(CONVENTION. By one or more persons and/or a Company.) Form 4

6

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

609548

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address (es).

~~I~~ We (1) HOECHST AKTIENGESELLSCHAFT

of 45 Bruningstrasse, D-6230 Frankfurt/Main 80,

Federal Republic of Germany

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)

PROCESS FOR THE PREPARATION OF TERTIARY N,N-DIMETHYLAMINES

(3) Here insert number(s) of basic application(s)

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered (3)

P37 41 726.6

(4) Here insert Name of basic Country or Countries, and basic date or dates

for a patent or similar protection made in (4) Federal Republic of Germany on 9th December 1987

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 6 · 2 · 91

~~My~~ Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys, 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 7th day of December 1988

(5) Signature (s) of Applicant (s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

(5) HOECHST AKTIENGESELLSCHAFT

by

D. B. Mischlewski

Registered Patent Attorney

08/12/88

To:

(CONVENTION. Company.)

Form 8.

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

(1) Here insert (in full) Name of Company.

In support of the Convention Application made by(1) HOECHST AKTIENGESELLSCHAFT

(2) Here insert title of Invention.

(hereinafter referred to as the applicant) for a patent for an invention entitled:(2) PROCESS FOR THE PREPARATION OF TERTIARY N,N-DIMETHYLAMINES

(3) Here insert full Name and Address, of Company official authorized to make declaration.

I,(3) X Dr. Karl-Heinz Reichelt

of X Hoechst Aktiengesellschaft Werk Ruhrchemie
X Postfach 13 01 60, 4200 Oberhausen 11

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.

(4) Here insert basic Country or Countries followed by date or dates and basic Applicant or Applicants.

2. The basic application as defined by Section 141 of the Act was made in(4) Federal Republic of Germany on the 9th day of December, 1987, ~~by~~ by HOECHST AKTIENGESELLSCHAFT

~~on the~~ .... ~~day of~~ .... ~~19~~ .... ~~, by.~~

(5) Here insert (in full) Name and Address of Actual Inventor or Inventors.

3.(5) DR. JÜRGEN WEBER, Bunsenstr. 17, D-4200 Oberhausen 11, DR. DETLEF KAMPMANN, Rankenweg 3, D-4630 Bochum 6 and CLAUS KNIEP, Rosenstr. 93, D-4200 Oberhausen 11; all of the Federal Republic of Germany

is/are the actual inventor of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The applicant is the assignee of DR. JÜRGEN WEBER, DR. DETLEF KAMPMANN and CLAUS KNIEP

4. The basic application referred to in paragraph 2 of this Declaration was .... the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at X Oberhausen 11

this X 18th day of X October 1990

(6) Signature.

(6) X Dr. Karl-heinz Reichelt

X (Dr. Karl-Heinz Reichelt
Procurist of
Hoechst Aktiengesellschaft)

To: THE COMMISSIONER OF PATENTS.

WATERMARK PATENT & TRADEMARK ATTORNEYS

(12) PATENT ABRIDGMENT (11) Document No. **AU-B-26670/88**
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. **609548**

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PROCESS FOR THE PREPARATION OF TERTIARY N,N-DIMETHYLAMINES

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(71) Applicant(s)
HOECHST AKTIENGESELLSCHAFT

(72) Inventor(s)
Dr. JURGEN WEBER; Dr. DETLEF KAMPMANN; CLAUS KNIEP

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS, Locked Bag 5, HAWTHORN VIC 3122

(56) Prior Art Documents
FR 2349569

(57) Claim

1.) Process for the preparation of tertiary N,N-dimethylamines by the reaction of primary amines with formaldehyde and hydrogen as starting materials under pressure and at elevated temperature on a nickel-containing hydrogenation catalyst in liquid phase, characterised in that the hydrogenation catalyst is suspended in a solvent, the nickel concentration is 0.1 to 10 % by weight, related to the primary amine to be used, the starting materials are separated from each other at 80 to 150°C and 1 to 15 MPa but are fed into the catalyst suspension at the same time with mixing and reacted in one reaction step to form tertiary N,N-dimethylamines.

609548

COMMONWEALTH OF AUSTRALIA

Form 10

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

		Class	Int. Class
Application Number:			
Lodged:			

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

This document contains the amendments made under Section 49 and is correct for printing.

