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PRODUCTION OF AMINES

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The present invention relates to the production of amines.

We have found that amines can be obtained in good yields by reacting a carboxylic acid substance with a mixture of an ammonia substance and hydrogen at elevated temperatures in the presence of catalysts.

The term "carboxylic acid substance" is intended to mean free carboxylic acids as well as anhydrides, amides and esters of carboxylic acids. The said carboxylic acids may be aliphatic open chain, cycloaliphatic, aromatic or heterocyclic carboxylic acids. Examples of saturated aliphatic open chain carboxylic acids which may be converted into amines according to the process of the present invention are acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, caprylic acid, nonylic acid, capric acid, lauric acid, myristic acid, pentadecylic acid, palmitic acid, margaric acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, melissic acid and montanic acid. Examples of suitable aliphatic unsaturated open chain carboxylic acids are acrylic acid, crotonic acid, vinylacetic acid, methacrylic acid, nonylenic acid, undecylenic acid, oleic acid, elaidic acid, linoleic acid, linolenic acid, erucic acid and sorbic acid. Suitable cycloaliphatic carboxylic acids are for instance cyclopentane carboxylic acid, hexahydrobenzene carboxylic acid, camphoric acid and decahydronaphthoic acid. Aromatic carboxylic acids, such as benzoic acid, the different toluic acids, the different ethylbenzoic acids, alpha-naphthoic acid, 10-phenanthrene carboxylic acid and the different anthracene monocarboxylic acids, may also be employed as well as aliphatic carboxylic acids substituted by aromatic radicles, such as phenylacetic acid and cinnamic acid. Polycarboxylic acids of the aliphatic and aromatic series may also be employed, for example oxalic acid, maleic acid, adipic acid, phthalic acid, and anthracene and phenanthrene polycarboxylic acids. Examples of heterocyclic carboxylic acids are furane-carboxylic acid, picolinic acid and the different pyridine carboxylic acids. The aforesaid acids may also bear substituents, such as hydroxyl, amino, nitro, ketonic and aldehydic groups. Acids of this kind are for example lactic acid, ricinoleic acid, mandelic acid, salicylic acid, pyroracemic acid, laevulic acid, benzoylacetac acid, glyoxalic acid, glycollic acid, alpha-amino-propionic acid, phenylaminoacetic acid, cyano-acetic acid, cyano-propionic acids. As already stated, the anhydrides, amides and esters

of the said acids may also be employed for the purpose of the present invention.

Esters of any kind may be subjected to the reaction. The aforesaid carboxylic acids may therefore be esterified with alcohols, such as methyl, ethyl, propyl, butyl, nonyl, octodecyl or oleyl alcohols, ethylene glycol, hexane-diol, glycerol, benzyl alcohol, hexahydrobenzyl alcohol, cyclohexanol, phenol, resorcinol, or sorbitol.

The aforesaid acids, esters, anhydrides or amides may be employed in admixture with each other. Very convenient initial materials are, however, the mixtures occurring in natural products, such as naphthenic acids and montanic acids, and, more particularly, the glycerol esters of long chain fatty acids known as fatty oils and fats, for example coconut oil, peanut oil, palm kernel oil, soya bean oil, olive oil, castor oil, train oil, tallow and the like. Similarly, the mixture of fatty acids obtainable by the liquid phase oxidation of paraffin hydrocarbons by means of oxygen-containing gases may also be subjected to the reaction.

The said carboxylic acid substances may be subjected to the reaction in the presence of inert organic diluents, such as ligroin, dodecane, gasoline fractions, cyclohexane, benzene, toluene, xylene, tetrahydronaphthalene. In some cases, the aromatic or partially saturated hydrocarbons are then converted into cycloaliphatic hydrocarbons, thus benzene may be simultaneously converted into cyclohexane.

