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(54) **Title**: BLOWING CATALYST

(57) **Abstract**: The invention relates to the use of a component according to one of the formulae (I) or (II), formula (I) being $(R^1R^2NR^3)_2NR^4$, formula (II) being $(R^1R^2NR^3)NH_2$, wherein - each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group and an n-propyl group; - R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2OCH_2CH_2CH_2CH_2-$; - R^4 is chosen from the group consisting of a hydrogen and $-CH_2CH_2CH_2NH_2$, as a blowing catalyst of a catalyst system in a reaction of at least one polyisocyanate component and at least one isocyanate-reactive component, the catalyst system further comprising at least one gelling catalyst different from said component of formula (I) or (II).

BLOWING CATALYST

The present invention relates to catalyst systems for polyurethane and/or polyurea foam production, and blowing catalysts of such catalyst system.

Polyurethane and polyurea products, and in particular foamed polyurethane products, are well known in the art and used for a multitude of different applications.
The foamed polyurethane products (hereinafter referred to as foamed PU), are obtained by reacting a polyisocyanate with a isocyanate reactive component, typically a polyalcohol (also called polyol).
The reaction to provide the foamed PU typically requires a catalyst system comprising at least two catalyst components. The first component is typically referred to as the gelling catalyst or gelation catalyst, mainly catalyzing the reaction of isocyanate groups and alcohol groups, thereby providing urethane groups in the polyurethane polymer obtained.
The second component is typically referred to as the blowing catalyst, mainly catalyzing the reaction of isocyanate groups and water, thereby providing urea groups in the polyurethane polymer obtained and carbon dioxide gas.

Additional additives such as chain extenders, other chemical or physical blowing agents, fillers, flame retarders, antioxidants and alike can be added.

Typically the catalyst system is to meet various criteria to a more or less extent, in order to be a suitable catalyst system for the foamed PU aimed for. Such criteria is a.o. the catalytic activity of the gelling catalyst, which typically is to be as high as possible, causing less catalyst to be used in order to obtain the proper reaction rate and obtaining a quick start of the reaction. An other criteria is a.o. the catalytic activity of the blowing catalyst, which typically is to be high in order to cause less catalyst to be used, but which may not be too high, as this might cause the developing foam to collapse due to the provision of too much gas in the reacting system. A blowing catalyst which has a constant catalytic activity during the whole reaction time of the foam may be desired. Other criteria of the catalytic system may be the release of low or even no VOC’s from

the manufactured foam. Still an other criteria of the catalytic system may be the provision of a foam showing less or no tendency to fogging.
Preferably the catalytic system is able to react different polyisocyanates with different isocyanate reactive components is a similar or even identical way.

A catalyst with formula $(R^1R^2NR^3)_3N$ or $(R^1R^2NR^3)_2NCH_3$, wherein each of R^1 and R^2 are a methyl group, and R^3 $-CH_2CH_2OCH_2CH_2-$ is known from DE2618280.

Surprisingly we found several components that are suitable as blowing catalyst of a catalyst system for use in polyurethane and/or polyurea foam providing reactions, which blowing catalysts meet one or more of the criteria as set out above.

According to a first aspect of the present invention, the use is provided of a component according to one of the formulae I or II, formula I being $(R^1R^2NR^3)_2NR^4$, formula II being $(R^1R^2NR^3)NH_2$, wherein

- each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group and an n-propyl group;
- R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$;
- R^4 is chosen from the group consisting of a hydrogen and $-CH_2CH_2CH_2NH_2$,

as a blowing catalyst of a catalyst system in a reaction of at least one polyisocyanate component and at least one isocyanate-reactive component, the catalyst system further comprising at least one gelling catalyst different from said component of formula I or II.

Hence it functions as the blowing catalyst in a reactive system of, on the one hand, at least one, but optionally more than one polyisocyanate component, and on the other hand the combination of the at least one, and possibly more than one, isocyanate-reactive component and all other components other than the isocyanates in the reaction system, such as, as the case may be, the polyol, water, any additives such as surfactants, flame retardants, antioxidants, and amine catalysts.

The component according to one of the formulae I or II can be provide, in general, by a method for providing a secondary or tertiary amine with formula $(R^1R^2NR^3)_2NR^4$, wherein

- each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group and an n-propyl group;
- R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$;
- $R^{4'}$ is chosen from the group consisting of a hydrogen, a methyl group, an ethyl group, an iso-propyl group, an n-propyl group and a group with formula $R^1R^2NR^3$,

the method comprising the steps:

(α)reacting $R^1R^2NR^3(OH)$ with ammonia, thereby providing a mixture comprising $(R^1R^2NR^3)_2NR^{4'}$;

(β) separating $(R^1R^2NR^3)_2NR^{4'}$ from said mixture.

It was found that the reaction of ammonia with the $R^1R^2NR^3(OH)$, preferably in presence of a catalyst, provides mixtures of components, which mixtures comprise, next to the corresponding $(R^1R^2NR^3)_2NH$, at least one of a corresponding primary amine $R^1R^2NR^3NH_2$, a secondary amine $R^1R^2NR^3NR^5H$, and/or a tertiary amine $R^1R^2NR^3NR^5R^6$, wherein R^5 and optionally R^6 are identical to R^1 or R^2. Further, it was noticed that also other amines, with general formula $(R^1R^2NR^3)_2NR^{4'}$ may be obtained, for which $R^{4'}$ equals either R^1, R^2 or $(R^1R^2NR^3)$.

Without wishing to be bound by any theory, it is believed that these latter amines are provided by trans-alkylation of the alkyl groups on the amines.

As an example, in case of an alkanol with formula $R^1R^2NR^3(OH)$ wherein each of R^1 and R^2 are a methyl group, and wherein R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$

and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$, a mixture comprising an amine with formula $((CH_3)_2NR^3)_2NH$, and further comprising a primary amine of the general formula $(CH_3)_2NR^3NH_2$, a secondary amine of formula $(CH_3)_2NR^3NH(CH_3)$ and a tertiary amine with formula $(CH_3)_2NR^3N(CH_3)_2$ may be obtained. Also present in this mixture are components with formula $((CH_3)_2NR^3)_3N$, next to $((CH_3)_2NR^3)_2NCH_3$.

The $R^1R^2NR^3(OH)$ may be reacted with ammonia in presence of a catalyst.
So-called copper-chromite catalysts are examples of typical oxidic catalysts of Group I B/ VI B of Periodic Table of elements, which catalysts are suitable for the reaction of N,N-2-dialkylaminoalkoxyalkanol with ammonia.
Numerous promoters may be used, mainly comprising elements of the Groups I A and II A, IV B, IV A, VIII B. Other suitable catalysts for alcohol amination reaction are supported or non-supported catalysts of the Group of VIII B. Carriers for group VIII B metals are Al_2O_3, SiO_2, TiO_2, activated carbon, etc. Also, it is popular to add different promoters to such catalyst, mainly of the Groups I A and II A, IV B, IV A.
Carriers like Al_2O_3, SiO_2, TiO_2 may show appreciable activity for alcohol amination reactions. Promoters can be added, which are covering a wide range of components.
The separation of $(R^1R^2NR^3)_2NR^{4'}$ from the mixture may typically be done by distillation.
The distillation provides different fractions, of which typically the heavy fraction comprises ($(R^1R^2NR^3)_2NR^{4'}$, together with isomers of this molecule. Typically, in case of an amine with formula $(R^1R^2NR^3)_2NH$ wherein

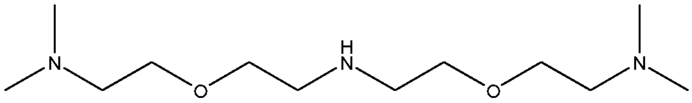
- each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group or an n-propyl group;
- R^3 being an alkoxyalkyl group chosen from the group consisting of -CH2CH2OCH2CH2-, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$,

the heavy fraction comprises $(R^1R^2NR^3)_2NH$, together with corresponding transalkylated amines with general formula $(R^1R^2NR^3)_2NR^{4'}$ for which $R^{4'}$ equals either R^1, R^2 or $(R^1R^2NR^3)$.

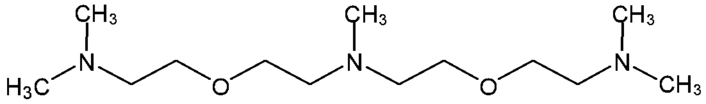
The component with formula $R^1R^2NR^3NH_2$, can be separated from the light fraction by a process as set out in the patent application PCT/EP2010/056143, hereby incorporated by reference in its entirety.

