

$$\begin{array}{ccc} \text{R}_1-\text{N} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array} & \text{R}_1 \begin{array}{l} \nearrow \text{N}-\text{CH}_3 \\ \searrow \text{R}_2 \end{array} & \text{N}-\text{CH}_3 \\ & & \text{---} \bigcirc \text{---} \end{array}$$

15 Mono- or dimethylated tertiary amines are the basis of at least three types of highly desired derivatives in industry: the quaternary ammonium salts, betaines and amine oxides, which have many applications in the field of detergents, in cosmetics, as bactericides and antibiotics, as agents for the treatment of textiles, or else for the manufacture of organophilic clays.

These processes have various major disadvantages. Thus, those which [sic] use the Leuckart reaction, already difficult to control, produce amines which are

5 additionally contaminated with formaldehyde; others which
use methylation by methyl chloride, besides generating
hydrochloric acid, have selectivity drawbacks, the
resulting products containing proportions of quaternary
10 ammonium salts which are difficult to control. Direct
hydrogenation of amides is carried out on a copper
chromite catalyst, which is incompatible with the nickel
catalysts otherwise used in plants which produce amines:
this increases the number of units and increases the
15 overall production cost [sic] of these plants.

The Applicant has now found that, under
conditions which will be specified,
hexamethylenetetramine could constitute an invaluable
methylating reagent for amines or nitriles, the
15 advantages of which will become clearly apparent in the
present description.

Hexamethylenetetramine (hereafter HMTA) is a well
known compound, of general formula $C_6H_{12}N_4$, listed under
the "registry number" [RN = 100-97-0], resulting from the
20 condensation of formaldehyde and ammonia. HMTA is a
tetracyclic compound, as shown by its official name of
1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane or, to recall
its spatial structure, by its name of 1,3,5,7-
tetraazaadamantane. HMTA is especially used, besides as
25 an antiseptic, in particular in urinary therapeutics
(urotropin), as a formaldehyde donor (hardener of phenol
formaldehyde resins, vulcanising agent for rubbers,
corrosion inhibitor for iron [lacuna]). It is also a base
capable of giving crystalline salts with inorganic or
30 organic acids. HMTA also behaves as a tertiary amine with
respect to quaternisation agents and provides quaternary
ammonium salts whose hydrolysis releases the
corresponding amine, whereby HMTA functions as an
aminating agent (see, for example, K.E. Schulte and
35 M. Goes, Arch. Pharm., 290, 118-30, 1957).

The general reactions which are the basis of the
present invention can be represented by one or other of

the equations below



or



5 or else



10 in which formulae the various coefficients y^i , p^i and q^i depend on and can be expressed as a function of the respective values x^i . If looked at, for simplification, in the case of the methylation of a primary amine, the optimum reaction can be represented overall by



15 In practice, the reaction is used with larger quantities of HMTA, especially when it is applied to precursors possessing long fatty chains. The degree of conversion of the nitrogenous precursor is governed by the molar ratio x of HMTA to nitrogen which can be methylated. This ratio is connected to the steric
20 hindrance of the nitrogenous site, and thus to the very structure of the precursors. It thus prescribes the quantity of hydrogen consumed y , and the composition of reaction byproducts, NH_3 and trimethylamine, in the gaseous effluents.

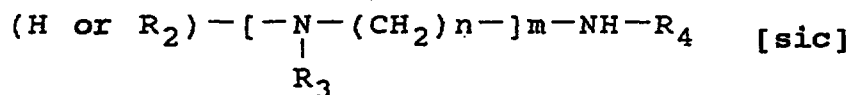
25 Methylating with HMTA is a selective reaction. This is understood to mean that, under the conditions which are those of the invention, only amine or nitrile functional groups participate in the reaction. It is thus possible to use, as nitrogenous precursors, products as
30 diverse as aminoalcohols, amidoamines or ether amines without affecting the functional groups which are combined with the amine or nitrile functional group of these precursors. The reaction thus makes it possible to arrive at very varied methylamines by being directed at
35 a great many nitrogenous precursors.

The process according to the invention thus makes it possible to produce fatty alkyl dimethylamines from nitrogenous precursors containing a primary amine functional group, molecules which can be represented by

a general formula R_1NH_2 : true monoamines, where R_1 is a linear or branched, saturated or unsaturated hydrocarbon residue R containing from 10 to 22 carbon atoms; aminoalcohols, with R_1 consisting of a monovalent residue such as $HO-CH_2-CH_2-$ or $HO-CH(CH_3)-CH_2-$; ether amines, in which R_1 is a group $R-O-(CH_2)_3-$, R having the same definition as above; ether amines, R_1 having the meaning $R-(OCH_2-CH_2)_p$, $R-[OCH(CH_3)-CH_2]_p$ or $R-[OCH_2-CH(CH_3)]_p$ [sic], in which R has the same meaning as above and where p is a number which can take any positive statistical value.

