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(71) Applicant(s)
Atofina

(72) Inventor(s)
Jean-Pierre Schirmann

(74) Agent/Attorney
SPRUSON and FERGUSON,GPO Box 3898,SYDNEY NSW 2001

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<p>(54) Title: METHOD FOR PREPARING HYDRAZINE HYDRATE</p> <p>(54) Titre: PROCEDE DE PREPARATION D'HYDRATE D'HYDRAZINE</p> <p>(57) Abstract</p> <p>The invention concerns a method for preparing hydrazine hydrate which consists in: (a) reacting ammonia, hydrogen peroxide and methyl ethyl ketone in the presence of a working solution to form an azine; (b) separating the working solution from the azine containing methyl ethyl ketone oxime and optionally the methyl ethyl ketone which has not reacted; (c) recycling the working solution to step (a) after an optional treatment; (d) hydrolyzing the azine to obtain hydrazine hydrate and regenerating the methyl ethyl ketone; (e) recycling to step (a) the methyl ethyl ketone. Said method is characterised in that in step (d) the methyl ethyl ketone oxime is purged.</p> <p>(57) Abrégé</p> <p>La présente invention concerne un procédé de préparation d'hydrate d'hydrazine dans lequel: (a) on fait réagir l'ammoniac, le peroxyde d'hydrogène et la méthyl éthyl cétone en présence d'une solution de travail pour former une azine; (b) on sépare la solution de travail d'avec l'azine contenant l'oxime de méthyl éthyl cétone et éventuellement la méthyl éthyl cétone n'ayant pas réagi; (c) on recycle la solution de travail à l'étape (a) après un traitement éventuel; (d) on hydrolyse l'azine pour obtenir de l'hydrate d'hydrazine et régénérer la méthyl éthyl cétone; (e) on recycle à l'étape (a) la méthyl éthyl cétone, ce procédé étant caractérisé en ce que, dans l'étape (d), on effectue une purge de l'oxime de méthyl éthyl cétone.</p>		

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PROCESS FOR THE PREPARATION OF HYDRAZINE HYDRATE

The present invention relates to a process for the preparation of hydrazine hydrate. The present invention relates more specifically to an improved
5 process for the manufacture of hydrazine hydrate from methyl ethyl ketone azine obtained by oxidation of ammonia with hydrogen peroxide in the presence of a coreactant or of a catalyst.

The industrial production of hydrazine
10 hydrate is carried out according to the Raschig, Bayer or hydrogen peroxide processes.

In the Raschig process, ammonia is oxidized with a hypochlorite in order to obtain a dilute hydrazine hydrate solution, which solution subsequently
15 has to be concentrated by distillation. This process is not very selective, has a low yield and is highly polluting, and is virtually no longer used.

The Bayer process is an alternative form of the Raschig process which consists in shifting a
20 chemical equilibrium by trapping, using acetone, the hydrazine formed in the azine form $(\text{CH}_3)_2\text{C}=\text{N}-\text{N}=\text{C}-(\text{CH}_3)_2$. The azine is subsequently isolated and then hydrolysed to hydrazine hydrate. The yields are improved but there is no improvement with respect to the discharges to the
25 environment.

The process with hydrogen peroxide consists in oxidizing a mixture of ammonia and a ketone with hydrogen peroxide in the presence of a means for



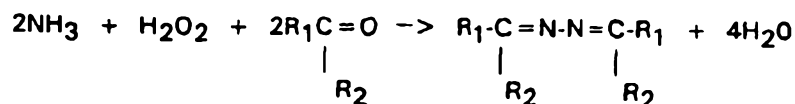
activating the hydrogen peroxide in order to directly form the azine, which it is sufficient subsequently to hydrolyse to hydrazine hydrate. The yields are high and the process is not polluting. This process with
 5 hydrogen peroxide is used by the Applicant Company and is disclosed in numerous patents, for example US 3,972,878, US 3,972,876, US 3,948,902 and US 4,093,656.

The hydrolysis of an azine to hydrazine hydrate is disclosed in Patents US 4,724,133 (Schirmann
 10 et al.), US 4,725,421 (Schirmann et al.) and GB 1,164,460. This hydrolysis is carried out in a distillation column which is fed with water and azine. The ketone is recovered at the top and the hydrazine hydrate at the bottom.