In case of bis-(N,N-2-dimethylamino-ethoxy-ethyl)-amine, the following compounds, additional to the primary amine of the general formula $(CH_3)_2NR^3NH_2$, the secondary amine of formula $(CH_3)_2NR^3NH(CH_3)$ and the tertiary amine with formula $(CH_3)_2NR^3N(CH_3)_2$, were found in the mixture obtained by reacting N,N-2-dimethylamino-ethoxy-ethanol with ammonia:

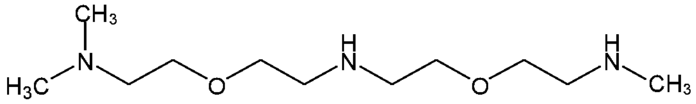
- bis(N,N-2-dimethylaminoethoxyethyl)amine



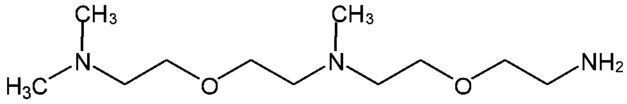
- bis(N,N-2-dimethylaminoethoxyethyl)methylamine:



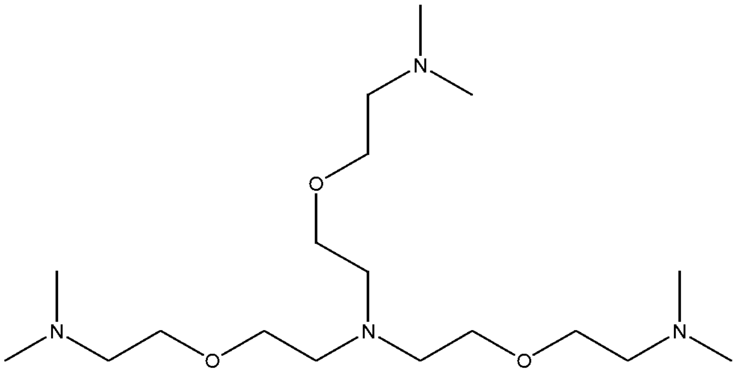
- [2-(2-Dimethylamino-ethoxy)-ethyl]-[2-(2-methylamino-ethoxy)-ethyl]-amine or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2-methyl-pentadecane:



- [2-(2-Amino-ethoxy)-ethyl]-[2-(2-dimethylamino-ethoxy)-ethyl]-methyl-amine or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2,8-dimethyl-tetradecane:



- and [2-(2-{Bis-[2-(2-dimethylamino-ethoxy)-ethyl]-amino}-ethoxy)-ethyl]-dimethyl-amine, (also referred to as TM33); MW 362,



Identification was done using by GC/MS- and NMR spectroscopy.

In order to separate $(R^1R^2NR^3)_2NH$ from $(R^1R^2NR^3)_2NR^{4'}$, $R^{4'}$ equaling either R^1 or R^2 or $(R^1R^2NR^3)$ can be done by first reacting the mixture of $(R^1R^2NR^3)_2NH$ and $(R^1R^2NR^3)_2NR^{4'}$, with formic acid HCOOH. Only $(R^1R^2NR^3)_2NH$ will undergo a formylation reaction, i.e. react with the formic acid, providing $(R^1R^2NR^3)_2NCOH$. This $(R^1R^2NR^3)_2NCOH$ can be separated from $(R^1R^2NR^3)_2NR^{4'}$ by distillation. The obtained $(R^1R^2NR^3)_2NCOH$ can thereafter be deformylated in alkalinic medium, e.g. in the presence of KOH, providing $(R^1R^2NR^3)_2NH$ and HCOOK.

As such $(R^1R^2NR^3)_2NH$ on the one hand, and $(R^1R^2NR^3)_2NR^{4'}$, $R^{4'}$ equaling either R^1 or R^2 or $(R^1R^2NR^3)$on the other hand may be obtained.

The $(R^1R^2NR^3)_2NH$ can be used as blowing catalyst as set out above, i.e. a product with formula $(R^1R^2NR^3)_2NR^4$, R^4 being hydrogen.

In the alternative, the tertiary amine with formula $(R^1R^2NR^3)_2NR^4$, wherein R^4 is $-CH_2CH_2CH_2NH_2$ can be obtained by first providing $(R^1R^2NR^3)_2NH$ as set out above, and thereafter converting this $(R^1R^2NR^3)_2NH$ into $(R^1R^2NR^3)_2NR^4$ by reacting $(R^1R^2NR^3)_2NH$ with acrilonitrile (R^4 being $-CH_2CH_2CH_2NH_2$).

According to some embodiments, the reaction of at least one polyisocyanate component and at least one isocyanate-reactive component may be carried out in presence of water.

According to some embodiments, the component may be a component according to formula I, R^4 being hydrogen.

According to some embodiments, R^1 and R^2 may be methyl

According to some embodiments, the component may be a component according to formula I, R^4 being $-CH_2CH_2CH_2NH_2$.

According to some embodiments, the at least one isocyanate-reactive component may be a polyamine.

By means of this use, a polyurea foam is provided.

Typical polyamines are e.g. amine terminated ethylene oxide and/or propylene oxide polymers, having two or more amine groups at the end of the polymer chain. Examples are the JEFFAMINE® polyoxyalkyleneamines of Huntsman International LLC.

According to some embodiments, the at least one isocyanate-reactive component may be a polyol.

By means of this use, a polyurethane foam is provided.

As good as any polyalcohol can be used. Typically polyether polyols or polyester polyols are used.

Given as examples of the polyether polyols are polyethylene glycol, polypropylene glycol, polypropylene glycol-ethylene glycol copolymer, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether polyols obtained by ring-opening copolymerisation of alkylene oxides, such as ethylene oxide and/or propylene oxide, with isocyanate-reactive initiators of functionality 2 to 8. The functionality of the isocyanate-reactive initiators is to be understood as the number of isocyanate-reactive hydrogen atoms per molecule initiator.

Polyester diols obtained by reacting a polyhydric alcohol and a polybasic acid are given as examples of the polyester polyols. As examples of the polyhydric alcohol, ethylene glycol, polyethylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,9-nonanediol, 2-methyl-1,8-octanediol, and the like can be given. As examples of the polybasic acid, phthalic acid, dimer acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid, sebacic acid, and the like can be given.

According to some embodiments, a polyurethane rigid foam may be provided
According to some embodiments, a polyurethane semi-rigid foam may be provided.
According to some embodiments, a polyurethane flexible foam may be provided.

According to some embodiments, the at least polyisocyanate component may be toluenediisocyanate (TDI) or diphenylmethane diisocyanate (MDI) – type polyisocyanate.

Suitable polyisocyanate compounds may comprise any number of polyisocyanates, including but not limited to, toluene diisocyanates (TDI), diphenylmethane diisocyanate (MDI) – type polyisocyanates, and prepolymers of these isocyanates., aliphatic isocyanates such as IPDI (isophoronediisocyanate) , and hexamethylene diisocyanate and derivatives thereof.

In case diphenylmethane diisocyanate (also known as methylene diphenyl diisocyanate, and referred to as MDI) is used, the diphenylmethane diisocyanate (MDI) can be in the form of its 2,4'-, 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof known in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates) having an isocyanate functionality of greater than 2, or any of their derivatives having a urethane, isocyanurate, allophonate, biuret, uretonimine, uretdione and/or iminooxadiazinedione groups and mixtures of the same.

Examples of other suitable polyisocyanates are tolylene diisocyanate (also known as toluene diisocyanate, and referred to as TDI), such as 2,4 TDI and 2,6 TDI in any suitable isomer mixture, hexamethylene diisocyanate (HMDI or HDI), isophorone diisocyanate

(IPDI), butylene diisocyanate, trimethylhexamethylene diisocyanate, di(isocyanatocyclohexyl)methane, e.g. 4,4'-diisocyanatodicyclohexylmethane (H_{12}MDI), isocyanatomethyl-1,8-octane diisocyanate and tetramethylxylene diisocyanate (TMXDI), 1,5-naphtalenediisocyanate (NDI), p-phenylenediisocyanate (PPDI), 1,4-cyclohexanediisocyanate (CDI), tolidine diisocyanate (TODI), any suitable mixture of these polyisocyanates, and any suitable mixture of one or more of these polyisocyanates with MDI in the form of its 2,4'-, 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof.

Preferred polyisocyanate compounds used for the present invention are polymeric or prepolymeric polyisocyanates, such a quasi-prepolymers, semi-prepolymers or full prepolymers, which may be obtained by reacting polyisocyanates, e.g. polyisocyanates as set out above, and preferably MDI-based polyisocyanates, with compounds containing isocyanate-reactive hydrogen atoms, typically polyamines or polyols.

In the use according to the invention, other additional catalytic components may be used.

Typically, when a polyurethane foamed material is to be provided, also a so-called gelling or gelating catalyst is added to catalyze the isocyanate-alcohol reaction. Typical catalysts are e.g. N-(3-dimethylaminopropyl) -N,N-diisopropanolamine (DPA), triethylenediamine (available from Huntsman as Jeffcat® TD-catalysts), N,N,N',N",N-pentamethyldipropylenetriamine, N,N,N-tris-(3-dimethylaminopropyl-)amine, N-(3-dimethylaminopropyl)-N,N-diisopropanolamine, N'-(3-(dimethylaminopropyl)-N,N-dimethyl-1,3-propanediamine, Jeffcat® LE-310, Jeffcat® Z-131, or combinations thereof.

Also additional blowing catalysts may be added, such as e.g. 2,2-dimorpholinodiethylether, N,N,N'-trimethyl-N'-hydroxyethyl-bisaminoethylether, , bis(2-dimethylaminoethyl)ether (available from Huntsman as Jeffcat® ZF catalysts), or combinations thereof.

According to some embodiments, the component may be a component according to formula I,

- each of R^1 and R^2 are a methyl group;
- R^3 being $-CH_2CH_2OCH_2CH_2-$;
- R^4 is hydrogen.