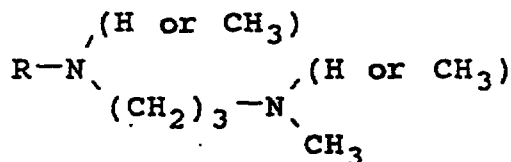
The nitrogenous precursors which can be used in the reaction according to the invention are also simple or complex secondary amines, of general formula R_1NHR_2 , where R_1 has the same definition as above, where R_2 can be CH_3 or R_1 , it being moreover possible for R_1 and R_2 to be involved in a ring, in this case a cyclic amine containing, if appropriate, a second nitrogen or oxygen heteroatom.

Methylating with HMTA is obviously applicable to polyamines, starting with the $\alpha-\omega$, $H_2N-(CH_2)_r-NH_2$ [sic] diamines where r is an integer which can take any whole value equal to or greater than 2 and which can be very large, although in practice it does not exceed the values of 14/16, and generally the polyamines which can be represented by a formula such as



where R_1 has the same definition as above,
 where R_2 has the above meaning of CH_3 or R_1 ,
 where R_3 is H or CH_3 or R_1 ,
 where R_4 is H or CH_3 or R or R_1 ,
 where n is an integer which can take the values 2 or 3,
 where m is an integer or any number with a statistical value greater than 1,
 it being possible, moreover, for R_2 and R_3 to be closed again to form a cyclic amine or even a nitrogenous ring containing another nitrogenous [sic] or oxygen-containing [sic] heteroatom.

These polyamines in particular comprise the diamines, such as the alkylpropylenediamines, which the process according to the invention converts into more or less complex mixtures of methylated polyamines such as

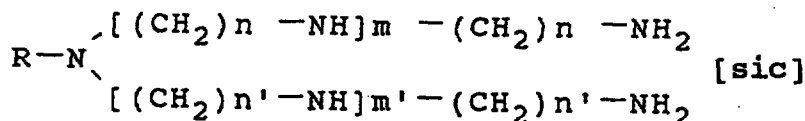


5 The corresponding derivatives possessing fatty chains, and more precisely possessing tallow chains, are industrially very advantageous. Indeed, the tallow base [sic] fatty alkylpropylenediamines are products which are much used by the road-building industry as emulsifying agents for bitumens. They have the disadvantage of being solids or pastes: the methylated diamines which are obtained by applying to them the process according to the invention have retained the notable emulsifying properties thereof, but have lower melting points, which makes it notably much easier to handle them and measure them out. Furthermore, they constitute the precursors of quaternary alkylpropylenediammonium chlorides also used in the road-building industry.

20 Among the many other polyamines which can be used as nitrogenous precursors for the process according to the invention, it is also useful to specify the fatty polyamines which are linear or branched on the nitrogen according to one or the other of the general formulae



25 or



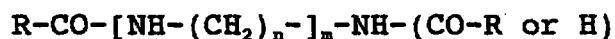
where R is a hydrocarbon chain containing from 10 to 22 carbon atoms;

30 where n and n' are integers which can take the values 2 or 3;

where m and m' can take any integral or statistical value from 0 [sic] to 3.

These products, and especially the polyamines possessing tallow chains which can be represented by the first of these formulae, and in which n is 3 and m a statistical value from approximately 2 to 3, are also used in the road-building industry as adhesiveness additives and emulsifying agents for bitumens; methylating according to the invention converts them into products with a controlled melting point, which depends on the degree of alkylation.

Fatty amidoamines or amidopolyamines, which are industrial products often in competition with the above and which can be represented by

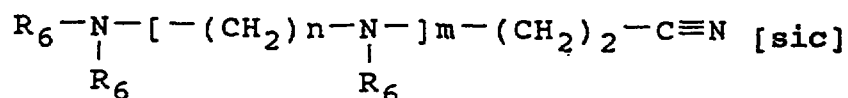


where R is a hydrocarbon residue as defined above, where n generally has the value 2 or 3, and m a statistical value from 1 to 6, as well as their derivatives more or less cyclised to imidazolines or tetrahydropyrimidines, can also be methylated by the process according to the invention.