15 EP 70,155 also discloses another hydrogen peroxide process.

These processes are also described in Ullmann's Encyclopedia of Industrial Chemistry (1989), vol. A 13, pages 182-183 and the references included.

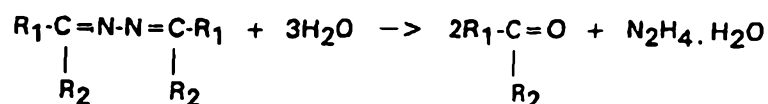
20 In hydrogen peroxide processes, ammonia is oxidized with hydrogen peroxide in the presence of a ketone and of a means for activating the hydrogen peroxide according to the following overall reaction, an azine being formed:



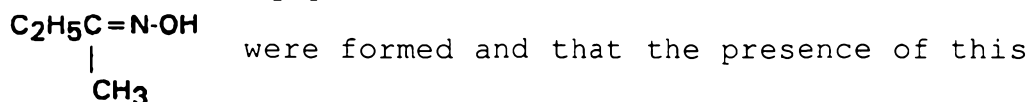
25



The activation means can be a nitrile, an amide, a carboxylic acid or a selenium, antimony or arsenic derivative. The azine is then hydrolysed to
 5 hydrazine and the regenerated ketone is recycled according to the following reaction:



10 This hydrolysis is carried out in a distillation column. The ketone is recovered at the top and the hydrazine hydrate at the bottom. The Applicant Company has discovered that, in these hydrogen peroxide processes and using methyl ethyl ketone (MEK), small
 15 amounts of a by-product, MEK oxime



oxime disrupted the operation of the process. In particular, the oxime is difficult to separate from the azine, it is found in the column for hydrolysis of the azine and it leads to decomposition of the hydrazine
 20 hydrate. The process of the invention consists in bleeding off this oxime.

The present invention is therefore a process for the preparation of hydrazine hydrate, in which:



(a) ammonia, hydrogen peroxide and methyl ethyl ketone are reacted in the presence of a working solution in order to form an azine;

(b) the working solution is separated from the azine comprising methyl ethyl ketone oxime and optionally methyl ethyl ketone;

5 (c) the working solution is recycled to the stage (a) after an optional treatment;

(d) the azine is hydrolysed in a distillation column in order to obtain hydrazine hydrate at the bottom and to regenerate the methyl ethyl ketone at the top;

(e) the methyl ethyl ketone is recycled to the stage (a), this process being characterised in that, in the stage (d), methyl ethyl ketone oxime is bled off in a
10 sidestream from the distillation column.

Stage (a)

The hydrogen peroxide can be used in the usual commercial form, for example as an aqueous solution containing between 30 and 90% by weight of H_2O_2 . One or more conventional stabilisers for peroxide solutions can advantageously be added, for example
15 phosphoric acid, pyrophosphoric acid, citric acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid or the ammonium or alkali metal salts of these acids. The amount to be used is advantageously between 10 and 1000ppm and preferably between 50 and 250ppm of the combined reactants and working solution at the reactor



inlet. The ammonia can be anhydrous or in aqueous solution.

The working solution comprises a means for activating the hydrogen peroxide, that is to say a product such that the azine can be produced from ammonia, hydrogen peroxide and methyl ethyl ketone.

This activator can be chosen from organic or inorganic oxyacids, their ammonium salts and generally their derivatives: anhydrides, esters, amides, nitriles, acyl peroxides, or their mixtures. Use is advantageously made of amides, ammonium salts and nitriles.

Mention may be made, by way of examples, of (i) amides of carboxylic acids of formula $R_5\text{COOH}$, in which R_5 is hydrogen, a linear alkyl radical having from 1 to 20 carbon atoms or a branched or cyclic alkyl radical having from 3 to 12 carbon atoms or a phenyl radical which can be substituted, or (ii) amides of polycarboxylic acids of formula $R_6(\text{COOH})_n$, in which R_6 represents an alkylene radical having from 1 to 10 carbon atoms and n being an integer greater than or equal to 2, or R_6 can be a single bond and then n has the value 2. The R_5 and R_6 radicals can be substituted by halogens or OH, NO_2 or methoxy groups. Mention may also be made of the amides of the organic acids of arsenic. The organic acids of arsenic are, for example, methylarsonic acid, phenylarsonic acid and cacodylic acid.



