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(54) **Title:** FORMATION OF HIGHER MOLECULAR WEIGHT CYCLIC POLYAMINE COMPOUNDS FROM CYCLIC POLYAMINE COMPOUNDS

(57) **Abstract:** The present invention provides strategies for making higher weight, cyclic polyamines from lower molecular weight, cyclic polyamine starting compounds via transamination. The higher molecular weight, cyclic polyamines are structurally similar to the lower molecular weight, cyclic polyamine starting compounds. The reactants used in the present invention include a cyclic polyamine component that comprises at least two amine groups separated from one another by at least a binary carbon atom spacing, and that can be transaminated to form a higher molecular weight, cyclic polyamine compound. The higher molecular weight, cyclic polyamine has at least two cyclic rings joined to one another through a nitrogen-containing hydrocarbyl group. Each of the cyclic rings contains two amine groups separated from one another by binary carbon atom spacing.

desired for some applications, and acyclic species are desired for other applications. For example, acyclic amines such as diethylenetriamine and triethylenetetramine formed from the transamination of ethylenediamine or the reductive amination of monoethanolamine are useful intermediates for wet strength resins and corrosion inhibitors. Cyclic polyamines are useful as epoxy hardeners. Additionally, they are a critical component in gas treating formulations for C(3/4) capture. In addition, because of their reactivity, cyclic polyamines are often used as intermediates for a variety of derivatives used in other applications. For example, methylation of piperazine (PIP) provides N,N'-dimethylpiperazine which is a useful polyurethane catalyst. Alkoxylation of PIP provides a starting material for polyurethanes, and reactions with diacids provide polyamides for use as hot-melt adhesives.

PIP is a solid at ambient (i.e., room) temperature, and can be a challenge to offer as a solid (e.g., flaking, prilling etc.). As a result, PIP is currently commercially offered by the DOW Chemical Company as a 68% aqueous solution (PIP68). However, the aqueous nature of the product limits its use in several applications that require anhydrous PIP due to time and energy costs to remove the water. Anhydrous PIP is a solid at room temperature and can be difficult to handle in many applications because of limited solubility in most common solvents.

As a result, there is a need to provide methodologies to provide compositions that have similar reactivity and functionality as PIP while being liquids at ambient temperature.

SUMMARY OF THE INVENTION

The present invention provides improved strategies for preparing higher molecular weight, cyclic polyamine products. Such higher molecular weight, cyclic polyamine products may comprise mixtures of the higher molecular weight, cyclic polyamines and lower molecular weight, cyclic polyamines.

The strategies of the present invention provide higher molecular weight, cyclic polyamines that are structurally similar to that of the starting cyclic polyamine, have similar reactivity to that of the starting cyclic polyamine, and have the benefit of being a liquid at room temperature. Additionally, the higher molecular weight, cyclic polyamine comprises at least two cyclic polyamine rings. It is expected that any extra amine functionality in the molecule will impart additional properties that are not present in the starting cyclic polyamine. Additionally, in some embodiments, the higher molecular weight, cyclic polyamine will have fewer volatile organic compound (VOC) issues than the lower molecular weight, cyclic polyamines or other lower molecular weight amines.

The present invention is based in part upon using reactants that include a cyclic polyamine component that comprises at least two amine groups separated from one another by

at least a binary carbon atom spacing, and that can be transaminated to form a higher molecular weight, cyclic polyamine compound. The higher molecular weight, cyclic polyamine has at least two cyclic rings joined to one another through a nitrogen-containing hydrocarbyl group. Each of the cyclic rings contains two amine groups separated from one another by binary carbon atom spacing.

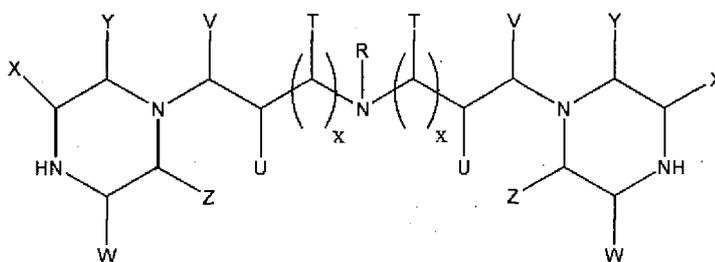
The reaction mixture further comprises at least one hydrogenation/dehydrogenation catalyst. Useful hydrogenation/dehydrogenation catalysts include both transamination and reductive amination catalysts.

As used herein, the term polyamine refers to a compound that includes at least two amine groups.

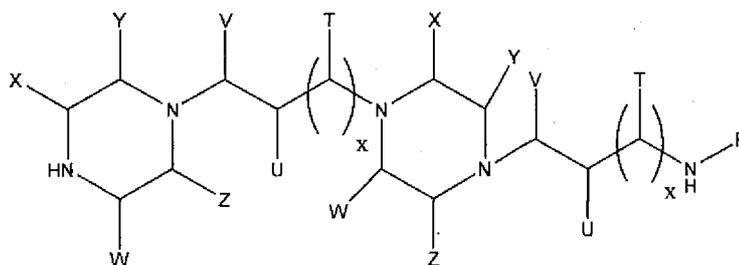
As used herein, the term "carbon atom spacing" refers to the number of carbon atoms between the various functional groups. For example, the term binary spacing refers to a two carbon atom spacing; the term ternary spacing refers to a three carbon atom spacing; etc. The binary, ternary, or other carbon atom spacing is that portion of the particular molecule that separates the various functional groups therein.

As used herein, the term high molecular weight refers to the molecular weight of a polyamine product(s) resulting from the practice of the present invention.

In one aspect, the present invention provides a reaction product comprising a higher molecular weight cyclic polyfunctional amine having the generic Formula I



and optionally an amine having the generic Formula II

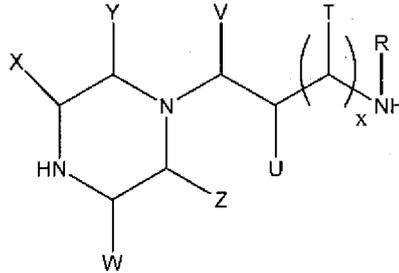


wherein each R, T, U, V, W, X, Y, and Z group is the same or different and is selected from hydrogen, or a hydrocarbyl group; and the value of x is 0 to 10, with the

proviso that if x is greater than 1, each T may be the same or different, the polyfunctional amine comprising the reaction product of:

- (a) an amine of the generic Formula III

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wherein each R, T, U, V, W, X, Y, and Z group is as described above; and the value of x is as described above; and

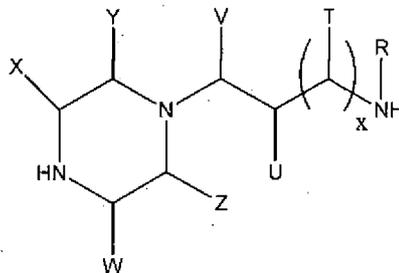
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- (b) a hydrogenation/dehydrogenation catalyst.