The reaction may also be carried out in the presence of substances capable of forming secondary or tertiary amines by reacting with the intermediate products of the reaction and/or with the amines formed, as for example, alcohols, phenols, nitriles, ketones, or aldehydes. The above enumerated alcohols and phenols which may form part of the initial carboxylic acid substances as esters, may also be employed as additional substances in the manner above described. Examples of suitable ketones and aldehydes are acetone, methyl ethyl ketone, cyclohexanone, acetaldehyde and benzaldehyde. Suitable nitriles are for example acetonitrile, propionitrile, valeronitrile, palmitonitrile, benzyl cyanide and the like. Thus, for example, an acid may be dissolved in a mixture of benzene and ethyl alcohol and the mixture subjected to the reaction.

The said ammonia substances comprise ammonia, primary and secondary amines, and substances which yield ammonia or primary or secondary amines under the reaction conditions. Substances capable of yielding ammonia are for

example ammonium carbonate, urea, aldehyde-ammonia, and the like. Examples of primary and secondary amines are methyl, ethyl, propyl, butyl, nonyl, undecyl, stearyl, oleyl amines, ethylene diamine, cyclohexyl amine, aniline, mono-N-alkylated aniline, beta-tetrahydronaphthyl amine, diethyl amine, dibutyl amine, dibenzyl amine, cyclohexyl methyl amine, piperidine, deka-hydroquinoline, primary and secondary alkylol
10 amine, such as hydroxyethyl amine, beta-amino-propionic acid and other amino acids. Substances capable of yielding primary or secondary amines under the reaction conditions are for example
15 pyridine, quinoline, nitrobenzene, hydrocyanic acid and nitriles, as those enumerated above.

The hydrogen or the mixture of hydrogen and ammonia may also be diluted by other gases or vapors, as for example nitrogen, carbon dioxide or steam, these diluents being employed for with-
20 drawing part of the heat evolved by the reaction.

The catalysts employed according to this invention essentially comprise hydrogenation catalysts, such as copper, cobalt, nickel, iron, platinum, ruthenium, rhodium, palladium, osmium
25 and iridium and the alloys of these metals. These hydrogenating metals may be prepared from the corresponding oxides, hydroxides, carbonates, nitrates, acetates or other salts or compounds which yield metals or oxides on heating, the oxides being converted into metals by heating at elevated
30 temperatures in the presence of hydrogen. Suitable hydrogenation catalysts are also mixtures comprising one or more of the following metals: zinc, cadmium, manganese, chromium and vanadium. Especially valuable catalysts are mixed
35 catalysts which contain one or more of the aforesaid metals having a hydrogenating action and, besides these metals, constituents having a dehydrating action. The said mixed catalysts will
40 hereinafter be called "combined hydrogenation-dehydration catalysts". The constituents having a dehydrating action are oxides, hydroxides, phosphates, carbonates or chromates of aluminium, titanium, zirconium, cerium, thorium, man-
45 ganese, chromium or silicon. The catalysts may further contain small amounts of activators, such as oxides, hydroxides, phosphates, carbonates, chromates and nitrates of alkali metals, such as sodium, potassium or lithium, of alkaline earth
50 metals, such as barium, calcium, or strontium, of vanadium, molybdenum, tungsten or uranium, small amounts of the corresponding compounds of aluminium, titanium, zirconium, cerium and thorium also acting as activators. The said catalysts may be deposited on inert carrier, such as
55 bleaching earth, kieselguhr, pumice, charcoal, magnesium oxide, silica gel, and the like. As examples of the combined hydrogenation-dehydration catalysts may be mentioned those containing the following elements: copper, aluminium and barium; cobalt, aluminium and an alkali metal; nickel, silicon and magnesium; copper, chromium, titanium and aluminium; copper and
60 manganese.

It is advantageous to subject the catalysts to a heat treatment, before use. Temperatures up to about 1000° C. are suitable for this purpose. It is possible to subject only one of the constituents of the combined hydrogenation-dehydration
70 catalysts to this preliminary treatment, for instance to heat alumina to a temperature between about 800 and about 900° C. and to mix it then with the hydrogenating metal in a finely divided state. The mixed catalysts are usually
75 heated to temperatures between about 300° and

about 500° C. This is the case for example when mixtures of compounds which are converted into oxides by heating are employed, the mixtures of oxides being then directly used for the reaction in the course of which the reducible oxides are converted into metals. It is, however, also possible to subject the mixtures of oxides to a reducing treatment by heating them in a stream of hydrogen or by dispersing them in an inert solvent, such as cyclohexane, and leading hydrogen into the heated dispersion. It is also possible to employ the catalytic metals in the form of salts, such as formates, acetates and carbonates, which have no deleterious effect on the reaction components and which do not impair the catalytic properties, the suitable metallic or oxidic state being thus produced in the course of the reaction. When the reaction is carried out discontinuously, that means with a given batch of initial materials, the aforesaid catalysts are usually employed in an amount of about 3 to about 10 per cent by weight of the reaction mixture, the next batch being, if so desired, treated with the same catalyst.

