanate compounds is known. For example, thermosetting compositions including the reaction products of these compounds are used in high solids coating compositions, such as paint compositions, and molding compositions for injection molding processes, such as reaction injection molding processes. Also, such reaction products can be used as blowing agents to produce a solid foamed product, such as polyurethane foam.

[0004] In addition, organic phosphorus containing compounds themselves can be used in very small amounts in such products as pot/bench life extenders, as acid catalysts that may enhance cross-linking on curing in paints, or as flame retardant agents. Further uses of organic phosphorus containing compounds include uses as emulsifiers, dispersants, clay stabilizing aids in drilling mud, water repellants for wood, herbicides, pesticides, corrosion inhibitors in lubricants, and anti-wear agents.

[0005] The use of isocyanate or polyisocyanate compounds is rapidly growing. Isocyanate or polyisocyanate compounds and their derivatives are manufactured and modified to form blends, prepolymerizations, and quasi-prepolymers. The resulting products have use in a wide variety of applications, such as those described above.

[0006] There exists an opportunity to use organic acid derivatives in certain amounts in isocyanate compositions to provide modified isocyanate compositions for various
applications. There also remains an opportunity to provide methods of preparing these compositions.

SUMMARY OF THE INVENTION

[0007] The present invention provides a composition that includes an isocyanate component and an organic acid derivative having the formula \((RO)_n(M)(E)(EH)^{3-n}\), wherein M is nitrogen, phosphorus, arsenic, antimony, or bismuth, n is the integer 1 or the integer 2, each E is independently oxygen, sulfur, selenium, or tellurium, each R is independently hydrogen, an alkyl group, a cyclic aryl group, an acyclic aryl group, a halogen-substituted alkyl group, a halogen-substituted cyclic aryl group, or a halogen-substituted acyclic aryl group, and wherein the ratio of the weight of the isocyanate component to the combined weight of the organic acid derivative and the isocyanate component is from 0.7 to 0.95.

[0008] The present invention also provides a modified isocyanate composition that includes the heated reaction product of a polyurethane including the reaction product of the isocyanate component and the organic acid derivative having the formula \((RO)_n(M)(E)(EH)^{3-n}\), wherein the organic acid derivative is present in an amount of at least 1 weight percent of the modified isocyanate composition.

DETAILED DESCRIPTION OF THE INVENTION

[0009] An advantage of the present invention is to provide modified isocyanate compositions, and methods of preparing the same, for use in a wide variety of applications, such as flexible, rigid, CASE (cast, adhesive, sealant, elastomer), foams and coatings applications. This invention provides modified isocyanate compositions that facilitate increased stability of pure isocyanates. The increased stabilization is useful in storage and transportation. The invention also provides modified isocyanate compositions that facilitate flame retardancy. For example, the compositions may be a flame retardant or may be applied to form flame retardant coatings. The method of this invention reduces the amount of organic fuel generated. This invention provides a composition that includes an isocyanate component and an organic acid derivative. The composition includes a reaction mixture including the isocyanate component and the organic acid derivative as well as other materials such as additives.
The isocyanate component is a compound terminated with at least one isocyanate group. The compound terminated with at least one isocyanate group may be terminated at each end with at least one isocyanate group. In this embodiment, the compound includes at least two isocyanate groups. The compound may be a liquid or a solid. The isocyanate component may be part of a composition that includes additional compounds that are also each terminated with at least one isocyanate group. The compound terminated with at least one isocyanate group may be selected from, but is not limited to, the group of aliphatic isocyanates, heterocyclic isocyanates, cycloaliphatic isocyanates, araliphatic isocyanates, aromatic isocyanates, and combinations thereof.

Suitable non-limiting examples of the isocyanate components that are compounds terminated with at least one isocyanate group may include alkylene diisocyanates having 4 to 12 carbons in an alkylene radical such as 1,12-dodecanediisocyanate, 2-ethyl-1,4-tetramethylene diisocyanate, 2-methyl-1,5-pentamethylene diisocyanate, 1,4-tetramethylene diisocyanate and 1,6-hexamethylene diisocyanate, cycloaliphatic diisocyanates such as 1,3- and 1,4-cyclohexane diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate), 2,4- and 2,6-hexahydrotoluene diisocyanate, 2,4'-dicyclohexylmethane diisocyanate, mixtures of 4,4'- and 2,4'-diphenylmethane diisocyanates and polyphenylenepolyethylene polyisocyanates (polymeric MDI), m-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, hexamethylene diisocyanate, tetramethylene diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene diisocyanate, naphthalene-1,5-diisocyanate, 1-methoxyphenyl-2,4-diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate and 3,3'-dimethyldiphenylmethan-4,4'-diisocyanate, 4,4',4''-triphenylmethane trisocyanate, toluene 2,4,6-triisocyanate; 4,4'-dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate, polymethylene polyphenylene polyisocyanate, isomers thereof, and combinations thereof. Particularly suitable compounds may include methylene diphenyl diisocyanates (MDI), polymeric MDI, toluene diisocyanate (TDI), or any combinations thereof.
The term MDI is used in this specification and claims as a general term for methylene(diphenyl diisocyanates) which include the isomers 2,2'-methylene(diphenyl diisocyanate), 2,4'-methylene(diphenyl diisocyanate), (2,4'-MDI) and 4,4'-methylene(diphenyl diisocyanate) (4,4'-MDI). These isomers are referred to together as monomeric MDI or simply MDI. The MDI may have a functionality of 2. The term polymeric MDI is used in this specification and claims as a general term for polymethylene polyphenylene polyisocyanates which includes polymeric MDI, which includes monomeric MDI and higher homologs of monomeric MDI. Isomers and isomer mixtures differing from MDI are commercially available, and 4,4'/2,4'-MDI mixtures and polymeric MDI are offered in addition to 4,4'-MDI. Polymeric MDI is a complex mixture of different MDI oligomers.