In another aspect, the present invention provides a reaction composition comprising

- (a) an amine of the Formula III

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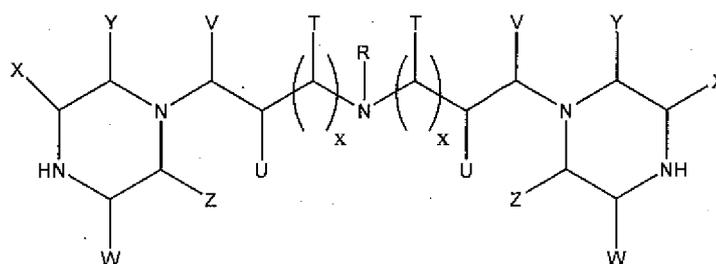


wherein each R, T, U, V, W, X, Y, and Z group is the same or different and is selected from hydrogen, or a hydrocarbyl group; and the value of x is 0 to 10, with the proviso that if x is greater than 1, each T may be the same or different; and

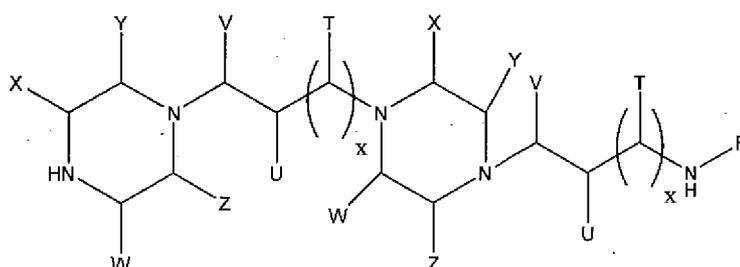
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- (b) a hydrogenation/dehydrogenation catalyst.

In still another aspect, the present invention comprises a method of manufacturing a polyfunctional amine having the Formula I

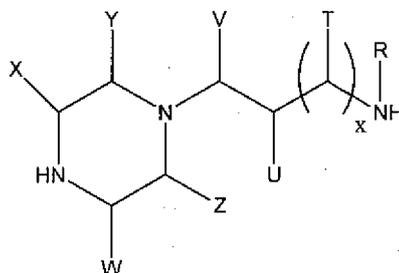


and, optionally, an amine having the Formula II



5 wherein each R, T, U, V, W, X, Y, and Z group is the same or different and is selected from hydrogen, or a hydrocarbyl group; and the value of x is 0 to 10, with the proviso that if x is greater than 1, T may be the same or different, the method comprising the steps of:

(a) providing an amine of the Formula III



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 wherein each R, T, U, V, W, X, Y, and Z group is as described above; and the value of x is as described above; and

15 (b) causing transamination of the amine of Formula III in the presence of a hydrogenation/dehydrogenation catalyst under conditions effective to cause the formation of the amine of Formula I.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

20 Reference will now be made in detail to representative embodiments of the invention. While the invention will be described in conjunction with the enumerated embodiments, it will be understood that they are not intended to limit the invention to those embodiments. On the

contrary, the invention is intended to cover all alternatives, modifications, and equivalents that may be included within the scope of the present invention as defined by the claims.

One skilled in the art will recognize many methods and materials similar or equivalent to those described herein, which could be used in and are within the scope of the practice of the present invention. The present invention is in no way limited to the methods, materials, and compositions described.

Unless defined otherwise herein, technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods, devices, and materials similar or equivalent to those described herein can be used in the practice or testing of the invention, the preferred methods, devices and materials are now described.

The present invention provides strategies for making cyclic polyamine compounds that have a higher molecular weight than the molecular weight of a starting cyclic polyamine by methodologies that comprise transaminating a first or lower molecular weight, cyclic polyamine compound that has at least two amine groups separated from one another by a binary carbon spacing (C2 spacing) in the cyclic ring to produce a second or higher molecular weight, cyclic polyamine compound. The second polyamine compound comprises at least two cyclic rings that each have at least two amine groups separated from one another by a binary carbon spacing (C2 spacing) in each cyclic ring.

Formula III, set forth above, represents an example of first cyclic polyamine compounds useful in the invention. Formula I and II, set forth above, represents an example of the second cyclic polyamine compounds produced by the present invention.

Hydrocarbyl groups that may be used in the practice of the invention may be substituted or unsubstituted, linear, branched, or cyclic hydrocarbyl such as alkyl, aryl, aralkyl, or the like; a monovalent moiety including one or more heteroatoms; polyether chains comprising one or more oxyalkylene repeating units such as $-R^xO-$, wherein R is often alkylene of 2 to 5 carbon atoms; other oligomeric or polymer chains of at least 2 repeating units. Preferably, R, R¹, T, U, V, W, X, and Y are H or straight, branched, or cyclic hydrocarbyl such as alkyl of 1 to 10 carbon atoms, preferably 1 to 3 carbon atoms. More preferably, R, R¹, T, U, V, W, X, and Y are H.

The values of x in the practice of the invention are typically in the range of from 1 to 10, preferably in the range of from 2 to 5, and more preferably in the range of from 2 to 3.

Examples of first or lower molecular weight, cyclic polyamines useful in the present invention include 2-(piperazin-1-yl)ethanamine (AEP), 3-(piperazin-1-yl)propan-1-amine, 4-(piperazin-1-yl)butan-1-amine, 5-(piperazin-1-yl)pentan-1-amine, 6-(piperazin-1-yl)hexan-1-amine, 1-(piperazin-1-yl)propan-2-amine and 2-(piperazin-1-yl)propan-1-amine.

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Examples of second or higher molecular weight, cyclic polyamines consistent with Formula I that are produced by the present invention include bis(2-(piperazin-1-yl)ethyl)amine (BPEA) (3-(piperazin-1-yl)propyl)amine, bis(4-(piperazin-1-yl)butyl)amine, bis(5-(piperazin-1-yl)pentyl)amine, bis(6-(piperazin-1-yl)hexyl)amine, bis(1-(piperazin-1-yl)propan-2-yl)amine, and bis(2-(piperazin-1-yl)propyl)amine.