According to some embodiments of the present invention, the amount of blowing catalyst may typically range between 0.01 and 7 pbw. The amount of gelling catalyst may typically be in the range of 0.01 to 6 pbw. A typical amount of water may range between 0.01 and 50 pbw. These pbw are to be understood as gram per 100 grams of the components of the combination of isocyanate reactive components and all other components other than the isocyanates in the reaction system, such as, as the case may be, the polyol, water, any additives such as surfactants, flame retardants, antioxidants, and amine catalysts.

According to a second aspect of the present invention a method for providing a polyurethane or polyurea foamed material is provided. The method comprises

a. Providing ingredients of a reaction mixture, said ingredients being at least
    - a polyisocyanate component;
    - an isocyanate-reactive component;
    - water;
    - a catalyst system comprising at least first catalyst suitable as a gelling catalyst in an reaction of an polyisocyanate component and an isocyanate-reactive component and a second catalyst, different from said first catalyst and suitable as a blowing catalyst in an reaction of an polyisocyanate component and an isocyanate-reactive component, said second catalyst being a component according to one of the formulae I or II, formula I being $(R^1R^2NR^3)_2NR^4$, formula II being $(R^1R^2NR^3)NH_2$ wherein
        - each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group and an n-propyl group;

  - R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$;
  - R^4 is chosen from the group consisting of a hydrogen and $-CH_2CH_2CH_2NH_2$,

b. Reacting said polyisocyanate component, said water and said isocyanate-reactive component in the presence of said catalyst system.

According to a further, third aspect of the present invention, a catalyst system suitable for catalyzing the reaction of said polyisocyanate component, water and a isocyanate-reactive component to provide a foamed polyurethane or polyurea material is provided. the catalyst system comprises at least a first catalyst suitable as a gelling catalyst in an reaction of an polyisocyanate component and an isocyanate-reactive component and a second catalyst, different from said first catalyst and suitable as a blowing catalyst in an reaction of an polyisocyanate component and an isocyanate-reactive component, said second catalyst being a component according to one of the formulae I or II, formula I being $(R^1R^2NR^3)_2NR^4$, formula II being $(R^1R^2NR^3)NH_2$ wherein

- each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group and an n-propyl group;
- R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$;
- R^4 is chosen from the group consisting of a hydrogen and $-CH_2CH_2CH_2NH_2$.

According to a further fourth aspect of the present invention, a primary amine is provided, which primary amine has the formula$(R^1R^2NR^3)_2NR^4$ wherein

  - each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group and an n-propyl group;
  - R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$

and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$;

- R^4 is $-CH_2CH_2CH_2NH_2$.

The independent and dependent claims set out particular and preferred features of the invention. Features from the dependent claims may be combined with features of the independent or other dependent claims as appropriate.

The above and other characteristics, features and advantages of the present invention will become apparent from the following detailed description which illustrates, by way of example, the principles of the invention. This description is given for the sake of example only, without limiting the scope of the invention.

The present invention will be described with respect to particular embodiments.
It is to be noticed that the term "comprising", used in the claims, should not be interpreted as being restricted to the means listed thereafter; it does not exclude other elements or steps. It is thus to be interpreted as specifying the presence of the stated features, steps or components as referred to, but does not preclude the presence or addition of one or more other features, steps or components, or groups thereof. Thus, the scope of the expression "a device comprising means A and B" should not be limited to devices consisting only of components A and B. It means that with respect to the present invention, the only relevant components of the device are A and B.
Throughout this specification, reference to "one embodiment" or "an embodiment" are made. Such references indicate that a particular feature, described in relation to the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment, though they could. Furthermore, the particular features or characteristics may be combined in any suitable manner in one or more embodiments, as would be apparent to one of ordinary skill in the art.

The following terms are provided solely to aid in the understanding of the invention.

A gelling catalyst is to be understood as a catalyst mainly catalyzing the reaction of isocyanate groups with alcohol groups, though sometimes also the reaction of isocyanate groups with water may be catalyzed to a minor extent.

A blowing catalyst is to be understood as a catalyst mainly catalyzing the reaction of isocyanate groups with water, though sometime also the reaction of isocyanate groups with alcohols or amines may be catalyzed to a minor extent.

Unless otherwise indicated, %w and w% of a component indicate the weight of the component over the total weight of the composition it forms part of.

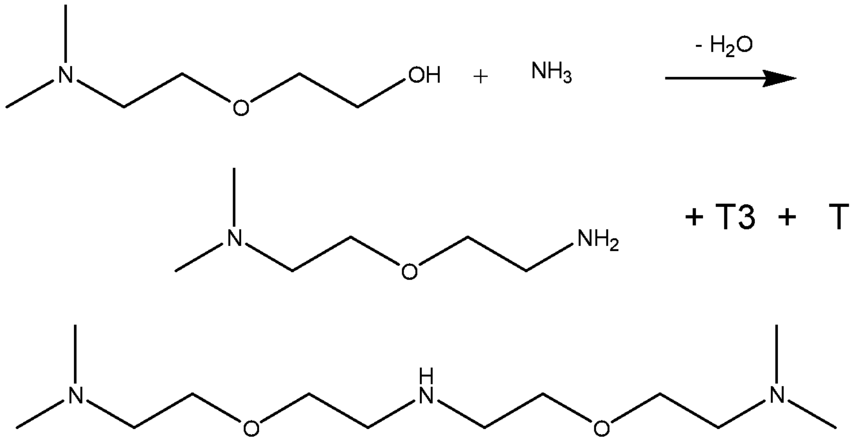
The various aspects of the present invention will further be described in detail by means of one or more examples relating to the use of Bis-(N,N-2-dimethylaminoethoxyethyl)amine (also referred to as T22), Bis-(N,N-2-dimethylaminoethoxyethyl)formamide (also referred to as T22-formamide) and the reduced adduct of acrilonitrile and Bis-(N,N-2-dimethylaminoethoxyethyl)amine (also referred to as T22-ACN-reduced).

First, the provision of Bis-(N,N-2-dimethylaminoethoxyethyl)amine from a mixture further comprising N,N-dimethylbisaminoethylether (T2MBAEE or T2), N,N,N'-trimethylbisaminoethylether (T3MBAEE or T3), and/or N,N,N',N'-tetramethylbisaminoethylether (T4MBAEE or T4) as well as the provision of Bis-(N,N-2-dimethylaminoethoxyethyl)amine and alkylated Bis-(N,N-2-dimethylaminoethoxyethyl)amin such as in particular Bis-(N,N-2-dimethylaminoethoxyethyl)methylamine, and [2-(2-{Bis-[2-(2-dimethylamino-ethoxy)-ethyl]-amino}-ethoxy)-ethyl]-dimethyl-amine will be explained.

The skilled person however understands that the same principle applies for preparation of any other secondary amines with formula $(R^1R^2NR^3)_2NH$ wherein

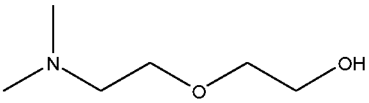
- each of R^1 and R^2 and are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group or an n-propyl group;
- R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$.

N,N-2-dimethylaminoethoxyethylamine, (also referred to as N,N-dimethylaminoethoxyethylamine, T2 or T2MBAEE), was synthesized by reacting N,N-2-dimethyl-aminoethoxyethanol with ammonia over a copper-chromite catalyst. The reaction scheme looks like:

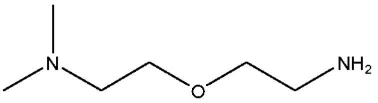


Wherein T3 refers to N,N,N'-trimethylbisaminoethylether (or T3MBAEE) and wherein T4 refers to N,N,N',N'-tetramethylbisaminoethylether (also known as T4MBAEE or JEFFCAT® ZF-20). N,N-2-dimethyl-aminoethoxyethanol is also known as JEFFCAT® ZR-70.

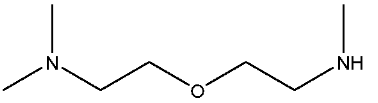
In the reactor effluent the following materials were identified:



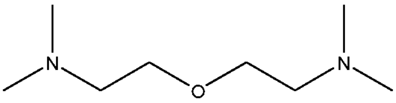
N,N-2-dimethylaminoethoxyethanol



N,N-2-dimethyaminoethoxyethylamine (also referred to as T2)

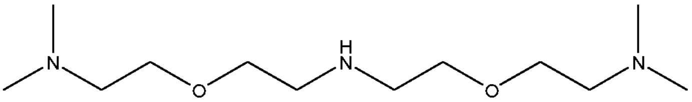


N,N,N'-trimethylbisaminoethylether (also referred to as T3) and



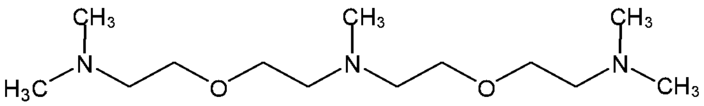
N,N,N',N'-tetramethylbisaminoethylether (also referred to as T4).