The term TDI is used in this specification and claims as a general term for toluene diisocyanates. The term toluene diisocyanates includes the isomers 2,4 toluene diisocyanate and 2,6 toluene diisocyanate.

Specific examples of suitable isocyanate components that are compounds terminated with at least one isocyanate group include LUPRANATE® M, LUPRANATE® MM103, LUPRANATE® MI, LUPRANATE® MP102, LUPRANATE® M20, LUPRANATE® M70, LUPRANATE® MS, LUPRANATE® T80 and LUPRANATE® 8020, all commercially available from BASF Corporation.

The organic acid derivate is represented by the formula \((RO)^n(M)(E)(EH)3_n\). The identifier \(n\) is the integer 1 or the integer 2. \(M\) is nitrogen (N), phosphorus (P), arsenic (As), antimony (Sn) or bismuth (Bi). In one embodiment of the invention, \(M\) is phosphorus. In further embodiments of the present invention, each \(E\) is independently oxygen (O), sulfur (S), selenium (Se), or tellurium (Te). In an embodiment, \(E\) is oxygen.

In embodiments of the present invention, the organic acid derivative may be structurally represented by each of the following chemical structures:

\[
\begin{align*}
R & \quad E \quad E \quad H \\
R & \quad E \quad E \quad H \\
R & \quad E \quad E \quad H \\
R & \quad E \quad E \quad H
\end{align*}
\]

\(R\) represents hydrogen, alkyl groups, cyclic groups, aryl groups, and alkyl-aryl groups containing from 1 to 10 carbons. In additional embodiments of the invention,
each R individually is the same or different from one another. Each R may independently be further defined as a substituted alkyl group, unsubstituted alkyl group, substituted cyclic aryl group, substituted acyclic aryl group, unsubstituted cyclic aryl group or unsubstituted acyclic aryl group. Each R may independently be further defined as a halogen-substituted alkyl group, a halogen-substituted cyclic aryl group or halogen-substituted acyclic aryl group. Each R may independently be further defined as a saturated alkyl group, unsaturated alkyl group, saturated aryl group, unsaturated aryl group, saturated cyclic aryl group, unsaturated cyclic aryl group, saturated acyclic aryl group or unsaturated acyclic aryl group. The organic acid derivative may be any such derivative with the proviso that the organic acid derivative is not a completely esterified derivative which has no functional group attached to the atom represented by M. Suitable organic acid derivatives include compounds that will react with the compound terminated with at least one isocyanate group. In various embodiments of the present invention, each alkyl group includes from 1 to 10 carbon atoms. This number of carbon atoms in the alkyl group aids in the reduction of organic fuel generated during the reaction. In a particular embodiment of the invention, R represents an unsubstituted or substituted butyl group, however, in additional applications, R may be a shorter chained unsubstituted or substituted alkyl group. The butyl group may be any of n-butyl, sec-butyl, iso-butyl or tert-butyl groups. In embodiments of the invention, M represents phosphorus and E represents oxygen.

[0018] In these embodiments of the present invention, the organic acid derivative may be structurally represented by each of the following chemical structures:

![Chemical structures](image)

[0019] In another embodiment of the invention, R is an unsubstituted n-butyl group.

[0020] Suitable organic acid derivatives include, but are not limited to, butyl acid phosphate, dibutyl acid phosphate, phosphoric acid monobutyl ester, phosphoric acid dibutyl ester, phosphoric acid monophenyl ester, phosphoric acid diphenyl ester, phosphoric acid 2-butoxy-1-ethyl ester, 2-ethylhexyl acid phosphate, cetyl acid phosphate, stearil acid phosphate, mono-methyl acid phosphate, dimethyl acid
phosphate, mono-ethyl acid phosphate, diethyl acid phosphate, mono-propyl acid phosphate, dipropyl acid phosphate, halogen substituted derivatives of these compounds, or any combinations thereof.

[0021] In addition to the compounds described above, the composition including the isocyanate component and the organic acid derivative may include other suitable additives to impart desired properties. These additives include but are not limited to fillers, surfactants, pigments, catalysts, etc. Other materials other than those described above may be incorporated into the composition depending on the particular end use of the modified isocyanate compositions.

[0022] In an embodiment of the present invention, the composition including the isocyanate component and the organic acid derivative may be reacted. The ratio of the weight of the isocyanate component to the combined weight of the organic acid derivative and the isocyanate component is at least 0.7. In alternative embodiments of the present invention, the ratio of the weight of the isocyanate component to the combined weight of the organic acid derivative and the isocyanate component is at least 0.8. In yet alternative embodiments, the ratio of the weight of the isocyanate component to the combined weight of the organic acid derivative and the isocyanate component is at least 0.9. In further embodiments, the ratio of the weight of the isocyanate component to the combined weight of the organic acid derivative and the isocyanate component is less than or equal to 0.95. A ratio of the weight of the isocyanate component to the combined weight of the organic acid derivative and the isocyanate component being at least 0.7 and less than or equal to 0.95 is preferred to maximize reactivity and control acidity.

