polyisocyanate products, decreasing yield and forming higher molecular weight impurities that increase viscosity and modify other characteristics of the product. They present a difficult separation problem if they are to be removed. The unreacted amines also can become phosgenated to form unwanted isocyanate species that are very difficult to remove from the desired product.

Isocyanate compounds are known to form carbodiimides when reacted in the presence of certain catalysts. *See*, for example, US Patent Nos. 4,014,935, 4,072,712, 4,120,884, 4,177,205, 4,199,524, 4,260,554 and 4,743,626 as well as US Published Patent Application Nos. 2007-0213432, 2007-0213496, 2008-0021176 and 2008-0085987. The carbodiimides thus formed can further react with isocyanate compounds to form uretonimines. The processes described in the foregoing references mainly deal with forming carbodiimide-modified and uretonimine-modified polyisocyanate compounds for polyurethane production. The thus-modified polyisocyanate compounds often are liquids and in some cases impart some desirable properties to polyurethanes from the modified polyisocyanates.

This present disclosure relates to an MDI and/or polymeric MDI manufacturing process, comprising the steps of:

a) reacting aniline with formaldehyde to produce a mixture of methylene dianiline (MDA), one or more polymethylene polyanilines having at least three aniline groups (PMDA) and unreacted aniline;

b) removing aniline from the mixture produced in step a) to produce a process stream containing the MDA, PMDA and residual aniline;

c) phosgenating the process stream from step b) in a non-polar solvent to form an isocyanate process stream containing the non-polar solvent, MDI, one or more polymethylene polyphenylisocyanates that have at least three phenyl isocyanate groups (PMDI) and at least one phenyl isocyanate;

d) separating MDI and PMDI from the isocyanate process stream obtained in step c) by distillation to produce a solvent stream containing the non-polar solvent, greater than zero up to 10 weight percent of the at least one phenyl isocyanate based on the weight of the solvent stream and 0 to 5 weight percent, based on the weight of the solvent stream, of MDI and/or PMDI;

e) reacting the solvent stream obtained in step d) in the presence of a catalytically effective amount of a carbodiimidization catalyst, to convert at least a portion of the at least one phenyl isocyanate to a N,N'-diphenylcarbodiimide,

f) optionally removing and/or deactivating the carbodiimidization catalyst and

g) optionally recycling the N,N'-diphenylcarbodiimide formed in step e), non-polar solvent and optionally the carbodiimidization catalyst and/or residues from the deactivation of the carbodiimidization catalyst, directly or indirectly into step d).

In one aspect, the present disclosure relates to an MDI and/or polymeric MDI manufacturing process, comprising the steps of:

a) reacting aniline with formaldehyde to produce a mixture of methylene dianiline (MDA), one or more polymethylene polyanilines having at least three aniline groups (PMDA) and unreacted aniline

b) removing aniline from the mixture produced in step a) to produce a process stream containing the MDA, PMDA and residual aniline;

c) phosgenating the process stream from step b) in a non-polar solvent to form an isocyanate process stream containing the non-polar solvent, MDI, one or more polymethylene polyphenylisocyanates that have at least three phenyl isocyanate groups (PMDI) and at least one phenyl isocyanate;

d) separating MDI and PMDI from the isocyanate process stream obtained in step c) by distillation to produce a solvent stream containing the non-polar solvent, greater than zero up to 10 weight percent of the at least one phenyl isocyanate based on the weight of the solvent stream and 0 to 5 weight percent, based on the weight of the solvent stream, of MDI and/or PMDI;

e) reacting the solvent stream obtained in step d) in the presence of a catalytically effective amount of a carbodiimidization catalyst, to convert at least a portion of the at least one phenyl isocyanate to an N,N'-diphenylcarbodiimide,

f) removing and/or deactivating the carbodiimidization catalyst, and

g) recycling an N,N'-diphenylcarbodiimide formed in step e), non-polar solvent and optionally the carbodiimidization catalyst and/or residues from the deactivation of the carbodiimidization catalyst, directly or indirectly into step d),

wherein the N,N'-diphenylcarbodiimide recycled in step d) reacts with MDI and/ors PMDI to form one or more uretonimine compounds.