Also, a dimerized form of T2 was detected in the reactor effluent as a main component, which is:



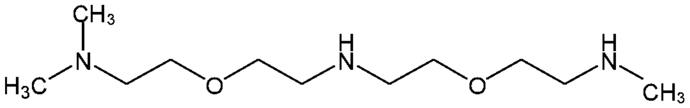
Bis-(N,N-2-dimethylaminoethoxyethyl)amine (hereinafter also referred to as "T22" or "T2-dimer"), molecular weight (hereinafter MW) 247.

Further other components were identified as various compounds structurally similar to bis-(N,N-2-dimethylamino-ethoxy-ethyl)-amine, e.g. the methylated derivative of N,N-bis(2-aminoethoxyethyl-)amine, having the structure:

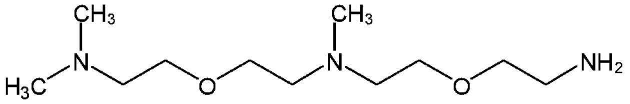


i.e. bis-(N,N-2-dimethylaminoethoxyethy-l)methylamine (also referred to as "TM22") or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2,8,14-trimethyl-pentadecane), MW 261.

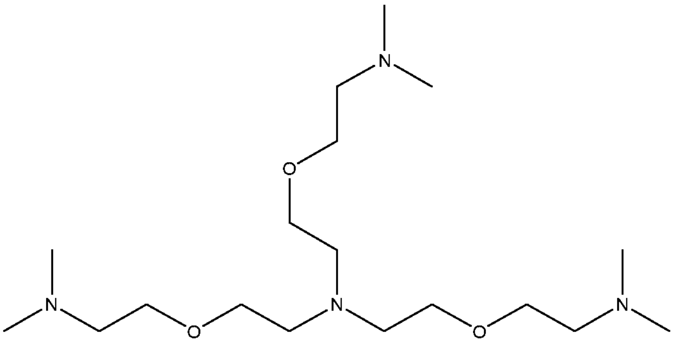
Further components having a similar structure as T22 are



[2-(2-Dimethylamino-ethoxy)-ethyl]-[2-(2-methylamino-ethoxy)-ethyl]-amine or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2-methyl-pentadecane, MW 233, and



[2-(2-Amino-ethoxy)-ethyl]-[2-(2-dimethylamino-ethoxy)-ethyl]-methyl-amine or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2,8-dimethyl-tetradecane; MW 233, and some minor amount of



[2-(2-{Bis-[2-(2-dimethylamino-ethoxy)-ethyl]-amino}-ethoxy)-ethyl]-dimethyl-amine; MW 362.

The reactor effluent was split by distillation into three fractions:

- a light fraction, essentially consisting of water and morpholines.
- a middle fraction containing T2, T3, T4 and N,N-2-dimethylaminoethoxyethanol, and
- a heavy fraction consisting mainly of bis-(N,N-2-dimethylaminoethoxyethyl)amine and the other heavy components.

Example 1: provision of T2/T3/T4/T22 mixture by reacting dimethylaminoethoxyethanol with ammonia.

A 1000 ml stainless steel reactor was charged with 2000 g commercial $2CuOxCr_2O_3$ catalyst (CAS# 99328-50-4, from Aldrich). The head of the continuous reactor system was connected with separate inlet lines and feed pumps for liquid ammonia and dimethylaminoethoxyethanol.

Ammonia and N,N-2-dimethylaminoethoxyethanol were charged to the reactor at different reaction conditions, as shown in Table 1. The reactor effluents were taken off at the bottom of the reactor, depressurized, degassed and collected for analysis and further use. All running conditions and compositions of the reactor effluents are shown in Table 1.

Table 1: Running conditions and product composition

Reaction conditions	unit	Run 1	Run 2	Run 3	Run 4	Run 5
Reactor temperature	°C	170	180	190	200	170
Reactor pressure	bar	70	70	70	70	70
Catalyst load - ammonia - N,N-2-dimethylaminoethoxyethanol	 ltr / h ltr / h	 0.1 0.5	 0.1 0.5	 0.1 0.5	 0.1 0.5	 0.1 0.13
Mol ratio ammonia versus N,N-2-dimethylaminoethoxyethanol		1.6 : 1	1.6 : 1	1.6 : 1	1.6 : 1	6 : 1
Product composition [wt.-%]						
Compound		Run 1	Run 2	Run 3	Run 4	Run 5
morpholine	[wt.-%]	0,18	0,53	0,79	1,12	0,37
N-methylmorpholine	[wt.-%]	0,26	0,70	1,16	1,89	0,30
N,N-2-dimethylaminoethoxyethylamine	[wt.-%]	6,63	6,61	8,60	7,96	13,88
N,N,N’-trimethylbisaminoethylether	[wt.-%]	0,38	0,95	1,69	2,31	0,08
N,N,N’,N’-	[wt.-%]	0,52	1,71	1,80	2,71	0,40

tetramethylbisaminoethylether						
N,N-2-dimethylaminoethoxyethanol	[wt.-%]	79,32	67,34	52,92	47,23	51,48
bis-(N,N-2-dimethylaminoethoxyethyl)amine	[wt.-%]	9,25	13,18	20,82	21,14	25,60
compounds structurally similar to bis-(N,N-2-dimethylamino-ethoxy-ethyl)-amine	[wt.-%]	3,64	8,98	12,22	15,64	7,12

All reactor effluents were combined (resulting in 8500 g crude material) and fractioned on a batch-type distillation tower, containing structured packings, having a total packing length of 100 cm. A main split was carried out to divide the combined reactor effluents in to three fractions. Fraction#1 and fraction#2 were collected as overhead products, whereas fraction#3 was taken as the residue stream.

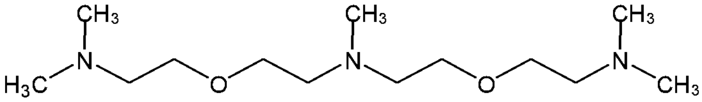
Fraction#1 was containing all reaction water and various light boiling components like morpholine, N-methylmorpholine and others. Fraction#2 contained mainly N,N-2-dimethylaminoethoxyethylamine, N,N,N'-trimethylbisaminoethylether, N,N,N',N'-tetramethylbisaminoethylether, and N,N-2-dimethyl-aminoethoxyethanol. Working conditions and results of the main split distillation are shown in Table 2.

Table 2: Conditions and results of main splitting distillation forming fractions#1 and fraction#2

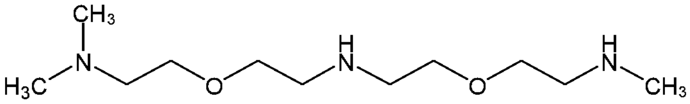
	unit	fraction #1, Example 1	fraction #2, Example 1
Boiling range, head temperature	°C	48-98	98-133
Boiling range, pot temperature	°C	92-143	143-145
Pressure	mbar	100	100
Reflux : take off ratio (vapour divider)		05:01	15:01
product composition [wt.-%] *)		fraction #1, Example 1	fraction #2, Example 1
morpholine	[wt.-%]	nd	0.43
N-methylmorpholine	[wt.-%]	nd	0.22
N,N-2-dimethylaminoethoxyethylamine (= A)	[wt.-%]	nd	40.07
N,N,N'-trimethylbis-aminoethylether (= B)	[wt.-%]	nd	11.01

N,N,N',N'-tetramethylbisaminoethylether (= C)	[wt.-%]	nd	14.70
N,N-2-dimethylaminoethoxyethanol	[wt.-%]	nd	29.51
bis-(N,N-2-dimethylaminoethoxyethyl)amine	[wt.-%]	nd	0.01
other components	[wt.-%]	nd	4.05
Ratio A : B : C * = based on water free material nd = not determined		nd	40:11:15

The bottom fractions was retained as residue fraction#3. GC-analysis of this residue-fraction#3, showed that it consists mainly of bis-(N,N-2-dimethylaminoethoxyethyl)amine and some other components. Further examination and analysis showed that these other components are structurally similar to bis-(N,N-2-dimethylaminoethoxyethyl)amine, some being identified as

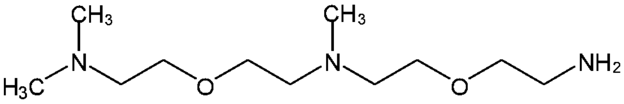


bis-(N,N-2-dimethylaminoethoxyethy-l)methylamine (also referred to as "TM22") or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2,8,14-trimethyl-pentadecane), MW 261, and



[2-(2-Dimethylamino-ethoxy)-ethyl]-[2-(2-methylamino-ethoxy)-ethyl]-amine or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2-methyl-pentadecane.

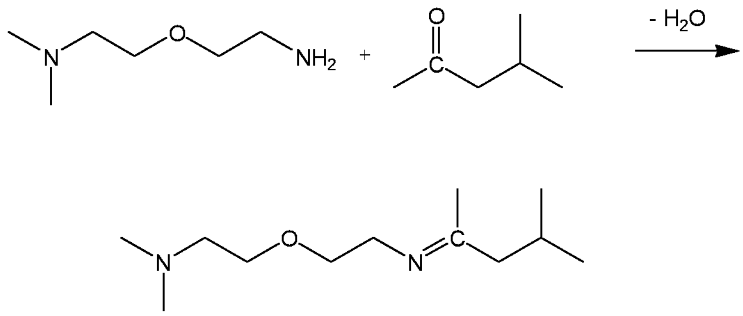
There are indications that another trace-impurity in T22 is



[2-(2-Amino-ethoxy)-ethyl]-[2-(2-dimethylamino-ethoxy)-ethyl]-methyl-amine or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2,8-dimethyl-tetradecane; MW 233. Also some [2-(2-{Bis-[2-(2-dimethylamino-ethoxy)-ethyl]-amino}-ethoxy)-ethyl]-dimethyl-amine was identified.

