

Process for the preparation and work-up of a reaction mixture containing triacetone amine

5 The present invention relates to a process for the preparation of triacetone amine, comprising the reaction of acetone and ammonia in the presence of a catalyst, and the subsequent work-up of the resulting reaction mixture.

Background of the invention

10 Triacetone amine (2,2,6,6-tetramethyl-4-piperidinone; TAA) is an important chemical intermediate which is used for the synthesis of numerous secondary products. Important secondary products in this connection are, for example, light stabilizers (hindered amine light stabilizers [HALS]), oxidizing agents and polymerization moderators (e.g. nitroxyl radicals).

15 The preparation of triacetone amine from acetone and ammonia is documented in the form of various processes. In this connection, the preparation processes are firstly subdivided roughly into the direct (one-stage) synthesis of TAA from the starting materials, described for example in DE2429937, US4536581, JP54088275 or in Zeitschrift für Naturforschung 1976, 328-337 and 338-345, and also the indirect (two-stage) synthesis via acetonin (2,2,4,4,6-pentamethyl-

20 1,2,5,6-tetrahydropyrimidine), described for example in DE2429935 or DE2429936, or via phorone (2,6-dimethyl-2,5-heptadien-4-one), e.g. in DE2352127. In the two-stage TAA synthesis via acetonin, this is formed firstly starting from acetone and ammonia and can then react further to give TAA in a subsequent step with the elimination of one equivalent of ammonia. In the case of the synthesis process via acetonin, however, both species (TAA and

25 acetonin) are always formed simultaneously, although the acetonin formation is greatly preferred in kinetic terms compared with the formation of TAA. In the "one-stage" TAA synthesis, the acetonin that is formed is simply not isolated.

The prior art discusses a TAA synthesis starting from acetone or acetone condensation

30 products. The basis for this is that during the reaction of acetone and ammonia firstly acyclic addition and condensation products (e.g. diacetone alcohol [4-hydroxy-4-methylpentan-2-one], diacetone amine [4-amino-4-methylpentan-2-one], mesityl oxide [4-methylpent-3-en-2-one], phorone etc.) are formed. These intermediates then react further to give TAA and can therefore

also be used directly as starting materials for the reaction, e.g. in the sense of an in-process recycle stream.

5 The preparation of TAA is fundamentally possible both under homogeneous catalysis (mostly by ammonium salts) and also under heterogeneous catalysis (e.g. over acidic ion exchangers).

Most of the documents from the prior art refer to homogeneously catalysed reactions. In this connection, mention is made most often of calcium chloride (e.g. in Chemical Industries 2003, 89, 559-564; Zeitschrift für Naturforschung 1976, 328-337 and 338-345), ammonium chloride
10 (e.g. in JP2003-206277; JP2001-031651; JP04154762) and hydrazine derivatives (e.g. in JP54088275; JP54112873A). However, problems arise when using these catalysts. Thus, for example, the use of calcium chloride has the disadvantage that a very slow reaction takes place. In the case of ammonium chloride, the reaction rate is higher, but the chloride used exhibits high corrosivity towards steel. By contrast, hydrazine derivatives exhibit very high
15 toxicity.

The preparation is described both in the batch process (see the aforementioned documents) and also in the continuous process (e.g. in JP02204480; JP02145571).

20 In general, TAA is prepared in a matrix in which the acetone is present in a large excess and serves both as reactant and also as solvent. Consequently, at the end of the reaction, a crude product is formed which, besides TAA, comprises a large fraction of acetone, and also unreacted ammonia, water formed by the condensation and, in the case of homogeneously catalysed processes, the catalyst. Moreover, further secondary components are present, such
25 as e.g. acyclic condensation products (e.g. diacetone alcohol, diacetone amine, mesityl oxide, phorone etc.), cyclic condensation products (e.g. acetonin, TMDH-pyridine [2,2,4,6-tetramethyl-2,3-dihydropyridine]) or higher molecular weight condensation products ("high boilers").

The most common processes for isolating pure TAA from said mixtures are in particular
30 distillative work-up and crystallization.

Distillative work-up can be carried out both in a batch process (e.g. in JP2003-206277; JP2001-031651; JP04154763; DE 2429937) and also in a continuous process (e.g. in

JP2003-160561). It is known that in the case of homogeneously catalysed processes, which are carried out e.g. using ammonium salts, the acid catalyst has to be deactivated before the distillation by adding base since otherwise a decomposition of the product takes place during the distillation (e.g. in JP04154763).

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Crystallization generally involves an addition of water to a concentrated solution of TAA in a nonpolar solvent (e.g. in hydrocarbons), precipitation of the TAA hydrate, optional washing thereof with a further solvent. This process step mostly takes place in combination with a prior distillative separation of the low boilers and thus merely replaces the purification by distillation (e.g. in JP04154763).

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The processes for the homogeneously catalysed preparation of TAA described in the prior art deal primarily with the reaction, the deactivation of the catalyst and also a subsequent isolation of the TAA by means of a batch distillation (e.g. JP2001-031651, JP04154763, US4536581, JP 05140104). These described processes are less suitable for industrial preparation since they are either problematic to carry out or problems arise during the work-up.

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Thus, synthesis using inorganic salts as catalysts leads to special and high-cost steels having to be used for plant construction in order to avoid corrosion problems. This is the case particularly when using halide-containing catalysts (thus e.g. in the case of the catalysts, ammonium chloride and calcium chloride specified most frequently in the prior art), which do not permit the use of many steels and stainless steels.

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Moreover, for all homogeneously dissolved inorganic catalysts, the problem arises that they accumulate in the distillation bottom during distillative work-up of the crude product. Particularly with regard to an industrial preparation, this accumulation leads to technical problems since deposits can form in the distillation boiler or on the heat exchanger. Although some of the prior art documents (e.g. JP2001-031651, JP04154763, US4536581, JP05140104) describe the addition of a base and the subsequent removal of an aqueous phase, this serves merely for the required deactivation of the catalyst described above (e.g. addition of NaOH when using NH_4Cl as catalyst and formation of NaCl, water and ammonia). After separating off the aqueous phase, some of the deactivated catalyst is still present in the organic phase and is accumulated in the bottom during a distillation.

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Although complete removal of the deactivated catalyst is technically possible, the known processes for removing the salt fraction by extraction are for their part likewise problematic since they require the use of a large amount of auxiliaries, which leads to a large amount of problematic waste waters. Thus, although the repeated, sequential admixing of the crude
5 product with a base, followed in each case by a phase separation (crossflow extraction; see e.g. K. Sattler, *Thermische Trennverfahren* [Thermal Separation Processes], 3rd Edition, **2001**, Wiley-VCH Weinheim, p. 542ff.), leads to a complete removal of salt, this is accomplished only using a large amount of base and its addition in solid form.

The alternative option of a countercurrent extraction (single addition of fresh extractant in the
10 last extraction step and recycling of the extract to the preceding extraction step) is described in JP2003-206277. JP2003-206277 describes a two-stage countercurrent extraction, although it can also be operated with a larger number of stages. However, the process described in JP2003-206277 also has the disadvantages specified above. Thus, adequate removal of salt is achieved only by using a large amount of base, which leads to the formation of a large waste
15 stream.

The object of the embodiments disclosed herein is therefore to provide an improved process for the industrial preparation of triacetone amine. This process should overcome the aforementioned problems. In particular, it should thus reduce the amount of waste materials
20 produced. It should proceed using a cost-effective and nontoxic catalyst which can also be used efficiently in a continuous process procedure. Finally, the improved process should also permit a simplified and efficient work-up of the triacetone amine.

Short description

Surprisingly, it has now been found that the aforementioned object is achieved by a process according to the present disclosure. Accordingly, a first subject matter of the present disclosure is

1. a process for the preparation of triacetone amine, comprising the reaction steps
 - a) reaction of an acetone equivalent with a first base, selected from ammonia, in the presence of a catalyst, giving a product mixture which comprises acetone;
 - b) deactivation of the product mixture from step a) by adding a further base, giving a triacetone amine crude product which comprises acetone;
 - c) removal of acetone from the triacetone amine crude product from step b), giving an acetone-depleted triacetone amine crude product;
 - d) extraction of the acetone-depleted triacetone amine crude product from step c) by adding an auxiliary, giving an extracted triacetone amine crude product.

In a first aspect, there is provided a process for the preparation of triacetone amine, comprising the reaction steps

- a) reaction of an acetone equivalent with a first base, selected from ammonia, in the presence of a catalyst, giving a product mixture which comprises acetone;
- b) stopping the catalytic activity of the catalyst used in step a) of the product mixture by adding a further base, wherein the further base is a base different from ammonia and has a lower pK_B value than ammonia, giving a triacetone amine crude product which comprises acetone;
- c) removal of acetone from the triacetone amine crude product from step b), giving an acetone-depleted triacetone amine crude product;
- d) extraction of the acetone-depleted triacetone amine crude product from step c) by adding an auxiliary, characterized in that a base is used as auxiliary in step d), thus desalting the solution obtained after step c) of the process, giving an extracted triacetone amine crude product.

2. In a further embodiment of the disclosure, the process as defined above is characterized in that in a further step e), the extracted triacetone amine crude product from step d) is purified to give triacetone amine.
- 5 The process according to the disclosure has the advantage that the catalyst used in step a) and deactivated in step b) is removed prior to the purification of the extracted triacetone amine crude product in step e), which can take place for example by distillation. This prevents an accumulation of the deactivated catalyst in the distillation bottom. In this connection, it permits the process as defined above to reduce the fraction of deactivated catalyst to below the limit of
10 detection, and in so doing to use a considerably smaller amount of auxiliaries compared to the prior art, as a result of which the amount of waste streams produced is also kept low.
3. In a further embodiment of the disclosure, the process as defined above is characterized in that the acetone equivalent is one or more of the compounds selected from the group
15 consisting of acetone, mesityl oxide, diacetone alcohol, phorone, diacetone amine, acetoin.

4. In a further embodiment of the disclosure, the process as defined above is characterized in that the acetone equivalent is acetone.
5. In a further embodiment of the disclosure, the process as defined above is characterized in that the removal of acetone from the triacetone amine crude product in step c) takes place by distillation.
6. In a further embodiment of the disclosure, the process as defined above is characterized in that the further base in step b) is selected from the group consisting of an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkali metal carbonate, an alkaline earth metal carbonate.
7. In a further embodiment of the disclosure, the process as defined above is characterized in that sodium hydroxide or potassium hydroxide is used as further base in step b).
8. In a further embodiment of the disclosure, the process as defined above is characterized in that sodium hydroxide is used as further base in step b).
9. In a further embodiment of the disclosure, the process as defined above is characterized in that an aqueous solution of sodium hydroxide is used as further base in step b).
10. In a further embodiment of the disclosure, the process as defined above is characterized in that an aqueous solution of sodium hydroxide, comprising 40-60% (mass percent) NaOH, is used as further base in step b).
11. In a further embodiment of the disclosure, the process as defined above is characterized in that an aqueous solution of sodium hydroxide, comprising 45-55% (mass percent) NaOH, is used as further base in step b).

12. In a further embodiment of the disclosure, the process as defined above is characterized in that potassium hydroxide is used as further base in step b).
- 5 13. In a further embodiment of the disclosure, the process as defined above is characterized in that an aqueous solution of potassium hydroxide is used as further base in step b).
14. In a further embodiment of the disclosure, the process as defined above is characterized in that an aqueous solution of potassium hydroxide, comprising 40-60% (mass percent) KOH, is used as further base in step b).
- 10 15. In a further embodiment of the disclosure, the process as defined above is characterized in that an aqueous solution of potassium hydroxide, comprising 45-55% (mass percent) KOH, is used as further base in step b).
- 15 16. In a further embodiment of the disclosure, the process as defined above is characterized in that the amount of further base added in step b) is in the range from 1.0 to 2.0 molar equivalents, based on the amount of catalyst used in step a).
- 20 17. In a further embodiment of the disclosure, the process as defined above is characterized in that the amount of further base added in step b) is in the range from 1.0 to 1.4 molar equivalents, based on the amount of catalyst used in step a).
- 25 18. In a further embodiment of the disclosure, the process as defined above is characterized in that the amount of further base added in step b) is 1.2 molar equivalents, based on the amount of catalyst used in step a).

19. In a further embodiment of the disclosure, the process as defined above is characterized in that a base is used as auxiliary in step d).
20. In a further embodiment of the disclosure, the process as defined above is characterized in that a base selected from the group consisting of an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkali metal carbonate, an alkaline earth metal carbonate is used as auxiliary in step d).
21. In a further embodiment of the disclosure, the process as defined above is characterized in that a base selected from the group consisting of sodium hydroxide or potassium hydroxide is used as auxiliary in step d).
22. In a further embodiment of the disclosure, the process as defined above is characterized in that a base, namely sodium hydroxide, is used as auxiliary in step d).
23. In a further embodiment of the disclosure, the process as defined above is characterized in that a base, namely an aqueous solution of sodium hydroxide, is used as auxiliary in step d).
24. In a further embodiment of the disclosure, the process as defined above is characterized in that a base, namely an aqueous solution of sodium hydroxide, comprising 40-60% (mass percent) NaOH, is used as auxiliary in step d).
25. In a further embodiment of the disclosure, the process as defined above is characterized in that a base, namely an aqueous solution of sodium hydroxide, comprising 45-55% (mass percent) NaOH, is used as auxiliary in step d).
26. In a further embodiment of the disclosure, the process as defined above is characterized in that a base, namely potassium hydroxide, is used as auxiliary in step d).