The preferred amides are formamide, acetamide, monochloroacetamide and propionamide.

Use is advantageously made, among ammonium salts, of the salts of hydracids, of inorganic oxyacids, of arylsulphonic acids, of $R_5\text{COOH}$ acids or of $R_6(\text{COOH})_n$ acids, R_5 , R_6 and n being defined above, or of the organic acids of arsenic.

The preferred ammonium salts are the formate, acetate, monochloroacetate, propionate, phenylarsonate and cacodylate. Mention may advantageously be made, among the nitriles, of the products of formula $R_7(\text{CN})_n$, it being possible for n to vary from 1 to 5, depending on the valency of R_7 , and R_7 is a cyclic or non-cyclic alkyl having from 1 to 12 carbon atoms or benzene or pyridine. R_7 can be substituted by groups which are not oxidized in the reactor of the stage a, for example halogens or carboxyl, carboxylic ester, nitro, amine, hydroxyl or sulphonic acid groups.

The preferred nitriles are acetonitrile and propionitrile.

The working solution is formed by dissolving one or more products chosen from organic or inorganic oxyacids, their ammonium salts and generally their derivatives: anhydrides, esters, amides, nitriles, acyl peroxides, or their mixtures. Use is advantageously made of the preceding amides, ammonium salts or nitriles.



This solution can be aqueous or based on an alcohol or on a mixture of alcohol and water. Use is advantageously made, among the alcohols, of saturated aliphatic alcohols having from 1 to 6 carbon atoms and
5 preferably 1 to 2 carbon atoms.

Use is also advantageously made of diols and more particularly of diols having from 2 to 5 carbon atoms. Mention may be made, for example, of glycol, propylene glycol, 1,3-propanediol, 1,3- and 1,4-butane-
10 diol and 1,5-pentanediol.

According to an advantageous form of the invention, the working solution is an alcoholic solution of an organic acid of arsenic and is disclosed in Patent EP 70,155, the contents of which are
15 incorporated in the present application. According to another advantageous form of the invention, the working solution is an aqueous solution of an amide of a weak acid and of the ammonium salt corresponding to this acid, such as disclosed in Patent EP 487,160.

20 These amides of weak acids are derived from the corresponding carboxylic acids which have a dissociation constant of less than 5×10^{-5} , that is to say acids which have a pK of greater than 4.3 in aqueous solution at 25°C.

25 For the polycarboxylic acids, these are the acids for which the constant of the first ionization is less than 5×10^{-5} .



Mention may be made, by way of example, of the carboxylic acids of formula $R_8\text{COOH}$, in which R_8 is a linear alkyl radical having from 1 to 20 carbon atoms or a branched or cyclic alkyl radical having from 3 to 12 carbon atoms or a phenyl radical which can be substituted, or of polycarboxylic acids of formula $R_9(\text{COOH})_n$, in which R_9 represents an alkylene radical having from 1 to 10 carbon atoms and n being a number greater than or equal to 2, or R_9 can be a single bond and then n has the value 2. The R_8 and R_9 radicals can be substituted by halogens or OH, NO_2 or methoxy groups. Use is preferably made of acetamide, propionamide, n-butyramide or isobutyramide.

The ammonium salt corresponding to acetamide is ammonium acetate.

It would not be departing from the scope of the invention to form the ammonium salt in situ, that is to say to use the corresponding carboxylic acid which gives the ammonium salt by reaction with ammonia.

The proportions of the amide and of the corresponding ammonium salt can vary within wide limits. Use is usually made of 1 to 25 parts of the ammonium salt per 5 parts of amide and preferably 2 to 10.

The reactants can be used in stoichiometric amounts. However, use is made, per mole of hydrogen peroxide, of 0.2 to 5 mol and preferably of 1.5 to 4 mol of methyl ethyl ketone and of 0.1 to 10 mol and

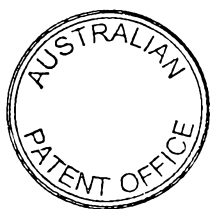


preferably of 1.5 to 4 mol of ammonia. The amount of working solution is between 0.1 and 1 kg per mole of hydrogen peroxide. This amount depends on its quality, that is to say on its catalytic strength or its activity which makes it possible to convert the reactants to azine. The proportions of the reactants laid down above make it possible to obtain complete conversion of the hydrogen peroxide and a production of azine corresponding to more than 50%, and which can reach 90%, of the hydrogen peroxide charged.