A thorough mixing of the single constituents of the catalysts is often sufficient, but in many cases it is preferable to effect an intimate mixing by mutual precipitation of the components of the catalysts from a solution, or to precipitate one or more of these constituents onto an inert carrier.

The mutual proportions of the hydrogenating, dehydrating and activating constituents may vary within wide limits. Thus, for example, the activator may be used in amounts of less than 1 per cent by weight of the hydrogenating constituents, but it is also possible to employ mixtures of, say, 10 to 30 parts of copper with 70 to 90 parts of manganese oxide and bleaching earth. Alumina is a valuable activator when employed in amounts of a few per cent or also less than 1 per cent by weight of the hydrogenating metal; if, however, larger amounts of alumina are employed, such as from 10 to 90 per cent by weight of the whole catalyst, it acts as carrier with dehydrating properties. The reaction temperatures usually lie between about 200° and about 500° C. preferably between about 250° and about 400° C. If the reaction is carried out in the liquid phase, that means discontinuously, temperatures between about 250° and about 300° C. are usually employed, whereas, if the reaction is carried out in the gaseous phase or continuously, while allowing the liquid reaction mixture to trickle down upon a rigidly arranged catalyst, temperatures between about 250° and 350° C. are preferably employed. The more active the catalysts, the lower may be the temperature for the formation of amines.

The reaction may be carried out at atmospheric pressure, pressures above atmospheric pressure being, however, preferred. The upper limit of pressure is determined only by the resistance of the apparatus. Thus, pressures of up to 1000 atmospheres or more may be employed. Usually pressures between about 200 and about 800 atmospheres are used. The employment of high pressures is especially advantageous because it allows of obtaining a high concentration of hydrogen and ammonia in the liquid reaction mixture; this is of special value for accelerating the course of the reaction.

If it is desired to obtain a greater yield of primary amines it is recommended to employ a high partial pressure of ammonia; similarly, 75

comparatively low temperatures between the aforesaid limits also favorize the formation of primary amines.

When working with comparatively low molecular initial materials it is preferable to carry out the reaction continuously in the gaseous phase by leading the vaporized reaction mixture over rigidly arranged catalysts; high molecular initial materials may, however, also be worked in the said manner. But it is more convenient to work high molecular initial materials, such as fatty oils and fats, in the liquid phase, care being taken to provide a good mixing of the reaction mixture, as for example by working in a stirring autoclave or by trickling the reaction mixture over a rigidly arranged catalyst, or by trickling a suspension of the catalysts in the reaction mixture over filler bodies, such as Raschig rings or aluminium grits.

The term "high concentration of ammonia and/or of hydrogen" is intended to mean a quantity of said substances considerably in excess over that theoretically necessary for the conversion of the initial carboxylic acid substances into amines. Since the ammonia substances and hydrogen which did not react may be returned to the reaction, the employment of the said high concentrations is by no means uneconomical.

The reaction according to the present invention is especially valuable for the production of amines from carboxylic acid substances containing at least 6 carbon atoms.

It is sometimes possible by working under comparatively moderate conditions, that means at a comparatively low temperature, with a comparatively low concentration of hydrogen and/or with catalysts having a comparatively low hydrogenating action, that means catalysts containing no metals of the 8th group of the periodic system, or only a very small amount thereof, such as those comprising one or more of the following metals: copper, zinc, cadmium, manganese, chromium, molybdenum or vanadium (in the form of the above stated compounds) for example a catalyst comprising zinc, manganese, chromium and aluminium, to carry out the formation of amines in such a manner that aliphatic double linkages of the original carboxylic acid substances remain unaffected by the reaction, unsaturated aliphatic amines being thus obtained.