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Examples of second or higher molecular weight, cyclic polyamines consistent with Formula II that are produced by the present invention include 2-(4-(2-(piperazin-1-yl)ethyl)piperazin-1-yl)ethanamine, 3-(4-(3-(piperazin-1-yl)propyl)piperazin-1-yl)propan-1-amine, 4-(4-(4-(piperazin-1-yl)butyl)piperazin-1-yl)butan-1-amine, 5-(4-(5-(piperazin-1-yl)pentyl)piperazin-1-yl)pentan-1-amine, 6-(4-(6-(piperazin-1-yl)hexyl)piperazin-1-yl)hexan-1-amine, 1-(4-(1-(piperazin-1-yl)propan-2-yl)piperazin-1-yl)propan-2-amine, and 2-(4-(2-(piperazin-1-yl)propyl)piperazin-1-yl)propan-1-amine.

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Any hydrogenation/dehydrogenation catalyst that can catalyze a transamination reaction can be used in the present invention. Such catalysts are well known. Hydrogenation generally refers to a chemical reaction involving the addition of hydrogen, and the process is often used to reduce or saturate organic materials. The reverse reaction in which hydrogen is removed from an organic molecule is referred to as dehydrogenation.

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Useful hydrogenation/dehydrogenation catalysts include transamination catalysts and reductive amination catalysts. Platinum group metals, particularly platinum, palladium, rhodium, and ruthenium form highly active hydrogenation/dehydrogenation catalysts. These are known to operate at lower temperatures and lower pressures of H_2 . Non-precious metal catalysts, especially those based on nickel (such as Raney nickel and Urushibara nickel) have also been developed as economical alternatives. Other hydrogenation/dehydrogenation catalysts might incorporate iron, copper, chromium, molybdenum, cobalt, osmium, iridium, and/or the like.

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In some aspects, the selectivity of the catalyst composition may be further enhanced by the use of metal promoter. The promoter may be a metal (or oxide) which when incorporated into the catalyst composition further enhances the productivity and/or

desirably, the weight ratio of nickel to rhenium is within these ranges with the proviso that the weight ratio is also greater than 1:1. In some preparations of the catalyst composition, the catalyst portion includes a mixture of nickel and rhenium in the composition in a predetermined weight ratio. In some cases, the weight ratio of the nickel and rhenium in the composition is in the range of about 3:1 to about 15:1. In some aspects, nickel is present in an amount in the range of about 23 weight percent to about 2 weight percent, and rhenium is present in the composition in the range of about 7 weight percent to about 0.5 weight percent. In some aspects, nickel is present in an amount in the range of about 5 weight percent to about 8.5 weight percent, and rhenium is present in the composition in the range of about 2.5 weight percent to about 1 weight percent. An exemplary catalyst portion includes nickel at about 6.8 weight percent and rhenium at about 1.8 weight percent.

In preferred embodiments in which a heterogeneous catalyst incorporates nickel and rhenium, useful support materials include silicas, aluminas, titanias, zirconias, magnesias, carbons, molecular sieves, or mixtures thereof.

In preferred embodiments in which a heterogeneous catalyst incorporates nickel and rhenium, a useful support are alumina-silicate particles. Such catalysts and methods of making such heterogeneous catalysts on such supports are further described in U.S. Pat. No. 6,534,441. Such catalysts are also further described in United States Published Patent Application Nos. 2010-0137642-A1, titled "LOW METAL LOADED, ALUMINA SUPPORTED, CATALYST COMPOSITIONS AND AMINATION PROCESS" by Stephen W. King et al.; 2010-0087682-A1, titled "LOW METAL CATALYST COMPOSITIONS INCLUDING ACIDIC MIXED METAL OXIDE AS SUPPORT" by Steven W. King et al; 2010-0087683-A1, titled "A PROCESS TO SELECTIVELY MANUFACTURE DETA OR OTHER DESIRABLE ETHYLENAMINES VIA CONTINUOUS TRANSAMINATION OF ETHYLENEDIAMINE (EDA), AND OTHER ETHYLENEAMINES OVER A HETEROGENEOUS CATALYST SYSTEM" by Ronald Gary Cook et al.; 2010-0087684-A1, (DOW0019P1) titled "METHODS FOR MAKING ETHANOLAMINE(S) AND ETHYLENEAMINE(S) FROM ETHYLENE OXIDE AND AMMONIA, AND RELATED METHODS" by David Do et al.; and 2010-0087681 -A1, titled "Method Of Manufacturing Ethyleneamines" by David M. Petraitis et al.

In some modes of practice the metals of the catalytic portion are deposited on the support using an incipient wetness technique, often referred to as incipient wetness impregnation (IW or IWI). In this technique an active metal precursor (or combination of active metal precursors) is dissolved in an aqueous or organic solution. The metal-

containing solution ("impregnation solution") is added to a catalyst support. Often, the impregnation solution is added in a volume that is the same as the pore volume of the support. Capillary action draws the impregnation solution into the pores of the support. The impregnated support can then be dried and calcined to drive off the volatile liquids of the impregnation solution. This process deposits the catalytic metals on the surface of the support portion.

In some modes of practice, the impregnation solution is an aqueous solution of a salt of the metal. Since more than one metal is to be immobilized on the support, the impregnation solution can include a mixture of salts of the desired metals. Alternatively, more than one impregnation solution can be prepared. The impregnation solution can be saturated with the metal salts, or the metal salts can be used in amounts less than saturation. The concentration of the metal salts in the impregnation solution can depend on factors such as the desired amount of metal(s) to be deposited on the support, and the solubility of the particular metal salt(s) used in the process.

Organic and inorganic salts of nickel include, but are not limited to, nickel nitrate hexahydrate, nickel formate, nickel acetate tetrahydrate, nickel acetate, nickel chloride, nickel carbonate and the like. A nickel -containing impregnation solution can be prepared containing one or more of these nickel salts. In some modes of practice, nickel nitrate or nickel formate is used to prepare the impregnation solution.

Precursor salts of rhenium include potassium and ammonium salts. Additionally, perrhenic acid may also be used. A rhenium-containing impregnation solution can be prepared containing one or both of these salts.

In many modes of practice, the one or more metals to be deposited on the support are dissolved in a suitable solvent, such as deionized water, for preparation of the impregnation solution.

One or more impregnation solutions can be prepared to provide the types and total amount of metals to be deposited on the support portion. Since a lower amount of metal is associated with the support, the total amount of metal can be deposited in a limited number of applications. For example, the total amount of metal deposited can be applied in one, two, three, or four applications. Although an impregnation solution can be prepared with a high concentration of metal salt (i.e., a minimal amount of water), in some cases the total amount of the impregnation solution to be applied may be more than what the alumina support can hold by absorption. Therefore, in some modes of practice, the impregnation solution is applied to the support in multiple steps, wherein a portion of the impregnation solution about equal to the absorption volume of the support is applied to the support in one

application step. Incorporation of additional metal(s) into the support may be further increased by techniques known to those skilled in the art, such as increasing the time the support is in contact with the solution.