Name of Applicant : HOECHST AKTIENGESELLSCHAFT

Address of Applicant : 45 Bruningstrasse, D-6230 Frankfurt/Main 80, Federal Republic of Germany

Actual Inventor: JURGEN WEBER, DETLEF KAMPMANN and CLAUS KNIEP

Address for Service :
EDWD. WATERS & SONS,
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

PROCESS FOR THE PREPARATION OF TERTIARY N,N-DIMETHYLAMINES

The following statement is a full description of this invention, including the best method of performing it known to : us

Process for the preparation of tertiary N,N-dimethylamines

The present invention relates to a process for the preparation of tertiary N,N-dimethylamines by the reaction of primary amines with formaldehyde and hydrogen on a hydrogenation catalyst in liquid phase. Any monovalent or multivalent primary amines as well as mixtures thereof can be used as the amines. The reaction takes place at elevated temperature and generally requires an elevated pressure. It results in the complete replacement of all the hydrogen atoms located on the amine nitrogen atom by a methyl group, water being formed. This reaction is also termed hydrogenating N-methylation of amines.

Tertiary amines are industrially significant compounds. They can serve as polymerisation and curing catalysts for the production of epoxy and urethane-based plastics. Moreover, they are suitable as corrosion inhibitors and adsorption agents for synthesis gas scrubbing. This applies in particular to the easily prepared dimethyl derivatives.

The hydrogenating methylation of primary amines with formaldehyde and hydrogen is an important synthesis route to the preparation of methylated amines. A summary of this process is to be found in Houben-Weyl, Methoden der organischen Chemie; Vol. XI/1, pages 641 to 643, 4th edition (1957).

According to DE-OS 19 32 422 the reaction can be performed using conventional fixed-bed catalysts in liquid phase.

The older application DE 37 21 539 describes a modified process. Here, the starting materials amine, formaldehyde and hydrogen are heated separately to a specified temperature and then mixed in the presence of a fixed-bed catalyst. The starting materials, in particular the formaldehyde, are to contain a reduced amount of water. The fixed catalysts are located in tubular reactors which can withstand the necessary high pressures.

However, it is also possible to dispense with the use of complicated high-pressure tubular reactors and to perform the reaction in stirred vessels or loop reactors, for example. In this case the hydrogenating N-methylation is conducted with the aid of a suspended hydrogenation catalyst. This process is also called the suspension method. The present invention relates to this process variation.

After prolonged use the hydrogenation catalysts decompose to an increasing extent. The resultant fine-grained particles are undesirable as they make the separation of the suspended catalyst after reaction more difficult. Normally, the suspended catalyst is removed by sedimentation and/or centrifugation and/or filtration. The finer the catalyst particles are, the more difficult it is to remove them from the reaction mixture. A smaller particle size means a reduction in the rate of sedimentation, which also has a negative effect on centrifugation. If filtration is employed to separate the catalyst, particularly small particles quickly block the filtration unit owing to clogging of the filter pores. This causes a rise in pressure in the apparatus with the result that filtration has to be interrupted to eliminate the clogging.

The incidence of formic acid, which probably forms from formaldehyde through the Cannizzaro reaction, is also undesirable. It removes a corresponding amount of amine from the reaction in the form of a salt. The free acid and the amine salt promote corrosion in the reactor system.

Further disruptive side reactions are a result of the polymerisation of formaldehyde with itself and the polycondensation between the amine and the formaldehyde to hexahydrotriazines or, in the case of multivalent amines, to higher molecular compounds. The formation of polymeric substances produces a reduction in the catalyst activity owing to caking of the suspended catalyst and can even lead to the reactor being blocked. The unavoidable consequence is that the catalyst has to be changed.

The EP-A 0 142 868 recommends for the N-alkylation of amines the use of special hydrogenation catalysts which contain at least one of the elements Co, Ni, Ru, Rh, Pd and Pt on carbon as a carrier. The catalyst is suspended in the amine and the carbonyl compound added continuously. Aluminium oxide, silicon dioxide and siliceous earth are undesirable as carriers for the hydrogenation catalysts since they do not ensure good distribution of the catalyst in the reaction system. Although metal catalysts without carriers, such as Raney nickel, Raney cobalt, palladium black and platinum black are very active, they do not produce good results, as comparative tests have shown.

The ES 538 216 produces comparable findings. While Pd and Pt-containing catalysts give good results on activated carbon, Raney nickel and a standard nickel carrier catalyst produce highly unfavourable results in the N-methylation of primary amines - confirmed in comparative tests.

