

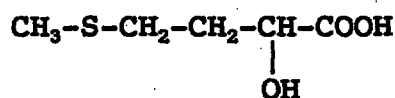
Description

A. SUBJECT OF THE INVENTION

The present invention relates to an improved process for preparing aqueous solutions of DL-2-hydroxy-4-methylthiobutyric acid, these solutions having less colour and odour, lower viscosity and a good thermal stability when they are compared with the same product prepared by other known processes.

B. BACKGROUND OF THE INVENTION

2-hydroxy-4-methylthiobutyric acid (hereinafter designated HMTBA) has the formula:



It is a known product analogous to the essential amino acid DL-methionine, which finds use mainly as a food supplement for animal nutrition. In contrast to the amino acid, it is not used directly by the organism in protein synthesis, because it must be converted anabolically to amino acid in order to be able to be used as such. HMTBA is not used in the pure form, but in various forms, that is to say:

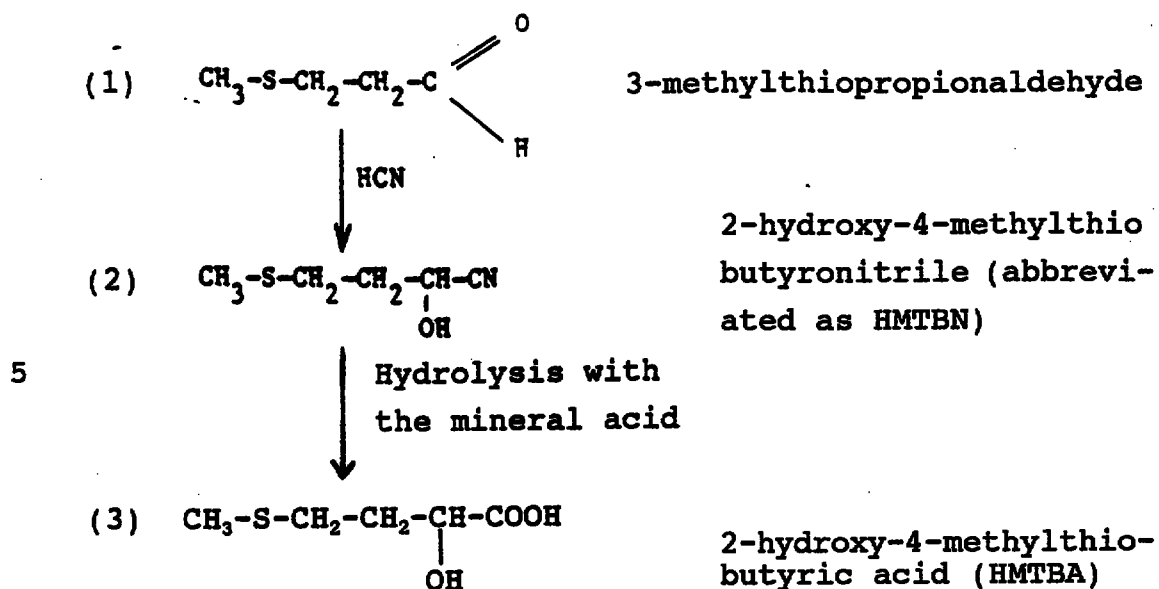
1) concentrates which contain a mixture of the calcium and ammonium salts of the said HMTBA, water and calcium sulphate, as is the case in US Patents 2,745,745 and 2,938,053 and GB Patents 722,024 and 915,193;

2) acid aqueous solutions having a HMTBA concentration of 85-90 % by weight, as is described in US Patents 4,353,924 and 3,773,927; and

3) the calcium salt of HMTBA obtained by the process of US Patent 3,175,000 of 23 March 1965.

C. PRIOR ART

The general process for obtaining HMTBA from 3-methylthiopropionaldehyde which may be summarized by the following scheme:



10 is amply described in the bibliography of the patents, specifically in US Patents 2,745,745 and 2,938,053, in which patents step (2) → (3) of the above scheme implies passage via the intermediate amide which, by means of an additional hydrolysis, leads to HMTBA. However, depending

15 on the hydrolysis conditions employed, the free acid or the intermediate amide is obtained. This hydrolysis reaction of the nitrile appears also to be described in US Patents 4,353,924 and 3,175,000, which specifically use sulphuric acid, and in US Patent 3,773,927 which uses

20 hydrochloric acid. The said patents of the prior art also describe the operating conditions of the process, such as the temperature, the duration and the molar ratios of mineral acid to nitrile. In these patents of the prior art, once the HMTBA is obtained by the hydrolysis

25 reaction it is isolated in the form indicated in paragraph (B) (salts or aqueous solution) by means of operations to which a further reference will be made when comparing the said processes of the prior art with the process of the present invention.