5 The impregnation solution can be applied to the support using various methods. For example, the solution can be applied by drip application, by immersion (e.g., dipping), or by spraying. During application, processes such as mixing, tumbling, stirring, or shaking can be used to agitate the support. Mechanical equipment can be used to facilitate agitation. Agitation during the application of the impregnation solution can increase the uniformity of the impregnation solution applied to the support.

10 After all or a portion of the impregnation solution is applied to the support, the support can be dried. In the drying step, the liquid which solvates the metal salt is volatilized and removed from the support. The drying may be accomplished by any technique that sufficiently evaporates the volatile constituents of the impregnation solution. The drying step can comprise a calcination step, as further discussed herein. Multiple drying steps can be performed if the impregnation solution is applied in more than one step. Therefore, an overall process for preparing the catalyst composition can include multiple steps of disposing the application composition, and then drying the impregnated support. The steps of depositing and then drying can be performed until all of the impregnation solution is used.

20 Typically, the impregnated support is dried at a temperature of above 100°C. The elevated temperature can also be accompanied by a reduced pressure environment to accelerate removal of the liquid from the support. The support can be dried in air or in the presence of an inert gas, such as nitrogen. Drying is carried out for a period of time sufficient for removal of most or all of the liquid of the impregnation solution. In some modes of practice, the step of drying is performed for a period of about one hour or more at elevated temperatures.

25 The process of preparing the catalytic composition can also involve one or more steps of calcining the support. One or more steps of calcining the support can be performed in the absence of the catalytic metals, and optionally in the presence of the catalytic metals, or both.

30 In some modes of practice, given the high heat of calcination, drying and removal of the liquid component of the impregnation solution occurs. Therefore, as used herein, calcination of the support meets the requirements of the drying step or steps, which are typically performed following application of the impregnation solution. In addition,

calcination can cause conversion of the metal salts into oxides. The choice of a particular calcination temperature can depend on the decomposition temperature of the salts used.

Calcination normally takes place at temperatures below the melting point of the materials used to form the support portion of the catalytic composition. For example,
5 calcination is typically performed in the range of about 200°C to about 1200°C, and more typically in the range of about 300°C to about 500°C. A calcination step can take a period of time in the range of a minute to hours (e.g., two or three or more hours). Calcination can be carried out in the presence of air, or under inert gas.

In some modes of practice calcination is performed after one or more steps of
10 applying the impregnation solution. After all of the impregnation solution has been applied the metal-loaded support can be calcined for a longer period of time to ensure substantial removal of the impregnation solution liquid. For example, in some specific modes of practice, the impregnation solution is applied to the support in two or more steps, with calcination at about 340°C for about one hour in air performed after each step of applying,
15 with a final calcination at about 340°C for about one hour in air.

Following metal impregnation and calcination, the catalyst composition can be reduced, converting the metal oxides produced in the calcination step to the reduced metal form. Typically, the metal-containing support is reduced in the presence of hydrogen. The metal-containing support can be contacted with hydrogen gas at a temperature that is about
20 in the same range as that used for calcination. The process of reduction can be carried out from about 30 minutes to about 24 hours, or more.

Following reduction, the catalyst composition can be stabilized with gentle oxidation. Typical stabilizing treatments involve contacting the reduced catalyst composition with oxygen or carbon dioxide. For example, in one mode of practice, the
25 catalyst composition is treated with about 1% O_2/N_2 . Prior to using in an animation reaction, the catalyst composition can be activated with hydrogen.

After impregnation and drying/calcination (with optional reduction) the catalyst composition can optionally be stored or handled in an inert environment.

In some embodiments, the morphology of the catalyst composition can be
30 controlled to reduce or minimize mass transfer resistance during transamination. Some illustrative methods for addressing mass transfer resistance include: adjusting the morphology of the catalyst composition, selecting the form of the catalyst composition (e.g., by providing a thin coating of the active catalyst metals on the surface of the support), and/or the selecting the size of the catalyst particles. For example, PCT Publication No.
35 WO 2006/060206 ("Transitional Alumina Particulate Materials Having Controlled

Morphology and Processing for Forming Same," Bauer et al.) describes alumina particulate material that contains particles comprising transitional alumina having an aspect ratio of not less than 3:1 and an average particle size of not less than about 110 nm and not greater than 1000 nm. Various shaped particles are described, including needle-shaped particles and platy-shaped particles.

In other embodiments, the catalyst portion is deposited on a porous support portion so that at least the active catalyst metals are provided in a very thin outer layer or "egg shell" structure, so as to minimize mass transfer resistance for the amine-containing solution. This catalyst structure can also lower the active metal requirement for the catalyst composition, and/or maximize contact of the active metals with the amine-containing elements within the reaction solution.

Thus, in accordance with these embodiments, useful catalyst composition diameters can be in the range of about 0.8 mm to about 3.1 mm; surface area can be in the range of about 10 m²/g to about 200 m²/g; catalytically active metal concentration can be in the range of about 1 weight percent to about 25 weight percent, and the catalyst portion can be provided as a thin outer shell on the support portion.

Methods described in U.S. Patent No. 5,851,948 can be utilized to create a similar "egg shell" structure for the present inventive catalyst compositions. For example, the catalytic metals comprising the catalyst portion (here, nickel and rhenium) can be added to the support portion as a thin outer layer or shell on the support portion. This small thickness for the catalyst portion can be influenced by the flow characteristics of the nickel and rhenium salts and a suitable carrier liquid solution of an alcohol and water, the porosity and surface area of the support portion, and the diffusion rate of the active metal liquid solution into the porous support portion. The flow characteristics of the nickel and rhenium in the alcohol-water carrier liquid having low surface tension is controlled so as to initially form a "cluster"-type structure of the nickel and rhenium in the carrier liquid on only the outer surface of the support portion. Such "cluster" type structures are formed because of valence differences between ions of the active nickel and rhenium and molecules of the alcohol carrier liquid, and such larger "clusters" effectively impede penetration of the active metal into smaller size pores of the support material. During the subsequent drying, reducing and calcining steps for making the catalyst, the carrier liquid is destroyed and removed so that only the active metals remain in uniformly dispersed sites in the thin outer "egg-shell" structure on the support portion. Suitable alcohol carrier liquids may include ethanol, methanol and isopropanol.

This technique of depositing an active metal such as nickel and/or rhenium in a thin layer or shell on only the outer surface of the support portion advantageously provides a high localized concentration of the active metals on the catalyst outer surface, where it is readily contacted by the amine-containing compounds in the reaction solution. Techniques described in U.S. Patent No. 5,851,948 (Chuang et al., "Supported Catalyst and Process for Catalytic Oxidation of Volatile Organic Compounds") can be instructive in accordance with these embodiments of the invention.

