

PATENT SPECIFICATION

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(54) PROCESS FOR THE MANUFACTURE OF TRIACETONE-AMINE

(71) We, CIBA-GEIGY AG., a Swiss Body Corporate, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a new process for the manufacture of triacetoneamine.

Various processes have been proposed for the manufacture of triacetoneamine. [E. G. Rozantsev, Pharm. Chem. J. 5 42-46 (1971)]. All these methods suffer from the disadvantage of a long reaction time coupled with relatively low yield. Furthermore, the by-products found in the aqueous liquors present serious ecological problems in the case of all these processes.

For example, in the known process for the manufacture of triacetoneamine starting from phorone and ammonia solution, a yield of 68% is obtained for a reaction time of 1 to 2 days. At the same time a relatively large amount of aqueous ammonia solution is required. To isolate the triacetoneamine, it must be salted out and filtered off. In spite of salting out, the aqueous mother liquor always retains 1 to 2% of the very readily water-soluble triacetoneamine, which means an additional contamination of the effluent.

A new more economical process for the manufacture of triacetoneamine by reaction of phorone with an aqueous solution of ammonia has now been discovered. According to the present invention, there is provided a process for the production of triacetoneamine, comprising reacting phorone with an aqueous solution of ammonia at elevated temperature and under gaseous ammonia at elevated pressure. This new process shortens the reaction time and increases the yield and it is furthermore possible to work with a substantially lower amount of water than in the case of the previously known processes. The reduced amount of water makes it possible to fill the reaction product directly into a container where it solidi-

fies to a mass of crystals after cooling. As a result, the filtration required in the previously known processes, and the effluent problems associated therewith, are eliminated.

An even better yield is obtained according to the new process if the reaction is carried out in the presence of alkali metal hydroxide or alkaline earth metal hydroxide. For example, 1 to 6 mol%, preferably 3 mol%, calculated relative to the phorone, can be added. Examples of alkali metal hydroxides which can be used are lithium hydroxide, sodium hydroxide or potassium hydroxide, and examples of alkaline earth metal hydroxides which can be used are magnesium hydroxide, calcium hydroxide, strontium hydroxide or barium hydroxide.

It is critical for the new process that the reaction is carried out at elevated temperature in a solution which is in contact with gaseous ammonia under excess pressure and that this excess pressure of the ammonia atmosphere is maintained during the reaction. The excess pressure should preferably be at least 0.2 bar and particularly preferably 1 to 5 and especially 1 to 3 bars. The elevated temperature is preferably 60 to 110°C and particularly to 90 to 100°C.

In a preferred embodiment of the new process, a small amount of water is used. In the preferred embodiment, the ratio of water to phorone should be at least 1:1 and should preferably be between 2:1 and 4:1. The triacetoneamine obtained is an intermediate product for the manufacture of light protection agents such as, for example, the light protection agents of French Patent No. 2,089,773 or of Belgian Patent No. 778,451. The invention is described in more detail in the Examples which follow. In these, per cent (%) denotes per cent by weight.

Example 1.

72 ml of 24% strength ammonia solution and 100 g of phorone are initially introduced into a 300 ml stainless steel autoclave at room

temperature. The autoclave is sealed and brought, three times in succession, to 2 bars excess pressure with ammonia gas for a short period, whilst stirring, the pressure in each case again being released. Thereafter the temperature is raised over the course of 1 hour to 95°C, starting at 1 bar excess pressure, whilst stirring well. During heating up, the ammonia pressure is allowed to rise to only 2 bars excess pressure by blowing off gas. Thereafter the reaction mixture is kept for approx. 4 hours at 95°C and 2 bars excess pressure. During the first 2 hours the mixture takes up ammonia whilst during the next 2 hours ammonia is evolved. The contents of the autoclave are cooled to 60°C and the liquid reaction mixture is run out. On cooling, it solidifies to a pale yellowish crystal mass of triacetamine hydrate. 160 g of crude product having a triacetamine content of 65% are obtained, corresponding to a theoretical yield of 93%.

Example 2.