The hydrogen peroxide, ammonia and methyl ethyl ketone can be brought into contact with the working solution in any way.

The reaction is advantageously carried out in a homogeneous medium or in a medium which provides at least sufficient solubilization of the reactants for it to be possible to obtain the azine. The reaction can be carried out in a very wide temperature range, for example between 0 and 100°C, and is advantageously carried out between 30 and 70°C. Although it is possible to carry out the reaction at any pressure, it is simpler to be at atmospheric pressure, but the pressure can rise up to approximately 10 bar if this is necessary in order to preferably maintain the reaction of the stage a in the liquid phase.

The reactants can be introduced simultaneously or separately and in any order into the working solution. It is possible to use all kinds of



reactors, stirred or nonstirred, or even simple tanks, which can be arranged in parallel or in series, cocurrentwise or countercurrentwise, or any combination of these possibilities.

5 Stage (b)

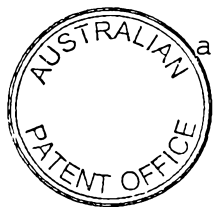
Known means, such as liquid-liquid extraction, distillation, separation by settling or any combination of these possibilities, are used to separate (i) the azine and optionally the excess methyl
10 ethyl ketone and (ii) the working solution.

Methyl ethyl ketone is advantageous because its azine is insoluble in the working solution.

The working solution can be treated in the stage (c).

15 The stages (a), (b) and (c) are disclosed, for example, in Patents EP 399,866 and EP 518,728, the contents of which are incorporated in the present application.

20 The Applicant Company has observed, for example, that the azine obtained in the stage (b), after separation from the working solution, is accompanied by unreacted methyl ethyl ketone and by various impurities. The Applicant Company, without being bound by this explanation, believes that these
25 impurities are formed during the stage (a) and are due to the simultaneous presence of hydrogen peroxide, ammonia, methyl ethyl ketone and the agent for
activating H_2O_2 .



These impurities include methyl ethyl ketone oxime
 $\text{C}_2\text{H}_5 \text{C}=\text{N}-\text{OH}$



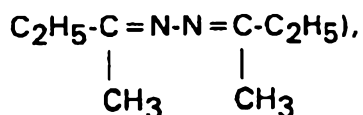
which is difficult to separate by distillation from the
 azine major product, with the result that, in
 5 industrial processes, they are conveyed simultaneously
 into the equipment which makes possible hydrolysis of
 the azine to hydrazine hydrate. Doing which, the
 Applicant Company has discovered that, when this
 hydrolysis is carried out in a reactive plate column,
 10 the oxime is concentrated on certain plates but an
 abnormal decomposition of the hydrazine hydrate is also
 observed, resulting in significant falls in yield.

The object of the present invention is to
 provide a means for not suffering from losses in yield
 15 by simply drawing off the oxime steadily via a side-
 stream, so as to prevent it from accumulating. Doing
 which, it is actually observed that the yield of
 hydrolysis of the azine to hydrogen hydrate remains
 high and does not decrease.

20 The stage (d) is carried out, for example, in
 a plate or packed column of distillation column type
 which is fed with the azine originating from the stage
 (b) and water. The following are obtained: (i) at the
 top, methyl ethyl ketone in the form of an azeotrope
 25 with water, and (ii) at the bottom, an aqueous
 hydrazine hydrate solution.



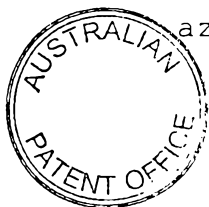
The hydrolysis of azines is known. For example, E. C. Gilbert, in an article in the Journal of the American Chemical Society, vol. 51, pages 3397-3409 (1929), describes equilibrium reactions for the formation of azine and the hydrolysis reactions of the latter and provides the thermodynamic parameters of the system in the case of water-soluble azines. For example, the hydrolysis of acetone azine is disclosed in US 4,724,133. As regards azines which are insoluble in aqueous solutions (for example, methyl ethyl ketone azine



the hydrolysis has to be carried out in a reactive column, such that, by continuously separating the methyl ethyl ketone at the distillation column top and the hydrazine hydrate at the column bottom, complete hydrolysis can be achieved. Of course, this system works best when the operation is carried out continuously, as disclosed in French Patent 1,315,348, British Patent 1,211,547 or Patent US 4,725,421.