Catalytic metal can also be deposited on the surface of the support portion according to techniques described by Komiyama et al. ("Concentration Profiles in Impregnation of Porous Catalysts: Nickel on Alumina," J. of Catalysis 63, 35-52 (1980)). Utilizing the principles described by Komiyama et al., radial concentration profiles in the catalyst compositions can be formed by impregnating the support portion with aqueous catalytic metal (e.g., nickel) solutions. In accordance with the present invention, a base can be used with nickel-formate to achieve surface deposition of nickel on alumina supports. More specifically, the pH effect on adsorption has been utilized to achieve surface impregnation of nickel by coimpregnating alumina supports with nickel formate ($\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$) and aqueous ammonia. The result was surface deposition of the nickel on the alumina supports. These principles can be further applied to catalyst compositions including more than one catalytic metal (e.g., more than one of cobalt, nickel, and/or copper).

In still further embodiments, selecting a desirable particle size for the support portion can control internal mass transfer resistance. As discussed in European Patent Application No. EP 1249440 A1 ("Process for Preparing Linear Alkylbenzenes," Wang et al.), both the catalyst particle size and porosity can be adjusted to provide a desired conversion and catalytic stability.

In use, the catalyst composition is added to promote the transamination process. The amount of catalyst composition that is used to promote transamination can be determined based on one or more of the following factors: the type and amount of reactants, the reactor (reaction vessel) configuration, the reaction conditions (such as temperature, time, flow rate, and pressure), the degree of conversion to a desired product(s), and the selectivity desired (i.e., the ratio of the desired product over an undesired product). The catalyst composition is present in the reaction zone in sufficient catalytic amount to enable the desired reaction to occur.

The particulate support may have a so-called guest/host structure, which may be prepared by adsorbing or adhering fine (less than 100 micrometers, preferably less than 50

micrometers and most preferably less than 10 micrometer in size) nanoporous particles on coarser (greater than 30 mesh) particles. The smaller particles are referred to as guests, while the large particles supporting them are referred to as hosts. This small-particle-supported-on-a-larger-particle composite structure provides very high total exterior surface area while retaining the desirable gas passing characteristics, i.e., low pressure drop, of a coarser particle. In addition, by using smaller particles in constructing these composite particles, inexpensive, coarser particles can be used. Thus, very inexpensive, highly active catalyst particles can be prepared since the bulk of the volume of a catalyst bed may be taken up by the inexpensive, underlying, coarser particles.

The catalyst material can be incorporated into or onto the guest and/or host particles. Often, the catalyst material is incorporated mainly onto the guest material before or after the guest/host composite is formed. Guest/host structures and methods of making these are further described in U.S. Publication No. 2005-00951 89 A1.

Preferably, the catalyst and/or the supported catalyst composition are calcined prior to use. Generally, calcining can occur in air or an inert atmosphere such as one based upon nitrogen, argon, carbon dioxide, combinations of these, and the like.

Catalyst material may be incorporated into heterogeneous catalyst systems in a variety of ways. In some instances, a catalyst precursor is first provided on the support, and then the precursor can be converted into the catalyst itself afterward. Exemplary procedures are well known in the industry and include solution impregnation, precipitation, vapor deposition such as by PVD or CVD techniques, and the like.

The transamination reaction can be practiced in any suitable reactor. These include batch reactor, continuous fixed bed reactors, slurry bed reactors, fluidized bed reactors, catalytic distillation reactors, combinations of these, and the like. In certain embodiments, a fixed bed reactor is preferred. A fixed bed reactor includes catalyst pellets that are held in place and do not substantially move with respect to fixed reference frame. At least a portion of the reactor feed material passes over (flows past) the catalyst pellets and reacts to form **produces**).

The, lower molecular weight cyclic polyamine to be transaminated can be contacted with the catalyst at any suitable temperature(s) that promotes the production of the desired higher molecular weight, cyclic polyamine. Typically, the temperature is maintained below about 350°C, preferably below 300°C. Preferred temperatures are in the range from 100°C to 220°C, more preferably from 120°C to 180°C. Below the preferred temperature ranges, the conversion to the desired higher cyclic polyamine may be too slow to be practical for commercial scale production. Above the preferred temperature ranges,

selectivity may be reduced to an undue degree, decreasing the yield of the desired cyclic polyamine compound.

Similarly, the transamination reaction can be contacted with catalyst at any suitable pressure(s) that promotes the production of the desired higher molecular weight, cyclic polyamine. Preferably, the pressure is sufficient to maintain the reactor contents in a liquid state as the reaction proceeds. In some instances, the pressure will vary as the reaction proceeds. For instance, ammonia is a by-product of a typical transamination process. The production of ammonia causes the pressure generally to increase as the reaction proceeds in pressure sealed reactors. Ammonia and/or other pressure-increasing products can be removed from the reactor in order to keep the pressure below a desired threshold. Typically, the pressure is at least 100 psi, preferably at least 200 psi, and preferably less than 1000 psi. Within these guidelines, the pressure is typically in the range from 100 psi to 1500 psi, preferably 200 psi to 1200 psi, more preferably 300 psi to 1000 psi. Pressures in the range of 300 psi to 800 psi are most preferred.

In many embodiments, the starting material used will be in liquid form such that no additional solvent is needed. Indeed, in many instances it may be preferred to carry out the desired reaction in the absence of solvent. However, one or more solvents may be used if desired. A variety of solvents or combinations of solvents may be used. Desirably, the solvent is not unduly reactive with the starting material or the resultant higher molecular weight, cyclic polyamine product(s) and does not unduly decompose under the reaction conditions. Some examples of solvents that could be used include saturated hydrocarbons such as pentane, hexane, octane, nonane, decane, or the like; aromatic hydrocarbons such as toluene, benzene, xylene, ether, combinations of these, and the like. Alcohols are desirably avoided, as many of these are capable of reacting with the amine reactants and/or products. If present, the amount of solvent used may vary over a wide range. In a typical instance, the solvent may constitute from about 5 to about 98 weight percent, desirably 10 to 80 weight percent, of the mixture. Optionally when solvent is used, the reaction medium can be diluted to favor intramolecular reactions and, hence, cyclization, relative to intermolecular interactions.

The reactant mixture for the transamination reaction optionally may, and preferably does, include hydrogen. When hydrogen is used, the level of hydrogen can be adjusted to favor the formation of the desired higher cyclic polyamine while minimizing the amount of hydrogenolysis that can lead to alkyl byproducts (e.g., 1-ethylpiperazine).

From 0.1 to about 100 mole percent, desirably about 1 to about 10 mole percent of hydrogen per mole of reactants would be suitable.