27. In a further embodiment of the disclosure, the process as defined above is characterized in that a base, namely an aqueous solution of potassium hydroxide, is used as auxiliary in step d).
- 5 28. In a further embodiment of the disclosure, the process as defined above is characterized in that a base, namely an aqueous solution of potassium hydroxide, comprising 40-60% (mass percent) of KOH, is used as auxiliary in step d).
- 10 29. In a further embodiment of the disclosure, the process as defined above is characterized in that an aqueous solution of potassium hydroxide, comprising 45-55% (mass percent) KOH, is used as base in step d).
- 15 30. In a further embodiment of the disclosure, the process as defined above is characterized in that the amount of base added in step d) as auxiliary is in the range from 1.0 to 6.0 molar equivalents, based on the amount of catalyst used in step a).
- 20 31. In a further embodiment of the disclosure, the process as defined above is characterized in that the amount of base added as auxiliary in step d) is in the range from 1.0 to 4.0 molar equivalents, based on the amount of catalyst used in step a).
- 25 32. In a further embodiment of the disclosure, the process as defined above is characterized in that the amount of base added as auxiliary in step d) is in the range from 1.0 to 2.0 molar equivalents, based on the amount of catalyst used in step a).
33. In a further embodiment of the disclosure, the process as defined above is characterized in that the amount of base added as auxiliary in

step d) is in the range from 1.0 to 1.4 molar equivalents, based on the amount of catalyst used in step a).

- 5 34. In a further embodiment of the disclosure, the process as defined above is characterized in that the amount of base added as auxiliary in step d) is 1.2 molar equivalents, based on the amount of catalyst used in step a).
- 10 35. In a further embodiment of the disclosure, the process as defined above is characterized in that a phase separation additionally takes place between step b) and step c).
36. In a further embodiment of the disclosure, the process as defined above is characterized in that a phase separation additionally takes place between step b) and step c), and the organic phase of the triacetone amine crude product is used in steps c) to d).
- 15 37. In a further embodiment of the disclosure, the process as defined above is characterized in that the acetone equivalent used in step a) is acetone and the molar ratio of acetone to ammonia used in the reaction in step a) is 3 : 1 to 20 : 1.
- 20 38. In a further embodiment of the disclosure, the process as defined above is characterized in that the acetone equivalent used in step a) is acetone and the molar ratio of acetone to ammonia used in the reaction in step a) is 6 : 1 to 9 : 1.
39. In a further embodiment of the disclosure, the process as defined above is characterized in that the reaction in step a) is carried out at temperatures in the range from 20-80°C.
- 25 40. In a further embodiment of the disclosure, the process as defined above is characterized in that the reaction in step a) is carried out at temperatures in the range from 40-80°C.

41. In a further embodiment of the disclosure, the process as defined above is characterized in that the reaction in step a) is carried out at temperatures in the range from 60-70°C.
- 5 42. In a further embodiment of the disclosure, the process as defined above is characterized in that the reaction in step a) is carried out at a pressure in the range from 1 to 16 bar.
43. In a further embodiment of the disclosure, the process as defined above is characterized in that the reaction in step a) is carried out at a pressure in the range from 1 to 10 bar.
- 10 44. In a further embodiment of the disclosure, the process as defined above is characterized in that the reaction in step a) is carried out at a pressure in the range from 1 to 6 bar.
45. In a further embodiment of the disclosure, the process as defined above is characterized in that ammonia is added in step a) in gaseous form or as a liquid.
- 15 46. In a further embodiment of the disclosure, the process as defined above is characterized in that, in a further step e), the extracted triacetone amine crude product from step d) is purified by distillation to give triacetone amine.
- 20 47. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is selected from the group consisting of Brönsted acids, ammonium salts of a Brönsted acid, phosphonium salts of a Brönsted acid, Lewis acids.
- 25 48. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is a Brönsted acid.

49. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is selected from the group consisting of hydrochloric acid, sulphuric acid, nitric acid, organic acids of the formula RCOOH , sulphonic acids of the formula RSO_3H , where R is selected from the group consisting of saturated, unsaturated, branched, unbranched, ring-closed, open-chain aliphatic, aromatic, substituted, unsubstituted hydrocarbon radicals.

50. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is a phosphonium salt of a Brönsted acid.

51. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is a phosphonium salt of a Brönsted acid, where the Brönsted acid is selected from the group consisting of hydrochloric acid, sulphuric acid, nitric acid, of an organic acid of the formula RCOOH , sulphonic acids of the formula RSO_3H , where R is selected from the group consisting of saturated, unsaturated, branched, unbranched, ring-closed, open-chain aliphatic, aromatic, substituted, unsubstituted hydrocarbon radicals.

52. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is an ammonium salt of a Brönsted acid.

53. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is an ammonium salt of a Brönsted acid, where the Brönsted acid is selected from the group consisting of hydrochloric acid, sulphuric acid, nitric acid, an organic acid of the formula RCOOH , sulphonic acids of the formula RSO_3H , where R is selected from the group consisting of saturated, unsaturated, branched, unbranched, ring-closed, open-chain aliphatic, aromatic, substituted, unsubstituted hydrocarbon radicals.

54. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is ammonium chloride or ammonium nitrate.
55. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is ammonium nitrate.
56. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is a Lewis acid.
57. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is a Lewis acid, where the Lewis acid is selected from compounds of the elements of the fourth group of the Periodic Table of the Elements, compounds of elements of the thirteenth group of the Periodic Table of the Elements, salts of alkali metals, salts of alkaline earth metals.
58. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is a Lewis acid, where the Lewis acid is selected from the group consisting of halides, alkoxides, alkyl compounds of the elements of the fourth and thirteenth groups of the Periodic Table of the Elements.
59. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is a Lewis acid, where the Lewis acid is selected from the group consisting of AlCl_3 , BF_3 , TiCl_4 , Al(OR)_3 , B(OR)_3 , Ti(OR)_4 , AlR_3 , where R is selected from the group consisting of saturated, unsaturated, branched, unbranched, ring-closed, open-chain aliphatic, aromatic, substituted, unsubstituted hydrocarbon radicals.
60. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is a

Lewis acid, where the Lewis acid is selected from the group consisting of salts of alkali metals, salts of alkaline earth metals.

- 5 61. In a further embodiment of the disclosure, the process as defined above is characterized in that the catalyst in step a) is a Lewis acid, where the Lewis acid is selected from the group consisting of CaCl_2 , MgCl_2 , LiCl .
- 10 62. In a further embodiment of the disclosure, the process as defined above is characterized in that the molar ratio of ammonia to catalyst in step a) is in the range 1 : 0.8 to 1 : 0.02.
63. In a further embodiment of the disclosure, the process as defined above is characterized in that the molar ratio of ammonia to catalyst in step a) is in the range 1 : 0.2 to 1 : 0.05.
- 15 64. In a further embodiment of the disclosure, the process as defined above is characterized in that in step d) a base is used as auxiliary and the base used in step d) and the base used in step b) are chemically identical.
- 20 65. In a further embodiment of the disclosure, the process as defined above is characterized in that the solvent in step a) is selected from the group consisting of aliphatic solvents, preferably pentane, hexane, heptane, octane, decane, cyclohexane, tetramethylsilane; aromatic solvents, preferably benzene, toluene, xylene; ether compounds, preferably diethyl ether, dipropyl ether, dibutyl ether, methyl tert-butyl ether; halogenated solvents, preferably dichloromethane, chloroform, tetrachloromethane; alcohols, preferably methanol, ethanol, propanol, isopropanol, butanol, tert-butanol; esters, preferably methyl acetate, ethyl acetate, propyl acetate, butyl acetate; acetone.
- 25 66. In a further embodiment of the disclosure, the process as defined above is characterized in that the solvent in step a) is acetone.

67. In a further embodiment of the disclosure, the process as defined above is characterized in that the extraction in step d) takes place at a temperature of 20-80°C.

68. In a further embodiment of the disclosure, the process as defined above is characterized in that the extraction in step d) takes place at a temperature of at least 20°C, preferably at 20-99°C, particularly preferably at 45-90°C, very particularly preferably at 45-80°C, most preferably at a temperature of 45 to 65°C, and ideally at a temperature of 60°C.

69. In a further embodiment of the disclosure, the process as defined above is characterized in that the acetone-depleted triacetone amine crude product obtained in step c) has an acetone content of less than 40% (mass percent), in particular of less than 20% (mass percent), preferably of less than 15% (mass percent), particularly preferably of less than 10% (mass percent), very particularly preferably of less than 2.5% (mass percent), most preferably of less than 1.5% (mass percent), ideally of less than 1% (mass percent).

70. In a further embodiment of the disclosure, the process as defined above is characterized in that the extraction of the acetone-depleted triacetone amine crude product in step d) is carried out as crossflow extraction.

71. In a further embodiment of the disclosure, the process as defined above is characterized in that the extraction of the acetone-depleted triacetone amine crude product in step d) is carried out as countercurrent extraction.

Detailed description of the invention

The process according to the invention is suitable for producing triacetone amine, but also for producing extracted triacetone amine crude product. In the first step [step a)] of the process according to the invention, the reaction of acetone with a first base, selected from ammonia, takes place in the presence of a catalyst, giving a product mixture which comprises acetone.

The reaction can be carried out continuously or in a batch operation. In the case of the batch operation, preferably all starting materials are combined, then the reaction mixture is heated. *Suitable reactors in this connection are all customary reactor types, e.g. stirred reactors, loop reactors or reactors with internal heat exchangers.*

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The reaction can take place in all solvents which do not prevent the reaction. In particular, the possible solvents are aliphatic solvents, preferably pentane, hexane, heptane, octane, decane, cyclohexane, tetramethylsilane; aromatic solvents, preferably benzene, toluene, xylene; ether compounds, preferably diethyl ether, dipropyl ether, dibutyl ether, methyl tert-butyl ether; halogenated solvents, preferably dichloromethane, chloroform, tetrachloromethane; alcohols, preferably methanol, ethanol, propanol, isopropanol, butanol, tert-butanol; esters, preferably methyl acetate, ethyl acetate, propyl acetate, butyl acetate; acetone.

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Particularly preferably, the reaction takes place in acetone by itself.

In a continuous operation, preferably all of the chemicals are metered in simultaneously at the reaction temperature. In the case of a continuous reaction, any reactor known to the person skilled in the art can be used, e.g. a continuous flow tube, a continuous stirred tank, a stirred-tank cascade, as well as possible combinations of these individual elements. In this connection, preference is given to using a combination of one or more reactors with internal or external circulation, followed by a post-reactor with flow tube characteristics.

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The reaction time in the batch operation is in the range 1 – 15 hours, preferably in the range 3 – 9 hours, particularly preferably in the range 5 – 7 hours. The reaction times for the continuous reaction procedure are given by the total residence time of the reactants in the reactor and are within the range specified for the batch operation.

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The reaction is preferably carried out at elevated temperature, in particular at temperatures in the range 20 – 80°C, preferably in the range 40 – 80°C, particularly preferably 60 – 70°C.

The reaction can either be carried out under the intrinsic pressure of the components or under increased pressure. Thus, the reaction can be carried out in the range 1 – 16 bar, preferably in the range 1 – 10 bar, particularly preferably in the range 1 – 6 bar.

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During the reaction, an acetone equivalent is reacted directly with ammonia. Within the context of the invention, the term "acetone equivalent" is understood here as meaning acetone itself and addition or condensation products of acetone with itself (e.g. mesityl oxide, diacetone alcohol, phorone) and/or addition or condensation products of acetone with ammonia (e.g. diacetone amine, acetoin), which can likewise be reacted productively to give TAA. In particular, the term "acetone equivalent" within the context of the invention means one or more compounds from the group consisting of mesityl oxide, diacetone alcohol, phorone, diacetone amine, acetoin, acetone. Preferably, the term "acetone equivalent" within the context of the invention means acetone. Moreover, the presence of inert or non-productive constituents in the reaction mixture is also possible.

Ammonia is preferably metered in as a pure substance, i.e. as gas, and is present during the reaction dissolved in acetone or dissolved in the reaction mixture.

The reaction takes place in the presence of a catalyst. Of suitability here are all catalysts described in the prior art for this type of reaction, e.g. Brönsted acids, salts of these acids or Lewis acids. The term "Brönsted acids" within the context of the invention encompasses in particular hydrochloric acid, sulphuric acid, nitric acid, organic acids (RCOOH) or sulphonc acids (RSO₃H), where R is selected from the group consisting of saturated, unsaturated, branched, unbranched, ring-closed, open-chain aliphatic, aromatic, substituted, unsubstituted hydrocarbon radicals. Within the context of the invention, substituted hydrocarbon radicals are hydrocarbon radicals substituted with heteroatoms, in particular hydrocarbon radicals substituted with one or more -OH, -NH, -CN, alkoxy and/or halogen radicals, preferably substituted with one or more halogen radicals, particularly preferably substituted with one or more radicals selected from F, Cl, Br and/or I, very particularly preferably with one or more radicals selected from F and/or Cl.