30 Finally, the European Patent Applications published under the numbers 0,142,488 and 0,143,100, both filed on 13 November 1984, relate specifically to the production of liquid forms of HMTBA by processes for the

extraction, with solvents, of the said HMTBA from the reaction mixture resulting from the hydrolysis of the HMTBN carried out in the first case with sulphuric acid and in the second case with a mineral acid. The two European patent applications describe, with all details, the conditions enabling the solvent extraction to be carried out, as well as the precise nature of the solvents employed.

However, the processes of the prior art taken up in the patents and applications mentioned suffer from various disadvantages derived from the specific way in which the isolation of the HMTBA end product is carried out. These disadvantages may be summarized as follows:

a) Presence of oligomers of HMTBA with the concomitant bad odour, colour and low free acid content.

b) Excessive viscosity.

c) Presence of particulate fines of calcium sulphate and/or soluble inorganic salts which render the product impure.

d) High cost of the final product because of the use of means such as solvent extraction.

e) Low recovery yields of HMTBA.

The said disadvantages are overcome by the process of the invention which, using the mixture resulting from the hydrolysis of HMTBN by sulphuric acid as the starting material, makes it possible, in a single step, to obtain an aqueous solution of HMTBA, devoid of the previous disadvantages owing to the use of a new process for the isolation of the HMTBA in the form of an aqueous solution.

D. DESCRIPTION OF THE PROCESS WHICH IS THE SUBJECT OF THE INVENTION

The process for the synthesis of 2-hydroxy-4-methylthiobutyronitrile (HMTBN), described below, is a variant of that disclosed in Spanish Patent 393,625 for the synthesis of the amino acid DL-methionine, the synthesis of the nitrile being similar in the two processes without any difference other than that of using an

aqueous ammonia solution as reaction means to obtain the nitrile corresponding to the amino acid, and water free from ammonia for the case of HMTBN.

The same may be stated with regard to the step following the synthesis, that is to say the acidification of the HMTBN. In the two cases, the product obtained in the synthesis step is brought into contact with concentrated sulphuric acid, preferably 98 % sulphuric acid, in an acidification loop where the two products are mixed. In order to avoid local heating leading to the destruction of the nitrile and to the formation of secondary reactions giving rise to increased coloration, the acidification is carried out continuously with large recirculation, by adding concentrated sulphuric acid to the acidified nitrile solution, this solution preferably having a concentration of 20-50 % by weight of acid.

Since it is necessary to remove the heat of dilution of the sulphuric acid, the acidification loop is provided with one or more heat exchangers such that the reaction temperature does not exceed a value of 50°C.

The molar ratio of the sulphuric acid/HMTBN must be between 0.5 and 2, preferably 0.8 and 1.5. The proportion of water must be adjusted in such a way that the acidified solution consists of a single phase and is capable of keeping in solution the ammonium sulphate which will be formed during the subsequent hydrolysis reaction and the later neutralization with ammonium hydroxide.

After a contact time of 30-60 minutes, the solution is heated to a temperature of between 60 and 140°C, preferably 90°C, to complete the hydrolysis reaction of the nitrile HMTBN in a single step, without the need to use different conditions in order to obtain the intermediate amide and then to modify the said conditions in order to obtain the HMTBA. The reaction time varies between 5 minutes and 6 hours, depending on the temperature chosen. Thus, for example, using 90°C and the abovementioned molar ratio, a quantitative conversion

of HMTBN to HMTBA is achieved after about 2 hours.

It is extremely important to control the temperature and the reaction time within the abovementioned ranges since the colour and the oligomer content fundamentally depend on the said values in the sense that higher temperatures and longer durations than those indicated lead to a product which has more colour and higher viscosity values, which is an obvious consequence of a higher oligomer content.