When the reaction is carried out with carboxylic acid substances containing aldehyde or keto groups, reaction products are obtained which contain a plurality of amino groups, the aldehyde or keto groups reacting in a similar way as the carboxyl group. Similarly polyamines are obtained from polycarboxylic acids. Thus, for example laevulic acid is converted into 2,5-di-amino-normal pentane.

The following examples will further illustrate the nature of this invention but the invention is not restricted to these examples. The parts are by weight, unless otherwise stated.

EXAMPLE 1

10 parts of a catalyst prepared by triturating with each part of an active aluminium oxide obtained by heating aluminium oxide at 950° C., 2 parts of a basic cobalt carbonate and reducing in a current of hydrogen at 325° C. are stirred into 100 parts of stearic acid methyl ester. The mixture is charged into a high pressure bomb and 40 parts of ammonia and sufficient hydrogen are pressed in to bring the total pressure up to

about 100 atmospheres. While stirring well, the whole is heated to 270° C., hydrogen being continually pressed in so that at the said temperature a pressure of about 200 atmospheres is maintained. When the absorption of hydrogen ceases, the reaction mixture is withdrawn, filtered while hot and while excluding air and subjected to distillation at a pressure of 2 millimetres (mercury gauge). Two fractions are obtained, 50 per cent boiling between 120° and 180° C., mainly at about 150° C. at the said pressure (Fraction I) and 46 per cent boiling between 230° and 280° C., mainly at about 270° C. (Fraction II).

Fraction I consists mainly of primary stearylamine $\text{CH}_3-(\text{CH}_2)_{16}-\text{CH}_2\text{NH}_2$. The amine may be obtained in the form of an entirely pure hydrochloride by dissolution in ether, precipitation with gaseous hydrochloric acid and dissolution in methyl alcohol.

Fraction II consists mainly of di-stearylamine $(\text{CH}_3-(\text{CH}_2)_{16}-\text{CH}_2)_2-\text{NH}$.

EXAMPLE 2

191 grams of copper and 330 grams of manganese in the form of their nitrates are dissolved in 9 litres of water. 300 grams of bleaching earth are added to the solution and, at from 45° to 50° C., a solution of 1512 grams of sodium bicarbonate in 18 litres of water is introduced while stirring well. The precipitate is filtered off by suction, washed, dried at from 90° to 100° C. in a vacuum drying cupboard and heated for 4 hours in a muffle furnace at 350° C.

15 grams of the catalyst thus prepared, 100 grams of acetic anhydride and 40 grams of ammonia gas are charged into a rotary high-pressure bomb of 1 litre capacity. Hydrogen is pressed in until the pressure at room temperature is 100 atmospheres. By heating the bomb to 270° C., the pressure increases to more than 200 atmospheres. By pressing in hydrogen, the pressure is kept at 250 atmospheres until no further decrease in pressure can be observed; the bomb is then allowed to cool. After releasing the pressure, by allowing the mixture of ammonia and hydrogen, with which may be admixed ethylamine, to escape, the reaction product is freed from catalyst by filtration and distilled. In addition to a first running containing amines and a small amount of residue, 65 grams of colourless, limpid liquid boiling between 180° and 209° C. are obtained of which 46 grams boil between 194° and 208° C. The nitrogen content of this fraction amounts to 16.26 per cent, i. e. it is practically pure ethylacetamide $\text{CH}_3-\text{CONHC}_2\text{H}_5$. Ethylamine may be obtained by saponification of the ethylacetamide.

EXAMPLE 3

1125 grams of crystalline aluminium nitrate, 873 grams of crystalline cobalt nitrate and 6 grams of barium nitrate are dissolved in 6 litres of water. A solution of 1344 grams of sodium bicarbonate in 16 litres of water is sprayed into the said solution at 40° C., while stirring. The whole is stirred for a further 30 minutes and the precipitate is filtered off. After it has been suspended in water several times and filtered again, the precipitate is dried in a vacuum drying cupboard at from 80° to 100° C. and the dry finely powdered product is reduced in a current of hydrogen at 350° C.