The process according to the invention also makes it possible to access methylated amines directly from nitriles, either from simple or complex fatty mononitriles such as



where R_5 is R or $R-O-(CH_2)_2-$, but also from aminonitriles



in which formula the R_6 groups can be, independently of each other, H or CH_3 or R_1 , it being additionally possible for two R_6 groups, when they are substituents on the same nitrogen, to be linked together to form a cyclic amine

which can even contain another nitrogenous [sic] or oxygen-containing [sic] heteroatom, and where n is an integer which can take the values 2 or 3, m is an integer or a number with a statistical value which can take any value from 0 to 3. The selectivity of the reaction which was indicated above makes it possible to methylate both amine and nitrile nitrogens of these precursors while leaving unaffected the other optionally combined functional groups.

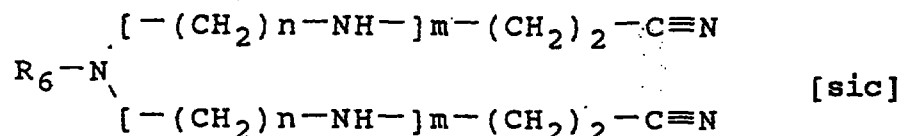
Among these products, mention must be made in particular of the dinitriles



where q is an integer which can take any value equal to or greater than 2, values which, however, do not exceed 14 in practice, and the intermediate aminonitriles in the industrial synthesis of polyamines by cyanoethylation, and which are represented by one or the other of the formulae



or



where R_6 is H or CH_3 or R_1 , where n is an integer which can take the values 2 or 3, and where m is an integer which can take any integral or statistical value from 0 to 3.

Generally, the preparation of methylated tertiary amines according to the invention by reacting nitrogenous precursors and HMTA is carried out on supported nickel catalysts under hydrogen pressures of between 3 and 50 bars, and at temperatures not greater than 160°C .

The process according to the invention has the advantage of not giving rise to the formation of foams, such as those which greatly impede the development of processes which use the Leuckart reaction. The implemented reactions generate the targeted tertiary amines with byproducts which are limited both qualitatively and quantitatively; it is therefore not

necessary to carry out repeated washes to remove the impurities from the final products. It is probably for this reason that the quaternary derivatives (quaternary ammonium salts or betaines) formed from the methylalkylamines obtained according to the invention do not show the pink colorations which affect these products when they result from the tertiary amines obtained according to the processes of the prior art.

The following examples will make the invention better understood.

Example 1: Methylation of coconut oil fatty monoamine

700 grams of a commercial monoalkylamine (Noram^C [sic] of CECA S.A., whose chain distribution is that of the coconut oil fatty acids from which it is derived, that is to say, rich in 12-14 carbon chains, with an alkalinity equal to 5.20; this product contains approximately 3.8 % by weight of dialkyl secondary amines), 363 grams of HMTA (amine/HMTA molar ratio = 0.70) and 7 grams of a supported nickel catalyst of the E 230 P type (Degussa) containing 63 % nickel (or 1 % nickel with respect to the monoalkylamine) are charged into a 2-litre reactor.

While stirring at 1100/1500 rev/min, degassing is carried out of the ammonia and the trimethylamine formed per stage at 130°C when the hydrogen uptake is zero, the temperature is then increased to 155°C and so on until uptake at 155°C has completely ceased. Hydrogen pressure is 20 bars. The operation lasts from 5 to 7 hours.

After separating the catalyst, the crude recovered amine has the following composition:

	Composition	% by weight
	Monoalkylamines	0.81
5	Monomethylmonoalkylamines R-NH-CH ₃	3.7
	Dimethylmonoalkylamines R-N-(CH ₃) ₂	89.1
10	Dialkylamines R-NH-R	3.4
	Monomethyldialkylamines (R-NCH ₃ -R)	3.0

15 The heavy dialkyl component, which arises, to a significant extent, from the dialkylamines present in the starting amine, can be easily separated therefrom by simple distillation. A mixture is then obtained whose composition is established as

20	Composition	% by weight
	Monoalkylamines	0.9
	Monomethylmonoalkylamines R-NH-CH ₃	3.9
25	Dimethylmonoalkylamines R-N-(CH ₃) ₂	95.2

Example 2: Preparation of dimethylalkylamine from a nitrile.

30 700 g of a nitrile derived from coconut oil fatty acid, 1.6 % of the same E 230 P catalyst as above and 371 g of HMTA (molar ratio 0.70) are charged into a reactor identical to that in Example 1. The reaction is carried out under the same conditions as in Example 1.

35 There is obtained:

	Composition	% by weight
	Monoalkylamines	negligible
5	Monomethylmonoalkylamines R-NH-CH ₃	negligible
	Dimethylmonoalkylamines R-N-(CH ₃) ₂	76.8
10	Dialkylamines R-NH-R	4.5
	Monomethyldialkylamines (R-NCH ₃ -R)	19.7

Example 3: Preparation of the N-methylated derivative of hydrogenated tallow dialkylamine from the corresponding dialkylamine.