In all these patents, the reaction is carried out in a packed distillation column or better still a plate distillation column operating under a pressure of 2 to 25 bar with a bottom temperature of 150°C to 200°C.

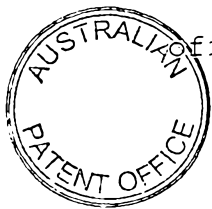
When the operation is carried out with pure azine, that is to say obtained from hydrazine hydrate



and methyl ethyl ketone, for example, it is actually found, by operating according to these patents, that dilute hydrazine hydrate solutions are obtained with a good yield.

5 In this column, the azine is hydrolysed and the hydrazine hydrate is separated from the methyl ethyl ketone. These conditions are known. A person skilled in the art easily determines the number of plates or the packing height, as well as the points for
10 feeding with azine and with water. Solutions comprising 30 or even up to 45% by weight of hydrazine hydrate are obtained at the bottom. This molar ratio of water to azine in feeding this column is at least greater than stoichiometry and advantageously between 5 and 8. The
15 column bottom is between 150°C and 200°C, preferably 175 to 190°C. The pressure depends on the boiling temperature of the azine, water and the reactant carrying a carbonyl group. Such a hydrolysis is disclosed in US 4,725,721.

20 A person skilled in the art can easily determine, according to the number of plates or the packing height, the position of the azine feed and the position of the water feed, the reflux, the nature of the azine, and the like, in what part of the column the
25 maximum oxime concentration is obtained. This is because it is simpler to bleed off the oxime by drawing off at the point of its maximum concentration. Drawing
off can be carried out continuously or batchwise, the

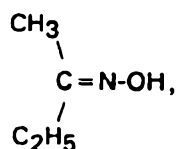


essential point being to avoid the accumulation of oxime in this column since its presence results in decomposition of the hydrazine hydrate.

The reaction of the stage (a) can produce an
5 azine comprising up to 2% by weight of oxime.

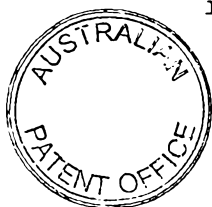
The concentration of oxime is prevented from exceeding 15% by weight on the plates or in the parts of the column of its maximum concentration.

For example, when the operation is carried
10 out with methyl ethyl ketone azine resulting from an oxidation operation with hydrogen peroxide according to Patent EP 70,155 or according to Patents EP 399,866, EP 518,728 or EP 487,160, it is observed that this azine is not pure but that it comprises an amount of
15 oxime which can vary between 0.1 and 1% of methyl ethyl ketone oxime



the boiling point of which is 151°C at atmospheric pressure, in comparison with 161°C for methyl ethyl
20 ketone azine. It is illusory to want to separate these two compounds by distillation. By means of recycling operations, the level of oxime can even rise to several percent.

The Applicant Company has found that,
25 industrially, the azine comprising the oxime could be introduced into the hydrolysis column and that this



oxime, because of its azeotropic behaviour with water, came to be distributed in the column at a level intermediate between the hydrazine hydrate and the methyl ethyl ketone and that, for this reason, it was possible, fairly easily, to separate it via a side-stream. This being the case, the Applicant Company has also found that, if the level of oxime is allowed to rise in the column, an increasing degree of decomposition of the hydrazine hydrate is concurrently observed. This decomposition is related to the presence of oxime, as is shown in the examples.

Example 1

In a column made of 316 L stainless steel, with a height of 3 m and a diameter $\varnothing = 70$ mm, which is equipped with 40 plates, each 80 mm apart, comprising a perforated single bell cap with a diameter of 27 mm [lacuna]. There are 14 holes in each bell cap, each with a diameter of 2 mm. The working volume of liquid retained on the plate is 33 ml. It can be adjusted by varying the height of the weir.