As can be seen from the preceding statements, the successful use of nickel-containing catalysts for the reaction of primary amines with formaldehyde and hydrogen is limited to a special nickel-activated carbon carrier catalyst.

Surprisingly, it has been found that the N-methylation of primary amines using any nickel-containing catalysts can be performed without any appreciable reduction in conversion and selectivity. With nearly quantitative conversion, the reaction produces distillative yields of 90% and more related to the amine used.

These tasks are solved by a process for the preparation of tertiary N,N-dimethylamines by the reaction of primary amines with formaldehyde and hydrogen as starting materials under pressure and at elevated temperature on a nickel-containing hydrogenation catalyst in liquid phase, characterised in that the hydrogenation catalyst is suspended in a solvent, the nickel concentration is 0.1 to 10 % by weight, related to the primary amine to be used, the starting materials are separated from each other at 80 to 150°C and 1 to 15 MPa but fed into the catalyst suspension at the same time with mixing and reacted in one reaction step to form tertiary N,N-dimethylamines.

The starting materials are reacted according to a proven method preferably at 90 to 130, in particular 95 to 125, most preferably 100 to 120°C. The pressure is preferably 1.5 to 12 MPa, in particular 3 to 10 MPa, most preferably 5 to 8 MPa.

The hydrogenation catalyst is preferably not to exhibit less than 10% by weight of Ni, related to the total amount of catalyst. Hydrogenation catalysts with at least 20% by weight of Ni, related to the total amount of catalyst, are well suited. These include a series of commercially available carrier catalysts having 20 to 80, in particular 40 to 70, preferably 50 to 65% by weight of Ni, related to the total amount of catalyst. In many cases catalysts having at least 40% by weight of Ni, related to the total amount of catalyst, are used.

The nickel-containing catalysts can be on carriers but can also be free of carriers. In addition to Ni they may also contain conventional additives and/or promoters, for example, alkaline earth oxides, SiO_2, Al_2O_3, MnO_2 and/or Cr_2O_3.

The use of carrier catalysts is advantageous. Al_2O_3, SiO_2, siliceous earth, silica gel, activated carbon and/or pumice stone, in particular Al_2O_3, SiO_2, siliceous earth and/or silica gel, preferably SiO_2, siliceous earth and/or silica gel serve as carriers.

The process according to the invention does not depend on the kind of primary amines used. In general, it can be used with all organic compounds with one or more primary amine groups. Monovalent and/or multivalent primary amines can be employed as amines. Aliphatic or cycloaliphatic amines can also be used in the N-methylation according to the invention as well as araliphatic, aromatic or heterocyclic amines. Mixtures of these can also be used.

The primary amines have a total of 1 to 40 carbon atoms. The substituents available can be straight-chain and/or branched alkyl groups having 1 to 24 carbon atoms, unsubstituted and/or substituted cycloalkyl groups having 5 to 20 carbon atoms, unsubstituted and/or substituted aromatic groups having 6 to 20 carbon atoms or heterocyclic groups having 4 to 20 carbon atoms which can contain oxygen, sulfur and/or nitrogen as the heteroatom.

Examples of primary aliphatic amines are: methylamine, ethylamine, propylamine, n- and i-butylamine, 3-methylbutylamine, n-pentylamine, 2-methylpentylamine, n-hexylamine, n- and i-heptylamine, n- and i-octylamine, n- and i-nonylamine, n- and i-decylamine, n- and i-undecylamine, 2-methylundecylamine, n-dodecylamine, n- and i-tridecylamine, n- and i-hexadecylamine, stearylamine, cerylamine, ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane (hexamethylenediamine-(1,6)), ω,ω'-polyalkylenediamines, aminoalcohols such as ethanolamine, propanolamine, diglycolamine.

The following are mentioned as examples of cycloaliphatic amines: cyclopentylamine, cyclohexylamine and tricyclodecanamines. The ring systems can exhibit substituents, in particular alkyl groups.

Examples of araliphatic amines are: benzylamine, alpha- and beta-phenylethylamine and phenylpropylamine.

Examples of aromatic amines are: aniline, toluidine, benzidine (4.4'-diaminodiphenyl), phenylene diamine, substituted and unsubstituted naphthylamines.

The process according to the invention has proved particularly successful in the N-methylation of straight-chain and/or branched primary aliphatic amines.