From fraction#2 containing mainly N,N-2-dimethylaminoethoxyethylamine, N,N,N’-trimethylbisaminoethylether, N,N,N’,N’-tetramethylbisaminoethylether, and N,N-2-dimethyl-aminoethoxyethanol, the N,N-2-dimethylaminoethoxyethylamine can be separated by reacting the mixture with e.g. MIBK.

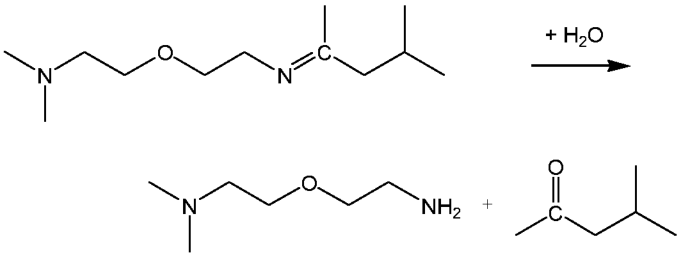
The separation of the product mixture was in particular obtained by using MIBK via a Schiff base formation by following reaction scheme.



MIBK – Schiff base of T2, being {2-[2-(1,3-Dimethyl-butylideneamino)-ethoxy]-ethyl}-dimethyl-amine.

This T2- based imine has a boiling point estimated above 300 °C. A boiling point of 160 to 161 °C was measured at 1 mbar vacuum.

This way, after the Schiff base is formed by dewatering, a mixture of N,N,N’-trimethylbisaminoethylether and N,N,N’,N’-tetramethylbisaminoethylether is removed by vacuum distillation from the high boiling Schiff base. Thereafter, the remaining Schiff base is hydrolyzed back by a large excess of water and simultaneously removal of the formed MIBK by an azeotropic distillation. Substantially pure N,N-2-dimethylaminoethoxyethylamine is remaining in the distillation flask and optionally a subsequent fine fractionation delivers purified N,N-2-dimethylbisaminoethylether.



The recovered N,N-2-dimethylaminoethoxyethylamine shows after distillation a purity of 99+ wt.-%, whereas the N,N,N'-trimethylbisaminoethylether / N,N,N',N'-tetramethylbisaminoethylether mixture was substantially free of N,N-2-dimethylaminoethoxyethylamine.

For Schiff base reaction, MIBK (methylisobutylketone) can be replaced by various other carbonyl compounds. Other carbonyl compounds are e.g. cyclohexanone, isovaleraldehyde and alike. In case of MIBK, no azeotropic entraining agent is necessary, because MIBK acts as both as reagent for the Schiff base formation and as entraining agent as well. If other carbonyl compounds are chosen usually suitable entraining solvents are needed, preferably being hydrocarbons, such as methylcyclohexane, toluene or xylene or a xylene isomer blend.

The bottom fractions which was retained as residue fraction#3, this heavy fraction could be recovered as follows:
The heavy fraction was distilled at different vacuum- and temperature conditions on a batch-type distillation tower, containing structured packing, having a total packing length of 100 cm. After a short transition fraction, fraction#4, two product fractions, fraction#5 and fraction#6 were taken.

Working conditions and results of distillation of residue-fraction#3 are shown in **Table 3.**

Table 3: conditions and results of distillation of residue-fraction#3

	unit	Example 1, fraction #4	Example 1, fraction #5	Example 1, fraction #6
Boiling range, head temperature	°C	20 - 20	120 - 125	125 - 128
Boiling range, pot temperature	°C	20 - 120	169 - 174	174 - 175
Pressure	mbar	7	7	7
Reflux : take off ratio (vapour divider)		2 : 1	2 : 1	2 : 1
product composition [wt.-%] *)	[wt.-%]	Example 1, fraction #4	Example 1, fraction #5	Example 1, fraction #6
morpholine	[wt.-%]	nd	0	0
N-methylmorpholine	[wt.-%]	nd	0	0
N,N-2-dimethylaminoethoxyethylamine (= **A**)	[wt.-%]	nd	0	0
N,N,N'-trimethylbis-aminoethylether (= **B**)	[wt.-%]	nd	0	0
N,N,N',N'-tetramethylbisaminoethylether (= **C**)	[wt.-%]	nd	0	0
N,N-2-dimethylaminoethoxyethanol	[wt.-%]	nd	0.17	0.01
bis-(N,N-2-dimethylaminoethoxyethyl)amine	[wt.-%]	nd	83.83	81.02
compounds structurally similar to bis-(N,N-2-dimethylamino-ethoxy-ethyl)-amine	[wt.-%]	nd	16.0	18.97
* = based on water free material nd = not determined				

868 g of **fraction#5/Example1** was filled in to a 2 liter distillation flask of a batch type distillation tower containing structured packings (packing length = 1 m).

A careful fractionation resulted 470.2 g of a product (fine fraction #2 in table 4) containing 87.7 wt.-% bis-(N,N-2-dimethyl-aminoethoxyethyl)amine ("T22").
Conditions and results are shown in **Table 4**.

Table 4: Conditions and results of fine fractionation of **fraction#5 / Example 1**

	unit	Fine fraction #1,	Fine fraction #2,
Boiling range, head temperature	°C	150-151	151-152
Boiling range, pot temperature	°C	173-174	174
Pressure	mbar	7	7
Reflux : take off ratio (vapour divider)		20:01	20:01

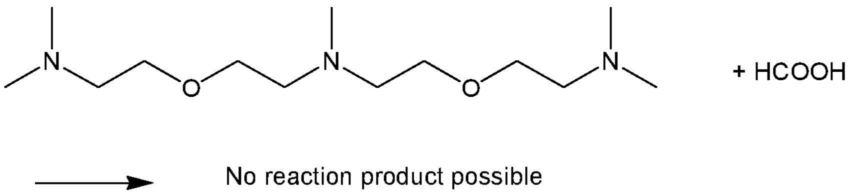
product composition [wt.-%] *)	[wt.-%]	Fine fraction #1,	Fine fraction #2,
N,N-2-dimethylaminoethoxyethanol	[wt.-%]	nd	0
bis-(N,N-2-dimethylaminoethoxyethyl)amine	[wt.-%]	nd	87.73
bis-(N,N-2-dimethylaminoethoxyethy-l)methylamine	[wt.-%]	nd	8.81
[2-(2-Amino-ethoxy)-ethyl]-[2-(2-dimethylamino-ethoxy)-ethyl]-methyl-amine	[wt.-%]	nd	3.46
* = based on water free material nd = not determined			

The structure of bis-(N,N-2-dimethyl-aminoethoxyethyl)amine was verified by GC/MS spectroscopy. The other components were identified as structural isomer of bis-(N,N-2-dimethylamino-ethoxy-ethyl)-amine or compounds structurally similar to bis-(N,N-2-dimethylamino-ethoxy-ethyl)-amine.

A boiling point of 300 °C is estimated for bis-(N,N-2-dimethylamino-ethoxy-ethyl)-amine. A boiling point of 150-152 °C at 7 mbar vacuum is measured

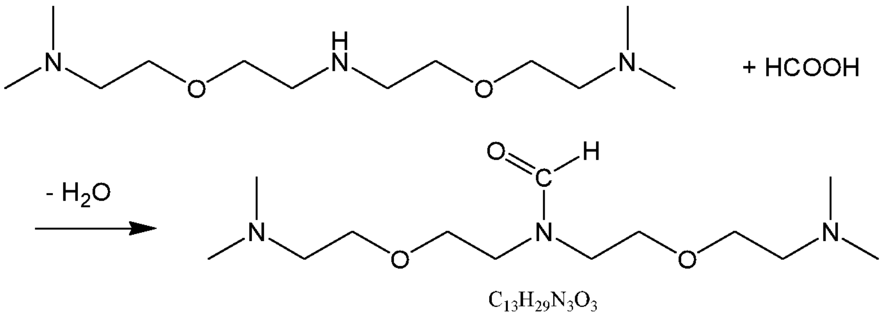
To separate and refine T22 from this mixture, the fractions #5 and/or #6 of example 1 were reacted with formic acid.