This column is equipped with temperature probes (thermocouples) on plates No. 3, 6, 10, 13, 15, 19, 26, 28, 31 and 37, as well as at the top and bottom. Sidestream outlets equipped with valves are installed at plates 3, 10, 19, 26, 31 and 37.

The reactants can be introduced at the level of plates 5, 8, 12, 19, 22, 26 and 34. The rate of reflux is measured using a precalibrated rotameter. The



heat supply at the column bottom is provided by electrical heating. The shaft of the column is rendered adiabatic by a sheath of hot air obtained by electrical heating, so as to equilibrate the temperatures inside
5 and outside the column.

The reactants are fed via metering pumps.

The condenser is fed with circulating hot oil maintained between 130 and 140°C.

The procedure is as follows:

10 400 cm³ of doubly deionized water are placed in the boiler (with a volume of 800 cm³) of the column. After the entire apparatus has been sealed, heating is begun and the pressure is allowed to rise to 8 bar. Then, as the water rises up into the column, the
15 inactive materials are bled off while maintaining the pressure at 8 bar. When the level of the boiler reaches 200 cm³, the injection of water is begun at the 34th plate in order to continue to form the water ballast in the column at the rate of 645 g over 1 h 15 minutes.
20 When the temperature reaches 162° at the 19th plate, the injection of azine is begun at the 26th plate at the rate of 543 g of 82.4% azine solution (3.2 mol) over 1 h 30 minutes. Bleeding of the inactive materials from the column is continued while maintaining the pressure
25 at 8 bar. Reflux is allowed to begin and the apparatus is left at total reflux until the reflux liquid is homogeneous. The continuous introduction of the reactants is then begun, as well as drawing off at the



bottom and top. The operation is carried out at reflux
1. The azine is introduced in the form of a mixture
with MEK at the rate of 275.4 g/h (assaying 82.4% of
azine and 3% of MEK oxime) and of 289 g/h of doubly
5 deionized water. The top temperature becomes
established at 148°C, whereas the bottom temperature is
180-181°C. Under stationary conditions, 200 g/h of
colourless 35% by weight aqueous hydrazine hydrate
solution are drawn off from the bottom. The content of
10 oxime in plate 26 is 14.5% after operating for a few
tens of hours. 20 ml of a mixture of azine, hydrazine,
oxime and water are drawn off from this plate every
five hours. The MEK-water azeotrope is drawn off at the
top, which azeotrope represents, after cooling to
15 normal temperature, an organic phase of 300 g/h,
assaying 86.5% of MEK, and an aqueous phase of 55 g/h,
assaying 20% of MEK.

Example 2

The operation is carried out as in Example 1
20 but with a synthetic MEK azine not comprising oxime.
Drawing off is not carried out. A similar result is
observed.

Example 3 (not in accordance with the
invention)

25 The operation is carried out as in Example 1
but drawing off from plate 26 is not carried out. It is
found that the hydrazine hydrate assay of the material



drawn off at the column bottom only assays 31% by weight of hydrazine hydrate.



The claims defining the invention are as follows:

1. A process for the preparation of hydrazine hydrate, in which:
 - (a) ammonia, hydrogen peroxide and methyl ethyl ketone are reacted in the presence of a working solution in order to form an azine;
 - 5 (b) the working solution is separated from the azine comprising methyl ethyl ketone oxime and optionally methyl ethyl ketone;
 - (c) the working solution is recycled to the stage (a) after an optional treatment;
 - (d) the azine is hydrolysed in a distillation column in order to obtain hydrazine hydrate at the bottom and to regenerate the methyl ethyl ketone at the top;
 - 10 (e) the methyl ethyl ketone is recycled to the stage (a), this process being characterised in that, in the stage (d), methyl ethyl ketone oxime is bled off in a sidestream from the distillation column.
2. A process according to claim 1, substantially as hereinbefore described.
3. A process for the preparation of hydrazine hydrate substantially as described
15 in Example 1.
4. Hydrazine hydrate prepared by the process claimed in any one of claims 1 to 3.

Dated 18 March, 2002
ATOFINA

20 **Patent Attorneys for the Applicant/Nominated Person**
SPRUSON & FERGUSON