Within the context of the invention "salts of a Brönsted acid" are in particular ammonium salts (i.e. salts with ammonia, amines, hydrazines, hydroxylamines) or phosphonium salts (i.e. salts with phosphanes). Within the context of the invention, Lewis acids are in particular compounds of the fourth or thirteenth group of the Periodic Table of the Elements, preferably halides (AlCl₃, BF₃, TiCl₄), alkoxides [Al(OR)₃, B(OR)₃, Ti(OR)₄] or alkyl compounds (e.g. AlR₃ where R is selected from the group consisting of saturated, unsaturated, branched, unbranched, ring-closed, open-chain aliphatic, aromatic, substituted, unsubstituted hydrocarbon radicals).

Within the context of the invention, Lewis acids are also salts of Lewis-acidic alkali metals or alkaline earth metals (e.g. CaCl_2 , MgCl_2 , LiCl).

Preferably, the catalyst is selected from the group of ammonium salts, in particular from the group comprising salts of ammonia and strong Brönsted acids [e.g. hydrochloric acid, sulphuric acid, nitric acid, organic acids (RCOOH) or sulphonic acids (RSO_3H), where R is selected from the group consisting of saturated, unsaturated, branched, unbranched, ring-closed, open-chain aliphatic, aromatic, substituted, unsubstituted hydrocarbon radicals.

Very particularly preferably, ammonium nitrate is used as catalyst in the reaction in step a). Ammonium nitrate has the advantage that it is favourable, nontoxic, halide-free and therefore less corrosive.

The use ratios of the starting materials can be selected within wide ranges, in particular acetone is used in an excess relative to ammonia. Preferably, the molar ratio of acetone used to ammonia is 3 : 1 to 20 : 1, with a ratio of 6 : 1 to 9 : 1 being preferred.

The catalyst used in the reaction is preferably used in substoichiometric amounts. The molar ratio of ammonia to catalyst, preferably ammonium nitrate, is particularly preferably in the range from 1 : 0.8 to 1 : 0.02. Very particularly preferably, the molar ratio of acetone: ammonia: ammonium nitrate is in the range 7 – 8: 0.9 – 1.1 : 0.085 – 0.98.

The result of the reaction that has taken place in step a) of the process is a product mixture which generally comprises 20 to 30% (mass percent) TAA, 50 to 60% (mass percent) acetone, 5 to 15% (mass percent) water, 10 to 20% (mass percent) of organic secondary components and 0.5 to 3% (mass percent) of catalyst, based on the product mixture, where the sum of the fraction of all components gives 100% (mass percent).

Within the context of the invention, the term “product mixture” means the reaction mixture which is obtained after the reaction has taken place [step a)] of the process according to the invention and is reacted with a base in subsequent step b).

The product mixture obtained in step a) of the process is deactivated in subsequent step b) by adding a further base, giving a triacetone amine crude product which comprises acetone. In this connection, the amount of the further base used, based on the amount of catalyst used in step a) of the process, is at least 1 molar equivalent. The amount of the further base used, based on
 5 the amount of the catalyst used in step a) of the process, is preferably in the range from 1.0 to 2.0 molar equivalents, particularly preferably in the range from 1.0 to 1.4 molar equivalents, and is most preferably 1.2 molar equivalents.

The addition of the further base in step b) brings about a deactivation of the catalyst, which
 10 prevents the triacetone amine which is located in the product mixture obtained after step a) from decomposing in the further process steps. In this connection, the addition of the further base in step b) according to the invention does not lead to an adequate removal of the deactivated catalyst from the organic phase, but serves merely to deactivate the catalyst.

15 Within the context of the invention, the term "deactivation" means that the catalytic activity of the catalyst used in step a) is stopped. This happens by means of a base $[M^+B^-]$, e.g. described in JP2003-206277; JP2001-031651; JP04154763; US4536581; G. Sosnovsky & M. Konieczny, Synthesis, 1976, 735-736; JP05140104; Plastic Additives 2006, 5(59), 46; A. Formenti & P. Piccinelli, Chimica e l'Industria, 2000, 82(5), 569-571]. This base reacts with the corresponding
 20 acidic catalyst from step a), for example an ammonium salt (AH^+X^-) to give the corresponding free amine (A), the conjugated acid (HB), and an inert salt (M^+X^-) . If e.g. the deactivation of ammonium chloride (AH^+X^-) with NaOH (M^+B^-) is contemplated, then ammonia (A), water (HB) and sodium chloride (M^+X^-) are formed.

25 Within the context of the invention, "further base" means in particular that the base added in step b) is a base different from ammonia. Preferably, the further base used in step b) is characterized in that it is a stronger base than ammonia. "Stronger base than ammonia" means that the further base used has a lower pK_B value than ammonia, preferably of an at least 5% aqueous solution of ammonia.

30 Further bases that can be used in step b) of the process may generally be all bases known to the person skilled in the art which satisfy these requirements. The further base can particularly preferably be selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal carbonates, alkaline earth metal carbonates. These can be used

individually or in combination. These can be used in solid form since the organic phase comprises water, and solid bases with the water of reaction can form an aqueous phase. However, the further base can also be used in liquid form. For example, it can be used as aqueous solution, the base preferably being present in a concentration of 40-60% (mass percent), particularly preferably in a concentration of 45-55% (mass percent). In a further embodiment, the base is sodium hydroxide (NaOH) or potassium hydroxide (KOH), particularly preferably sodium hydroxide.

KOH or NaOH, preferably NaOH, can be used here in solid form. In a further advantageous embodiment of the present invention, KOH or NaOH are used in liquid form, for example dissolved in a solvent, in particular as aqueous solution. This embodiment is particularly advantageous for a continuous process procedure. Here, an aqueous solution of KOH or NaOH is used, where the concentration of KOH or NaOH is preferably 40-60% (mass percent), particularly preferably 45-55% (mass percent). A very particular preference here is given to using an aqueous solution of NaOH, where the concentration of NaOH is preferably 40-60% (mass percent), particularly preferably 45-55% (mass percent).

Reaction of the product mixture obtained after step a) with further base according to step b) then produces a solution ("TAA crude product") which has an organic phase and an aqueous phase. The organic phase here comprises the triacetone amine. The aqueous phase can be left in the crude product and the subsequent step c) can be carried out in the presence of this aqueous phase.

Within the context of the invention, the term "triacetone amine crude product" refers here to the solution which is formed when, in step b), the product mixture from step a) is admixed with a further base. This solution has an aqueous phase and an organic phase.

In a further advantageous embodiment of the present invention, this aqueous phase can be separated off before carrying out the subsequent step c) and only the organic phase ("organic phase of the TAA crude product") can be used in the further process. Surprisingly, it has been found that by separating off the aqueous phase after step b) and further processing the organic phase of the TAA crude product obtained as a result of phase separation in subsequent steps c) to d) according to the process of the present invention, the stability of TAA is increased. This

additionally contributes to an increased process efficiency. This is particularly advantageous if, in step b), more base was added than is necessary for deactivation of the catalyst, i.e. more than 1 molar equivalent of base, based on the amount of catalyst used in step a).

5 In this embodiment [in which a phase separation takes place only after adding the further base in step b) and only the resulting organic phase of the TAA crude product is used in the subsequent step c)], within the context of the invention, the term "triacetone amine crude product" in step c) is to be understood as meaning the organic phase of the triacetone amine crude product obtained in step b).

10 In step c) of the process, the removal of acetone from the triacetone amine crude product in step b) takes place, giving an acetone-depleted triacetone amine crude product. Consequently, the extraction in step d) takes place not at the stage of the acetone-containing triacetone amine crude product, but only following removal of the acetone from the triacetone amine crude product. In this connection, it has surprisingly been found that the extraction in step d) proceeds considerably more effectively after removing the acetone.

Within the context of the invention, "removal of acetone from the triacetone amine crude product obtained in step b)" means a removal of the acetone from the triacetone amine crude product or the organic phase of the triacetone amine crude product, such that an acetone content of less than 40% (mass percent), in particular of less than 20% (mass percent), preferably of less than 15% (mass percent), particularly preferably of less than 10% (mass percent), very particularly preferably of less than 2.5% (mass percent), most preferably of less than 1.5% (mass percent), ideally of less than 1% (mass percent) is present in the resulting acetone-depleted triacetone amine crude product. In a further embodiment, the acetone content in the acetone-depleted triacetone amine crude product is 20%, 19%, 18%, 17%, 16%, 15%, 14%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1% (the percentages indicate percent by mass), the acetone content being more preferred the smaller it is.

30 The removal of the acetone from the triacetone amine crude product can take place in particular by means of distillation. Distillative removal of acetone from the triacetone amine crude product can be carried out e.g. in a distillation at atmospheric pressure or under reduced pressure. Here, all apparatuses known to the person skilled in the art can be used, thus e.g. a stirred reactor, a falling-film evaporator or a thin-film evaporator, in each case in combination with a

suitable distillation column or another apparatus suitable for the distillation. The distillation can take place either discontinuously or continuously, the exact distillation conditions and residence times being selected such that the desired acetone content in the bottom can be achieved. The pressure used during the distillation is particularly in the range 0.4 – 2 bar.

5

Within the context of the invention, the term "acetone-depleted triacetone amine crude product" refers here to the solution which is formed after carrying out step c) if the removal of acetone from the triacetone amine crude product is carried out in step c) of the process.

10 The special feature of the process according to the invention lies in step d) of the process. In step d), the extraction of the acetone-depleted triacetone amine crude product from step c) takes place by adding an auxiliary, giving an extracted triacetone amine crude product. Within the context of the invention, the term "extracted triacetone amine crude product" refers to the organic phase obtained in step d) which comprises the triacetone amine. The auxiliary used can
15 be the aqueous solution of a salt, where the salt may be an alkali metal hydroxide, preferably NaOH, KOH; an alkaline earth metal hydroxide, preferably $\text{Ca}(\text{OH})_2$; an alkali metal carbonate, preferably Na_2CO_3 , K_2CO_3 ; an alkaline earth metal carbonate; an alkali metal halide, preferably NaCl; an alkaline earth metal halide. The auxiliary is particularly preferably a base. The base used in this preferred embodiment in step d) of the process corresponds here very particularly
20 preferably to the base used in step b). Within the context of the invention, "corresponds" means that the chemically identical base is used in both steps b) and d). For example, sodium hydroxide is used in both steps b) and d).

As a result of the process configuration according to the invention, the extraction takes place at
25 the stage of the acetone-depleted triacetone amine crude product which is obtained in step c), and not at the stage of the triacetone amine crude product which is obtained in step b) and still contains acetone.

Surprisingly, it has been shown that the extraction of the acetone-depleted triacetone amine crude product takes place significantly more effectively than that of the triacetone amine crude
30 product which still contains a large fraction of acetone. Consequently, the amount of required auxiliary, preferably of required base, can be reduced significantly compared to the prior art. Additionally, this permits the reduction in the organic burden of the resulting aqueous phase. As a further advantage, this permits the use of liquid base, e.g. aqueous NaOH, in step d) of the

process with the advantages specified previously. A direct removal of the acetone from the product mixture obtained after step a) of the process is not possible as described since, for example, the distillation preferably undertaken to remove the acetone would lead, in the presence of the active catalyst, to an at least partial decomposition of the triacetone amine.

- 5 Surprisingly, it has now been found that a removal of acetone from the triacetone amine crude product is nevertheless possible if the catalyst obtained in the triacetone amine crude product is deactivated by adding base. After the deactivation of the catalyst that has taken place in step b) of the process, the preferably distillative removal of the acetone from the triacetone amine crude product can then take place in step c) of the process. After step c) of the process, the acetone-
- 10 depleted triacetone amine crude product then results as described above, still containing salt and water, even in the case of the above-described embodiment of the invention in which a phase separation is carried out between steps b) and d) of the process and only the organic phase of the triacetone amine crude product is used in step c) of the process. In step d) of the process, the solution obtained after step c) of the process is then desalted by adding further
- 15 auxiliaries, preferably further base.

- Within the context of the invention, "desalting" means that the salt produced during the deactivation of the catalyst in step b) is removed from the solution obtained in step c), in particular to a value of less than 250 ppm, preferably of less than 150 ppm, particularly
- 20 preferably of less than 100 ppm, very particularly preferably of less than 50 ppm, most preferably of less than 25 ppm, ideally of less than 1 ppm.

- The amount of auxiliary added in step d), preferably the base added, is in the range from 1.0 to 6.0 molar equivalents, preferably in the range from 1.0 to 4.0 molar equivalents, particularly
- 25 preferably in the range from 1.0 to 2.0 molar equivalents, very particularly preferably in the range from 1.0 to 1.4 molar equivalents, based on the amount of catalyst used in step a) of the process. Most preferably, the auxiliary, in particular the base, is used in step d) of the process in an amount of 1.2 molar equivalents based on the amount of catalyst used in step a) of the process.

- 30 If a base is used as auxiliary in step d), the base used can be any base known to the person skilled in the art. In particular, the base can be selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal carbonates and alkaline earth metal

carbonates. These can be used individually or in combination. These can be used in solid form. They can also be used in liquid form. For example, they can be used as aqueous solution, where the base is preferably present in a concentration of 40-60% (mass percent), particularly preferably in a concentration of 45-55% (mass percent).