30 g of water and 100 g of phorone are initially introduced at room temperature into a 300 ml stainless steel autoclave. The autoclave is sealed and is brought three times in succession to 2 bars excess pressure with ammonia gas for a short time, whilst stirring, the pressure being released in each case. Thereafter, the temperature is raised to 95°C over the course of 1 hour, whilst stirring well. During heating up, the ammonia pressure is allowed to rise to only 1.3 bars excess pressure, by blowing off gas. Thereafter the reaction mixture is kept for approx. 5 hours at 95°C and 1.3 bars excess pressure. During the first 2.5 hours the mixture takes up ammonia and during the next 2.5 hours ammonia is

evolved. The contents of the autoclave are cooled to 60°C and the liquid reaction mixture is run out. On cooling, it solidifies to a pale yellowish crystal mass of 142 g of triacetamine hydrate with a triacetamine content of 72.5%, which corresponds to a theoretical yield of 92%.

Example 3.

72 ml of 24% strength ammonia solution, 100 g of phorone and 0.05 g of lithium hydroxide (= 0.002 mol), dissolved in 4 ml of water, are initially introduced at room temperature into a 300 ml stainless steel autoclave. The autoclave is sealed and brought three times in succession to 2 bars excess pressure with ammonia gas for a short time, whilst stirring, the pressure being released in each case. Thereafter, the temperature is raised to 95°C over the course of 1 hour, starting at 1 bar excess pressure, whilst stirring well. During heating up, the ammonia pressure is allowed to rise to only 2 bars excess pressure, by blowing off gas. Thereafter the reaction mixture is kept at 95°C and 2 bars excess pressure for approx. 4 hours. During the first 2 hours the mixture takes up ammonia and during the next 2 hours ammonia is evolved. The autoclave contents are cooled to 60°C and the liquid reaction mixture is run out. On cooling, it solidifies to a pale yellowish crystal mass of triacetamine hydrate. 169 g of crude product having a triacetamine content of 65% are obtained, corresponding to a theoretical yield of 98%.

On replacing the 0.002 ml of lithium hydroxide used in this Example by equimolar amounts of other alkali metal hydroxides or alkaline earth metal hydroxides, the following yields are obtained:

Alkali metal hydroxide or alkaline earth metal hydroxide	Amount	Yield of triacetamine % of theory
NaOH	0.002 mol	96%
Ca(OH) ₂	0.002 mol	94%
Ba(OH) ₂	0.002 mol	93%

WHAT WE CLAIM IS:—

1. A process for the production of triacetamine comprising reacting phorone with an aqueous solution of ammonia, at elevated temperature and under gaseous ammonia at elevated pressure.
2. A process according to Claim 1 wherein the reaction is carried out under gaseous ammonia at not less than 0.2 bar excess pressure at 60 to 110°C and a molar ratio of water to phorone of at least 1:1 is used.

3. A process according to Claim 1 or 2 wherein the reaction is carried out under gaseous ammonia at 1 to 5 bars excess pressure.

4. A process according to any of the preceding claims wherein the reaction is carried out under gaseous ammonia at 1 to 3 bars excess pressure.

5. A process according to any of the preceding claims wherein the reaction is carried out at 90 to 100°C.

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temperature. The autoclave is sealed and brought, three times in succession, to 2 bars excess pressure with ammonia gas for a short period, whilst stirring, the pressure in each case again being released. Thereafter the temperature is raised over the course of 1 hour to 95°C, starting at 1 bar excess pressure, whilst stirring well. During heating up, the ammonia pressure is allowed to rise to only 2 bars excess pressure by blowing off gas. Thereafter the reaction mixture is kept for approx. 4 hours at 95°C and 2 bars excess pressure. During the first 2 hours the mixture takes up ammonia whilst during the next 2 hours ammonia is evolved. The contents of the autoclave are cooled to 60°C and the liquid reaction mixture is run out. On cooling, it solidifies to a pale yellowish crystal mass of triacetoneamine hydrate. 160 g of crude product having a triacetoneamine content of 65% are obtained, corresponding to a theoretical yield of 93%.

Example 2.