As the hydrolysis proceeds, it is expedient to apply a slight vacuum to the reactor (between about 20 and 200 mm) so as to remove the small excess of HCN used in the synthesis of the HMTBN, as well as the volatile impurities which could have formed in the reaction and to which the bad odour of the end product is attributed.

It is when the hydrolysis reaction is complete that the isolation of the HMTBA, which is the essential aspect of the present invention, actually starts. The reaction mixture from the hydrolysis is cooled to 60-70°C and its excess acid is neutralized with a 20-35 % by weight ammonia solution, the said solution optionally being able to be formed in situ by bubbling gaseous NH_3 . The said neutralization may necessitate cooling so as not to exceed the temperature of 60-70°C.

The neutralized composition obtained comprises two phases, which are easy to separate by settling, because they have distinctly different densities. The following step of the process is therefore to separate off the organic phase, which contains 93-95 % of the HMTBA formed, from the aqueous phase, which contains the rest, by means of settling. The ammonium sulphate which has formed during the hydrolysis reaction and the neutralization of the acid used in excess is also distributed between the two phases, the aqueous phase being the richest, containing 70-75 % by weight.

It is an essential part of the present invention that the two phases are separated by settling, centrifuging or by another standard process for liquid/liquid

separation which does not involve extraction with solvents, which to an extraordinary degree facilitates the subsequent processes of purification and total recovery of the HMTBA, on the one hand, and of the ammonium sulphate, on the other hand, with a high yield and efficiency.

Separating processes of the type involving extraction with a water-immiscible solvent are not necessary; they do not substantially improve either the quality or the yield, but increase the price of the process and make the installation more complicated.

The ammonium sulphate is precipitated from the aqueous phase by evaporation of the water under atmospheric pressure or under reduced pressure. The resulting solid is separated off by any standard solid/liquid separation process, such as filtration and/or centrifuging, and the liquid thus obtained, containing the portion of ammonium sulphate which has not precipitated and the HMTBA, is recycled to the neutralization vessel. With this process, ammonium sulphate is obtained which, once it has been dried, is of high purity and is virtually free from HMTBA; the latter is recovered in its entirety by recycling to the head of the separation process, while remaining incorporated in the organic phase.

The organic phase which issues from the settler and contains the HMTBA from the two streams (neutralization and recycling) is led to an evaporator, operating under vacuum, where the water is evaporated until its content is lowered to 1 % and preferably to 0.5 %, in order to precipitate all of the ammonium sulphate which it contained in solution. The suspension obtained is readily transportable because it contains, in suspension, only 25-30 % of the ammonium sulphate produced in total in the synthesis and neutralization steps and it may be separated off very easily by filtration and/or centrifuging. The HMTBA obtained by this process is of high purity and its ammonium sulphate content is less than 1 %.

The ammonium sulphate cake originating from the abovementioned separator system contains amounts of HMTBA which vary between 15 and 30 % by weight. The two products are recovered by recycling them to the neutralization vessel by preliminary dissolution with water and, in the same way as for the previous recycling, the dissolved ammonium sulphate is preferably incorporated in the aqueous phase and the HMTBA in the organic phase, which ensures that the recovery of the two products is quantitative.

The HMTBA obtained by this process must subsequently be diluted with water and, if necessary, stabilized with a small amount of sulphuric acid, to give a solution which contains 65-95 % of HMTBA and between 0.1 and 0.5 % of free sulphuric acid. The solution thus obtained is in equilibrium with its polymer or oligomer esters and is stable over time. In the end product the ratio between the monomer HMTBA and the sum of the oligomers is higher than 3, its colouring is less than 2000 degrees APHA and its ammonium sulphate content is less than 1 % by weight.

Purely by way of illustration, the process is now described with reference to the single figure of drawings showing a flow diagram of the improved process of the invention. HMTBN, represented by (A), is introduced into the acidification vessel (1), where it is mixed with concentrated sulphuric acid, represented by (B). The arrangement of the acidification loop formed by the vessel (1), the pipes (C) and (D) and the heat exchanger (E) makes it possible to obtain a sulphuric acid concentration of 20-50 % by weight in the vessel (1). The reaction mixture passes via the pipe (F) into the hydrolysis reactor (2), in which the reaction is carried out under the temperature and time conditions specified above. The said hydrolysis reactor is provided with communication to the atmosphere (G) for ventilation and an outlet pipe (H), which leads to a neutralization and mixing vessel (3) into which the ammonium hydroxide

5 solution is introduced via (I) (optionally it would be possible to introduce gaseous ammonia in order to form the ammonium hydroxide solution in situ). From the vessel (3), the neutralized solution passes via the pipe (J) to the phase separator (4), in which the organic phase (Ph O) and the aqueous phase (Ph A) form.