700 g of a hydrogenated tallow dialkylamine (Noram² SH [sic] of CECA S.A.), 1.6 % by weight of the same E 230 P catalyst as above and 72.3 g of HMTA (amine/HMTA molar ratio = 1/0.37) are charged into a reactor identical to that of Example 1. After reaction, there is obtained:

	Composition	% by weight
25	Monoalkylamines	negligible
	Monomethylmonoalkylamines R-NH-CH ₃	negligible
30	Dimethylmonoalkylamines R-N-(CH ₃) ₂	negligible
	Dialkylamines R-NH-R	56.0
35	Monomethyldialkylamines (R-NCH ₃ -R)	44.0

For the charge of 136 g of HMTA, (molar ratio 1/0.70), all the other details remaining unchanged, there is obtained:

	Composition	% by weight
	Monoalkylamines	negligible
5	Monomethylmonoalkylamines $R-NH-CH_3$	negligible
	Dimethylmonoalkylamines $R-N-(CH_3)_2$	negligible
10	Dialkylamines $R-NH-R$	28.4
	Monomethyldialkylamines $(R-NCH_3-R)$	71.6

The reaction of HMTA with the fatty dialkylamines is particularly advantageous in that there is no reaction byproduct and in that the final product which is collected is the methyldialkylamine with the starting dialkylamine.

Example 4: Reaction of diethanolamine and HMTA.

700 g of diethanolamine and 346 g of HMTA (molar ratio = 1/0.35) are charged into the equipment used in Example 1. After reaction under the conditions of Example 1, there is obtained:

	Composition	% by weight
25	Diethanolamine $(HOCH_2CH_2)_2NH$	8.1
30	Methyldiethanolamine $(HOCH_2CH_2)_2NCH_3$	91.9

The product of this reaction is a simple product, a mixture of the sole reaction product, methyldiethanolamine, with the starting diethanolamine.

Methyldiethanolamine is a very advantageous intermediate for preparing amino esters and their quaternary ammonium derivatives, which can be used, especially, for the formulation of biodegradable textile softening agents.

The example is directly transposable to the methylation of monoethanolamine, to give essentially monomethylethanolamine and dimethylethanolamine.

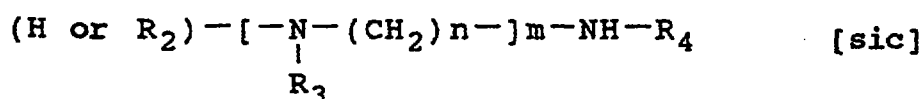
CLAIMS

1. Process for preparing methylated tertiary amines, characterised in that hexamethylenetetramine is reacted with nitrogenous precursors taken from the group consisting of the primary or secondary amines, nitriles and aminonitriles, the reaction being carried out under hydrogen pressure and in the presence of a hydrogenation catalyst, at a temperature not greater than 160°C.
2. Process according to Claim 1, in which the catalyst is a supported nickel hydrogenation catalyst.
3. Process according to Claims 1 or 2, characterised in that the nitrogenous precursor is a primary monoamine R_1NH_2 , where R_1 is:
 - a linear or branched, saturated or unsaturated hydrocarbon residue R containing from 10 to 22 carbon atoms, or
 - a $HO-CH_2-CH_2-$ or $HO-CH(CH_3)-CH_2-$ group, or
 - a group $R-O-(CH_2)_3-$, in which R is a linear or branched, saturated or unsaturated hydrocarbon residue containing from 10 to 20 carbon atoms, or
 - a group $R-(OCH_2-CH_2)_p$, $R-[OCH(CH_3)-CH_2]_p$ or $R-[OCH_2-CH(CH_3)]_p$ [sic], in which R has the same meaning as above and where p is a number which can take any positive statistical value.
4. Process according to Claims 1 or 2, characterised in that the nitrogenous precursor is a secondary monoamine R_1NHR_2 , where R_1 has the same definition as in Claim 3, where R_2 can be CH_3 or R_1 , it being possible for R_1 and R_2 to be closed in a cyclic amine, it being possible for the ring to secondarily contain another nitrogenous or oxygen-containing [sic] heteroatom.
5. Process according to Claim 4, characterised in that the nitrogenous precursor is monoethanolamine or diethanolamine.
6. Process according to Claims 1 or 2, characterised in that the nitrogenous precursor is a primary diamine $H_2N-(CH_2)_r-NH_2$ where r is an integer which can take any



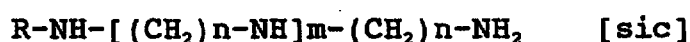
value equal to or greater than 2, generally between 2 and 16.