86 grams of capric acid and 129 grams of aniline together with 20 grams of the catalyst thus prepared are treated in a stirring autoclave for

hours at 270° C. under a pressure of hydrogen of 200 atmospheres. The reaction product obtained is freed from catalyst by filtration and distilled. The amine content of the single fractions are determined by titrating the product dissolved in methyl alcohol with normal hydrochloric acid using methyl red as the indicator. In the following table, the values given in the column of amine contents are the number of cubic centimetres of normal hydrochloric acid required for the titration of 1 gram of the fraction concerned.

Table

Amount employed for the distillation: 162 grams

Fraction	Temperature	Amount	Amine content
		Grams	
1.....	Up to 120° 760 mm.	5.4	3.80
2.....	120° to 160° 760 mm.	30.8	6.01
3.....	160° to 200° 760 mm.	4.3	4.06
4.....	104° to 160° 13 mm.	46.6	5.05
5.....	180° to 180° 13 mm.	28.0	3.41
6.....	180° to 200° 13 mm.	3.3	2.29
7.....	200° to 220° 13 mm.	36.8	0.88
8.....	220° to 230° 13 mm.	3.0	0.45
9.....	Residue	2.5	
25		160.7	

Fractions 2 and 4 contain mainly cyclohexylamine or dicyclohexylamine. Fraction 5 corresponds to cyclohexyldecylamine. This base may be obtained from Fraction 5 as the hydrochloride or in the pure state by careful fractionation. Fraction 7 contains in addition to tertiary bases probably capric acid amide which is substituted on the nitrogen atom.

EXAMPLE 4

86 grams of capric acid and 186 grams of butylamine are treated at 270° C. with hydrogen under a pressure of 200 atmospheres with an addition of 20 grams of the catalyst prepared according to Example 3. When there is no further absorption of hydrogen, the whole is allowed to cool, the reaction product is filtered from catalyst and dried with caustic alkali. A part of the filtrate is distilled; it boils in the following fractions:

	Boiling range	Pressure in millimetres	Yield in grams
	Degrees		
1.....	80 to 90	760	9
2.....	90 to 135	760	2
3.....	Up to 70	17	79
4.....	70 to 105	17	16
5.....	105 to 144	17	6
6.....	144 to 160	17	20
7.....	160 to 175	17	7.4
8.....	175 to 195	17	15.2
9.....	195 to 215	17	15.4
10.....	Residue		6.5

Fraction 1 consists mainly of butylamine, Fraction 3 of dibutylamine, Fraction 4 of tributylamine, Fraction 6 of butyldecylamine. Fractions 8 and 9 probably contain alkylated capric acid amides as well as amines.

EXAMPLE 5

150 grams of dekahydronaphthalene, 100 grams of stearic methyl ester, 10 grams of a catalyst prepared as described in Example 3, 40 grams of ammonia and sufficient hydrogen to produce a pressure of about 235 atmospheres at 270° C., are introduced into a high-pressure bomb and allowed to act on each other as long as a decrease in pressure can be observed. By pressing in hy-

drogen, the pressure is kept constant at from 230 to 240 atmospheres. A part of the reaction product obtained is filtered and distilled under a pressure of 16 millimetres (mercury gauge). The fraction boiling between 167° and 235° C. contains (as determined by titrimetric observations) 25.7 grams of stearylamine while the distillation residue of 33 grams boiling above 235° C. has a content of 25.5 grams of distearylamine.

EXAMPLE 6

100 grams of stearic acid methyl ester, 40 grams of ammonia and 20 grams of a catalyst prepared according to Example 2 are introduced into a high-pressure bomb and hydrogen is pressed in until the total pressure at room temperature is 100 atmospheres. The bomb is heated to 270° C. and allowed to cool as soon as there is no further decrease in pressure. The reaction product is freed from catalyst by filtration while still hot and distilled at from 2 to 3 millimetres (mercury gauge).

25 per cent boil at from 151° to 172° C.—Fraction 1.

6 per cent boil at from 172° to 230° C.—Fraction 2.

57 per cent boil at from 230° to 300° C.—Fraction 3.