- 5 Preferably, the base is sodium hydroxide (NaOH) or potassium hydroxide (KOH), particularly preferably sodium hydroxide. In a further advantageous embodiment of the present invention, KOH or NaOH are used in liquid form, for example dissolved in a solvent, preferably as aqueous solution. This embodiment is particularly advantageous for a continuous process procedure. Particular preference is given in this connection to using an aqueous solution of
 - 10 KOH or NaOH, where the concentration of KOH or NaOH is 40-60% (mass percent), particularly preferably 45-55% (mass percent). Very particular preference is given in this connection to using an aqueous solution of NaOH, where the concentration of NaOH is 40-60% (mass percent), particularly preferably 45-55% (mass percent).
 - 15 The extraction according to step d) takes place at a temperature at which both phases are liquid, in particular at a temperature of at least 20°C, preferably at 20-99°C, particularly preferably at 45-90°C, very particularly preferably at 45-80°C, most preferably at a temperature of 45 to 65°C, and ideally at a temperature of 60°C.
 - 20 The extraction can take place in principle in different ways, e.g. the extraction can take place both discontinuously and also in a continuous manner. In the case of a discontinuous extraction, e.g. a mixing of the solution obtained from step c) with the auxiliary, preferably the base, in a stirred tank, followed by a phase separation in the same container or a second container can take place. In a continuous embodiment, the extraction can take place by mixing the solution
 - 25 obtained from c) with the auxiliary, preferably the base, paired with phase separation in one or more mixer-settler containers or one or more extraction columns.
- The extraction methods according to the invention are described in W.R.A. Vauck, H.A. Müller, Grundoperationen chemischer Verfahrenstechnik [Basic Operations of Chemical Processing Technology], 11th Edition, pages 787-805, where the countercurrent extraction is described in
- 30 particular on pages 792-794, and the crossflow extraction is described in particular on pages 790-792.

The crossflow extraction can be carried out here in at least one stage, preferably in at least two stages, particularly preferably at least three, very particularly preferably at least four stages. For the crossflow extraction, the term "stage" refers here to the individual operation in which a carrier liquid laden with extract substance to be extracted is mixed with fresh extractant until the partition equilibrium is established, and is then separated off by settling.

The countercurrent extraction in this connection can be carried out in at least one theoretical separation stage, preferably in at least two theoretical separation stages, particularly preferably at least three theoretical separation stages, very particularly preferably at least four theoretical separation stages. For the countercurrent extraction, the term "theoretical separation stage" refers to the mixing of two liquid phases with extract substance transfer and separation after attained partition equilibrium.

An optional step e) of the process is characterized in that the extracted triacetone amine crude product from step c) is purified to give triacetone amine. The purification preferably takes place by distillation. Here, the distillation can take place either batchwise or continuously. Particular preference is given to a continuous distillation in a plurality of steps, in particular in three steps, comprising a separation off of mesityl oxide/water, a subsequent separation off of medium boilers and a final TAA purification by distillation.

Even without further details, it is assumed that a person skilled in the art can utilize the above description in the widest scope. The preferred embodiments and examples are therefore merely to be interpreted as a descriptive disclosure and in no case as limiting in any way.

The present invention is illustrated below by reference to examples. Alternative embodiments of the present invention are obtainable analogously.

Examples

1. General procedures

A) Reaction of acetone with ammonia in the presence of a catalyst, giving a product mixture

A1) Preparation of product mixture according to a batch process – small scale

5

A 2 L steel autoclave is charged at room temperature with acetone (1000 g, 17.2 mol) and ammonium nitrate (17.6 g, 0.220 mol). Ammonia (40.0 g, 2.35 mol) is metered in as gas, and the mixture is heated to 65°C and stirred at 65°C for 6 hours. After cooling to room temperature, the autoclave is decompressed and the crude product (1050 g) is discharged. This gives a

10 homogeneous product mixture having the following composition (Table 1):

Table 1: Composition of the product mixture which is obtained in Example A1. Data in % (mass percent)

Water	Ammonium nitrate	Acetone	Mesityl oxide	Diacetone alcohol	Diacetone-amine	TMDH-pyridine	Acetonin	Phorone	TAA	Remainder
8.61	1.67	51.18	2.85	0.60	1.88	1.97	1.79	0.06	25.03	4.41

The product mixture described in Table 1 is that which was further used in Examples 1-10.

15 *A2) Preparation of product mixture according to a batch process – large scale*

Additionally, product mixture is prepared on a larger scale. For this purpose, a 90 L steel autoclave is charged at room temperature with acetone (56.0 kg, 964 mol) and ammonium nitrate (990 g, 12.4 mol). Ammonia (2.24 kg, 132 mol) is metered in as gas, and the mixture is

20 heated to 65°C and stirred at 65°C for 6 hours. After cooling to room temperature, the autoclave is decompressed and the crude product (59 kg) is discharged. This gives a homogeneous crude product having the following composition (Table 2):

25

Table 2: Composition of the product mixture which is obtained in Example A2. Data in % (mass percent)

Water	Ammonium nitrate	Acetone	Mesityl oxide	Diacetone alcohol	Diacetone-amine	TMDH-pyridine	Acetonin	Phorone	TAA	Remainder
9.34	1.63	50.23	2.15	0.55	1.69	2.04	0.84	0.06	27.39	4.08

A3) Preparation of product mixture according to a continuous process

For the continuous process, a heatable continuous stirred tank is used in which acetone, ammonia and an ammonium nitrate solution can be metered in continuously. The discharge from the stirred tank is passed through a separately heatable post-reactor (1.6 L), which has flow-tube characteristics. At the start of the reaction, the stirred tank is filled with the desired amount of starting materials and the desired temperatures in the stirred tank and also in the post-reactor are established. The starting material metered addition is started, and the reaction discharge from the post-reactor is collected. In this connection, the molar ratio of the starting materials during the initial filling corresponds to the ratio of the starting materials during the continuous metered addition. A starting material ratio of acetone: ammonia = 7.33 : 1 and ammonia: ammonium nitrate = 10.6 : 1 is chosen.

Depending on the exact reaction parameters [temperatures, residence times (RT) in the reactors], the product mixtures shown in Table 3 [5 experiments i) to v) were carried out] were obtained:

Table 3: Continuous preparation TAA – composition of the product mixture which is obtained in Example A3. Data in % (mass percent)

Experiment	Reaction conditions			Composition										
		Residence- time in h	Temperature in °C	Water	Ammonium nitrate	Acetone	Mesityl oxide	Diacetone alcohol	Diacetone amine	TMDH- pyridine	Acetonin	Phorone	TAA	Remainder
i)	Stirred tank	2.5	65	9.22	1.54	56.95	1.33	0.56	2.21	2.16	6.28	0.04	15.61	4.11
	Post-reactor	2.5	65	10.03	1.56	52.75	2.01	0.78	2.05	2.93	2.99	0.05	20.27	4.58
ii)	Stirred tank	2.5	65	9.17	1.55	57.23	1.19	0.50	3.02	1.68	6.33	0.02	15.95	3.36
	Post-reactor	2.5	60	9.93	1.56	53.74	1.64	0.67	2.63	2.20	3.92	0.04	20.15	3.51
iii)	Stirred tank	2,5	70	10.43	1.54	55.62	1.63	0.58	2.81	1.84	6.09	0.05	15.65	3.76
	Post-reactor	2,5	60	10.98	1.55	52.44	1.98	0.74	2.41	2.38	3.78	0.05	19.19	4.51
iv)	Stirred tank	3,0	65	9.38	1.55	57.30	1.20	0.47	2.97	1.60	6.14	0.04	16.17	3.19
	Post-reactor	2,5	65	10.02	1.56	54.45	1.74	0.62	2.42	2.10	3.41	0.05	20.52	3.10
v)	Stirred tank	2,5	65	8.03	1.55	60.00	0.93	0.41	3.18	1.44	6.45	0.04	14.72	3.26
	Post-reactor	3,0	65	8.84	1.57	55.24	1.85	0.68	2.52	2.09	3.08	0.06	20.20	3.88

B) Reaction of the product mixture from A) with a further base to give the triacetone amine crude product

5 The reaction product from A1) [1000 g, comprising 16.7 g (0.208 mol) of ammonium nitrate, 512 g of acetone and 250 g of TAA] is admixed with 20.0 g of a 50% (mass percent) aqueous solution of NaOH (0.250 mol; corresponding to 1.20 molar equivalents of NaOH based on the catalyst). The mixture is stirred for 15 minutes at room temperature. This gives 1018 g of a two-phase triacetone amine crude product which comprises 250 g of triacetone amine. This consists of 1001 g of an organic phase (comprising 12.6 g of sodium nitrate, 510 g of acetone and 249 g
10 of TAA) and 17.0 g of an aqueous phase (comprising 4.9 g of sodium nitrate and 1.7 g of sodium hydroxide).

**C) Removal of acetone from the triacetone amine crude product, as a result of which
15 an acetone-depleted triacetone amine crude product is obtained**

C1) Removal of acetone from the triacetone amine crude product obtained in B)

20 The two-phase mixture from B) is heated to boiling under atmospheric pressure. The acetone is separated off via a distillation column (30 cm glass column with vapour divider and reflux condenser) (top temperature 57-62°C).

C2) Removal of acetone in the preferred embodiment such that the organic phase of the
25 triacetone amine crude product obtained in B) is used

30 The organic phase of the triacetone amine crude product obtained in B) is separated off. This is then heated to boiling under atmospheric pressure. The acetone is separated off over a distillation column (30 cm glass column with vapour divider and reflux condenser) (top temperature 57-62°C).

D) Extraction of the acetone-depleted triacetone amine crude product from step C) by adding an auxiliary to give the extracted triacetone amine crude product

D1 General procedure for carrying out a crossflow extraction (two- or three-stage)

5

The feed product is the acetone-depleted crude product from C1 or C2. This is separated at 60°C into its two phases (1st extraction step). The organic phase is admixed with sodium hydroxide, and the mixture is stirred for 15 minutes and the phases are separated (2nd extraction step). The organic phase is optionally admixed again with sodium hydroxide, the mixture is stirred for 15 minutes and the phases are separated (3rd extraction step).

10

D2) General procedure for carrying out a countercurrent extraction (three-stage)

The feed product is the acetone-depleted crude product from C1) or C2). To this is added, at 60°C, the aqueous phase from the second extraction step, and the mixture is stirred for 15 minutes and the phases are separated (1st extraction step). To the resulting organic phase is added the aqueous phase from the 3rd extraction step, and the mixture is stirred for 15 minutes and the phases are separated (2nd extraction step). Sodium hydroxide is added to the resulting organic phase, and the mixture is stirred for 15 minutes and the phases are separated (3rd extraction step). The addition of the aqueous phase in each case from the subsequent extraction step takes place expediently from an analogous experiment carried out beforehand. It is also possible to carry out a two-stage or multistage countercurrent extraction analogously to this three-stage countercurrent extraction [as in Examples G9), G10].

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E) Comparative examples: Removal of salts from the crude product from the product mixture without previously carrying out steps B) and C)

E1) General procedure for carrying out a crossflow extraction without previously carrying out steps B) and C)

The feed product is the product mixture from A1), A2) or A3). This is admixed at room temperature with sodium hydroxide, and the mixture is stirred for 15 minutes and the phases are separated (1st extraction step). The organic phase is admixed a second time with sodium hydroxide, and the mixture is stirred for 15 minutes and the phases are separated (2nd extraction step). Optionally, the organic phase is admixed a third time with sodium hydroxide, and the mixture is stirred for 15 minutes and the phases are separated (3rd extraction step).

E2) General procedure for carrying out a countercurrent extraction (three-stage)

The feed product is the reaction product from A1), A2) or A3). To this is added, at room temperature, the aqueous phase from the second extraction step, and the mixture is stirred for 15 minutes and the phases are separated (1st extraction step). To the resulting organic phase is added the aqueous phase from the third extraction step, and the mixture is stirred for 15 minutes and the phases are separated (2nd extraction step). Sodium hydroxide is added to the resulting organic phase, and the mixture is stirred for 15 minutes and the phases are separated (3rd extraction step).

The addition of the respective aqueous phase from the subsequent extraction step expediently takes place here from an analogous experiment carried out beforehand.

It is also possible to carry out a two-stage or multistage countercurrent extraction analogously to this three-stage [as in examples G3), G4), G5)] countercurrent extraction.

F) Measurement methodsF1) Determination of the nitrate content

- 5 The nitrate ions were determined via ion chromatography in accordance with DIN EN ISO 10304. The instrument used was a Metrohm ion chromatograph with conductivity detection. The column used was a Metrohm Metrosep Anion Dual 2. The eluent used was an aqueous solution of 2.0 mmol NaHCO₃, 1.3 mmol Na₂CO₃, 2% acetone. Injection loops of 10 µl or 100 µl (for samples with a threshold value < 20 mg/kg) were used.
- 10 The calibration range of the 10 µl loop was 0.5-100 mg/l. The calibration range of the 100 µl loop was 0.05-2.0 mg/l.

F2) Determination of the content of organic components

- 15 The content of all organic components was determined using gas chromatography over a gas chromatograph HP 5890. The column used was a HP-50+, 30m × 0.25 mm × 0.25 mm. The carrier gas used was nitrogen. The temperature of the detector was 280°C, the temperature of the injector was 250°C. The temperature profile was 50°C for 2 min, then heating at a rate of
- 20 5°C/min to 260°C (0 min).

F3) Determination of the water content

- The water content was determined by Karl-Fischer Titration on a Mettler Toledo V20 Volumetric
- 25 Karl-Fischer Titrator. The solution used was Hydranal Composite 5K /Medium K.