As their number of carbon atoms increases, primary aliphatic amines tend to transalkylate in the presence of nickel-containing hydrogenation catalysts forming correspondingly substituted dialkylamines and trialkylamines.

When the process according to the invention is employed, these undesirable transfers of an alkyl group from one amine nitrogen atom to another do not occur. Thus this procedure is admirably suited for the reaction of primary aliphatic amines having 4 to 24, in particular 6 to 20 and preferably 8 to 16 carbon atoms.

The nickel-containing catalyst can be used in lump form, for example as filaments, tablets, pellets or granules but also in crushed form or as a powder. The grains should not be too fine nor too coarse. Coarse catalyst particles have an unfavourable effect because they have too small a surface for the reaction to take place on. On the other hand, the fine-grained catalysts are highly reactive owing to their large surface but it is difficult to separate them by sedimentation, centrifugation or filtration owing to their small particle size. The removal of nickel-containing catalysts after the reaction has been completed is necessary in order to avoid undesirable side reactions during purification. During distillation even minor amounts of nickel lead to rearrangements and transalkylations. The by-products thus formed contaminate the desired tertiary N,N-dimethylamine.

Before the reaction begins, the nickel-containing hydrogenation catalyst is suspended in a solvent. This solvent is to be inert to the reaction taking place, i.e. it must not intervene in the N-methylation as a reactant.

Suitable solvents are the reaction product, aliphatic, cycloaliphatic, aromatic hydrocarbons, ether and/or alcohols.

In many cases cyclic ether and/or aliphatic alcohols have proved their worth.

Tetrahydrofuran, dioxane and/or aliphatic alcohols having 1 to 6 carbon atoms, in particular methanol, ethanol, propanol, i-propanol, n-butanol and/or i-butanol have proved particularly successful.

In view of their good solubility in water methanol, ethanol and/or propanols, in particular methanol and/or ethanol, preferably methanol are recommended as solvents.

The solvent is to be selected depending on the primary amine to be reacted. Aminec with a relatively high molecular weight require solvents of low polarity, e.g. benzene, toluene and/or xylene, but mixtures of different solvents can also be used. In order to adjust the required polarity, it may be necessary to mix unpolar solvents with polar solvents.

When primary amines are reacted with formaldehyde and hydrogen, water is formed. Apart from this reaction water, water also enters the reaction with the feed materials, in particular with the formaldehyde.

It is recommended to limit the water content. At the end of the reaction it should be max. 35, in particular 25, preferably 15 % by weight, related to the total reaction mixture. If there is too much water, this can lead to the formation of a heterogeneous water phase and also to damage of the nickel-containing catalyst.

A heterogeneously forming water phase settles at the bottom of the reactor and prevents the reaction at least in the area where it surrounds the catalyst. This part of the catalyst which is surrounded by water is no longer available for the reaction.

Too high a water content, particularly over an extended period of time, leads to an impairment of the catalyst activity and reduces both the conversion and the selectivity of the reaction. Moreover, rapid decomposition of the catalyst is promoted. This applies to a great extent to a number of carrier catalysts. Obviously the water attacks the carrier material and quickly reduces its life.

Rapid decomposition of the suspended catalyst is disadvantageous owing to the poor separability of fine-grained catalyst particles.

The water in the reaction mixture can be limited by the type and quantity of solvent and also by the formaldehyde to be used, which can contain about 60 % by weight and more of water, related to the formaldehyde solution.

Solvents which can dissolve water to a limited or high degree prevent the formation of a heterogeneous water phase. They should be present in a percentage of at least 5 % by volume, related to the volume of all the liquid starting materials, but for economic reasons not more than 50 % by volume.

In many cases adding 5 to 40, in particular 10 to 30, preferably 15 to 25 % by volume of solvent, related to the volume of all the liquid starting materials, is sufficient. If less reaction water forms per volume unit of amine, it is sufficient to add 5 to 20 % by volume; if more reaction water is released per volume unit, it is recommended to add 10 to 30 or 15 to 35 % by volume, related to the volume of all the liquid starting materials.

At least some of the solvent is placed in the reactor at the beginning with the nickel-containing hydrogenation catalyst. More can be added to the reaction with one of the starting materials, preferably with formaldehyde.

The use of a low-water, solvent-containing formaldehyde has proved particularly successful. Such solutions consist of formaldehyde, 5 to 15, in particular 7 to 12 % by weight of water and 25 to 55, in particular 30 to 40 % by weight of an aliphatic alcohol, in particular methanol.