The amine contents of the three fractions are determined by titration and are as follows:

Fraction 1 contains 98 per cent of stearylamine. Fraction 2 contains 74 per cent of stearylamine. Fraction 3 contains 90 per cent of distearylamine.

EXAMPLE 7

100 grams of acetic acid ethyl ester, 15 grams of a catalyst prepared according to Example 3 and 40 grams of ammonia are treated under pressure with hydrogen at 270° C. in a high-pressure autoclave of 1 litre capacity. The total pressure is about 250 atmospheres. When there is no further decrease in pressure, the whole is allowed to cool and the hydrogen and ammonia are allowed to escape, any ethylamine formed as escaping with them. After filtration, 78 grams of a strongly ammoniacal-odored liquid are obtained. 47.4 grams thereof boil up to 135° C. (Fraction 1), 1.5 grams boil between 135° and 198° C. (Fraction 2) and 22.4 grams between 198° and 210° C. (Fraction 3). The distillation residue is about 1 gram. The hydrochlorides of a mixture of amines which are soluble in chloroform may be isolated from Fraction 1, of which 1 gram requires 6.40 cubic centimetres of normal hydrochloric acid for neutralization. The said solubility indicates the hydrochlorides of diethylamine and triethylamine. Fraction 3 is practically pure ethyl-acetamide.

EXAMPLE 8

700 cubic centimetres of pumice stone (average diameter of the grains: 5 to 10 millimetres) are moistened with 100 cubic centimetres of distilled water and strewed with 150 grams of a catalyst prepared according to Example 2 while being stirred round. 700 cubic centimetres of the catalyst thus obtained are charged into a tube and reduced in a current of hydrogen at 350° C. By moving the tube in an electric heating jacket, care is taken that every part of the catalyst contained in the tube is effectively heated to 350° C. during the reduction.

45 grams of nonylenic acid methyl ester, 25 litres of ammonia gas and 75 litres of hydrogen

are led per hour over the catalyst at 350° C. The reaction product obtained by condensation consists of two layers, the lower being aqueous and the upper oily, the layers being in the ratio of 1:5. The oily layer is separated, dried and distilled in vacuo. Of the 340 parts, 200 boil between 86° and 107° at 10 millimetres (mercury gauge); their amine content (calculated as non-ylamine) is 7.9 per cent. 75 parts boil between 107° and 200° C.; the amine content (calculated as dinonylamine) is 23 per cent. 32 parts remain as a distillation residue.

EXAMPLE 9

100 grams of benzoic acid ethyl ester and 20 grams of a catalyst prepared according to Example 2 are treated as described in Example 2 with ammonia and hydrogen at 270° C. and at about 200 atmospheres pressure.

The reaction product, freed from catalyst by filtration, is distilled at 11 millimetres (mercury gauge). The main fraction passes over at between 68° and 72° C. It consists substantially of benzylamine. 1 gram of the main fraction requires 7.97 cubic centimetres of normal hydrochloric acid for neutralization. A second fraction passes over between 153° and 164° C. in an amount of about 40 per cent of the main fraction. 1 gram of this distillate requires 2.80 cubic centimetres of normal hydrochloric acid for neutralization. Dibenzylamine may be obtained in the form of its hydrochloride in a state of analytical purity from the fraction boiling between 153° and 164° C.

EXAMPLE 10

258 grams of dibutylamine and 86 grams of capric acid are treated with 30 grams of a catalyst prepared according to Example 3 and hydrogen under a pressure of 230 atmospheres at 270° C.

180 grams of the filtered reaction product are distilled. The following amounts boil at the given temperature under a pressure of 8 millimetres (mercury gauge):

Below 50° C.—86 grams (dibutylamine)
50° to 82° C.—30 grams (tributylamine).

Amine content in ccs. of n-HCl (see Example 3)

82° to 131° C. 6.5 grams----- 4.52
131° to 134° C. 14.2 grams----- 4.38
134° to 150° C. 11.2 grams----- 3.05
150° to 153° C. 10.0 grams----- 2.98
Above 153° C. 6.5 grams----- 1.87
Residue 3.5 grams.

Butyldecylamine hydrochloride may be isolated in a pure state from the fraction boiling between 131° and 134° C. The fraction boiling between 150° and 153° C. is probably almost pure dibutyldecylamine.