TM22 could not react with the formic acid



Following reactions occurred:

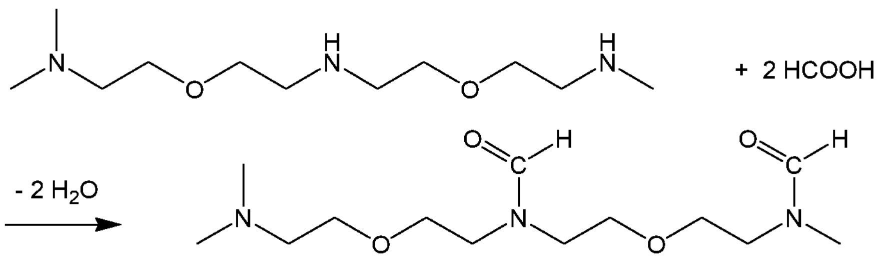
Reaction 1



$C_{13}H_{29}N_3O_3$
Mol. Wt.: 275,39

N,*N*-Bis-[2-(2-dimethylamino-ethoxy)-ethyl]-formamide

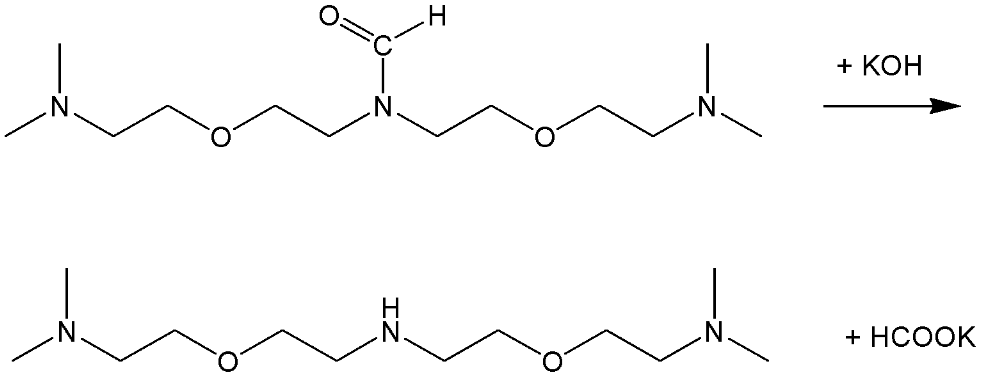
Reaction 2



It can be easily seen from these reactions, that TM22 does not form any formylation product. T22 is provided by such a formylation reaction and by addition of one formyl group a mono formamide, namely N,N-Bis-[2-(2-dimethylamino-ethoxy)-ethyl]-formamide (reaction 1), whereas the formylation reaction shown by reaction 2 is resulting a product having two formyl groups in the molecule. A result of this measure is a large differentiation of the boiling points of TM22 and the formed formamides. By a simple vacuum distillation, optionally even without utilizing a fractionation tower, TM22 appears as a "light end component". The N,N-bis-[2-(2-dimethylamino-ethoxy)-ethyl]-formamide is forming the main fraction, having a purity of 98 % or more (the remainder being impurities due to the reaction steps as described above), whereas the other formamide as shown in reaction 2 is remaining in the distillation residue due to the difference of its boiling point with the N,N-Bis-[2-(2-dimethylamino-ethoxy)-ethyl]-formamide.

Subsequent deformylation of the N,N-bis-[2-(2-dimethylamino-ethoxy)-ethyl]-formamide provides T22 in good yield and appreciable purity. Such a deformylation reaction can be carried out under acidic or alkalinic reaction condition. In the following reaction 3 alkalinic conditions were chosen using e.g. potassium hydroxide.

Reaction 3



The fraction 5 was further refined and bis-(N,N-2-dimethyl-aminoethoxyethyl)amine was separated from the other bis-(N,N-2-dimethyl-aminoethoxyethyl)amine isomers, by distillation. To remove the light fraction, the temperature of the mixture in the reactor may be chosen in the range of 173-175 °C, the temperature of the head of the column may be chosen in the range of 150-151 °C. The pressure can be 7 mbar. To remove the middle fraction, the temperature of the mixture in the reactor may be chosen in the range of 174-175 °C, the temperature of the head of the column may be chosen in the range of 151-152 °C. The pressure may be 7 mbar. The column may comprise of 15-30 trays of structured packing.

Substantially pure bis-(N,N-2-dimethyl-aminoethoxyethyl)amine was obtained, i.e. bis-(N,N-2-dimethyl-aminoethoxyethyl)amine with a purity of 87 w%. Remaining compounds are bis-(N,N-2-dimethylaminoethoxyethy-l)methylamine (also referred to as "TM22") or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2,8,14-trimethyl-pentadecane), MW 261 (0.1 – 18 w%) and [2-(2-Dimethylamino-ethoxy)-ethyl]-[2-(2-methylamino-ethoxy)-ethyl]-amine or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2-methyl-pentadecane (0.1-18 w%) and [2-(2-Amino-ethoxy)-ethyl]-[2-(2-dimethylamino-ethoxy)-ethyl]-methyl-amine or by IUPAC nomenclature: 2,8,14-triaza-5,11-dioxa-2,8-dimethyl-tetradecane; MW 233 (0.1-18 w%). Some other unknown high boiling components may be present.

To provide the reduced adduct of N,N-Bis-[2-(2-dimethylamino-ethoxy)-ethyl]- amine and acrylonitrile, following multiple step process was applied.

a- Cyanoethylation of bis-(N,N-2-dimethylaminoethoxyethyl)amine

400 g of “crude T22” bis-(N,N-2-dimethylaminoethoxyethyl)amine were recycled through a reactor column of 27 mm inner diameter, 80 cm length, filled with 200 ml of Amberlyst® A26 (Rohm & Haas, via Aldrich). Over a total period 24 hours were 71 g of acrylonitrile added to the recycle stream. During this cyanoethylation step the reaction temperature was kept at 50 °C. After the end of the reaction period the reaction mixture was carefully filtered and used for the subsequent nitrile hydrogenation step.

b- Nitrile hydrogenation of the cyanoethylated bis-(N,N-2-dimethylaminoethoxyethyl)amine.

The cyanoethylated bis-(N,N-2-dimethylaminoethoxyethyl)amine of step a-) was hydrogenated over a Raney® 2786 catalyst (Grace Corp., available from Aldrich) placed in a 100 ml reactor at 70 bar and 120°C. The hydrogenation feedstock was sent over the catalyst bed by a total chargetime of 24 hours and aprox. 10 g ventgas / liquid*hours. Apart of some losses by washing the catalyst bed all hydrogenated material was collected for further working up.

c- Distillation of hydrogenated nitrile

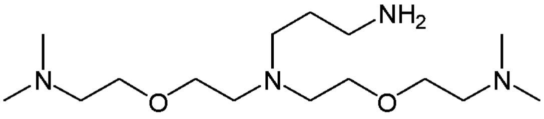
400 g hydrogenated reactor effluent were transferred in to a Büchi-Rotavapor® apparatus an subsequently flash-distilled. After a small fore-cut, taken up to 80°C head temperature

at a pressure of 100 mbar, the bulk of material was distilled at 1 mbar up to 180 °C head temperature. In total were 340 g distillate collected. The flash-distillate was fractionated on a batch-type distillation tower, containing structured packings (Sulzer® EX), having a total packing length of 100 cm. Working conditions and results of this distillation are shown in **Table 5.**

Table 5: Purification of N,N-bis-[2-(2-dimethylaminoethoxy)ethyl]propanane-1,3-diamine

	unit	Example7 fraction #1	Example7 fraction #2	Example7 fraction #3
Boiling range, head temperature	°C	166 - 170	170	170
Boiling range, pot temperature	°C	20 - 215	215 - 264	264 - 268
Pressure	mbar	2	2	2
Reflux : take off ratio (vapour divider)		10 : 1	10 : 1	10 : 1
product composition [wt.-%] *)	[wt.-%]	Example7 fraction #1	Example7 fraction #2	Example7 fraction #3
N,N-bis-[2-(2-dimethylaminoethoxy)ethyl]-propanane-1,3-diamine	[wt.-%]	nd	97.19	97.19
∑ unknowns	[wt.-%]	nd	2.81	2.81
nd = not determined				

The fractions #2 and #3 combined, straight after the end of the distillation resulting 250 g product in total. This material was investigated by GC analysis and GC/MS spectroscopy. The product was identified by GC/MS spectroscopy to be N,N-bis-[2-(2-dimethylaminoethoxy)ethyl]propanane-1,3-diamine and is therewith in conformity with the structure:



$C_{15}H_{36}N_4O_2$
Mol. Wt.: 304,47

N,N-bis-[2-(2-dimethylaminoethoxy)ethyl]propanane-1,3-diamine

The purity of the product was found to be 97.19 wt.-% by GC. The estimated atmospheric boiling point is expected to be between 380 and 450 °C, the liquid density at 20 °C was determined as 0.94 g/ml.

Following different components were used as a blowing catalyst component of a catalyst system in the production of flexible polyurethane foam:

A*	Jeffcat® ZF-22 = bis-(2-dimethylaminoethyl)ether at 70%w in dipropyleneglycol
B	T2 = N,N-dimethylbisaminoethylether
C	T22 = N,N-Bis-[2-(2-dimethylamino-ethoxy)-ethyl]- amine
D*	TM22 = N,N-Bis-[2-(2-dimethylamino-ethoxy)-ethyl]-methyl- amine
E*	T22-formamide = N,N-Bis-[2-(2-dimethylamino-ethoxy)-ethyl]-formamide
F	T22-ACN-adduct reduced = N,N-Bis-[2-(2-dimethylamino-ethoxy)-ethyl]-N-3-aminopropylamine, also referred to as [2-(2-{[2-(2-aminoethoxy)ethyl](3-aminopropyl)amino}ethoxy)ethyl]dimethylamine

* are comparative catalyst components

Component B is a component according to formula II, i.e. $(R^1R^2NR^3)NH_2$.