A solution containing about 55 % by weight of formaldehyde, 10 % by weight of water and 35 % by weight of methanol is well suited. A product with this composition is on the market.

The solvent can also be added to the reaction with the amine. This is to be recommended especially with pasty or solid primary amines of higher molecular weight.

Normally the reaction is performed in a pressure-tight vessel. The required mixing can be performed by circulating the suspended hydrogenation catalyst and/or by stirring. In many cases a conventional stirred vessel can be used. The reaction can be performed continuously or discontinuously; it is particularly suitable for discontinuous operation.

The optionally crushed, nickel-containing hydrogenation catalyst is placed in the pressure vessel together with the solvent and suspended by mixing. The suspension is heated to 80 to 150°C. The pressure of 1 to 15 MPa is adjusted by adding hydrogen.

A major feature of the invention is that the starting materials are introduced separately but simultaneously into the catalyst suspension with mixing.

This means that amine, formaldehyde and hydrogen are fed through their own separate lines into the reaction zone where the suspended catalyst is located.

It is also possible to add the hydrogen to the reaction in a mixture with the amine or in a mixture with the formaldehyde. It is furthermore possible to distribute the hydrogen between the amine and formaldehyde.

All three starting materials, amine, formaldehyde and hydrogen, may only come into contact with each other in the presence of the suspended catalyst.

If the hydrogen is fed into the reaction together with one of the other starting materials, the amine and the formaldehyde may only be added in the presence of the suspended nickel-containing catalyst. In this case as well, all three starting materials only come into contact with each other in the presence of the catalyst.

It is possible to have the lines of two or all three starting materials terminating in the zone of the suspended catalyst. The arrangement of the lines to be selected depends both on the amounts of material and on the geometry of the reaction zone and the required flow conditions. If the throughput of the substances per time unit is to be substantial, it is recommended to use not only one but several lines per starting material. Should the flow conditions not ensure adequate mixing of the reactants in the catalyst zone, the use of additional distributing equipment is useful. These distributors can, for example, be mounted as ring showers or shower heads at the end of a line. However, other distribution systems such as jets, frits or pipe bundles can also be used.

In accordance with a special embodiment of the invention primary amine and formaldehyde are introduced into the catalyst suspension through two separate dip pipes. The hydrogen can be introduced either through another dip pipe into the reaction zone or through a pipe nozzle into the gas chamber located above the suspension.

The reaction conditions, especially the pressure, temperature and duration of reaction, also depend to a certain extent on the type of primary amine and the suspended hydrogenation catalyst.

Amines of low thermal stability are reacted at 80 to 100°C, amines of medium reactivity at 100 to 120°C and those of low reactivity at 120 to 150°C.

Nickel-containing catalysts with high activity permit a reaction at relatively low temperatures whereas catalysts with medium activity require higher temperatures.

The activity of a catalyst drops as a function of its length of use. Catalysts which have been re-used several times in hydrogenating N-methylation require ever higher reaction temperatures in the course of time in order to ensure an optimum synthesis process. Even originally very active catalysts can require reaction temperatures of 140°C and more.

The amount of formaldehyde required depends on the number of hydrogen atoms on the primary amine nitrogen.

preferably 1 to 2, in particular 1 to 1.5, most preferably 1.1 to 1.25 moles of formaldehyde are used per gramme atom of hydrogen to be substituted. As a rule a stoichiometric excess of 5 to 30 mol. % of formaldehyde will have a positive effect on the reaction.

The amount of hydrogen required is governed by the stoichiometry of the reaction. Normally, the hydrogen is added in an amount which ensures that a specified pressure is maintained. Excess hydrogen used can be separated from the reaction and fed back into the reaction process.

The primary amine and formaldehyde are added separately but simultaneously. This must not take place too quickly owing to the risk of undesirable by-products being formed. Slightly too rapid dosing of amine and formaldehyde can be corrected by an after-reaction without appreciable amounts of by-products being formed. In most cases a time of 0.5 to 2 hours is sufficient for this purpose. However, too slow addition can promote the formation of higher-boiling substances.