7. Process according to Claims 1 or 2, characterised in that the nitrogenous precursor is a polyamine which can be represented by the general formula

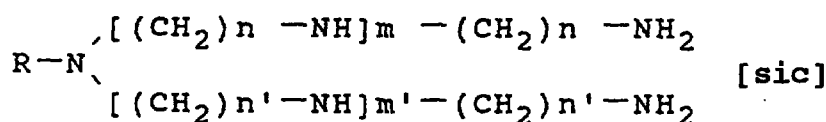


where R_1 has the same definition as in Claim 3,
 where R_2 can be CH_3 or R_1 ,
 where R_3 can be H or CH_3 or R_1 ,
 10 where R_4 is H or CH_3 or R or R_1 ,
 where n is an integer which can take the values 2 or 3,
 where m is an integer or any number with a statistical value greater than 1,
 it being possible, moreover, for R_2 and R_3 to be closed to
 15 form a cyclic amine or even a nitrogenous ring containing another nitrogenous [sic] or oxygen-containing [sic] heteroatom.

8. Process according to Claims 1 or 2, characterised in that the nitrogenous precursor is a fatty polyamine
 20 corresponding to one or the other of the formula [sic]



or



where R is a hydrocarbon chain containing from 10 to
 25 22 carbon atoms;

where n and n' are integers which can take the values 2 or 3;

where m and m' can take any integral or statistical value from 0 [sic] to 3.

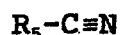
30 9. Process according to Claim 8, characterised in that the nitrogenous precursor is a fatty diamine corresponding to the general formula $T - NH - (CH_2)_3 - NH_2$, T being a tallow base [sic] hydrocarbon chain.



10. Process according to Claim 8, characterised in that the nitrogenous precursor is a fatty polyamine containing a tallow chain, of formula $\text{RNH}-[(\text{CH}_2)_3\text{-NH}]_m\text{-(CH}_2)_3\text{-NH}_2$, where m has a statistical value of approximately 2 to 3.

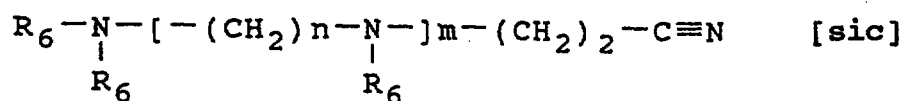
5 11. Process according to Claims 1 or 2, characterised in that the nitrogenous precursors are fatty amidoamines or amidopolyamines which can be represented by $\text{R-CO-[NH-(CH}_2)_n\text{]}_m\text{-NH-(CO-R or H)}$, where R is a hydrocarbon residue as defined above, where n generally
10 has the value 2 or 3, and m a statistical value from 1 to 6, as well as their derivatives more or less cyclised to imidazolines or tetrahydropyrimidines.

12. Process according to Claims 1 or 2, characterised in that the nitrogenous precursor is a mononitrile which can
15 be represented by the general formula



where R_5 is R or $\text{R-O-(CH}_2)_2\text{-}$, R having the definition given above.

13. Process according to Claims 1 or 2, characterised in
20 that the nitrogenous precursor is an aminonitrile which can be represented by the general formula



in which

- the R_6 groups can be, independently of each other, H or
25 CH_3 or R_1 ,

it being possible for two R_6 groups, when they are substituents on the same nitrogen, to additionally constitute a ring with a nitrogenous [sic] or oxygen-containing [sic] heteroatom,

30 and where

- n is an integer which can take the values 2 or 3,

- m can take any value from 0 [sic] to 3.

14. Process according to Claims 1 or 2, characterised in that the nitrogenous precursor is a dinitrile

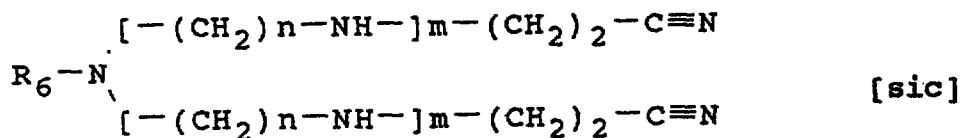


where q is an integer which can take any value greater than 2, generally of between 2 and 14.

15. Process according to Claims 1 or 2, characterised in that the nitrogenous precursor is an aminonitrile which
5 can be represented by one or the other of the formulae



or



- where n is an integer which can take the values 2 or 3,
10 where m can take any integral or statistical value from 0 [sic] to 3,
where R_6 is H or CH_3 or R_1 .