Components C, and F are components according to the formula I, i.e.
$(R^1R^2NR^3)_2NR^4$

In both formulae,

- each of R^1 and R^2 are a methyl groups;
- R^3 are $-CH_2CH_2OCH_2CH_2-$;
- R^4 is
  - a hydrogen (component C),
  - $-CH_2CH_2CH_2NH_2$ (component F)

In the formulations, Jeffcat® DPA was used as the gelling catalyst component, being N-(3-dimethylaminopropyl) -N,N-diisopropanolamine.

The amount of blowing catalyst was defined for each of the components A to G, for providing a flexible foam with comparable Cream- , Top of Cup and Gelation times, in order to obtain comparable foam systems. Following formulations were compared:

Formulations:

	fA*	fB	fC1	fD*	fE*	fF	fC2
JEFFOL® G31-28	60.00	60.00	60.00	60.00	60.00	60.00	60.00
JEFFOL® PPG-3706	40.00	40.00	40.00	40.00	40.00	40.00	40.00
TEGOSTAB® B 8734 LF2	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Diethanolamine, 85% Low Freeze Grade	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Deionized Water	3.85	3.85	3.85	3.85	3.85	3.85	3.85
A: JEFFCAT® ZF-22 Amine Catalyst	0.10						
B: T2		0.60					
C: T22			0.53				
D: TM22				0.15			
E: T22-Formamide					0.72		
F: T22-ACN-Adduct (Reduced)						0.36	
C: T22							0.53
JEFFCAT® DPA Amine Catalyst	1.13	1.13	1.13	1.13	1.13	1.13	1.13
Formula Weight	106.68	107.18	107.11	106.73	107.30	106.94	107.11
Isocyanate Index	90	90	90	90	90	90	90
SUPRASEC® 7320	67.4	68.6	67.7	67.5	67.9	67.6	67.7

* formulations fA , fD and fE are comparative formulations
all amounts of the various components are expressed by weight parts

The component C (T22) used in fC1 comprises 88.7%w of T22, 9.2w% of TM22 and 2.1% of other components.

The component C (T22) used in fC2 comprises 87.7%w of T22, 8.8w% of TM22 and 3.5% of other components.

Jeffol® G31-28 of Huntsman International LLC is an EO tipped, dipropyleneglycol initiated PO-diol with Molecular weight of about 3800.

Jeffol® PPG-3706 of Huntsman International LLC is an EO tipped, glycerine initiated PO-triol with Molecular weight of about 6000

Tegostab® B 8734 LF2 is a silicone surfactant of Evonic.

SUPRASEC® 7320 of Huntsman International LLC is an MDI-based polyisocyanate being a mixture of polymeric MDI, an MDI prepolymer and an MDI isomer mixture.

A blend of the components set out above, except the polyisocyanate component, was made, containing the catalyst use level as set out in the table above. The blend was mixed for 5 minutes at 900 RPMs using the RYOBI® 10” Drill Press with EXACTLINE™ Laser System. To produce foam in an open box, 250 grams of the blend was poured into a Solo® 64 ounce lined paper cup and mixed with a 2 inch ITC Style Conn Blade® for 24 seconds and at 3050 RPMs, using the RYOBI® 10” Drill Press with EXACTLINE™ Laser System. A calculated amount of SUPRASEC® 7320 Isocyanate (Huntsman Corporation) was added and mixed for 6 seconds. At the end of 6 seconds, the contents were poured into a 12 inch by 6 inch by 6 inch open box and the foam was allowed to rise until completion was made.

The foam bun was allowed to cure for 30 minutes and after curing, three foam samples were extracted, using a Feather® No. 11 Disposable Scalpel, from three different areas and placed into three labeled 4 dram GC vials. Three 2 inch by 2 inch by 1 inch foam blocks were cut from three different areas, using the CRAFTSMAN® Professional 18 inch 4 Speed Metal/Wood Cutting Band Saw, and were analyzed for air flow and density. To determine the air flow, the Gulbrandsen Foam Porosity Measurement Instrument was turned on and the foam block was inserted. The high air flow valve was opened until the pressure read 125 kilopascals and the air flow reading was recorded in standard cubic feet per minute. To determine the density, the volume of the foam block was calculated and the weight of the foam sample was determine and using these two values, the density was calculated into pounds per cubic feet.

The Daimler thermal desorption analysis method PB VWL 709 which has both a VOC and a FOG component to the resultant data report was used to specify the VOC and FOG properties of the foams obtained. In this quantitative and dynamic headspace type test, VOC emissions are measured from a very small foam sample that is placed in a thermal desorption tube and continually flushed with an inert gas for thirty minutes at 90°C. The volatiles carried away by the flush gas are collected in a -150°C cryogenic trap and later reheated and conveyed into a GC/MS instrument for further analysis and calculation of total VOC (volatile organic chemicals) expressed in parts per million (ppm). In the FOG portion of the test, the same sample is heated to 120°C and is swept by the carrier gas for an additional one hour. Volatiles collected in the cryogenic trap are then analyzed by the GC/MS instrumentation to obtain the final FOG results.

Following results were obtained

formulation	Cream time (sec)	Top of cup time (sec)	Gelation time (sec)	Air flow (scfm)	Free rise density (pcf)
fA*	7	39	58	3.1	2.21
fB	7	40	55	3.4	1.93
fC1	7	40	55	3.2	2.14
fC2	8	39	56	3.1	2.13
fD*	7	38	55	2.9	2.9
fE*	7	39	54	3.1	3.1
fF	7	39	58	2.9	2.9

* are comparative formulations

In the VOC and FOG test, the components emitted were characterized and quantified as follows

VOC

Component (ppm)							
	fA*	fB	fC1	fC2	fD*	fE*	fF
A	137.6	0	0	0	0	0	0
B	0	0	0	0	0	0	0
C	0	0	0	0	0	0	0
D	0	0	19.8	38.4	71.95	0	0
E	0	0	0	0	0	0	0
F	0	0	0	0	0	0	0
DPA	0	0	0	0	0	0	0

Total VOC	219.9	55.2	102.19	61.22	148.35	79.22	51.88

FOG

Component (ppm)							
	fA*	fB	fC1	fC2	fD*	fE*	fF
A	0	0	0	0	0	0	0
B	0	0	0	0	0	0	0
C	0	0	0	0	0	0	0
D	0	0	29.4	38.4	125.45	0	0
E	0	0	0	0	0	719.1	0
F	0	0	0	0	0	0	0
DPA	0	0	0	0	0	0	0
Total FOG	120.7	79.95	139.8	168.35	281.85	843.95	125.8

As is clear from the figures above, the components T2, T22 and T22-ACN-adduct reduced does not show in the VOC and FOG tests. JEFFCAT® ZF-22 (fA) and TM22, either used as such (fD) of as a contaminant in the T22 (fC1 and fC2) contributes to VOC, and TM22 shows up in the FOG tests.

Thence using pure T22, comprising only about 0.1%w of TM22, will have a lower score rate at the total VOC and total FOG.

Also the component T22–formamide (fE) does not show up on the VOC tests, but does contribute in the FOG test.

Other polyurethane foams were made as follows:

1728 grams of a master batch solution composed of 100 parts of VARNOL 3136 (Dow chemical Co), 2.8 parts of deionized water, 1.0 parts of SURFONIC L-620 (Momentive Performance Materials), and JEFFCAT® TD-33a catalysts, 0.3 parts were thoroughly mixed together for 1 hour on a roller mixer. This polyol mixture, 249.84 grams, was added to a 1.8 liter paper cup. The correct amount of blowing catalysts, as indicated in the table below, was added to the cup. The mixture was then mixed at 2500 RPM for 7 seconds. Kosmos 15P, 0.72 ml (Evonik Goldschmidt) is added to the mixture and mixed with the 2500 RPM stirrer for seven seconds. Mondur TD-80, toluendediidocyanate (TDI) (Bayer), 93.89 grams is added and an additional seven seconds of mixing this mixture, using the 2500 RPM mixer, is completed. This mixture is then poured into a Cardboard box having a dimension of 30.4 by 15.2 by 15.2 cm. The cream time is noted. The time for the foam to rise above the top of the box is noted. The blow off time is also noted. After the foam is cured, three 5.1 by 5.1 by 2.54 cm foam blocks are cut from the center of the foam block. Air flow measurements are completed on these samples and averaged. The airflow data is also shown in the table.