EXAMPLE 11

100 grams of lauric acid, 180 grams of ethylene diamine (about 70 per cent) and 20 grams of a catalyst according to Example 2 are treated with hydrogen at 270° C. under a pressure of about 300 atmospheres according to Example 2.

A part of the resulting filtered reaction product is distilled. Unchanged ethylene diamine and water pass over between 100° and 129° C. and the distillation is then continued under a pressure of 2 millimetres (mercury gauge). The temperature rises immediately to 168° C. 41.5 grams boil between 168° and 190° C., 6.5 grams

between 190° and 240° C. and the residue amounts to 24.0 grams. 1 gram of the main fraction boiling between 168° and 190° C. requires 4.74 cubic centimetres of normal hydrochloric acid for neutralization. The oxygen content of this fraction amounts to only 2.57 per cent.

EXAMPLE 12

100 grams of butyric acid octodecyl ester, 40 grams of ammonia and 20 grams of a catalyst according to Example 2 are treated as described in Example 2 with hydrogen at 270° C. under a pressure of 220 atmospheres. The greater part of the reaction product is separated from the catalyst by extraction with diethyl ether. The ether, which is distilled off from the reaction product, contains amines. The butylamine formed is probably for the greater part volatile with the ether. The residue remaining after the distillation of the ether boils as follows:

Pressure in millimetres	Temperature centigrade	Yield	Amine content in cubic centimetres of n-HCl (according to Example 3)
	Degrees	Grams	
760-----	60 to 68	2.0	2.15
7-----	82 to 145	2.2	3.92
7-----	145 to 190	1.5	1.53
7-----	190 to 240	29.5	2.59
7-----	213 to 272	29.0	1.60
1-----	Residue	11.0	0.99

EXAMPLE 13

100 grams of stearic acid methyl ester, 40 grams of ammonia, and 20 grams of a catalyst prepared by heating for 4 hours basic cobalt carbonate at about 350° C. are heated in a high pressure rotary bomb at between about 250° and 270° C., hydrogen being pressed in so that the pressure is maintained at 250 atmospheres. The reaction product is freed from the catalyst by filtration and subjected to fractional distillation. About 55 per cent of monostearylamine and about 43 per cent of distearylamine are obtained, calculated on the amount of stearic ester employed.

EXAMPLE 14

100 grams of coconut oil, 40 grams of ammonia and 20 grams of the catalyst employed according to Example 13 are heated at 250° C. in a rotary high pressure bomb while maintaining a pressure of 250 atmospheres by means of hydrogen. After removing the catalyst by filtration the resulting mixture of amines obtained is subjected to fractional distillation in vacuo. About 40 per cent of monoamines, calculated on the amount of coconut oil employed, are thus distilled over between about 125° and about 223° C., at a pressure of 17 millimetres mercury gauge, and about 50 per cent of diamines at between about 183° and about 260° C. at a pressure of 2 millimetres mercury gauge.

EXAMPLE 15

A solution of 14.5 kilograms of copper nitrate, 22.5 kilograms of aluminium nitrate and 0.12 kilogram of barium nitrate in 120 kilograms of water is warmed to 40° C. 26.88 kilograms of sodium bicarbonate, dissolved in 320 kilograms of water are slowly stirred into the solution. The resulting precipitate is separated from the liquid by filtration, washed with water, dried and then heated for 4 hours at about 350° C. The resulting dry catalyst is comminuted to fragments having an average diameter between about 3 and

about 10 millimetres and is then brought into a vertical pressure-tight tower. The catalyst is then reduced in the tower by means of streaming hydrogen at between about 300 and about 350° C.

- 5 Lauric acid methyl ester is allowed to trickle down through the tower at 270° C. and at a hydrogen pressure of about 200 atmospheres, at the rate of from 2 to 6 times the volume occupied by the catalyst in the course of 24 hours, together with liquefied ammonia in an amount of from 1 to 3 times the volume occupied by the catalyst. The hydrogen is employed in a cycle. A mixture consisting of from 70 to 75 per cent of monododecyl amine and of from 30 to 25 per cent of didodecylamine is continuously withdrawn at the bottom of the tower.