The present disclosure also relates to a method for converting a phenyl isocyanate to an N,N'-diphenylcarbodiimide. The method comprises reacting a solution of phenyl isocyanate in a liquid non-polar solvent in the presence of an effective amount of a carbodiimidization catalyst to convert at least a portion of the phenyl isocyanate to N,N'-diphenylcarbodiimide. In preferred examples, the method of this aspect of the disclosure includes a further step of deactivating the carbodiimidization catalyst. Steps a), b) and c) of the process as described above are well-known in the art and described, for example, in US Patent Application Nos. 4,189,354, 4,118,410, 4,294,666, WO 1999/054289A, WO 2013/081873 and US Published Patent Application No. 2007-0117997, among many others. Aniline and aqueous formaldehyde are typically condensed in a molar ratio from about between about 20:1 and about 1.6:1. The reaction is generally acid-catalyzed. A weight ratio of aniline to acid catalyst from between about 20:1 and about 1.1:1 is useful. The temperature of the reaction mixture is typically 30°C to 250°C. After the reaction, the reaction mixture is typically neutralized with a base, such as a hydroxide of an alkali metal or an alkaline earth metal (*e.g.*, sodium hydroxide). In this process, a portion of the aniline is typically not converted to MDA (methylene dianiline) or polymethylene polyanilines (PMDA) and remains in the product mixture obtained from the reaction.

The reaction mixture generally includes an aqueous phase and an organic phase which contains the amines (including unreacted aniline). The phases typically are separated, and aniline removed from the organic phase using methods such as crystallization, extraction or, preferably, distillation. The distillation may be performed at a temperature at or above the boiling temperature of aniline at the pressure employed. The pressure may be atmospheric but is preferably subatmospheric.

A residual portion of the aniline typically remains in the distilled MDA and PMDA product. When this product is taken to the subsequent phosgenation step, at

WHAT IS CLAIMED IS:

1. An MDI and/or polymeric MDI manufacturing process, comprising the steps of:

a) reacting aniline with formaldehyde to produce a mixture of methylene dianiline (MDA), one or more polymethylene polyanilines having at least three aniline groups (PMDA) and unreacted aniline

b) removing aniline from the mixture produced in step a) to produce a process stream containing the MDA, PMDA and residual aniline;

c) phosgenating the process stream from step b) in a non-polar solvent to form an isocyanate process stream containing the non-polar solvent, MDI, one or more polymethylene polyphenylisocyanates that have at least three phenyl isocyanate groups (PMDI) and at least one phenyl isocyanate;

d) separating MDI and PMDI from the isocyanate process stream obtained in step c) by distillation to produce a solvent stream containing the non-polar solvent, greater than zero up to 10 weight percent of the at least one phenyl isocyanate based on the weight of the solvent stream and 0 to 5 weight percent, based on the weight of the solvent stream, of MDI and/or PMDI;

e) reacting the solvent stream obtained in step d) in the presence of a catalytically effective amount of a carbodiimidization catalyst, to convert at least a portion of the at least one phenyl isocyanate to an N,N'-diphenylcarbodiimide,

f) removing and/or deactivating the carbodiimidization catalyst, and

g) recycling an N,N'-diphenylcarbodiimide formed in step e), non-polar solvent and optionally the carbodiimidization catalyst and/or residues from the deactivation of the carbodiimidization catalyst, directly or indirectly into step d),

wherein the N,N'-diphenylcarbodiimide recycled in step d) reacts with MDI and/or PMDI to form one or more uretonimine compounds.

2. The manufacturing process of claim 1 wherein the carbodiimization catalyst is one or more of a phospholene compound; a phospholidine compound; a phosphate ester; a phosphine oxide; a diazaphospholane; an oxaza-phospholane; a diazaphosphorinanes; an oxazaphosphorinane; a triaryl arsine; an arsine oxide; a metallic derivative of acetylacetone; a metal complex derived from a d-group transition element and a T-

bonding ligand; a urea compound; a biuret compound; an amide compound; an imide compound; and an anilide compound.

3. The manufacturing process of any preceding claim wherein the carbodiimization catalyst is a phospholidine.

4. The manufacturing process of any preceding claim wherein the carbodiimization catalyst is a phospholidine oxide.

5. The manufacturing process of any preceding claim wherein the carbodiimization catalyst is a phospholene oxide.

6. The manufacturing process of any preceding claim wherein step f) is performed and is performed by adding a chemical deactivator.

7. The manufacturing process of claim 6 wherein the chemical deactivator includes a Lewis acid.

8. The manufacturing process of claim 7 wherein the Lewis acid includes tin(II) chloride.

9. The manufacturing process of any preceding claim wherein step (g) is performed.