G) Examples according to the invention and comparative examples

G1) Example 1 (comparative example; triple crossflow extraction from the product mixture without acetone removal)

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1 kg of the product mixture from A1) [Table 1; 250 g TAA, 1.67% (mass percent) NH_4NO_3] is admixed at room temperature with 20 g of a 50% (mass percent) aqueous NaOH, the mixture is stirred for 15 min and the phases are separated (1st extraction step). This results in 1001 g of an organic phase OP1 [comprising 249 g TAA and 1.26% (mass percent) NaNO_3] and 17 g of an aqueous phase WP1 [comprising 28.8% (mass percent) NaNO_3]. OP1 is admixed again at room temperature with 20 g of a 50% (mass percent) aqueous NaOH, the mixture is stirred for 15 minutes and the phases are separated (2nd extraction step). This results in 960 g of an organic phase OP2 [comprising 248 g TAA and 0.53% (mass percent) NaNO_3] and an aqueous phase WP2 [comprising 16.6% (mass percent) NaNO_3]. OP2 is then admixed at room temperature a third time with 20 g of a 50% (mass percent) aqueous NaOH, the mixture is stirred for 15 minutes and the phases are separated (3rd extraction step). This results in 932 g of an organic phase OP3 [comprising 244 g TAA and 1800 ppm NaNO_3] and an aqueous phase WP3 [comprising 7.9% (mass percent) NaNO_3].

The TAA content in OP3 was determined by gas chromatography and ion chromatography as 244 g TAA [97.6% based on the TAA content in the product mixture from A1, determined by gas chromatography]. The content of NaNO_3 in OP3 was 1800 ppm (determined by ion chromatography). This corresponds to an NaOH feed of 123 g of NaOH per kg of purified TAA or 3.61 molar equivalents based on the ammonium nitrate catalyst used.

Example 1 shows that if acetone removal is not carried out the use of 3.61 molar equivalents, based on the amount of ammonium nitrate catalyst used in step A1) does not suffice in the crossflow process in order to completely remove NaNO_3 from the OP3.

G2) Example 2 (comparative example; triple crossflow extraction from the product mixture without acetone removal)

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1 kg of the product mixture from A1) [Table 1; 250 g TAA, 1.67% (mass percent) NH_4NO_3] is admixed at room temperature with 15 g of solid NaOH, the mixture is stirred for 15 min and the

phases are separated (1st extraction step). This results in 972 g of an organic phase OP1 [comprising 250 g TAA and 0.71% (mass percent) NaNO₃] and an aqueous phase WP1 [comprising 25.1% (mass percent) NaNO₃]. OP1 is again admixed at room temperature with 15 g of solid NaOH, the mixture is stirred for 15 min and the phases are separated (2nd extraction step). This results in 925 g of an organic phase OP2 [comprising 248 g TAA and 0.12% (mass percent) NaNO₃] and 56.1 g of an aqueous phase WP2 [comprising 10.3% (mass percent) NaNO₃]. OP2 is then admixed at room temperature a third time with 15 g of solid NaOH, the mixture is stirred for 15 min and the phases are separated (3rd extraction step). This results in 895 g of an organic phase OP3 [comprising 247 g TAA, the content of NaNO₃ is below the detection limit] and an aqueous phase WP3 [comprising 2.7% (mass percent) NaNO₃]. The TAA content in OP3 was determined as 247 g TAA [98.8% based on the TAA content in the product mixture from A1, determined by gas chromatography]. The content of NaNO₃ in OP3 was below the detection limit of < 25 ppm; determined by ion chromatography. This corresponds to an NaOH feed of 182 g of NaOH per kg of purified TAA or 5.41 molar equivalents based on the ammonium nitrate catalyst used.

The comparison between Example 1 and 2 shows that in the case of crossflow extraction a depletion of NaNO₃ in OP3 to below the detection limit without diminishing the acetone content in the triacetone amine crude product is possible only with the use of 182 g of NaOH per kg of purified TAA or 5.4 molar equivalents [based on the ammonium nitrate catalyst used in A1)]. Additionally, NaOH must be present in solid form.

G3) Example 3 (comparative example; triple countercurrent extraction from the product mixture without acetone removal)

1st pass:

Step 1/1): 1 kg of the product mixture from A1) {Table 1; 250 g TAA, 16.7 g, [0.208 mol, 1.67% (mass percent)] NH₄NO₃} is admixed at room temperature with a first simulated aqueous phase SWP1. SWP1 consisted of 73.2 g water, 14.8 g NaNO₃, 20.0 g NaOH. After adding SWP1, the mixture was stirred for 15 min at room temperature and the resulting organic phase OP1/1 was separated. The resulting aqueous phase WP1/1* was discarded.

Step 1/2): OP1/1 was then admixed with a second simulated aqueous phase SWP2. This second simulated aqueous phase SWP2 consisted of 50.0 g of water, 6.1 g of NaNO_3 and 20.0 g of NaOH. After adding SWP2, the mixture was stirred for 15 min at room temperature and the resulting organic phase OP1/2 was separated off from the aqueous phase WP1/2*. The phase WP1/2* was stored.

Step 1/3): OP1/2 was then admixed with 20 g of solid NaOH. The mixture was stirred for 15 min at room temperature and the resulting organic phase OP1/3 was separated off from the resulting aqueous phase WP1/3*. The phase WP1/3* was stored.

Step 1/4): The content of TAA and NaNO_3 in OP1/3 was determined (not shown in Table 4).

2nd pass:

Step 2/1): Repetition of step 1/1, except that the extraction was not carried out with SWP1, but with WP1/2* from step 1/2. A new organic phase was obtained (OP2/1). The resulting aqueous phase WP2/1* was discarded.

Step 2/2): OP2/1 was then admixed with WP1/3* from step 1/3 and the mixture was stirred for 15 min at room temperature. A new organic phase was obtained (OP2/2). The resulting aqueous phase WP2/2* was stored.

Step 2/3): Repetition of step 1/3, except that the phase OP2/2 was used instead of OP1/2. A new organic phase OP2/3 was obtained. The resulting aqueous phase WP2/3* was stored.

Step 2/4): The content of TAA and NaNO_3 in OP2/3 was determined (not shown in Table 4).

3rd pass:

Step 3/1): Repetition of step 1/1, except that the extraction was carried out not with SWP1, but with WP2/2* from step 2/2. A new organic phase was obtained (OP3/1). The resulting aqueous phase WP3/1* was stored. The content of NaNO_3 and triacetone amine in OP3/1 and WP3/1* was determined and is shown in Table 4.

Step 3/2): OP3/1 was then admixed with WP2/3* from step 2/3, and the mixture was stirred for 15 min at room temperature. A new organic phase was obtained (OP3/2). The resulting aqueous phase WP3/2* was stored. The content of NaNO_3 and triacetone amine in OP3/2 and WP3/2* was determined and is shown in Table 4.

Step 3/3): Repetition of step 1/3, except that the phase OP3/2 was used instead of OP1/2. A new organic phase OP3/3 was obtained. The resulting aqueous phase WP3/3* was stored.

Step 3/4): The content of TAA and NaNO_3 in OP3/3 and WP3/3* was determined.

- 5 The contents of NaNO_3 and TAA in the organic phases OP3/1, OP3/2 and OP3/3 were determined and are shown in Table 4. The contents of NaNO_3 and TAA in the aqueous phases WP3/1*, WP3/2* and WP3/3* were likewise determined and are shown in Table 4.

Overall, in the third pass of Example 3, 20 g of NaOH (solid; 0.500 mol) were used for the
 10 extraction of the salt NaNO_3 (0.208 mol) in 1 kg of the product mixture. Consequently, 2.40 mol equivalents of NaOH were consumed per NaNO_3 present in the product mixture, which in turn results directly from the amount of ammonium nitrate catalyst used. Calculated relative to the amount of TAA present in the product mixture, the amount of sodium hydroxide used is 80 g NaOH/kg TAA. In the resulting organic phase OP3/3, a value of 800 ppm NaNO_3 was still
 15 established. This shows that this amount of NaOH does not suffice during the countercurrent extraction in order to remove NaNO_3 from the organic phase to below the detection limit if no acetone removal from the triacetone amine crude product is undertaken.

20 G4) Example 4 (comparative example: triple countercurrent extraction from the product mixture without acetone removal)

1st pass:

Step 1/1): 1 kg of the product mixture from A1) {Table 1; 250 g TAA, 16.7 g, [0.208 mol, 1.67%
 25 (mass percent) NH_4NO_3]} is admixed at room temperature with a first simulated aqueous phase SWP1. SWP1 consisted of 89.3 g of water, 15.2 g of NaNO_3 , 30.0 g of NaOH. After adding SWP1, the mixture was stirred for 15 min at room temperature and the resulting organic phase OP1/1 was separated off. The resulting aqueous phase WP1/1* was discarded.

Step 1/2): OP1/1 was then admixed with a second simulated aqueous phase SWP2. This
 30 second simulated aqueous phase SWP2 consisted of 62.5 g of water, 6.3 g of NaNO_3 and 30.0 g of NaOH. After adding SWP2, the mixture was stirred for 15 min at room temperature and the resulting organic phase OP1/2 was separated off from the aqueous phase WP1/2*. The phase WP1/2* was stored.

Step 1/3): OP1/2 was then admixed with 30 g of solid NaOH. The mixture was stirred for 15 min at room temperature and the resulting organic phase OP1/3 was separated off from the resulting aqueous phase WP1/3*. The phase WP1/3* was stored.

Step 1/4): The content of TAA and NaNO₃ in OP1/3 was determined (not shown in Table 4).

5

2nd pass:

Step 2/1): Repetition of step 1/1, except that the extraction was carried out not with SWP1, but with WP1/2* from step 1/2. A new organic phase was obtained (OP2/1). The resulting aqueous phase WP2/1* was discarded.

10

Step 2/2): OP2/1 was then admixed with WP1/3* from step 1/3, and the mixture was stirred for 15 min at room temperature. A new organic phase was obtained (OP2/2). The resulting aqueous phase WP2/2* was stored.

Step 2/3): Repetition of step 1/3, except that the phase OP2/2 was used instead of OP1/2. A new organic phase OP2/3 was obtained. The resulting aqueous phase WP2/3* was stored.

15

Step 2/4): The content of TAA and NaNO₃ in OP2/3 was determined (not shown in Table 4).

3rd pass:

Step 3/1): Repetition of step 1/1, except that the extraction was carried out not with SWP1, but with WP2/2* from step 2/2. A new organic phase was obtained (OP3/1). The resulting aqueous phase WP3/1* was stored. The content of NaNO₃ and TAA in OP3/1 and WP3/1* was determined and is shown in Table 4.

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Step 3/2): OP3/1 was then admixed with WP2/3* from step 2/3, and the mixture was stirred for 15 min at room temperature. A new organic phase was obtained (OP3/2). The resulting aqueous phase WP3/2* was stored. The content of NaNO₃ and TAA in OP3/2 and WP3/2* was determined and is shown in Table 4.

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Step 3/3): Repetition of step 1/3, except that the phase OP3/2 was used instead of OP1/2. A new organic phase OP3/3 was obtained. The resulting aqueous phase WP3/3* was stored.

Step 3/4): The content of TAA and NaNO₃ in OP3/3 and WP3/3* was determined.

30

The contents of NaNO_3 and TAA in the organic phases OP3/1, OP3/2 and OP3/3 were determined and are shown in Table 4. The contents of NaNO_3 and TAA in the aqueous phases WP3/1*, WP3/2* and WP3/3* were likewise determined and are shown in Table 4.

- 5 In total, in the third pass of Example 4, 30 g of NaOH (solid; 0.750 mol) were used for the extraction of the salt NaNO_3 (0.208 mol) in 1 kg of the product mixture. Consequently, 3.61 mol equivalents of NaOH were consumed per NaNO_3 , present in the product mixture, which in turn results directly from the amount of ammonium nitrate catalyst used. Calculated on the basis of the amount of purified TAA, the amount of NaOH used is 121 g of NaOH/ kg of TAA. In the
- 10 resulting organic phase OP3/3, a value of NaNO_3 was established, which is below the detection limit of 25 ppm. This shows that only an amount of 3.6 molar equivalents of NaOH (solid; based on the amount of ammonium nitrate catalyst present in the product mixture) suffices during the countercurrent extraction in order to remove NaNO_3 from the organic phase to below the detection limit if no acetone removal from the triacetone amine crude product is carried out.

G5) Example 5 (comparative example; triple countercurrent extraction from the product mixture without acetone removal)

1st pass:

5

Step 1/1): 1 kg of the product mixture from A1) {Table 1; 250 g of TAA, 16.7 g, [0.208 mol, 1.67% (mass percent)] NH_4NO_3 } is admixed at room temperature with a first simulated aqueous phase SWP1. SWP1 consisted of 166.0 g of water, 8.5 g of NaNO_3 , 30.0 g of NaOH. After adding SWP1, the mixture was stirred for 15 min at room temperature and the resulting organic phase OP1/1 was separated off. The resulting aqueous phase WP1/1* was discarded.

10

Step 1/2): OP1/1 was then admixed with a second simulated aqueous phase SWP2. This second simulated aqueous phase SWP2 consisted of 76.0 g of water, 1.5 g of NaNO_3 and 30.0 g of NaOH. After adding SWP2, the mixture was stirred for 15 min at room temperature and the resulting organic phase OP1/2 was separated off from the aqueous phase WP1/2*. The phase WP1/2* was stored.