[0023] In an embodiment of the invention, a polyurethane is formed by reacting the isocyanate component and the organic acid derivative. The polyurethane may be formed as an intermediate product in the reaction of the isocyanate component and the organic acid derivative.

[0024] The formation of a polyurethane as an intermediate product may be schematically represented by the general reaction chemistry as shown immediately below. In the representation, the isocyanate component is 4,4’-MDI and the organic
acid derivative is a mixture of butyl acid phosphate and dibutyl acid phosphate.

[0025] In an alternative embodiment, the formation of a polyurethane as an intermediate product may be schematically represented by the general reaction chemistry as shown immediately below. In this embodiment, the polyurethane is terminated at each end with an NCO group. In the representation, 4,4'-MDI is the isocyanate component and M represents phosphorus, E represents oxygen and R represents an unsaturated or saturated alkyl or aryl group in the organic acid derivative.

[0026] In an alternative embodiment, the formation of a polyurethane as an intermediate product may be schematically represented by the general reaction chemistry as shown immediately below. In this embodiment, the polyurethane is terminated at each end with an OH group. In the representation, 4,4'-MDI is the isocyanate component and M represents phosphorus, E represents oxygen and R represents an unsaturated or saturated alkyl or aryl group in the organic acid derivative.

[0027] In yet another alternative embodiment, the formation of a polyurethane as an intermediate product may be schematically represented by the general reaction chemistry as shown immediately below. In this embodiment, the polyurethane is
terminated at one end with an NCO group and is terminated at the other end with an OH group. In the representation shown, 4,4’-MDI is the isocyanate component and M represents phosphorus, E represents oxygen and R represents an unsaturated or saturated alkyl or aryl group in the organic acid derivative.

![Chemical structure](image)

[0028] A method of forming a modified isocyanate composition from the reaction of an isocyanate component and an organic acid derivative is also provided. The isocyanate component is a compound terminated with at least one isocyanate group. The method includes combining the isocyanate component and the organic acid derivative.

[0029] The isocyanate component and the organic acid derivative may be combined in any number of reaction vessels or mediums as selected by one of ordinary skill in the art. The reaction mixture may be agitated, stirred, mixed or any agitation technique as appreciated by one of ordinary skill in the art. The reaction mixture may then be heated to a first temperature which is maintained for a first time period. Any heating technique suitable for heating the reaction vessel or medium as appreciated by one of ordinary skill in the art may be employed.

[0030] The first temperature may be less than or equal to 70 degrees Celsius. In another embodiment of the invention, the first temperature may be less than or equal to 75 degrees Celsius. Not to be bound by theory, it is believed that carbon dioxide is released when the temperature of the reaction mixture reaches the first temperature.

[0031] The method may further include heating the reaction mixture to a second temperature higher than the first temperature and maintaining the second temperature for a second time period. Typically this forms a modified isocyanate compound. Not to be bound by theory, it is believed that the modified isocyanate compound is formed after carbon dioxide is released from the reaction of the reaction mixture.

[0032] For example, in the embodiment where the isocyanate component is 4,4’-MDI and the organic acid derivative is a mixture of butyl acid phosphate and dibutyl acid
phosphate, the general reaction chemistry showing the theoretically release of carbon
dioxide may be schematically represented as follows:

\[
\text{OCN} \quad \begin{array}{c}
\text{P} \quad \text{O} \\
\text{H} \quad \text{N} \\
\text{O}
\end{array}
\quad +
\begin{array}{c}
\text{P} \quad \text{O} \\
\text{H} \quad \text{N} \\
\text{O}
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{N} \quad \text{C} \quad \text{O} \\
\text{P} \quad \text{O} \\
\text{H} \quad \text{N} \\
\text{O}
\end{array}
\]

-\text{CO}_2

5 [0033] In this representation, the chemical structure of the modified isocyanate
compound may be represented by:

\[
\begin{array}{c}
\text{O} \quad \text{P} \quad \text{N} \quad \text{O} \\
\text{H} \quad \text{N} \quad \text{O} \\
\text{O} \quad \text{P} \quad \text{N} \quad \text{O}
\end{array}
\]

[0034] It is to be understood that the modified isocyanate composition may
additionally include an unreacted amount of organic acid derivative as described
below. The modified isocyanate composition may additionally include an average
free NCO content as described below.

[0035] In one embodiment of the invention, the second temperature is about 70 to
about 90 degrees Celsius. In another embodiment of the invention, the second
temperature is about 90 to about 100 degrees Celsius. In another embodiment of the
invention, the second temperature is about 100 to about 110 degrees Celsius. In another
embodiment of the invention, the second temperature is about 110 to about 125 degrees Celsius. In another embodiment of the invention, the second temperature is about 125 to about 130 degrees Celsius. In another embodiment of the invention, the second temperature is less than or equal to 125 degrees Celsius. In another
embodiment of the invention, the second temperature is less than or equal to 130 degrees Celsius.

[0036] In an additional embodiment of the invention, the first time period and the second time period when added together are at least one hour. In a further embodiment, the first time period and the second time period when added together are about two hours.

[0037] The modified isocyanate composition may include the modified isocyanate compound and an unreacted amount of organic acid derivative. In one embodiment, the organic acid derivate is present in the modified isocyanate composition in an amount of at least one weight percent based on the total weight of the modified isocyanate composition. In another embodiment, the organic acid derivate is present in the modified isocyanate composition in an amount of not more than 50 weight percent based on the total weight of the modified isocyanate composition. In still another embodiment, the organic acid derivate is present in the modified isocyanate composition in an amount of about four weight percent based on the total weight of the modified isocyanate composition. In a further embodiment, the organic acid derivate is present in the modified isocyanate composition in an amount of about nine weight percent based on the total weight of the modified isocyanate composition. The organic acid derivate being present in an amount of at least one weight percent and in an amount less than or equal to 50 percent of the modified isocyanate composition is preferred to control NCO content.