The charging rate should be the same for all feed materials, especially for the primary amine and the formaldehyde. It depends on various factors such as size of the batch, reactivity of the amine, type of amine, reactor geometry, type of catalyst, nickel concentration, intensity of mixing, pressure and temperature. It is to be adapted to the prevailing conditions and, if necessary, is to be determined by experiment. Here, the consumption of hydrogen per time unit is a useful aid to check the progress of the reaction. When no more hydrogen is consumed, the reaction is completed.

The following examples substantiate the invention without limiting it.

Example 1:

The reactor vessel consists of a 2 l stirred autoclave which has 2 dip pipes in addition to an inlet for the supply of hydrogen.

5 g of a pulverised nickel catalyst (~50 to ~53 % by weight of Ni and roughly 25 to 30 % by weight of diatomaceous earth as carrier; proprietary product of Hoechst AG: RCH Ni 52/35) and 100 g of methanol are poured into this vessel. The pulverised catalyst is suspended with stirring and the desired conditions (10 MPa hydrogen pressure; 120°C) are adjusted.

After the desired conditions have been reached, 258 g (2 moles) of n-octylamine and 275 g of a formaldehyde solution (~55 % by weight of formaldehyde, ~ 10 % by weight of water and ~ 35 % by weight of methanol) - corresponding to 5 moles of formaldehyde - are simultaneously pumped into the catalyst suspension via the two dip pipes over a period of 2 hours.

Examples 2 to 4

The procedure is analogous to example 1 but the pumping time varies for the feed materials n-octylamine and formaldehyde. It is 90 minutes in example 2, 60 minutes in example 3 and 30 minutes in example 4.

Example 5

The procedure is analogous to example 1 but 5 g of a different pulverised nickel catalyst are used (~55 % by weight of nickel on diatomaceous earth as the carrier, proprietary product of Hoechst AG: RCH Ni 55/5).

Comparative test A

Using the reactor vessel described in example 1, 258 g (2 moles) of n-octylamine and 5 g of the nickel catalyst used in example 1 are taken. The addition of methanol is dispensed with.

The pulverised catalyst is suspended with stirring and the desired conditions (10 MPa hydrogen pressure, 120°C) are adjusted.

After the desired conditions have been reached, 275 g of the formaldehyde solution used in example 1 - corresponding to 5 moles of formaldehyde - are pumped in over a period of 2 hours. The reaction product consists of 2 phases, the lower phase consisting of 98 % by weight of water and 2 % by weight of N,N-dimethyl-n-octylamine. The composition of the organic phase is shown in table 1 under A. A comparison with example 1 shows a clear deterioration in the yield of value product.

In the following table 1 the results of the GC analysis (sampling directly after end of the pumping process) are given for examples 1 to 5 and comparative test A. Table 2 contains the results of examples 2 to 5, in each case after 1 hour after-reaction.

Table 1

Example	1	2	3	4	5	A
Composition *)						
n-octylamine	-	< 0.1	< 0.1	< 0.1	-	< 0.1
N-methyl-n-octylamine		0.2	0.9	1.1	2.3	1.1
N,N-dimethyl-n-octylamine	93.1	93.3	96.2	98.1	96.7	78.26
N,N-dioctyl-methylamine	2.5	4.6	1.0	-	0.3	15.9

*) all figures in % by weight; H_2O and methanol excluded from calculation.

Table 2

Example	2	3	4	5
Composition *)				
n-octylamine	-	-	-	-
N-methyl-n-octylamine	0.2	0.5	0.6	1.1
N,N-dimethyl-n-octylamine	93.7	96.7	98.4	97.8
N,N-dioctyl-methylamine	4.7	0.7	-	0.1

*) all figures in % by weight; H_2O and methanol excluded from calculation.

Example 6:

The procedure is analogous to example 1.

After the desired conditions have been reached, 185 g (1 mole) of n-dodecylamine and 138 g of the formaldehyde solution used in example 1 - corresponding to 2.5 moles of formaldehyde - are pumped in through the two dip pipes separately but simultaneously over a period of 2 hours. The reaction mixture contains 0.6 % by weight of N-methyl-n-dodecylamine, 93.6 % by weight of N,N-dimethyl-n-dodecylamine and 0.6 % by weight of N,N-didodecylmethylamine (GC analysis; H_2O and methanol excluded from calculation).

Comparative test B

The procedure is analogous to the comparative test A but instead of n-octylamine 185 g (1 mole) of n-dodecylamine and 3 g of the nickel catalyst used in example 1 are taken. 138 g of the formaldehyde solution are added as described in comparative test A.