The one or more cyclic polyamines contained in the reaction product mixture made according to the present invention can be separated (refined) by any method known in the art. For example, the ethyleneamines can be refined using
5 conventional distillation technology known in the art. Preferably, dividing wall columns are used. Other separation techniques such as membrane separation, melt crystallization, and reactive distillation may also be employed. Alternatively, the lower molecular weight polyamine can be removed and recycled back to the reactor,
10 and the higher molecular weight polyamine can be used as a mixture or further separation can be employed to give the products with higher purity.

The present invention will now be further described with reference to the following illustrative examples.

Catalyst Preparation

15 Unless otherwise noted, the catalyst compositions employed were prepared using the following procedure. Precursor salts of nickel and rhenium were dissolved in 70-80°C water to form an impregnation solution. The final volume of the impregnation solution was adjusted to equal the adsorption volume required for the number of times that the carrier was impregnated, and the quantities of the precursor salts were calculated to give
20 a nominal composition of 6.8 and 1.8 wt. percent nickel and rhenium, respectively. An alumina/silica (80:20 wt. percent) carrier was impregnated to incipient wetness by the addition of the appropriate amount of impregnation solution and gently agitated until all the liquid was adsorbed. The sample was then calcined in air at 340°C. When the support had cooled, additional impregnations were performed until all of the solution had been added. A
25 calcination step at 340°C was done after each impregnation. The material was reduced in hydrogen at 340°C. After reduction, the catalyst was passivated with a small amount of oxygen in an inert gas so the material could be handled in air.

Those skilled in the art will readily appreciate that impregnation with the impregnation solution can optionally be performed in one, two, three or more incipient
30 wetness applications, as dictated by such variables as the solubility of the precursor salts, the porosity of the support to be impregnated, and the desired weight loading of the metal.

Reactor/Reaction Conditions

The reaction was run in a 1 inch by 8 foot packed bed reactor with 400 grams of the catalyst described above. The reactor bed was made of 1 inch seamless Swagelok tubing (1 inch outside diameter, 0.095 in wall thickness). The length of the reactor tube was approximately 8 feet. It is incased in 1.5 inch diameter Swagelok tubing through which heat transfer fluid was pumped via a standard laboratory heating bath. This allowed for isothermal operation of the reactor tube. A multipoint thermocouple was inside the reactor bed for temperature monitoring. Temperature and pressure was monitored at various points in the reactor system. The 2-(piperazin-1-yl)ethanamine (AEP) feed material was pumped via a 500 ml Isco syringe pump through a flow meter, a preheater, and into the bottom of the reactor. Just prior to the reactor tube inlet (bottom), the hydrogen gas was introduced to the AEP stream. There was a sampling system that allowed for a timed sample to be taken of the product stream. The sample time was dependent on the feed flowrate, but routinely samples were taken in the range of 5-30 minutes. The sampling system consisted of a stainless reservoir to collect the AEP reaction mixture, followed by a small scrubber, and a wet test meter. This allowed for quantification of the feed flow, ammonia generation, and hydrogen flow during sampling. The product mixture is analyzed by gas chromatography and the peaks identified using electron impact mass spectrometry. In some cases the total weight percent was greater than 100 percent due to different response factors with higher molecular weight oligomers.

EXAMPLES

Reactions were run as described above in the Reactor/Reaction Conditions section. The results of these reactions are set forth in the following tables in which Table 1 shows the difference in the final product mix as a function of AEP space velocity; Table 2 shows the effect on AEP conversion at different reactor pressures and a constant temperature and feed rate; and Table 3 shows that the effect upon BPEA selectivity at various AEP conversions at a constant pressure and feed rate.

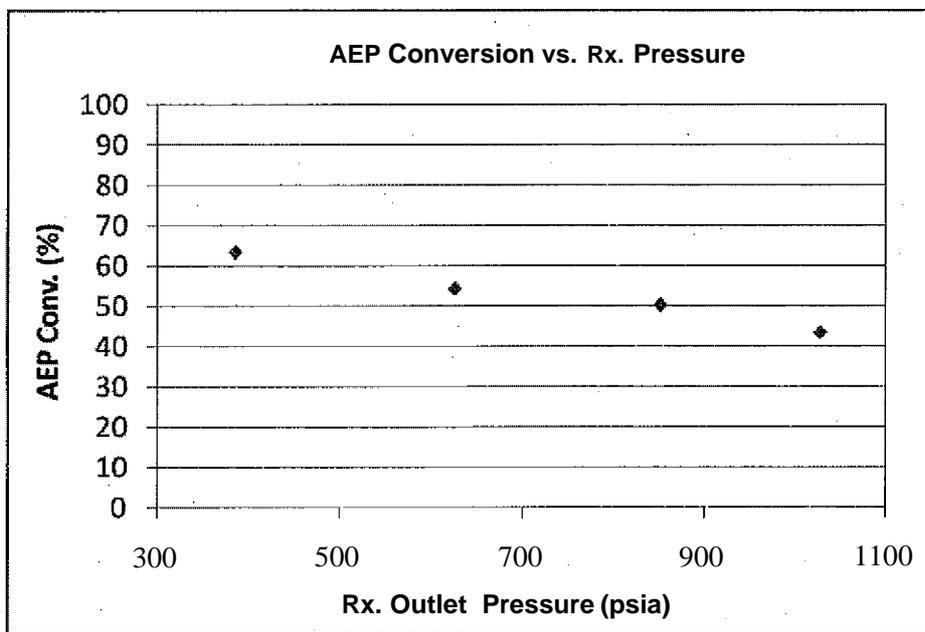
Table 1

	Condition 1	Condition 2
Product GC Analysis	Oil bath at 155C. AEP feed at 1.5 mL/min. 150 sccm of H2 flow. 800 psig of pressure	Oil bath at 155C. AEP feed at 3 mL/min. 150 sccm of H2 flow. 800 psig of pressure
AEP (wt%)	30.5	53.8
BPEA (wt%)	61.6	42.9
Others (, wt%)*	14.6	9.3
GC Total	106.7	106.0
AEP conversion, %	68.8	44.9
AEP Product (BPEA) Selectivity, %	80.9	82.2
AEP By-Product Selectivity, %	19.1	17.8

- Others include piperazine, higher cyclic polyamine oligomers, and 2-(4-(2-(piperazin-1-yl)ethyl)piperazin-1-yl)ethanamine.