[0038] The modified isocyanate composition including the modified isocyanate compound and the unreacted amount of organic acid derivative may additionally include an average free NCO content. In one embodiment, the average free NCO content of the modified isocyanate composition is at least 19 weight percent based on the total weight of the modified isocyanate composition. In another embodiment, the average free NCO content of the modified isocyanate composition is not more than 30 weight percent based on the total weight of the modified isocyanate composition. In another embodiment, the average free NCO content of the modified isocyanate composition is about 25 weight percent based on the total weight of the modified isocyanate composition. An average free NCO content is of at least 19 weight percent
and less than or equal to 30 weight percent of the modified isocyanate composition is preferred to maximize reactivity and stability.

[0039] The average free NCO content is measured potentiometrically as known and practiced by one of ordinary skill in the art by typical gas phase chromatography as appreciated by one of ordinary skill in the art.

[0040] In an embodiment of a further method, the modified isocyanate composition may additionally be reacted with another isocyanate component which is a compound terminated with at least one isocyanate group. The compound terminated with at least one isocyanate group may include MDI, polymeric MDI, TDI, or any combinations thereof, as described above. The compound may be a liquid or a solid.

In an embodiment of the invention, the modified isocyanate composition is reacted in an amount of at least 45 percent of the combined weight of the modified isocyanate composition and the isocyanate component. The isocyanate component is reacted in the balance amount.

[0041] The composition of the present invention may additionally include catalysts, plasticizers, solvents, etc. For example, triethylphosphate may be included in the composition of the present invention. In addition or alternatively, the composition of the present invention may include Fyrol PCF or similar compounds as is appreciated by one of ordinary skill in the art, TXIB, gamma-butyrolactone, propylene carbonate, aliphatic hydrocarbon solvents, aromatic solvents, mesamoll, or similar compounds as may be appreciated by one of ordinary skill in the art.

[0042] The following examples are intended to illustrate the invention and are not to be viewed in any way as limiting the scope of the invention.

**EXAMPLES**

**Example 1**

[0043] A modified isocyanate composition is formed by charging methylene diphenyl diisocyanate (Lupranate® MI) and butyl acid phosphate in a one liter flask under agitation and heating the contents of the flask to 120 degrees Celsius. The methylene diphenyl diisocyanate is present in an amount of 80.54 percent and the butyl acid phosphate is present in an amount of 19.46 percent. The temperature of the reaction mass is maintained for 2 hours. At about 70 degrees Celsius during heating, carbon dioxide release is observed. The carbon dioxide release peaks during the first hours
and is observed until completion of the reaction. The resultant product is then cooled to room temperature. The resultant product is then collected for observations and analysis. The average free NCO content of the resultant product is 20.42 percent. The percent of butyl acid phosphate in the resultant product is 0.02 percent. Average free NCO content is measured using potentiometric titration.

Example 2
[0044] A modified isocyanate composition is formed by charging methylene diphenyl diisocyanate (Lupranate® M) and butyl acid phosphate in a one liter flask under agitation and heating the contents of the flask to 105 degrees Celsius. The methylene diphenyl diisocyanate is present in an amount of 94.08 percent and the butyl acid phosphate is present in an amount of 5.92 percent. The temperature of the reaction mass is maintained for 1 hour. At about 70 degrees Celsius during heating, carbon dioxide release is observed. Most of the carbon dioxide is released during the first 15 minutes of the reaction. The resultant product is then cooled to room temperature. The resultant product is then collected for observations and analysis. The product appears clear. After being stored at room temperature for two days, 40 percent by volume of the product materializes into solids. The product is placed in an oven at 120 degrees Celsius for one hour and the solids mostly disappear. After being cooled to room temperature, solids appear again. The average free NCO content of the resultant product is 20.52 percent. The percent of butyl acid phosphate in the resultant product is 0.03 percent. Average free NCO content is measured using potentiometric titration.

Example 3
[0045] A modified isocyanate composition is formed by charging molten methylene diphenyl diisocyanate (Lupranate® M) and butyl acid phosphate in a preheated one liter flask under agitation and heating the contents of the flask to 105 degrees Celsius. The methylene diphenyl diisocyanate is present in an amount of 87.38 percent and the butyl acid phosphate is present in an amount of 12.62 percent. The temperature of the reaction mass is maintained for 2 hours. At about 70 degrees Celsius during heating, carbon dioxide release is observed. At about 85 degrees Celsius, large amounts of carbon dioxide release are observed. The reaction mass solidifies quickly but in about 15 minutes, the reaction mass completely liquefies. The temperature is increased to
120 degrees Celsius for 30 minutes, ensuring the dissolution of all solids. The temperature is then decreased to 105 degrees Celsius. The resultant product is then cooled to room temperature. The resultant product is then collected for observations and analysis. The average free NCO content of the resultant product is 24.90 percent. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration. The resultant product, when stored at room temperature for a day, appears clear. On the second day, the product, stored at room temperature, exhibits gelling.