The reaction mixture consists of 2 phases, the lower one consisting of 89.7 % by weight of water and 10.3 % by weight of methanol. The upper organic phase contains 0.9 % by weight of N-methyl-n-dodecylamine, 80.3 % by weight of N,N-dimethyl-n-dodecylamine and 16.7 % by weight of N,N-didodecylmethylamine (GC analysis; H_2O and methanol excluded from the calculation).

A comparison with example 6 shows a clear deterioration in the yield of value product.

P~~atent Clai~~ms

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1.) Process for the preparation of tertiary N,N-dimethylamines by the reaction of primary amines with formaldehyde and hydrogen as starting materials under pressure and at elevated temperature on a nickel-containing hydrogenation catalyst in liquid phase, characterised in that the hydrogenation catalyst is suspended in a solvent, the nickel concentration is 0.1 to 10 % by weight, related to the primary amine to be used, the starting materials are separated from each other at 80 to 150°C and 1 to 15 MPa but are fed into the catalyst suspension at the same time with mixing and reacted in one reaction step to form tertiary N,N-dimethylamines.

2.) Process according to claim 1, characterised in that the starting materials are introduced into the catalyst suspension and reacted at 90 to 130, particularly 95 to 125, preferably 100 to 120°C.

3.) Process according to one or both of the claims 1 to 2, characterised in that the starting materials are introduced into the catalyst suspension and reacted at 1.5 to 12 MPa, in particular 3 to 10 MPa.

4.) Process according to one or more of the claims 1 to 3, characterised in that the concentration of nickel is 0.2 to 5, in particular 0.3 to 2.0, preferably 0.6 to 1.3 % by weight, related to the primary amine to be used.

5.) Process according to one or more of the claims 1 to 4, characterised in that the catalyst contains 20 to 80, in particular 40 to 70, preferably 50 to 65 % by weight of nickel.

6.) Process according to one or more of the claims 1 to 5, characterised in that the nickel-containing catalyst exhibits Al_2O_3, SiO_2, siliceous earth, silica gel, activated carbon and/or pumice stone as carriers.

7.) Process according to one or more of the claims 1 to 5, characterised in that the nickel-containing catalyst exhibits Al_2O_3, SiO_2, siliceous earth, and/or silica gel as carriers.

8.) Process according to one or more of the claims 1 to 5, characterised in that the nickel-containing catalyst exhibits SiO_2, siliceous earth and/or silica gel as carriers.

9.) Process according to one or more of the claims 1 to 8, characterised in that straight-chain and/or branched aliphatic amines having 4 to 24, in particular 6 to 20, preferably 8 to 16 carbon atoms are used as the primary amine.

10.) Process according to one or more of the claims 1 to 9, characterised in that the reaction product, aliphatic, cycloaliphatic, aromatic hydrocarbons, ether and/or alcohols are used as solvents.

11.) Process according to one or more of the claims 1 to 9, characterised in that cyclic ether and/or aliphatic alcohols are used as solvents.

12.) Process according to one or more of the claims 1 to 9, characterised in that tetrahydrofuran, dioxane and/or aliphatic alcohols having 1 to 6 carbon atoms, especially methanol, ethanol, propanol, i-propanol, n-butanol and/or i-butanol are used as solvents.

13.) Process according to one or more of the claims 1 to 9, characterised in that methanol is used as the solvent.

14.) Process according to one or more of the claims 1 to 13, characterised in that the proportion of the solvent is at least 5 % by volume, related to the volume of all the liquid starting materials.

15.) Process according to one or more of the claims 1 to 14, characterised in that the proportion of the solvent is 5 to 40, in particular 10 to 30, preferably 15 to 25 % by volume, related to the volume of all the liquid starting materials.

16.) Process according to one or more of the claims 1 to 15, characterised in that formaldehyde is used as a solution, which apart from formaldehyde contains 5 to 15 % by weight of water and 25 to 55 % by weight of an aliphatic alcohol, in particular methanol.

17.) Process according to one or more of the claims 1 to 15, characterised in that formaldehyde is used as a solution, which apart from formaldehyde contains 7 to 12 % by weight of water and 30 to 40 % by weight of an aliphatic alcohol, in particular methanol.

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HOECHST AKTIENGESELLSCHAFT

EDWD. WATERS & SONS
PATENT ATTORNEYS
50 QUEEN STREET
MELBOURNE. VIC. 3000.