What we claim is:

1. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at a temperature between about 200° C. and about 500° C. in the presence of a combined hydrogenation-dehydration catalyst.

- 25 2. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at a temperature between about 200° C. and about 500° C. in the presence of an activated, combined hydrogenation-dehydration catalyst.

3. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at between about 200° and about 500° C. in the presence of an activated, combined hydrogenation-dehydration catalyst.

- 40 4. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at between about 200° and about 500° C. in the presence of an activated, combined hydrogenation-dehydration catalyst and at a pressure between atmospheric and 1000 atmospheres.

- 50 5. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of ammonia and hydrogen at between about 200° and about 500° C. in the presence of an activated, combined hydrogenation-dehydration catalyst and at a pressure between about 200 and about 1000 atmospheres.

- 60 6. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at between about 200° and about 500° C. in the presence of a hydrogenation catalyst.

- 70 7. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at between about 250° and about 400° C. in the presence of a hydrogenation catalyst.

8. A process for the production of amines which comprises reacting a long chain fatty acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at between about 200° and

about 500° C. in the presence of a hydrogenation catalyst.

9. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at between about 250° and about 400° C. in the presence of an activated combined hydrogenation-dehydration catalyst, the hydrogenating constituent of which comprises essentially copper.

10. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at between about 250° and about 400° C. in the presence of an activated combined hydrogenation-dehydration catalyst, the hydrogenating constituent of which comprises essentially at least one metal selected from the 8th group of the periodic system.

11. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at between about 250° and about 400° C. in the presence of an activated combined hydrogenation-dehydration catalyst, the hydrogenating constituent of which comprises essentially cobalt and the dehydrating constituent of which comprises essentially a substance selected from the group consisting of alumina, silica gel and bleaching earth.

12. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms in the acid radical with a mixture of an ammonia substance and hydrogen at between about 250° and about 400° C. in the presence of an activated combined hydrogenation-dehydration catalyst, the hydrogenating constituent of which comprises essentially copper and the dehydrating constituent of which comprises essentially a substance selected from the group consisting of alumina, silica gel and bleaching earth.

13. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms with a mixture of ammonia, an alcoholic substance and hydrogen at between about 200° and about 500° C. in the presence of a hydrogenation catalyst.

14. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms with a mixture of ammonia, a compound containing a carboxyl group and hydrogen at between about 200° and about 500° C. in the presence of a hydrogenation catalyst.

15. A process for the production of amines which comprises reacting a carboxylic acid substance containing at least 6 carbon atoms with a mixture of ammonia, a nitrile and hydrogen at between about 200° and about 500° C. in the presence of a hydrogenation catalyst.

16. The process of preparing dodecylamines which comprises heating ammonium laurate with hydrogen at about 250° C. and at a pressure of from about 50 to about 500 atmospheres in the presence of a copper hydrogenation catalyst.

17. The process of producing amines which comprises bringing a mixture of a member of the group consisting of mono- and dicarboxylic acids and a member of the group consisting of ammonia and the primary and secondary amines with hydrogen, into contact with a hydrogenation

catalyst at a temperature between about 200° C. and about 450° C. and at a pressure between about 10 and about 600 atmospheres.

5 18. The process which comprises hydrogenating a mixture of a lower alkyl ester of a soap-forming fatty acid and ammonia with hydrogen in the presence of a hydrogenation catalyst at a temperature between about 200° C. and about 450° C. and at a pressure between about 10 and about 600 atmospheres.

10 19. The process which comprises hydrogenating a mixture of capric acid with one of the group consisting of ammonia, primary and secondary amines, with hydrogen in the presence of a hy-

drogenation catalyst at a temperature of about 270° C. and between about 200 and about 275 atmospheres.

20. The process of producing amines which comprises hydrogenating with hydrogen a mixture of a carboxylic acid ester of a straight chain lower aliphatic alcohol and one of the group consisting of ammonia, primary and secondary amines in the presence of a hydrogenation catalyst and at a temperature between about 200° C. and about 450° C. and at a pressure between about 10 and about 600 atmospheres.

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