Example 4

[0046] A modified isocyanate composition is formed by charging molten methylene diphenyl diisocyanate (Lupranate® M) in a preheated one liter flask under agitation and heating the contents of the flask to 105 degrees Celsius. Butyl acid phosphate is added dropwise to the flask. The methylene diphenyl diisocyanate is present in an amount of 87.38 percent and the butyl acid phosphate is present in an amount of 12.62 percent. The temperature of the reaction mass is maintained for 2 hours. The resultant product is then cooled to room temperature. The resultant product is then collected for observations and analysis. The average free NCO content of the resultant product is 24.97 percent. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration. The resultant product, when stored at room temperature for a day, appears clear. On the second day, the product, stored at room temperature, appears oily due to the stable emulsion.

Example 5

[0047] The modified isocyanate composition of Example 4 is blended with methylene diphenyl diisocyanate (Lupranate® M). The modified isocyanate composition of Example 4 is charged in a 16-ounce glass container. The container is heated in an oven to 105 degrees Celsius for 15 minutes. Molten methylene diphenyl diisocyanate (Lupranate® M) is added. The modified isocyanate composition of Example 4 is present in an amount of 46.93 percent and the methylene diphenyl diisocyanate is present in an amount of 53.07 percent. The glass container is agitated. The next day, the blended product, which had been stored at room temperature, appears cloudy with solids at the bottom of the container. The product is melted and analyzed. The
average free NCO content of the product is 29.38 percent. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration.

Example 6

[0048] The modified isocyanate composition of Example 4 is blended with a methylene diphenyl diisocyanate (Lupranate® M) and another methylene diphenyl diisocyanate (Lupranate® MI). The modified isocyanate composition of Example 4 and the Lupranate® MI are charged in a 16-ounce glass container. The container is heated in an oven to 80 degrees Celsius for 15 minutes. Molten Lupranate® M is added. The modified isocyanate composition of Example 4 is present in an amount of 46.94 percent, Lupranate® MI is present in an amount of 26.53 percent and Lupranate® M is present in an amount of 26.53 percent. The glass container is agitated. The blended product, stored at room temperature, appears clear after five days. The average free NCO content of the product is 29.44 percent. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration.

Example 7

[0049] The modified isocyanate composition of Example 3 is blended with a methylene diphenyl diisocyanate (Lupranate® M) and another methylene diphenyl diisocyanate (Lupranate® MI). The modified isocyanate composition of Example 3 and the Lupranate® MI are charged in a 16-ounce glass container. The container is heated in an oven to 80 degrees Celsius for 15 minutes. Molten Lupranate® M is added. The modified isocyanate composition of Example 3 is present in an amount of 46.39 percent, Lupranate® MI is present in an amount of 10.72 percent and Lupranate® M is present in an amount of 42.89 percent. The glass container is agitated. The blended product, stored at room temperature, appears almost clear and has a very slight cloudiness after five days. After an additional five days, the blended product, which has been stored at room temperature, appears very slightly cloudy. The average free NCO content of the product is 29.27 percent. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration.

Example 8
A modified isocyanate composition is formed by charging pure methylene diphenyl diisocyanate (Lupranate® M) in a preheated two liter flask under agitation and heating the contents of the flask to 105 degrees Celsius. Butyl acid phosphate is added dropwise to the flask while the temperature is maintained below 110 degrees Celsius. The methylene diphenyl diisocyanate is present in an amount of 79.94 percent and the butyl acid phosphate is present in an amount of 20.06 percent. The temperature of the reaction mass is maintained for 2 hours at 105 degrees Celsius. The resultant product is then transferred to a 32 ounce glass container cooled to room temperature. The resultant product, stored at room temperature for a day, appears clear. The average free NCO content of the resultant product is 19.70 percent. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration.

Example 9

The modified isocyanate composition of Example 3 is blended with a methylene diphenyl diisocyanate (Lupranate® M) and triethyl phosphate (TEP). The TEP acts as a solvent and may be used to impart stability to the blend. Any solvent or plasticizer as described above may be used to impart stability to the blend.

The modified isocyanate composition of Example 3 is charged in a 16-ounce glass container. The container is heated in an oven to 80 degrees Celsius for 15 minutes. Molten Lupranate® M and TEP are added. The modified isocyanate composition of Example 3 is present in an amount of 26.91 percent, Lupranate® M is present in an amount of 68.09 percent and TEP is present in an amount of 5.0 percent. The glass container is agitated. The blended product, stored at room temperature for six days, has some solids at the bottom of the container. About 1 percent of the solids are at the top of the container. The product is melted and analyzed. The average free NCO content of the product is 29.47 percent. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration.

Example 10

The modified isocyanate composition of Example 8 is blended with a methylene diphenyl diisocyanate (Lupranate® M). The modified isocyanate composition of Example 8 is charged in a 4-ounce glass container. The container is
heated in an oven to 80 degrees Celsius for 15 minutes. Molten methylene diphenyl diisocyanate (Lupranate® M) is added. The modified isocyanate composition of Example 8 is present in an amount of 28.88 percent and the methylene diphenyl diisocyanate is present in an amount of 71.12 percent. The glass container is agitated. About 1 volume percent of the blended product, stored at room temperature for six days, is in solid form at the bottom of the container. The product is melted and analyzed. The average free NCO content of the product is 29.42 percent. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration.