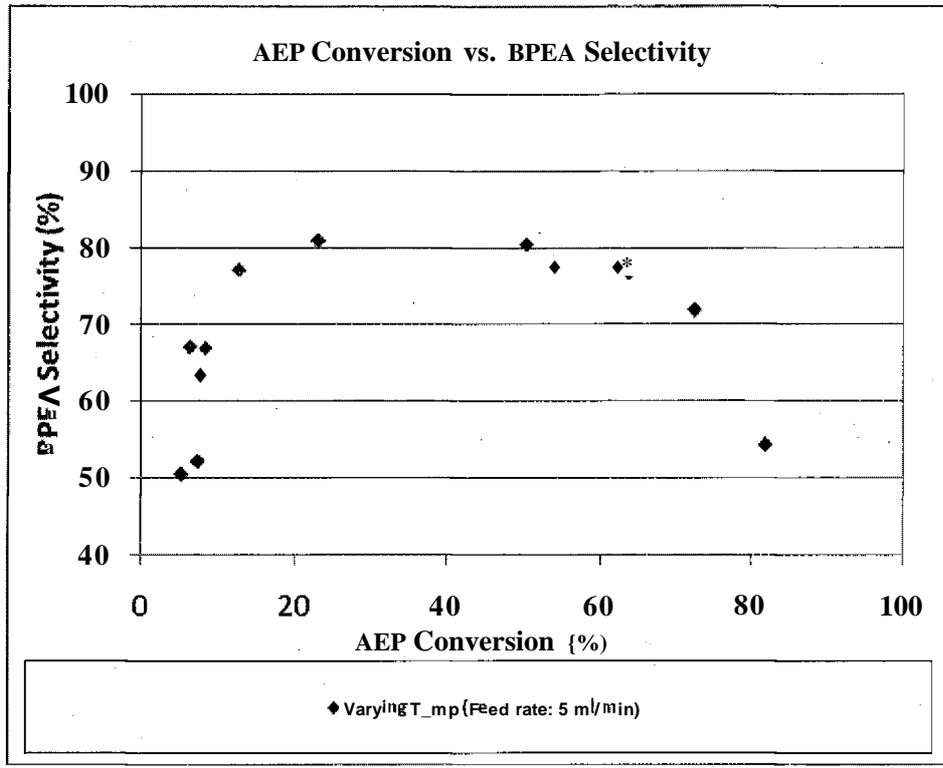
Table 1 shows that as the feed rate of AEP increases, the AEP conversion to BPEA decreases. However, the selectivity to BPEA remains similar across the AEP conversion range of ca. 30-54 percent.

Table 2



The Table above shows that under similar reaction conditions higher conversions of AEP are obtained at lower pressures.

Table 3



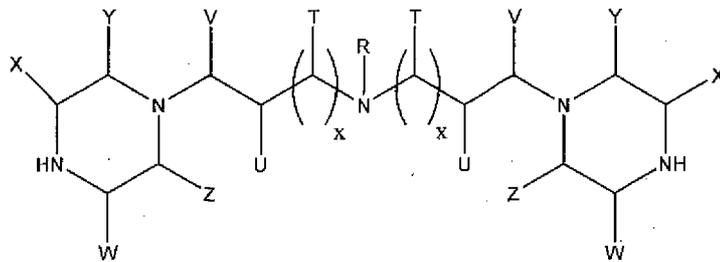
This graph shows that at a constant pressure and feed rate, BPEA selectivity reaches a maximum at ca. 20% AEP conversion and remains essentially flat to 65% AEP conversion.

5

CLAIMS

1. A reaction product comprising a higher molecular weight cyclic polyfunctional amine having the generic Formula I

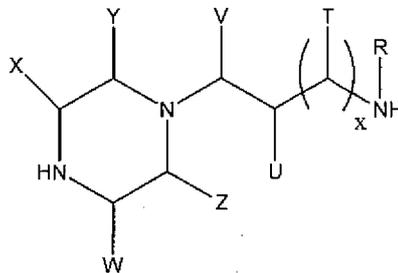
5



wherein each R, T, U, V, W, X, Y, and Z group is the same or different and is selected from hydrogen, or a hydrocarbyl group; and the value of x is 0 to 10, with the proviso that if x is greater than 1, each T may be the same or different, the polyfunctional amine comprising the reaction product of:

10

(a) an amine of the Formula III



15

wherein each R, T, U, V, W, X, Y, and Z group is as described above; and the value of x is as described above in this claim; and

(b) a hydrogenation/dehydrogenation catalyst.

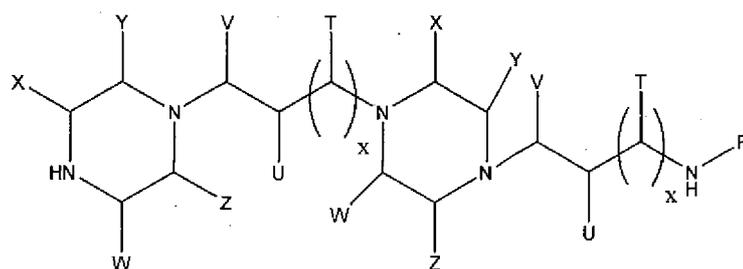
20

2. The reaction product of claim 1, wherein x has a value of from 2 to 3.

3. The reaction product of claim 2, wherein R, T, U, V, W, X, Y, and Z are each hydrogen.

25

4. The reaction product of claim 1, further comprising a polyfunctional amine product having the Formula II

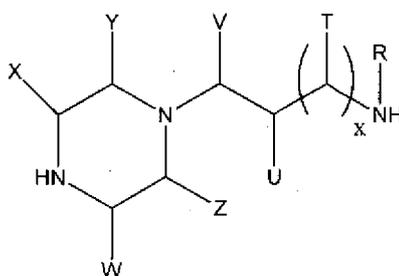


5 wherein each R, T, U, V, W, X, Y, and Z group is as described above; and the value of x is as described in claim 1.

5. The reaction product of claim 4, wherein the polyfunctional amine of
 Formula I comprises bis(2-piperazin-1-ylethyl)amine and the polyfunctional amine
 10 of the Formula II comprises 2-(4-(2-(piperazin-1-yl)ethyl)piperazin-1-yl)ethanamine.

6. A reaction composition comprising
 (a) an amine of the Formula HI

15



wherein each R, T, U, V, W, X, Y, and Z group is the same or different and is
 selected from hydrogen, or a hydrocarbyl group; and the value of x is 0 to 10, with the
 proviso that if x is greater than 1, each T may be the same or different; and

20 (b) a hydrogenation/dehydrogenation catalyst.

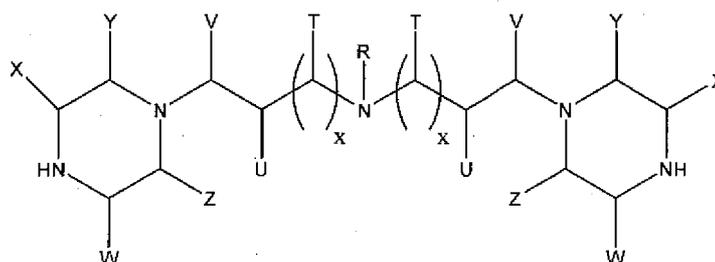
7. The reaction composition of claim 6, wherein the
 hydrogenation/dehydrogenation catalyst comprises a transamination catalyst or a reductive
 animation catalyst.