15

Step 1/3): OP1/2 was then admixed with 60 g of a 50% (mass percent) aqueous solution of NaOH. The mixture was stirred for 15 min at room temperature and the resulting organic phase OP1/3 was separated off from the resulting aqueous phase WP1/3*. The phase WP1/3* was stored.

20 Step 1/4): The content of TAA and NaNO_3 in OP1/3 was determined (not shown in Table 4).

2nd pass:

Step 2/1): Repetition of step 1/1, except that the extraction was carried out not with SWP1, but with WP1/2* from step 1/2. A new organic phase was obtained (OP2/1). The resulting aqueous phase WP2/1* was discarded.

25

Step 2/2): OP2/1 was then admixed with WP1/3* from step 1/3, and the mixture was stirred for 15 min at room temperature. A new organic phase was obtained (OP2/2). The resulting aqueous phase WP2/2* was stored.

30 Step 2/3): Repetition of step 1/3, except that the phase OP2/2 was used instead of OP1/2. A new organic phase OP2/3 was obtained. The resulting aqueous phase WP2/3* was stored.

Step 2/4): The content of TAA and NaNO_3 in OP2/3 was determined (not shown in Table 4).

3rd pass:

Step 3/1): Repetition of step 1/1, except that the extraction was carried out not with SWP1, but with WP2/2* from step 2/2. A new organic phase was obtained (OP3/1). The resulting aqueous phase WP3/1* was stored. The content of NaNO₃ and TAA in OP3/1 and WP3/1* was determined and is shown in Table 4.

Step 3/2): OP3/1 was then admixed with WP2/3* from step 2/3, and the mixture was stirred for 15 min at room temperature. A new organic phase was obtained (OP3/2). The resulting aqueous phase WP3/2* was stored. The content of NaNO₃ and TAA in OP3/2 and WP3/2* was determined and is shown in Table 4.

Step 3/3): Repetition of step 1/3, except that the phase OP3/2 was used instead of OP1/2. A new organic phase OP3/3 was obtained. The resulting aqueous phase WP3/3* was stored.

Step 3/4): The content of TAA and NaNO₃ in OP3/3 was determined.

The contents of NaNO₃ and TAA in the organic phases OP3/1, OP3/2 and OP3/3 were determined and are shown in Table 4. The contents of NaNO₃ and TAA in the aqueous phases WP3/1*, WP3/2* and WP3/3* were likewise determined and are shown in Table 4.

In total, in the third pass of the Example 5, 30 g of NaOH (0.750 mol) were used for the extraction of the salt NaNO₃ (0.208 mol) in 1 kg of the product mixture. In contrast to Example 4, however, this was added in the form of a 50% (mass percent) aqueous solution. This thus corresponds to a ratio of 3.61 molar equivalents of NaOH per ammonium nitrate catalyst present in the product mixture. Calculated on the basis of amount of TAA present in the product mixture, the amount of NaOH used is 121 g of NaOH/ kg of TAA. In the resulting organic phase OP3/3, a value of 600 ppm of NaNO₃ was established. This shows that in Comparative Example 4 it was only possible to suppress the content of NaNO₃ in the organic phase to below the detection limit using 3.6 equivalents of solid NaOH.

G6) Example 6 (example according to the invention; triple crossflow extraction from the acetone-depleted triacetone amine crude product with acetone removal)

The product mixture from A1) (1 kg, comprising 16.7 g (0.208 mol) of ammonium nitrate, 512 g of acetone and 250 g of TAA) is admixed with 20 g of a 50% (mass percent) aqueous solution of NaOH (10 g of NaOH, 0.250 mol, 1.2 molar equivalents of NaOH, based on the ammonium nitrate catalyst). The mixture is stirred for 15 min at room temperature, giving a triacetone amine crude product. This is subjected to an acetone distillation. Here, heating is carried out to boiling under atmospheric pressure and the acetone is separated off via a distillation column (30 cm glass column with vapour divider and reflux condenser) (top temperature 57 - 62°C). This gives 420 g of a distillate which, besides acetone, comprises traces of water [0.9% (mass percent)] and 0.05% (mass percent) mesityl oxide. The residue obtained is 578 g of a two-phase mixture which comprises 90 g of acetone and 240 g of TAA. The acetone content of the acetone-depleted triacetone amine crude product is thus 16% (mass percent).

The two-phase mixture is separated into its phases at 60°C, giving 545 g of an organic phase OP1 [comprising 240 g of TAA and 1.5% (mass percent) of NaNO_3] and 30.9 g of an aqueous phase WP1 [comprising 26.3% (mass percent) of NaNO_3]. The organic phase is separated off (1st extraction step) and admixed with 20 g of a 50% (mass percent) aqueous NaOH, and the mixture is stirred for 15 min and the phases are separated (2nd extraction step). This gives 501 g of an organic phase OP2 [comprising 237 g of TAA and 0.33% (mass percent) of NaNO_3] and 57.9 g of an aqueous phase WP2 [comprising 16.2% (mass percent) of NaNO_3]. OP2 is admixed again at 60°C with 20 g of a 50% (mass percent) aqueous NaOH, and the mixture is stirred for 15 minutes and the phases are separated (3rd extraction step). This gives 475 g of an organic phase OP3 (comprising 237 g of TAA and 500 ppm of NaNO_3) and 39.7 g of an aqueous phase WP3 [comprising 3.2% (mass percent) NaNO_3].

The TAA content in OP3 was determined by gas chromatography and ion chromatography as 244 g of TAA [98.8% based on the TAA content in the product mixture A1, determined by gas chromatography]. The content of NaNO_3 in OP3 was 500 ppm (determined by ion chromatography). This corresponds to an NaOH feed of 127 g of NaOH per kg of purified TAA or 3.6 molar equivalents of NaOH based on the ammonium nitrate catalyst used. This example demonstrates the effect of the acetone removal on the content of NaNO_3 in the solution. At 16% acetone content in the two-phase distillation residue, 500 ppm of NaNO_3 still remain in the organic phase OP3 after the extraction.

G7) Example 7 (example according to the invention; triple crossflow extraction from the acetone-depleted triacetone amine crude product with acetone removal)

The product mixture of the TAA preparation from A1) [1 kg, comprising 16.7 g (0.208 mol) of ammonium nitrate, 512 g of acetone and 250 g of TAA] is admixed with 20 g of a 50% (mass percent) aqueous solution of NaOH (10 g of NaOH, 0.250 mol, 1.2 molar equivalents of NaOH, based on the ammonium nitrate catalyst), resulting in a triacetone amine crude product. The mixture is stirred for 15 min at room temperature. The resulting mixture is subjected to an acetone distillation. Here, the mixture is heated to boiling under atmospheric pressure and the acetone is separated off via a distillation column (30 cm glass column with vapour divider and reflux condenser) (top temperature 57 - 62°C).

This gives 490 g of a distillate which, besides acetone, comprises traces of water [(1.1% (mass percent)] and 0.3% (mass percent) of mesityl oxide. As residue, the acetone-depleted triacetone amine crude product, 528 g of a two-phase mixture are obtained, which comprises 19 g of acetone and 235 g of TAA. The acetone content of the residue is thus 3.6% (mass percent).

The two-phase mixture is separated into its phases at 60°C, giving 444 g of an organic phase OP1 [comprising 233 g of TAA and 0.30% (mass percent) of NaNO_3] and 80.4 g of an aqueous phase WP1 [comprising 26.3% (mass percent) NaNO_3]. The organic phase is separated off (1st extraction step) and admixed with 20 g of a 50% (mass percent) aqueous NaOH, and the mixture is stirred for 15 minutes and the phases are separated (2nd extraction step). This results in 417 g of an organic phase OP2 (comprising 232 g of TAA and 300 ppm of NaOH) and 42.3 g of an aqueous phase WP2 [comprising 3.3% (mass percent) NaNO_3]. OP2 is admixed again at 60°C with 20 g of a 50% (mass percent) aqueous NaOH, and the mixture is stirred for 15 min and the phases are separated (3rd extraction step). This results in 399 g of an organic phase OP3 (comprising 228 g of TAA and < 25 ppm of NaNO_3) and 31.5 g of an aqueous phase WP3 [comprising 0.3% (mass percent) NaNO_3].

The TAA content in OP3 was determined by gas chromatography and ion chromatography. Accordingly, OP3 comprised 228 g of TAA [97.0% based on the TAA content in the product mixture from A1, determined by gas chromatography]. The content of NaNO_3 in OP3 was below the detection limit of 25 ppm (determined by ion chromatography). This corresponds to an NaOH feed of 132 g of NaOH per kg of purified TAA or 3.61 molar equivalents of NaOH, based on the ammonium nitrate catalyst used. This example demonstrates the effect of the acetone

removal on the content of NaNO_3 in the solution. At 16% acetone content in the two-phase distillation residue, 500 ppm of NaNO_3 still remain in the organic phase OP3 after the extraction whereas if the acetone content is reduced to 3.6% (mass percent) in the acetone-depleted triacetone amine crude product, under otherwise identical conditions as in this example, the
 5 fraction of NaNO_3 in the phase OP3 drops to below the detection limit.

G8) Example 8 (example according to the invention; double crossflow extraction from the acetone-depleted TAA crude product)

10 The product mixture of the TAA preparation from A1 [1 kg, comprising 16.7 g (0.208 mol) of ammonium nitrate, 512 g of acetone and 250 g of TAA] is admixed with 20 g of a 50% (mass percent) aqueous solution of NaOH (10 g of NaOH, 0.250 mol, 1.2 molar equivalents of NaOH, based on the ammonium nitrate catalyst). The mixture is stirred for 15 min at room temperature. The mixture obtained is subjected to an acetone distillation. Here, the mixture is heated to
 15 boiling under atmospheric pressure and the acetone is separated off via a distillation column (top temperature 57 – 62°C).

This gives 490 g of a distillate which, besides acetone, comprises traces of water [1.1% (mass percent)] and 0.3% (mass percent) of mesityl oxide. The residue obtained is 528 g of a two-
 20 phase mixture, the acetone-depleted triacetone amine crude product, which comprises 19 g of acetone and 235 g of TAA. The acetone content of the residue is thus 3.6% (mass percent).

The two-phase mixture is separated into its phases at 60°C, giving 441 g of an organic phase OP1 [comprising 234 g of TAA and 0.27% (mass percent) of NaNO_3] and 81 g of an aqueous
 25 phase WP1 [comprising 21.7% (mass percent) NaNO_3]. The organic phase is separated off (1st extraction step) and admixed with 40 g of a 50% (mass percent) aqueous NaOH, and the mixture is stirred for 15 min and the phases are separated (2nd extraction step). This results in 405 g of an organic phase OP2 (comprising 231 g of TAA and 110 ppm of NaNO_3) and 69.4 g of an aqueous phase WP2 [comprising 1.92% (mass percent) NaNO_3].

30 The TAA content in OP2 was determined by gas chromatography and ion chromatography. Accordingly, OP2 comprised 231 g of TAA [98.3% based on the TAA content in the product mixture A1, determined by gas chromatography]. The content of NaNO_3 in OP2 was 110 ppm

(determined by ion chromatography). This corresponds to an NaOH feed of 130 g of NaOH per kg of purified TAA or 3.61 molar equivalents of NaOH, based on the ammonium nitrate catalyst used. This example demonstrates that it is advantageous to carry out a three-stage crossflow extraction to completely remove NaNO_3 from the organic phase.

5

G9) Example 9 (example according to the invention; triple countercurrent extraction from the product mixture with acetone removal)

The product mixture from A1) (1 kg, comprising 16.7 g (0.208 mol) of ammonium nitrate, 512 g of acetone and 250 g of TAA) is admixed with 20 g of a 50% (mass percent) aqueous solution of NaOH (10 g of NaOH, 0.250 mol, 1.2 molar equivalents of NaOH, based on the ammonium nitrate catalyst). This triacetone amine crude product is stirred for 15 min at room temperature. The resulting mixture is subjected to an acetone distillation. Here, the mixture is heated to boiling under atmospheric pressure and the acetone is separated off via a distillation column (top temperature 57 - 62°C). As soon as acetone no longer passes over, the distillation is ended. 490 g of a distillate are obtained which, besides acetone, comprises traces of water [1.1% (mass percent)] and 0.3% (mass percent) mesityl oxide. The residue obtained is 528 g of a two-phase mixture, the acetone-depleted triacetone amine crude product, which comprises 19 g of acetone and 235 g of TAA. The acetone content of the residue is thus 3.6% (mass percent). The residue is then subjected to a countercurrent extraction, which is carried out at 60°C, and the procedure is as follows:

1st pass:

Step 1/1): 528 g of the two-phase mixture [235 g of TAA, 17.7 g (0.208 mol, 3.35 mass percent) of NaNO_3] is admixed at 60°C with a first simulated aqueous phase SWP1. SWP1 consisted of 70.0 g of water, 14.0 g of NaNO_3 , 10.0 g of NaOH. After adding SWP1, the mixture was stirred for 15 min and the resulting organic phase OP1/1 was separated off. The resulting aqueous phase WP1/1* was discarded.