Example 11

[0054] The modified isocyanate composition of Example 8 is blended with a methylene diphenyl diisocyanate (Lupranate® M) and another methylene diphenyl diisocyanate (Lupranate® MI). The modified isocyanate composition of Example 8 and the Lupranate® MI are charged in a 4-ounce glass container. The container is heated in an oven to 80 degrees Celsius for 15 minutes. Molten Lupranate® M is added. The modified isocyanate composition of Example 8 is present in an amount of 28.88 percent, Lupranate® MI is present in an amount of 14.22 percent and Lupranate® M is present in an amount of 56.90 percent. The glass container is agitated. The blended product, stored at room temperature, appears clear. The blended product is placed in an incubator at 10 degrees Celsius. The next day, at the temperature of 10 degrees Celsius, the blended product is completely solidified. When the product is stored at room temperature for 30 days, 20 percent by volume of the product is observed to have solids. The average free NCO content of the product is 29.45 percent. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration.

Example 12

[0055] A modified isocyanate composition is formed by charging toluene diisocyanate (Lupranate® T80, type 1) in a three liter flask under agitation and heating the contents of the flask to 105 degrees Celsius. Butyl acid phosphate is added dropwise while the temperature is maintained below 110 degrees Celsius. The toluene diisocyanate is present in an amount of 72.36 percent and the butyl acid phosphate is present in an amount of 27.64 percent. The temperature of the reaction
mass is maintained for 2 hours at 105 degrees Celsius. The resultant product is then collected for observations and analysis. The average free NCO content of the resultant product is 26.85 percent. The resultant product, stored at room temperature for 14 months and appears clear at 14 months. The percent of butyl acid phosphate in the resultant product is 1.75 percent. Average free NCO content is measured using potentiometric titration.

Example 13

[0056] A modified isocyanate composition is formed by charging polymeric MDI (Lupranate® M20) in a two liter glass flask under agitation and heating the contents of the flask to 105 degrees Celsius. Butyl acid phosphate is added dropwise while the temperature is maintained below 110 degrees Celsius. The polymeric TDI is present in an amount of 90.66 percent and the butyl acid phosphate is present in an amount of 9.34 percent. The temperature of the reaction mass is maintained for 2 hours at 105 degrees Celsius. The resultant product is then collected for observations and analysis. The average free NCO content of the resultant product is 25.72 percent. The resultant product, stored at room temperature for 14 months and appears clear at 14 months. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration.

Example 14

[0057] The modified isocyanate composition of Example 8 is blended with a methylene diphenyl diisocyanate (Lupranate® M) and another methylene diphenyl diisocyanate (Lupranate® MI). The modified isocyanate composition of Example 8 and the Lupranate® MI are charged in a 1-liter glass flask. Agitation is started and the container is heated to 60 degrees Celsius. Under agitation, molten Lupranate® M is added and the reaction mass is stirred for 15 minutes. While agitating, at 60 degrees Celsius, PLURACOL® 1062 polyol (having 0.0274 weight percent water), a polyol commercially available from BASF Corporation, is added while the temperature is maintained below 80 degrees Celsius. The modified isocyanate composition of Example 8 is present in an amount of 21.72 percent, Lupranate® MI is present in an amount of 10.69 percent, Lupranate® M is present in an amount of 42.79 percent and the PLURACOL® 1062 polyol is present in an amount of 24.80 percent. The temperature of the reaction mass is maintained for 1 hour at 80 degrees Celsius and
then for 1 hour at 100 degrees Celsius. At 100 degrees Celsius, the reaction mass changes color from light yellow to brown and then became clear. Upon cooling to 70 degrees Celsius, the reaction mass becomes cloudy. The resultant product is then collected and analyzed. After being maintained at room temperature for one day, the product appears cloudy. After being maintained at room temperature for five days, the product separates into two layers. The bottom layer is dark and oily and comprises about 5 volume percent of the total product. The average free NCO content of the product is 21.42 percent. The percent of butyl acid phosphate in the resultant product is zero percent. Average free NCO content is measured using potentiometric titration.

Example 15

[0058] A composition is formed by charging molten methylene diphenyl diisocyanate (Lupranate® M) in a preheated one liter flask under agitation and heating the contents of the flask to 60 degrees Celsius. PLURACOL® 1062 polyol (having 0.0274 weight percent water), a polyol commercially available from BASF Corporation, is added dropwise while the temperature is maintained below 80 degrees Celsius. After the polyol is added, butyl acid phosphate is added dropwise to the flask while the temperature is maintained below 90 degrees Celsius. The methylene diphenyl diisocyanate is present in an amount of 70.25 percent, the butyl acid phosphate is present in an amount of 4.36 percent and the PLURACOL® 1062 polyol is present in an amount of 25.39 percent. The temperature of the reaction mass is maintained for 2 hours at 80 degrees Celsius. The resultant product is then collected for observations and analysis. After being maintained at room temperature for one day, the product appears cloudy. After being maintained at room temperature for four days, the product separates into two layers. After being maintained at room temperature for 32 days, 20 percent of the volume of the product is in solid form. The average free NCO content of the product is 22.05 percent. The percent of butyl acid phosphate in the resultant product is 0.2 percent. Average free NCO content is measured using gas phase chromatography.

[0059] The examples are summarized in the following table. The components of each aforementioned composition are set forth below in approximate weight percentages.
M is Lupranate®, MI is Lupranate® MI, M20 is Lupranate® M20, TEP is triethylphosphate and BAP is butyl acid phosphate.