30 g of water and 100 g of phorone are initially introduced at room temperature into a 300 ml stainless steel autoclave. The autoclave is sealed and is brought three times in succession to 2 bars excess pressure with ammonia gas for a short time, whilst stirring, the pressure being released in each case. Thereafter, the temperature is raised to 95°C over the course of 1 hour, whilst stirring well. During heating up, the ammonia pressure is allowed to rise to only 1.3 bars excess pressure, by blowing off gas. Thereafter the reaction mixture is kept for approx. 5 hours at 95°C and 1.3 bars excess pressure. During the first 2.5 hours the mixture takes up ammonia and during the next 2.5 hours ammonia is

evolved. The contents of the autoclave are cooled to 60°C and the liquid reaction mixture is run out. On cooling, it solidifies to a pale yellowish crystal mass of 142 g of triacetoneamine hydrate with a triacetoneamine content of 72.5%, which corresponds to a theoretical yield of 92%.

Example 3.

72 ml of 24% strength ammonia solution, 100 g of phorone and 0.05 g of lithium hydroxide (= 0.002 mol), dissolved in 4 ml of water, are initially introduced at room temperature into a 300 ml stainless steel autoclave. The autoclave is sealed and brought three times in succession to 2 bars excess pressure with ammonia gas for a short time, whilst stirring, the pressure being released in each case. Thereafter, the temperature is raised to 95°C over the course of 1 hour, starting at 1 bar excess pressure, whilst stirring well. During heating up, the ammonia pressure is allowed to rise to only 2 bars excess pressure, by blowing off gas. Thereafter the reaction mixture is kept at 95°C and 2 bars excess pressure for approx. 4 hours. During the first 2 hours the mixture takes up ammonia and during the next 2 hours ammonia is evolved. The autoclave contents are cooled to 60°C and the liquid reaction mixture is run out. On cooling, it solidifies to a pale yellowish crystal mass of triacetoneamine hydrate. 169 g of crude product having a triacetoneamine content of 65% are obtained, corresponding to a theoretical yield of 98%.

On replacing the 0.002 ml of lithium hydroxide used in this Example by equimolar amounts of other alkali metal hydroxides or alkaline earth metal hydroxides, the following yields are obtained:

Alkali metal hydroxide or alkaline earth metal hydroxide	Amount	Yield of triacetone amine % of theory
NaOH	0.002 mol	96%
Ca(OH) ₂	0.002 mol	94%
Ba(OH) ₂	0.002 mol	93%

WHAT WE CLAIM IS:—

1. A process for the production of triacetoneamine comprising reacting phorone with an aqueous solution of ammonia, at elevated temperature and under gaseous ammonia at elevated pressure.
2. A process according to Claim 1 wherein the reaction is carried out under gaseous ammonia at not less than 0.2 bar excess pressure at 60 to 110°C and a molar ratio of water to phorone of at least 1:1 is used.

3. A process according to Claim 1 or 2 wherein the reaction is carried out under gaseous ammonia at 1 to 5 bars excess pressure.

4. A process according to any of the preceding claims wherein the reaction is carried out under gaseous ammonia at 1 to 3 bars excess pressure.

5. A process according to any of the preceding claims wherein the reaction is carried out at 90 to 100°C.

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6. A process according to any of the preceding claims wherein the molar ratio of water to phorone is 2:1 to 4:1.
- 5 7. A process according to any of the preceding claims wherein the reaction is carried out in the presence of alkali metal hydroxide or alkaline earth metal hydroxide.
- 10 8. A process according to Claim 7 wherein the reaction is carried out in the presence of 1 to 6 mol% of alkali metal hydroxide or alkaline earth metal hydroxide calculated relative to the phorone.
- 15 9. A process according to Claim 8 wherein the reaction is carried out in the presence of 3 mol% of alkali metal hydroxide or alkaline earth metal hydroxide calculated relative to the phorone.
- 20 10. A process according to Claim 7 or 8 wherein lithium hydroxide is used as the alkali metal hydroxide.
11. A process according to Claim 7 or 8 wherein sodium hydroxide is used as the alkali metal hydroxide.
12. A process according to Claim 7 or 8 wherein calcium hydroxide is used as the alkaline earth metal hydroxide. 25
13. A process according to Claim 7 or 8 wherein barium hydroxide is used as the alkaline earth metal hydroxide.
14. A process according to Claim 1 substantially as described with reference to any of the Examples. 30
15. Triacetoneamine when produced by a process claimed in any of claims 1 to 14.

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