Step 1/2): OP1/1 was then admixed with a second simulated aqueous phase SWP2. This second simulated aqueous phase SWP2 consisted of 40.0 g of water, .6.0 g of NaNO_3 and 10.0 g of NaOH. After adding SWP2, the mixture was stirred for 15 min at 60°C and the

resulting organic phase OP1/2 was separated off from the aqueous phase WP1/2*. The phase WP1/2* was stored.

Step 1/3): OP1/2 was then admixed with 20 g of a 50% (mass percent) aqueous solution of NaOH. The mixture was stirred for 15 min at 60°C and the resulting organic phase OP1/3 was separated off from the resulting aqueous phase WP1/3*. The phase WP1/3* was stored.

Step 1/4): The content of TAA and NaNO₃ in OP1/3 was determined (not shown in Table 4).

2nd pass:

Step 2/1): Repetition of step 1/1, except that the extraction was carried out not with SWP1, but with WP1/2* from step 1/2. A new organic phase (OP2/1) was obtained. The resulting aqueous phase WP2/1* was discarded.

Step 2/2): OP2/1 was extracted with WP1/3* from step 1/3. A new organic phase (OP2/2) was obtained. The resulting aqueous phase WP2/2* was stored.

Step 2/3): Repetition of step 1/3, except that the phase OP2/2 was used instead of OP1/2. A new organic phase OP2/3 was obtained. The resulting aqueous phase WP2/3* was stored.

Step 2/4): The content of TAA and NaNO₃ in OP2/3 was determined (not shown in Table 4).

3rd pass:

Step 3/1): Repetition of step 1/1, except that the extraction was carried out not with SWP1, but with WP2/2* from step 2/2. A new organic phase was obtained (OP3/1). The resulting aqueous phase WP3/1* was stored. The content of NaNO₃ and TAA in OP3/1 and WP3/1* was determined and is shown in Table 4.

Step 3/2): OP3/1 was extracted with WP2/3* from step 2/3. A new organic phase was obtained (OP3/2). The resulting aqueous phase WP3/2* was stored. The content of NaNO₃ and TAA in OP3/2 and WP3/2* was determined and is shown in Table 4.

Step 3/3): Repetition of step 1/3, except that the phase OP3/2 was used instead of OP1/2. A new organic phase OP3/3 was obtained. The resulting aqueous phase WP3/3* was stored.

Step 3/4): The content of TAA and NaNO₃ in OP3/3 was determined.

The contents of NaNO_3 and TAA in the organic phases OP3/1, OP3/2 and OP3/3 were determined and are shown in Table 4. Likewise, the contents of NaNO_3 and TAA in the aqueous phases WP3/1*, WP3/2* and WP3/3* are determined and are shown in Table 4.

5 Overall, in the third pass of Example 9, 20 g of NaOH [in the form of a 50% (mass percent) aqueous solution; 0.500 mol] was used, with 10 g of NaOH being used for the deactivation and again 10 g of NaOH being used for the extraction of the salt NH_4NO_3 (0.208 mol) in 1 kg of the product mixture. This thus corresponds to a ratio of 2.40 molar equivalents of NaOH per NH_4NO_3 present in the product mixture. Calculated on the basis of the amount of TAA (235 g)
 10 obtained from the two-phase residue, the amount of NaOH used is thus 87 g of NaOH/kg of TAA. In the resulting organic phase OP3/3, no NaNO_3 could be ascertained; the value was below the detection limit, i.e. < 25 ppm. This indicates that for an acetone removal from the TAA crude product and extraction of the acetone-depleted TAA crude product with an acetone content of 3.6% (mass percent), the amount of 2.40 equivalents of NaOH, based on the amount
 15 of NaNO_3 present in the product mixture, suffices in order to remove NaNO_3 from the organic phase to below the detection limit.

G10) Example 10 (example according to the invention; triple countercurrent extraction from the product mixture with acetone removal and using the organic phase of the triacetone amine crude product)

The product mixture from A1) [1 kg, comprising 16.7 g (0.208 mol) of ammonium nitrate, 512 g of acetone and 250 g of TAA] is admixed with 20 g of a 50% (mass percent) aqueous solution of NaOH (10 g of NaOH, 0.250 mol, 1.2 molar equivalents of NaOH, based on the ammonium
 25 nitrate catalyst). The mixture is stirred for 15 min at room temperature. This gives 1001 g of an organic phase (comprising 12.6 g of NaNO_3 , 510 g of acetone, 249 g of TAA) and 17.0 g of an aqueous phase (comprising 4.9 g of NaNO_3 , 1.7 g of NaOH). The organic phase of the triacetone amine crude product is separated off from the aqueous phase and heated to boiling under atmospheric pressure. The acetone is separated off over a distillation column (top
 30 temperature 57 - 62°C). As soon as acetone no longer passes over, the distillation is ended. This gives 488 g of a distillate which, besides acetone, comprises traces of water [0.9% (mass percent)] and also 0.3% (mass percent) of mesityl oxide. The residue obtained is 531 g of a

two-phase mixture which comprises 22 g of acetone and 247 g of TAA. The acetone content of the residue is thus 4.1% (mass percent).

5 The residue is then subjected to a countercurrent extraction, which is carried out at 60°C, and the procedure is as follows:

1st pass:

10 Step 1/1): 531 g of the two-phase mixture [247 g of TAA, 17.7 g (0.208 mol, 3.35 mass percent) of NaNO₃] is admixed at 60°C with a first simulated aqueous phase SWP1. SWP1 consisted of 60.0 g of water, 4.6 g of NaNO₃, 10.0 g of NaOH. After adding SWP1, the mixture was stirred for 15 min and the resulting organic phase OP1/1 was separated off. The resulting aqueous phase WP1/1* was discarded.

15 Step 1/2) OP1/1 was then admixed with a second simulated aqueous phase SWP2. This second simulated aqueous phase SWP2 consisted of 30.0 g of water, 0.6 g of NaNO₃ and 10.0 g of NaOH. After adding SWP2, the mixture was stirred for 15 min at 60°C and the resulting organic phase OP1/2 was separated off from the aqueous phase WP1/2*. The phase WP1/2* was stored.

20 Step 1/3) OP1/2 was then admixed with 20 g of a 50% (mass percent) aqueous solution of NaOH. The mixture was stirred for 15 min at 60°C and the resulting organic phase OP1/3 was separated off from the resulting aqueous phase WP1/3*. The phase WP1/3* was stored.

Step 1/4): The content of TAA and NaNO₃ in OP1/3 was determined (not shown in Table 4).

2nd pass:

25 Step 2/1): Repetition of step 1/1, except that the extraction was carried out not with SWP1, but with WP1/2* from step 1/2. A new organic phase was obtained (OP2/1). The resulting aqueous phase WP2/1* was discarded.

30 Step 2/2): OP2/1 was extracted with WP1/3* from step 1/3. A new organic phase was obtained (OP2/2). The resulting aqueous phase WP2/2* was stored.

Step 2/3): Repetition of step 1/3, except that the phase OP2/2 was used instead of OP1/2. A new organic phase OP2/3 was obtained. The resulting aqueous phase WP2/3* was stored.

Step 2/4): The content of TAA and NaNO₃ in OP2/3 was determined (not shown in Table 4).

3rd pass:

Step 3/1): Repetition of step 1/1, except that the extraction was carried out not with SWP1, but
 5 with WP2/2* from step 2/2. A new organic phase was obtained (OP3/1). The resulting aqueous
 phase WP3/1* was stored. The content of NaNO₃ and TAA in OP3/1 and WP3/1* was
 determined and is shown in Table 4.

Step 3/2): OP3/1 was extracted with WP2/3* from step 2/3. A new organic phase was obtained
 (OP3/2). The resulting aqueous phase WP3/2* was stored. The content of NaNO₃ and TAA in
 10 OP3/2 and WP3/2* was determined and is shown in Table 4.

Step 3/3): Repetition of step 1/3, except that the phase OP3/2 was used instead of OP1/2. A
 new organic phase OP3/3 was obtained. The resulting aqueous phase WP3/3* was stored.

Step 3/4): The content of TAA and NaNO₃ in OP3/3 was determined.

15 The contents of NaNO₃ and TAA in the organic phases OP3/1, OP3/2 and OP3/3 were
 determined and are shown in Table 4. Likewise, the contents of NaNO₃ and TAA in the aqueous
 phases WP3/1*, WP3/2* and WP3/3* were determined and are shown in Table 4.

Overall, in the third pass of Example 10, 20 g of NaOH [in the form of a 50% (mass percent)
 20 aqueous solution; 0.500 mol] were used, with 10 g of NaOH being used for the deactivation and
 again 10 g being used for the extraction of the salt NaNO₃ (0.208 mol) in 1 kg of the product
 mixture. This thus corresponds to a molar ratio of 2.40 molar equivalents of NaOH per NaNO₃
 present in the product mixture, which in turn results directly from the amount of ammonium
 nitrate catalyst used. Calculated on the basis of the amount of TAA obtained from the two-
 25 phase residue (235 g), the amount of NaOH used is thus 82 g of NaOH/kg of TAA. No NaNO₃
 could be ascertained in the resulting organic phase OP3/3; the value was below the detection
 limit, i.e. < 25 ppm. This shows that when using the organic phase of the triacetone amine crude
 product and removing the acetone from the organic phase of the triacetone amine crude
 product with reduction of the acetone content to 4.1% (mass percent), the amount of
 30 2.40 equivalents of NaOH, based on the amount of the NaNO₃ present in the product mixture,
 suffices in order to remove NaNO₃ from the organic phase OP3 to below the detection limit.
 Additionally, the comparison of Comparative Examples 9 and 10 shows that the TAA yield,
 based on the product from the TAA synthesis, (97.9% compared with 99.2% in Comparative

Example 9 or 10) is higher if a phase separation is carried out before the countercurrent extraction and only the organic phase is subjected to the countercurrent extraction.

For all of the examples according to the invention in which a countercurrent extraction was carried out (Examples 9 and 10), the amount of NaOH used, based on the TAA obtained, was 87 or 82, respectively [g of NaOH used per kg of triacetone amine obtained]. By contrast, this value in the countercurrent process according to JP2003-206277 is 169 [g of TAA/1 kg of TAA]. This process is detailed in Table 4 as Example 11. These results show that the process according to the invention offers the surprising advantage compared with that described in JP2003-06277 that a removal of salts from the organic phase is possible using only half of the amount of NaOH.

This surprising result is also evident in the comparison with Examples 1 to 5. Thus, it is not possible in a countercurrent extraction according to Example 4 to eliminate NaNO_3 from the organic phase OP3 to below the detection limit using 2.4 molar equivalents of NaOH (based on the ammonium nitrate catalyst present in the product mixture). 800 ppm residue content remain. By contrast, in Examples 9 and 10 it is possible to reduce the NaNO_3 content of the organic phase to below the detection limit using 2.4 molar equivalents of NaOH (based on the ammonium nitrate catalyst present in the product mixture).

Without acetone removal, this is accomplished only using 3.61 molar equivalents of NaOH (based on the ammonium nitrate catalyst present in the product mixture) and even then only if solid NaOH is used (Example 4). 2.4 molar equivalents of NaOH (based on the ammonium nitrate catalyst present in the product mixture) do not suffice (Example 3). When using an aqueous solution of NaOH (Example 5), the reduction of NaNO_3 in the organic phase OP3 is not accomplished even with 3.61 molar equivalents of NaOH based on the ammonium nitrate catalyst present in the product mixture. As is evident in the comparison with Examples 1 to 5, it is moreover possible by virtue of the process according to the invention to reduce considerably the use of NaOH [based on the ammonium nitrate catalyst used in step A1)].

It is evident from the comparison of Example 7 with Examples 1 and 2 that in the case of the crossflow extraction without acetone removal, it is only possible using 5.41 molar equivalents of NaOH, used as solid NaOH, based on the ammonium nitrate catalyst present in the product mixture, to reduce the NaNO_3 in the organic phase OP3 to below the detection limit

(Example 2). When using 3.61 molar equivalents of NaOH, used as aqueous solution, based on the ammonium nitrate catalyst present in the product mixture, this is not accomplished (Example 1).

- 5 Consequently, the process according to the invention permits a more efficient removal of salts from the organic phase since this proceeds using a significantly reduced amount of NaOH. This permits a considerable saving of material and thereby achieves the object of the present invention. The results are summarized in Table 4.