**TABLE**

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<th>Type</th>
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<th>Reaction Temp.</th>
<th>%NCO</th>
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<td>Reaction 1</td>
<td>MI 80.54%; BAP 19.46%</td>
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<td>M 94.08%; BAP 5.92%</td>
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</table>

[0060] It is to be understood that the appended claims are not limited to express and particular compounds, compositions, or methods described in the detailed description, which may vary between particular embodiments which fall within the scope of the appended claims. It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come
within the scope of the appended claims and their equivalents. With respect to any Markush groups relied upon herein for describing particular features or aspects of various embodiments, it is to be appreciated that different, special, and/or unexpected results may be obtained from each member of the respective Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and or in combination and provides adequate support for specific embodiments within the scope of the appended claims.

[0061] It is also to be understood that any ranges and subranges relied upon in describing various embodiments of the present invention independently and collectively fall within the scope of the appended claims, and are understood to describe and contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. One of skill in the art readily recognizes that the enumerated ranges and subranges sufficiently describe and enable various embodiments of the present invention, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range "of from 0.1 to 0.9" may be further delineated into a lower third, i.e., from 0.1 to 0.3, a middle third, i.e., from 0.4 to 0.6, and an upper third, i.e., from 0.7 to 0.9, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of the appended claims. In addition, with respect to the language which defines or modifies a range, such as "at least," "greater than," "less than," "no more than," and the like, it is to be understood that such language includes subranges and/or an upper or lower limit. As another example, a range of "at least 10" inherently includes a subrange of from at least 10 to 35, a subrange of from at least 10 to 25, a subrange of from 25 to 35, and so on, and each subrange may be relied upon individually and/or collectively and provides adequate support for specific embodiments within the scope of the appended claims. Finally, an individual number within a disclosed range may be relied upon and provides adequate support for specific embodiments within the scope of the appended claims. For example, a range "of from 1 to 9" includes various individual integers, such as 3, as well as individual numbers including a decimal point (or fraction), such
as 4.1, which may be relied upon and provide adequate support for specific embodiments within the scope of the appended claims.
CLAIMS

What is claimed is:

1. A composition comprising:
   an isocyanate component; and
   an organic acid derivative having the formula \((RO)_{n}(M)(E)(EH)_{3-n}\),
   wherein M is nitrogen, phosphorus, arsenic, antimony, or bismuth,
   \(n\) is the integer 1 or the integer 2,
   each E is independently oxygen, sulfur, selenium, or tellurium,
   each R is independently hydrogen, an alkyl group, a cyclic aryl group,
   an acyclic aryl group, a halogen-substituted alkyl group, a halogen-
   substituted cyclic aryl group or a halogen-substituted acyclic aryl
   group; and
   wherein the ratio of the weight of said isocyanate component to the combined
   weight of said organic acid derivative and said isocyanate component is from
   0.7 to 0.95.

2. The composition of claim 1, wherein M is phosphorus, E is oxygen, and R is
   a butyl group and wherein said isocyanate component is selected from the group of
   MDI, polymeric MDI, TDI, and combinations thereof.

3. The composition of claim 1, wherein said organic acid derivative is selected
   from the group of phosphoric acid monobutyl ester, phosphoric acid dibutyl ester,
   phosphoric acid monophenyl ester, phosphoric acid diphenyl ester, phosphoric acid
   2-butoxy-l-ethyl ester, 2-ethylhexyl acid phosphate, cetyl acid phosphate, stearyl acid
   phosphate, butyl acid phosphate, dibutyl acid phosphate, mono-methyl acid phosphate,
   dimethyl acid phosphate, mono-ethyl acid phosphate, diethyl acid phosphate, mono-
   propyl acid phosphate, dipropyl acid phosphate, halogen substituted derivatives thereof
   and combinations thereof.

4. A polyurethane comprising:
   a reaction product of
   an isocyanate component, and
   an organic acid derivative having the formula \((RO)_{n}(M)(E)(EH)_{3-n}\),
   wherein M is nitrogen, phosphorus, arsenic, antimony, or bismuth,
n is the integer 1 or the integer 2,
each E is independently oxygen, sulfur, selenium, or tellurium,
each R is independently hydrogen, an alkyl group, a cyclic aryl group,
an acyclic aryl group, a halogen-substituted alkyl group, a halogen-substituted cyclic aryl group or a halogen-substituted acyclic aryl group, and

wherein the ratio of the weight of said isocyanate component to the combined weight of said organic acid derivative and said isocyanate component is from 0.7 to 0.95 prior to reaction.

5. The polyurethane of claim 4, wherein M is phosphorus, E is oxygen, and R is a butyl group and wherein said isocyanate component is selected from the group of MDI, polymeric MDI, TDI, and combinations thereof.

6. The polyurethane of claim 4, wherein said organic acid derivative is selected from the group of phosphoric acid monobutyl ester, phosphoric acid dibutyl ester, phosphoric acid monophenyl ester, phosphoric acid diphenyl ester, phosphoric acid 2-butoxy-1-ethyl ester, 2-ethylhexyl acid phosphate, cetyl acid phosphate, stearyl acid phosphate, dimethyl acid phosphate, mono-ethyl acid phosphate, diethyl acid phosphate, monopropyl acid phosphate, dipropyl acid phosphate, halogen substituted derivatives thereof and combinations thereof.