Examples 1-7 – Flexible slab foams made with JEFFCAT TD-33A gel catalysts

	fH*	fI	fJ	fK	fL*	fM*	fN
Voranol 3136	240	240	240	240	240	240	240
Water	6.72	6.72	6.72	6.72	6.72	6.72	6.72
Niax L-620	2.4	2.4	2.4	2.4	2.4	2.4	2.4
JEFFCAT®TD-33A catalyst	0.72	0.72	0.72	0.72	0.72	0.72	0.72
Total Masterbatch	249.84	249.84	249.84	249.84	249.84	249.84	249.84
JEFFCAT®ZF-22 catalyst	0.24						
T2 -		1.32					
T22 -			1.06				
T22 crude -				1.06			
TM22 -					0.34		
T22-formamide -						1.06	
T22-ACN-adduct (reduced) -							0.79
Kosmos 15p	0.84	0.84	0.84	0.84	0.84	0.84	0.84
Index	110	110	110	110	110	110	110
Mondur TD-80 TDI	93.88	93.88	93.88	93.88	93.88	93.88	93.88
Properties of the foam							
Rise profile (times in seconds)							
CREAM TIME	9	9	9	9	9	9	9
TOP OF CUP	39	42	43	43	38	46	42
BLOWOFF TIME	99	102	103	103	96	103	102
Air flow, liters/min	90.6	53.8	62.3	68.0	84.9	90.6	68.0
DENSITY g/in^3	34.60	33.48	34.76	33.48	35.08	33.80	33.80

* formulations fH , fL and fM are comparative formulations
all amounts of the various components are expressed by weight parts

Examples 8-14 Flexible slab foams made with JEFFCAT DPA gel catalysts

	fO*	P	Q	fR	fS*	fT*	fU
Voranol 3136	240	240	240	240	240	240	240
Water	6.72	6.72	6.72	6.72	6.72	6.72	6.72
Niax L-620	2.4	2.4	2.4	2.4	2.4	2.4	2.4
JEFFCAT® DPA catalyst	0.72	0.72	0.72	0.72	0.72	0.72	0.72
Total Masterbatch	249.84	249.84	249.84	249.84	249.84	249.84	249.84
JEFFCAT® ZF-22 catalyst	0.24						
T2 -		1.32					
T22 -			1.06				
T22 crude -				1.06			
TM22 -					0.53		
T22-formamide -						1.2	
T22-CAN-adduct (reduced) -							0.79
Kosmos 15p	0.84	0.84	0.84	0.84	0.84	0.84	0.84
Index	110	110	110	110	110	110	110
Mondur TD-80 TDI	93.88	93.88	93.88	93.88	93.88	93.88	93.88
(Formulation Factor x 0.9)							
Rise profile (time in seconds)							
CREAM TIME	9	10	9	9	9	9	8
TOP OF CUP	41	42	45	42	39	42	38
BLOWOFF TIME	101	99	105	103	101	101	96
Air flow, liters/min	118.9	96.3	113.3	107.6	118.9	101.9	56.6
DENSITY g/in^3	34.44	35.72	33.16	33.00	33.80	33.32	36.36

* formulations fO , fS and fT are comparative formulations
all amounts of the various components are expressed by weight parts

It is to be understood that although preferred embodiments and/or materials have been discussed for providing embodiments according to the present invention, various modifications or changes may be made without departing from the scope and spirit of this invention.

CLAIMS

1.- The use of a component according to one of the formulae I or II, formula I being $(R^1R^2NR^3)_2NR^4$, formula II being $(R^1R^2NR^3)NH_2$, wherein

- each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group and an n-propyl group;
- R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$;
- R^4 is chosen from the group consisting of a hydrogenand $-CH_2CH_2CH_2NH_2$,

as a blowing catalyst of a catalyst system in a reaction of at least one polyisocyanate component and at least one isocyanate-reactive component, the catalyst system further comprising at least one gelling catalyst different from said component of formula I or II.

2.- The use according to claim 1, wherein the reaction of at least one polyisocyanate component and at least one isocyanate-reactive component is carried out in presence of water.

3.- The use according to claim 1 or 2, wherein said component is a component according to formula I, R^4 being hydrogen.

4.- The use according to claim 3, wherein R^1 and R^2 are methyl

5.- The use according to claim 1 or 2, wherein said component is a component according to formula I, R^4 being $-CH_2CH_2CH_2NH_2$.

6.- The use according to claim 1, wherein said component is a component according to formula I,

- each of R^1 and R^2 are a methyl group;
- R^3 being $-CH_2CH_2OCH_2CH_2-$;
- R^4 is hydrogen.

7.- The use according to any one of the claims 1 to 6, wherein the at least one isocyanate-reactive component is a polyamine.

8.- The use according to any one of the claims 1 to 6, wherein the at least one isocyanate-reactive component is a polyol.

9.- The use according to claim 8 for providing a polyurethane rigid foam or a semi-rigid foam.

10.- The use according to claim 8 for providing a polyurethane flexible foam.

11.- The use according to any one of the preceding claims, wherein the at least polyisocyanate component is toluenediisocyanate (TDI) or diphenylmethane diisocyanate (MDI) – type polyisocyanate.

12.- A method for providing a polyurethane or polyurea foamed material, said method comprising

a. Providing ingredients of a reaction mixture, said ingredients being at least
   - a polyisocyanate component;
   - an isocyanate-reactive component;
   - water;
   - a catalyst system comprising at least first catalyst suitable as a gelling catalyst in an reaction of an polyisocyanate component and an isocyanate-reactive component and a second catalyst, different from said first catalyst and suitable as a blowing catalyst in an reaction of an polyisocyanate component and an isocyanate-reactive component, said second catalyst being a component according to one of the formulae I or

II, formula I being $(R^1R^2NR^3)_2NR^4$, formula II being $(R^1R^2NR^3)NH_2$ wherein

- each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group and an n-propyl group;
- R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$;
- R^4 is chosen from the group consisting of a hydrogen and $-CH_2CH_2CH_2NH_2$,

b. Reacting said polyisocyanate component, said water and said isocyanate-reactive component in the presence of said catalyst system.

13.- A catalyst system suitable for catalyzing the reaction of said polyisocyanate component, water and a isocyanate-reactive component to provide a foamed polyurethane or polyurea material, said catalyst system comprising at least a first catalyst suitable as a gelling catalyst in an reaction of an polyisocyanate component and an isocyanate-reactive component and a second catalyst, different from said first catalyst and suitable as a blowing catalyst in an reaction of an polyisocyanate component and an isocyanate-reactive component, said second catalyst being a component according to one of the formulae I or II, formula I being $(R^1R^2NR^3)_2NR^4$, formula II being $(R^1R^2NR^3)NH_2$ wherein

- each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group and an n-propyl group;
- R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$;
- R^4 is chosen from the group consisting of a hydrogen and $-CH_2CH_2CH_2NH_2$.

14.- A primary amine having the formula$(R^1R^2NR^3)_2NR^4$ wherein

- each of R^1 and R^2 are chosen from the group consisting of a methyl group, an ethyl group, an iso-propyl group and an n-propyl group;
- R^3 being an alkoxyalkyl group chosen from the group consisting of $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2CH_2-$ and $-CH_2CH_2CH_2OCH_2CH_2CH_2-$;
- R^4 is $-CH_2CH_2CH_2NH_2$,

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/070611

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/18 C08G18/48 C08G18/66 C07C217/00 C07C213/02
C07C217/08
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)
C08G C07C

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/117479 A2 (HUNTSMAN SPEC CHEM CORP [US]; GRIGSBY ROBERT A [US]; RISTER ERNEST L [] 24 September 2009 (2009-09-24)	1,2,7-13
A	page 2, paragraph 2 - page 4, paragraph 1 page 7 pages 12-14; example 7 -----	3-6,14
A	DE 26 18 280 A1 (BAYER AG) 17 November 1977 (1977-11-17) cited in the application page 6, paragraph 3 - page 8, paragraph 2 pages 11,12,14 pages 14-25 -----	1-14
A	EP 2 196 493 A1 (AIR PROD & CHEM [US]) 16 June 2010 (2010-06-16) paragraphs [0030] - [0042]; examples 1-3; tables 1-4 ----- -/--	1-14

☒ 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

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search 14 May 2012	Date of mailing of the international search report 22/05/2012
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 Neugebauer, Ute

3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/070611

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 213 584 A (IZAIKU HIROUMI [JP] ET AL) 25 May 1993 (1993-05-25) example 4 -----	14

3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2011/070611

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: 1-13

   Use of an amine compound as specified in formulae I or II (see claim 1) as a blowing catalyst of a catalyst system in a reaction of at least one polyisocyanate component and at least one polyisocyanate-reactive component; a method for providing a polyurethane or polyurea foamed material; a catalyst system suitable for catalyzing the reaction of said components and water to provide a foamed polyurethane or polyurea material.

   ---

2. claim: 14

   Primary amine as specified.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/070611

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009117479 A2	24-09-2009	AU 2009225611 A1	24-09-2009
		CA 2717573 A1	24-09-2009
		CN 101977977 A	16-02-2011
		EP 2257592 A2	08-12-2010
		JP 2011515540 A	19-05-2011
		TW 201011051 A	16-03-2010
		US 2011009512 A1	13-01-2011
		WO 2009117479 A2	24-09-2009
DE 2618280 A1	17-11-1977	NONE	
EP 2196493 A1	16-06-2010	AT 546485 T	15-03-2012
		CN 101831043 A	15-09-2010
		EP 2196493 A1	16-06-2010
		ES 2380429 T3	11-05-2012
		US 2010152312 A1	17-06-2010
US 5213584 A	25-05-1993	AT 101390 T	15-02-1994
		CA 2020726 A1	11-01-1991
		DE 69006552 D1	24-03-1994
		DE 69006552 T2	30-06-1994
		DK 0407950 T3	06-06-1994
		EP 0407950 A1	16-01-1991
		ES 2062209 T3	16-12-1994
		JP 1971522 C	27-09-1995
		JP 3128933 A	31-05-1991
		JP 6102724 B	14-12-1994
		US 5213584 A	25-05-1993