Table 4: Experimental data relating to the experiments carried out in Examples 1-10 (Examples 1-5 were carried out without acetone removal in step C; “%” data mean percent by mass)

Example/ sequence/ comments	Parameter	1 st Extraction step				2 nd Extraction step				3 rd Extraction step				Overall process			
		Feed materials		Phases obtained		Feed materials		Phases obtained		Feed materials		Phases obtained		TAA yield [based on product from A1]	NaOH feed [g]	NaOH feed [mol/mol NH ₄ NO ₃ - cat.]	NaOH feed [g/kg TAA]
		Organic phase	Extractant	Organic phase	Aqueous phase	Organic phase	Extractant	Organic phase	Aqueous phase	Organic phase	Extractant	Organic phase	Aqueous phase				
1./A1-E1/ 3 x crossflow; use of an NaOH solution	Phase/ Substance	from (A1)	NaOH (50%)	OP1	WP1		NaOH (50%)	OP2	WP2		NaOH (50%)	OP3	WP3				
	Mass [g]	1000	20	1001	17		20	960	56.1		20	932	42.7				
	Content of TAA [g]	250	-	249	-	OP1	-	248	-	OP2	-	244	-	97.6%	30	3.61	123
	Content of NaNO ₃	1.67% NH ₄ NO ₃ ²⁾	-	1.26%	28.8%		-	0.0053	0.166		-	1800 ppm	7.9%				
2./A1-E1/ 3 x crossflow; use of solid NaOH	Phase/ Substance	from (A1)	NaOH (solid)	OP1	WP1		NaOH (solid)	OP2	WP2		NaOH (solid)	OP3	WP3				
	Mass [g]	1000	15	972	42.1		15	925	56.1		15	895	38.3				
	Content of TAA [g]	250	-	250	-	OP1	-	248	-	OP2	-	247	-	98.8%	45	5.41	182
	Content of NaNO ₃	1.67% NH ₄ NO ₃ ²⁾	-	0.71%	25.1%		-	0.12%	10.3%		-	<25 ppm ¹⁾	2.7%				
3./ A1-E2/ 3 x counter- current; use of solid NaOH; only pass 3 is shown	Phase/ Substance	from (A1)		OP3/1	WP3/1*			OP3/2	WP3/2*		NaOH (solid)	OP3/3	WP3/3*				
	Mass [g]	1000		1024	83.5			985	107		20	901	74.1				
	Content of TAA [g]	250	WP2/2*	250	-	OP3/1	WP2/3*	249	-	OP3/2	-	249	-	99.6%	20	2.40	80
	Content of NaNO ₃	1.67% NH ₄ NO ₃ ²⁾		1.27%	20.4%			0.51%	11.1%		-	800 ppm	5.6%				

4./ A1-E2/ 3 x counter-current; use of solid NaOH; only pass 3 is shown	Phase/ Substance	from (A1)	OP3/1	WP3/1*			OP3/2	WP3/2*		NaOH (solid)	OP3/3	WP3/3*				
	Mass [g]	1000	1001	121			949	123		30	893	77.2				
	Content of TAA [g]	250	250	-	OP3/1	WP2/3*	250	-	OP3/2	-	249	-	99.4%	30	3.61	121
	Content of NaNO ₃	1.67% NH ₄ NO ₃ ²⁾	0.82%	15.4%			0.18%	6.9%		-	<25 ppm ¹⁾	2.06%				
5/ A1-E2/ 3 x counter-current; use of an NaOH solution; only pass 3 is shown	Phase/ Substance	from (A1)	OP3/1	WP3/1*			OP3/2	WP3/2*		NaOH (50%)	OP3/3	WP3/3*				
	Mass [g]	1000	1010	129			971	141		60	914	107				
	Content of TAA [g]	250	249	-	OP3/1	WP2/3*	248	-	OP3/2	-	248	-	99.2%	30	3.61	121
	Content of NaNO ₃	1.67% NH ₄ NO ₃ ²⁾	0.88%	11.4%			0.36%	5.6%		-	600 ppm	2.5%				

¹⁾ Means that the value ascertained for the content of NaNO₃ is below the detection limit.

²⁾ Takes into consideration that still no sodium nitrate is present in the product mixture from A1, but ammonium nitrate [1.67% (mass percent)]

Table 4 (continuation): Experimental data relating to the experiments carried out in Examples 1-10 (Examples 6-10 were carried out with acetone removal; Example 11 shows a comparative experiment)																	
Example/ sequence/ comments	Parameter	1 st Extraction step				2 nd Extraction step				3 rd Extraction step				Overall process			
		Feed materials		Phases obtained		Feed materials		Phases obtained		Feed material		Phases obtained		TAA yield {based on product from A1}	NaOH feed [g]	NaOH feed [mol/mol NH ₄ NO ₃ - cat.]	NaOH feed [g/kg TAA]
		Organic phase	Extract- ant	Organic phase	Aqueous phase	Organic phase	Extract- ant	Organic phase	Aqueous phase	Organic phase	Extract- ant	Organic phase	Aqueous phase				
6/ A1-B-C1-D1/ 3 x crossflow; use of an NaOH solution; acetone content 16%	Phase/ Substance	from C1		OP1	WP1		NaOH (50%)	OP2	WP2		NaOH (50%)	OP3	WP3				
	Mass [g]	578	none, only phase separ- ation	545	30.9		20	501	57.9		20	475	39.7				
	Content of TAA [g]	240				OP1	-	237	-	OP2	-	237	-	98.8%	30	3.61	127
	Content of NaNO ₃ ³⁾	3.1%			1.5%	26.3%		-	0.33%	16.2%		-	500 ppm	3.2%			
7/ A1-B-C1-D1/ 3 x crossflow; use of an NaOH solution; acetone content 3.6%	Phase/ Substance	from C1		OP1	WP1		NaOH (50%)	OP2	WP2		NaOH (50%)	OP3	WP3				
	Mass [g]	528	none, only phase separ- ation	444	80.4		20	417	42.3		20	399	31.5				
	Content of TAA [g]	235				OP1	-	232	-	OP2	-	228	-	97.0%	30	3.61	132
	Content of NaNO ₃ ³⁾	3.35%			0.30%	21.4%		-	300 ppm	3.3%		-	<25 ppm ¹⁾	0.3%			
8/ A1-B-C1-D1/ 2 x crossflow; use of an NaOH solution; acetone content 3.6%	Phase/ Substance	from C1		OP1	WP1		NaOH (50%)	OP2	WP2								
	Mass [g]	528	none, only phase separ- ation	441	81		40	405	69.4								
	Content of TAA [g]	235				OP1	-	231	-	Only two-stage extraction				98.3%	30	3.61	130
	Content of NaNO ₃ ³⁾	3.35%			0.27%	21.7%		-	110 ppm	1.92%							

9/A1-B-C1-D1/ 3 x counter-current; use of an NaOH solution; acetone content 3.6%; only pass 3 is shown	Phase/ Substance	from C1	OP3/1	WP3/1*		OP3/2	WP3/2*		NaOH (50%)	OP3/3	WP3/3*						
	Mass [g]	528		449	121		429	46.9		20	410	32.4					
	Content of TAA [g]	235	WP2/2*	234	-	OP3/1	WP2/3*	233	-	OP3/2	-	230	-	97.9%	20	2.40	87
	Content of NaNO ₃ ³⁾	3.35%			900 ppm			14.5%			70 ppm	2.5%					
10/ A1-B-C2-D1/ 3 x counter-current; use of an NaOH solution; acetone content 4.1%; organic phase/only pass 3 is shown	Phase/ Substance	from C2	OP3/1	WP3/1*		OP3/2	WP 3/2*		NaOH (50%)	OP3/3	WP 3/3*						
	Mass	531		454	123		425	47.8		20	415	24.5					
	Content of TAA [g]	247	WP2/2*	247	-	OP3/1	WP2/3*	245	-	OP3/2	-	245	-	99.2%	20	2.40	82
	Content of NaNO ₃ ³⁾	2.37%			0.16%			9.5%			140 ppm	1.20%					
11/ JP200320627 7/Examples [018]-[022]	Phase/ Substance	-	OP1	WP1		NaOH (48%)	OP2	WP2									
	Mass	400	WP2	n.s. ⁴⁾	n.s. ⁴⁾	OP1	37.3	340	60	Only two-stage extraction				-	17.9	169	
	Content of TAA [g]	n.s. ⁴⁾		n.s. ⁴⁾	-		106	-									
	Content of chloride	1.82%		280 ppm	n.s. ⁴⁾		-	< 25 ppm ¹⁾	n.s. ⁴⁾								

¹⁾ Means that the value ascertained for the content of NaNO₃ is below the detection limit.

³⁾ The sodium nitrate contents after incipient distillation are higher since the crude product volume has reduced as a result of the acetone removal. The resulting absolute mass of NaNO₃, however, is identical to that in the respective triacetone amine crude product prior to the distillation.

⁴⁾ n.s. = not specified.

H) Purification of the extracted triacetone amine crude product

An extracted triacetone amine crude product corresponding to the organic phase OP3/3 from Example 9 (Table 4) is worked-up by distillation. This takes place in a fractional distillation using a column with eight theoretical plates. The distillation takes place firstly under atmospheric pressure and then under reduced pressure. The precise conditions and compositions of the individual fractions can be found in Table 5.

It is evident that particularly diacetone alcohol, diacetone amine and acetonin are not stable under the distillation conditions. TAA, however, exhibits no tendency towards decomposition under the distillation conditions. The TAA yield during the distillation is 93.3% (mass percent) for a purity of 94.9%.

Table 5: Distillative purification of triacetone amine; “%” data of the constituents in mass percent											
Sample	Amount kg	Water %	Acetone %	Mesityl oxide %	Diacetone alcohol %	Diacetone amine %	TMDH pyridine %	Aceto- nin %	TAA %	Remainder %	Total %
Feed	28.00	2.10	2.89	5.38	7.00	3.41	1.97	3.23	61.00	13.02	100.00
Fr. 1	0.21	3.53	93.67	0	0	0	0	0.09	1.72	0.99	100.00
Fr. 2	0.99	17.54	42.17	28.08	0	3.05	0	0.59	0.02	8.55	100.00
Fr. 3 lower phase	0.10	81.12	6.9	0.22	0.10	6.91	0.38	4.25	0.02	0.10	100.00
Fr. 3 upper phase	1.40	5.01	5.22	77.56	0.26	0.99	5.28	0.2	0.02	5.46	100.00
Fr. 4	1.04	7.53	0.19	0.23	0.51	0.64	46.83	5.38	17.66	21.03	100.00
Fr. 5	16.80	0.08	0.03	0.01	0.00	0.00	0.02	0.03	94.87	4.97	100.00
Residue	3.04	4.14	0.47	0.07	0	0	0.13	0	4	91.19	100.00
Cool trap	3.50	1.5	2.55	0.20	0.03	0.06	0.12	0.02	0.22	95.30	100.00
Feed mass [kg]	28.00	0.59	0.81	1.51	1.96	0.95	0.55	0.90	17.08	3.65	
Mass in the distillate [kg]	27.08	0.60	0.80	1.38	0.01	0.06	0.57	0.07	16.26	7.32	
Error [%]	3.29	-2.36	0.66	8.63	99.48	93.74	-3.77	91.82	4.82	-100.85	

No sediment formation is established during the distillation. Even if the distillation is repeated without interim purification of the distillation bottom, no sediment formation and/or the formation of deposits on reactor surfaces or heat exchanger surfaces is seen.

Patent claims

1. Process for the preparation of triacetone amine, comprising the reaction steps
 - a) reaction of an acetone equivalent with a first base, selected from ammonia, in the presence of a catalyst, giving a product mixture which comprises acetone;
 - b) stopping the catalytic activity of the catalyst used in step a) of the product mixture by adding a further base, wherein the further base is a base different from ammonia and has a lower pK_B value than ammonia, giving a triacetone amine crude product which comprises acetone;
 - c) removal of acetone from the triacetone amine crude product from step b), giving an acetone-depleted triacetone amine crude product;
 - d) extraction of the acetone-depleted triacetone amine crude product from step c) by adding an auxiliary, characterized in that a base is used as auxiliary in step d), thus desalting the solution obtained after step c) of the process, giving an extracted triacetone amine crude product.
2. Process according to Claim 1, characterized in that, in a further step e), the extracted triacetone amine crude product from step d) is purified to give triacetone amine.
3. Process according to Claim 1 or 2, characterized in that the acetone equivalent is one or more of the compounds selected from the group consisting of acetone, mesityl oxide, diacetone alcohol, phorone, diacetone amine, acetoin.
4. Process according to one or more of Claims 1 to 3, characterized in that the further base in step b) is selected from the group consisting of an alkali metal hydroxide, an alkaline earth metal hydroxide, an alkali metal carbonate, an alkaline earth metal carbonate.
5. Process according to one or more of Claims 1 to 4, characterized in that the amount of further base added in step b) is in the range from 1.0 to 2.0 molar equivalents, based on the amount of catalyst used in step a).
6. Process according to one or more of Claims 1 to 5, characterized in that a phase separation additionally takes place between step b) and step c).

7. Process according to one or more of Claims 1 to 6, characterized in that the reaction in step a) is carried out at temperatures in the range from 40 - 80°C.
8. Process according to one or more of Claims 1 to 7, characterized in that the removal of acetone from the triacetone amine crude product in step c) takes place by distillation.
9. Process according to one or more of Claims 1 to 8, characterized in that the catalyst in step a) is selected from the group consisting of Brönsted acids, ammonium salts of a Brönsted acid, phosphonium salts of a Brönsted acid, Lewis acids.
10. Process according to one or more of Claims 1 to 9, characterized in that the catalyst in step a) is ammonium chloride or ammonium nitrate.
11. Process according to one or more of Claims 1 to 10, characterized in that the molar ratio of ammonia to catalyst in step a) is in the range 1 : 0.8 to 1 : 0.02.
12. Process according to one or more of Claims 1 to 11, characterized in that the extraction of the acetone-depleted triacetone amine crude product in step d) is carried out as a crossflow extraction or as a countercurrent extraction.
13. Process according to one or more of Claims 2 to 12, characterized in that the extracted triacetone amine crude product in step e) is purified by distillation to give triacetone amine.

Process for the preparation and work-up of a reaction mixture containing triacetone amine

Abstract

5

The present invention relates to a process for the preparation of triacetone amine, comprising the reaction of acetone and ammonia in the presence of a catalyst, and the subsequent work-up of the resulting reaction mixture.

10

(No suitable figure)