25

8. The reaction composition of claim 7, wherein the transamination catalyst comprises Ni and Re in a ratio in the range of 3:1 to 14:1.

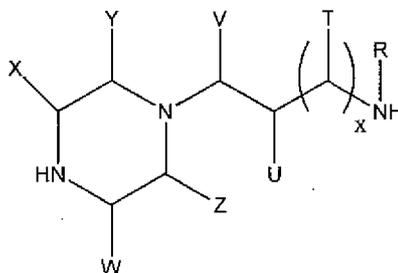
9. The reaction composition of claim 6, wherein the amine of Formula III is 2-(piperazine-1-yl)ethylamine.

10. A method of manufacturing a polyfunctional amine having the Formula I



10 wherein each R, T, U, V, W, X, Y, and Z group is the same or different and is selected from hydrogen, or a hydrocarbyl group; and the value of x is 0 to 10, with the proviso that if x is greater than 1, T may be the same or different, the method comprising the steps of:

(a) providing an amine of the Formula III



15 wherein each R, T, U, V, W, X, Y, and Z group is as described above; and the value of x is as described above in this claim;

and

(b) reacting the amine of Formula III in the presence of a catalyst under conditions effective to cause the formation of the amine of Formula I.

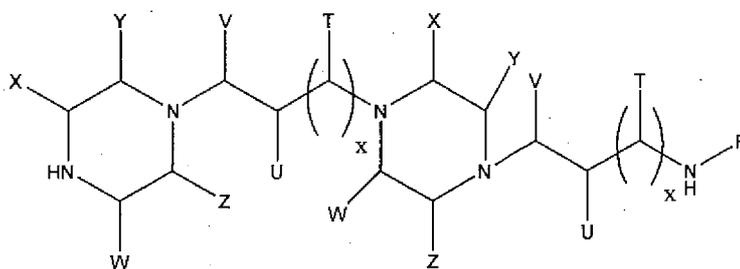
11. The method of claim 10, wherein the hydrogenation/dehydrogenation catalyst is a transamination catalyst or a reductive amination catalyst.

12. The method of claim 10, wherein the hydrogenation/dehydrogenation catalyst comprises a transamination catalyst selected from nickel (Ni), copper (Cu), cobalt (Co),

ruthenium (Ru), rhenium (Re), rhodium (Rh), platinum (Pt), palladium (Pd), iridium, and combinations thereof.

13. The method of claim 12, wherein the transamination catalyst comprises Ni and Re
5 in a ratio in the range of 3:1 to 14:1 on an alumina-silica support.

14. The method of claim 10, further comprising the formation of a polyfunctional amine product of the Formula II



wherein each R, T, U, V, W, X, Y, and Z group is as described above; and the value of x is as described above in claim 10.

15. The method of claim 14, wherein the polyfunctional amine of Formula I is bis(2-
15 piperazin-1-ylethyl)amine, the polyfunctional amine of Formula II is 2-(4-(2-(piperazin-1-yl)ethyl)piperazin-1-yl)ethanamine, and the amine of Formula III is 2-(piperazin-1-yl)ethanamine.

20

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/064971

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D295/13
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)
C07D

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 , CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 256 786 A (BOWMAN ROBERT G [US] ET AL) 26 October 1993 (1993-10-26)	1, 3, 6, 10, 11
Y	examples 2b, 3b, 4b, 5b, 6b, 7b, 8b, 9b, 10b; table I	10-15
X	US 2010/094007 AI (KING STEPHEN W [US] ET AL) 15 April 2010 (2010-04-15) Table 10, runs 4-10	6-15
	----- -/- .	

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	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 10 May 2013	Date of mailing of the international search report 21/05/2013
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Grassi , Dami an
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/064971

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	C. BAZZICALUPI ET AL: "Reinforced piperazine rings containing polyamines: metal complex equilibria and structural studies", INORGANICA CHIMICA ACTA, vol. 268, no. 1, 1998, pages 63-68, XP055054759, ISSN: 0020-1693, DOI: 10.1016/S0020-1693(97)05720-4 compounds L1, L2 -----	1, 3, 6
X	EP 0 412 611 A (UNION CARBIDE CHEM) 13 February 1991 (1991-02-13) pages 15, 17, 54-56, 60-67 -----	1-5
Y	Wo 2010/042157 AI (UNION CARBIDE CHEM PLASTIC [US]; KING STEPHEN W [US]; MIERAU STEFAN K) 15 April 2010 (2010-04-15) cited in the application page 22, lines 20-25; claims 1, 11; example 1A -----	10-15
X	EP 0 737 669 AI (UNION CARBIDE CHEM PLASTIC [US]) 16 October 1996 (1996-10-16) claim 1; examples 4-66 -----	6-9
X	US 2010/087683 AI (COOK RONALD G [US] ET AL) 8 April 2010 (2010-04-08) tables 1-5 -----	6-9
X	US 4 973 692 A (BURGESS LLOYD M [US] ET AL) 27 November 1990 (1990-11-27) claim 3; examples 1-4 -----	6-9
X	US 4 977 266 A (BURGESS LLOYD M [US] ET AL) 11 December 1990 (1990-12-11) claim 3; tables A-F -----	6-9
X	US 5 196 588 A (BURGESS LLOYD M [US] ET AL) 23 March 1993 (1993-03-23) claim 4; examples 1-7 -----	6-9
X	US 5 410 086 A (BURGESS LLOYD M [US]) 25 April 1995 (1995-04-25) claim 5; examples 1-42 -----	6-9
	-/--	

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/064971

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>MARCHAND ALAN P ET AL: "Synthesis and electrospray ionization mass spectrometric evaluation of the metal cation complexation behavior of cage-annulated azacrown ethers" , HETEROCYCLES. INTERNATIONAL JOURNAL FOR REVIEWS AND COMMUNICATIONS IN HETEROCYCLIC CHEMISTRY, ELSEVIER SCIENCE PUBLISHERS B.V. AMSTERDAM, NL, vol . 62, 2004, pages 279-296, XP001526098, ISSN: 0385-5414 compound 25</p> <p style="text-align: center;">-----</p>	1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/064971

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos. :

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos. :

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-5, 10-15

Compounds according to claim 1 and a process for their preparation according to claim 10 (the group is still not unitary) .

2. claims: 6-9

Compositions according to claim 6 (the group is still not unitary) .

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2012/064971
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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us 5410086	A	25-04-1995	NONE