7. A method comprising:
providing an isocyanate component;
providing an organic acid derivative having the formula (RO)_n(M)(E)(EH)_{3-n},
wherein M is nitrogen, phosphorus, arsenic, antimony, or bismuth,
n is the integer 1 or the integer 2,
each E is independently oxygen, sulfur, selenium, or tellurium,
each R is independently hydrogen, an alkyl group, a cyclic aryl group,
an acyclic aryl group, a halogen-substituted alkyl group, a halogen-substituted cyclic aryl group or a halogen-substituted acyclic aryl group; and
combining said isocyanate component and said organic acid derivative, wherein the ratio of the weight of said isocyanate component to the combined
weight of said organic acid derivative and said isocyanate component is from
0.7 to 0.95 prior to reaction;
heating said isocyanate component and said organic acid derivative at a first
temperature; and
maintaining the first temperature for a first time, such that said isocyanate
component and said organic acid derivative react to form a polyurethane.
8. The method of claim 7, further comprising the step of heating the
polyurethane at a second temperature higher than the first temperature and the step of
maintaining the second temperature for a second time such that a modified
isocyanate compound is formed optionally in the presence of said isocyanate
component and said organic acid derivative.
9. The method of claim 8, wherein the first temperature is less than or equal to
70 degrees Celsius and wherein the second temperature is less than or equal to 130
degrees Celsius.
10. The method of claim 8, wherein the first time and the second time together
are at least one hour.
11. The method of claim 8, wherein said organic acid derivative is present in an
amount of at least one weight percent of the combined weight of said modified
isocyanate compound, said isocyanate component and said organic acid derivative.
12. The method of claim 11, wherein said organic acid derivative is present in an
amount of less than or equal to 50 weight percent of the combined weight of said
modified isocyanate compound, said isocyanate component and said organic acid
derivative.
13. The method of claim 11, wherein the modified isocyanate compound has an
average free NCO content of at least 19 percent and not more than 30 percent.
14. The method of claim 7, wherein M is phosphorus, E is oxygen, and R is a
butyl group and wherein said isocyanate component is selected from the group of
MDI, polymeric MDI, TDI, and combinations thereof.
15. The method of claim 7, wherein said organic acid derivative is selected from
the group of phosphoric acid monobutyl ester, phosphoric acid dibutyl ester,
phosphoric acid monophenyl ester, phosphoric acid diphenyl ester, phosphoric acid
2-butoxy-1-ethyl ester, 2-ethylhexyl acid phosphate, cetyl acid phosphate, stearyl acid
phosphate, butyl acid phosphate, dibutyl acid phosphate, mono-methyl acid phosphate, dimethyl acid phosphate, mono-ethyl acid phosphate, diethyl acid phosphate, mono-propyl acid phosphate, dipropyl acid phosphate, halogen substituted derivatives thereof and combinations thereof.

16. The method of claim 11, further comprising the step of reacting the modified isocyanate composition with a second isocyanate component.

17. The method of claim 16, wherein the second isocyanate component is selected from the group of MDI, polymeric MDI, TDI, and combinations thereof.

18. A modified isocyanate composition comprising:

the heated reaction product of a polyurethane comprising the reaction product of

an isocyanate component; and

an organic acid derivative having the formula \((RO)_n(M)(E)(EH)_{3-n}\),

wherein \(M\) is nitrogen, phosphorus, arsenic, antimony, or bismuth,
\(n\) is the integer 1 or the integer 2,
each \(E\) is independently oxygen, sulfur, selenium, or tellurium,
each \(R\) is independently hydrogen, an alkyl group, a cyclic aryl group, an acyclic aryl group, a halogen-substituted alkyl group, a halogen-substituted cyclic aryl group or a halogen-substituted acyclic aryl group; and

wherein said organic acid derivative is present in an amount of at least 1 weight percent of the modified isocyanate composition.

19. The modified isocyanate composition of claim 18, wherein said organic acid derivative is present in an amount of less than or equal to 50 weight percent of the modified isocyanate composition.

20. The modified isocyanate composition of claim 18 wherein the heated reaction product has an average free NCO content of at least 19 percent and not more than 30 percent.

21. The modified isocyanate composition of claim 18, wherein \(M\) is phosphorus, \(E\) is oxygen, and \(R\) is a butyl group and wherein said isocyanate component is selected from the group of MDI, polymeric MDI, TDI, and combinations thereof.
22. The modified isocyanate composition of claim 18, wherein said organic acid derivative is selected from the group of phosphoric acid monobutyl ester, phosphoric acid dibutyl ester, phosphoric acid monophenyl ester, phosphoric acid diphenyl ester, phosphoric acid 2-butoxy-l-ethyl ester, 2-ethylhexyl acid phosphate, cetyl acid phosphate, stearyl acid phosphate, butyl acid phosphate, dibutyl acid phosphate, monomethyl acid phosphate, dimethyl acid phosphate, mono-ethyl acid phosphate, diethyl acid phosphate, mono-propyl acid phosphate, dipropyl acid phosphate, halogen substituted derivatives thereof and combinations thereof.

23. The modified isocyanate composition of claim 18, wherein the composition is a flame retardant.
INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/030783

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07F9/141 C07F9/32 C08G18/76 C08G18/80 C08K5/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07F C08G C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 2010/256286 AI (BERNARD JEAN-MARI E [FR] ET AL) 7 October 2010 (2010-10-07) page 9; examples 1-19</td>
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<td>X</td>
<td>WO 98/56843 AI (BASF AG [DE]; TREIBER REINHARD [DE]; RENZ HANS [DE]; HAEBERLE KARL [DE] 17 December 1998 (1998-12-17) claims 1-3; examples 2,3</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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Date of the actual completion of the international search
24 July 2013

Date of mailing of the international search report
09/08/2013

Name and mailing address of the ISA/
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NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, 340-3016

Authorized officer
Bergmeier, Martin
## INTERNATIONAL SEARCH REPORT

### Information on patent family members

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