10 The organic phase (Ph O) is fed via the pipe (K) to the evaporator under vacuum (7), provided with its steam inlet (SI) for heating, its outlet for emptying (EO) and its pipe (N) for aqueous effluent. A transportable suspension consisting of ammonium sulphate and HMTBA leaves via the pipe (M); this suspension then arrives in the separator device (filter/centrifuge) (8), allowing, on the one hand, recovery of a solid cake of impure ammonium sulphate containing HMTBA, which is transported by the means represented by (O) to the dilution vessel (10), from where an ammonium sulphate solution containing a small proportion of HMTBA leaves via the pipe (P), which solution is recycled to the neutralization vessel (3). On the other hand, liquid HMTBA is withdrawn, via the pipe (Q), from the separator device (8), which liquid HMTBA, after dilution with water to adjust its concentration in the mixer (9) and, if necessary, stabilization with sulphuric acid, is collected as the main product of the process.

30 The aqueous phase (Ph A), withdrawn from the settler (4) via the pipe (L), is concentrated in the evaporator (5), in which the references EO and SI have the same meanings as in the evaporator (7). The aqueous effluent is collected via the pipe (R) and an aqueous suspension of impure ammonium sulphate containing HMTBA is collected via (S), which suspension is separated by filtering and/or centrifuging in (6) in order to withdraw ammonium sulphate by-product, which, after drying, may be used as fertilizer. The aqueous liquid which contains ammonium sulphate which has not precipitated and dissolved HMTBA is returned via the pipe (T) to the neutralization vessel (3).

Only the main elements have been shown in the diagram of drawings, customary devices and accessories, such as pumps, flow meters, heating means, temperature measuring devices, and the like, having been deliberately omitted.

As can be seen, the improved process according to the invention makes it possible to lose virtually no HMTBA in effluent streams and it may be stated that the recovery is 99 %.

The improved process according to the invention is extremely advantageous compared with the prior art. In fact, US Patent 2,745,745 describes a process for obtaining an alkaline-earth metal salt, the calcium salt of HMTBA, by means of the two-step hydrolysis of HMTBN, proceeding via the corresponding amide and obtaining the salt by addition of an alkaline-earth metal hydroxide or carbonate. This method has the disadvantage of requiring a change in the HMTBN hydrolysis conditions in order first to obtain the corresponding hydroxyamide and then, under different conditions, to obtain the HMTBA. We have found that the solution acidified by our process may be hydrolysed in a single step with virtually quantitative yields. This is also valid for US Patent 2,983,053, which essentially relates to the synthesis of HMTBA, proceeding via the intermediate hydroxyamide, in order to obtain the calcium salt of HMTBA. US Patent 2,745,745 uses a calcium hydroxide or calcium carbonate solution to neutralize the sulphuric acid used in the hydrolysis. This method has the disadvantage of necessitating the separation of the corresponding calcium sulphate from the remainder of the solution; moreover, this sulphate precipitates in very fine form, which gives rise to considerable losses of product in the cake obtained. Moreover, the corresponding alkali metal salt of the HMTBA is obtained in impure form, which necessitates heating the filtrate with the addition of more hydroxide or carbonate, which complicates the process and makes it more expensive. US Patent 2,745,745 also establishes that the free acid may be

directly obtained from the hydrolysis composition by extraction with a water-immiscible solvent. However, it appears that the yields obtained by the extraction process described in this patent are low; it is therefore
5 doubtful that the said process has practical application.

US Patent 3,175,000 improves the yield in which the calcium salt of HMTBA is obtained by the following means: addition of ammonium sulphate to the hydrolysis composition until it is saturated; extraction of the
10 aqueous phase with a water-immiscible polar solvent, preferably an ether; mixing of the extract with the organic phase; evaporation of the solvent; and addition of a calcium hydroxide or carbonate in order to form the HMTBA salt.

15 GB Patent 722,024 also yields calcium sulphate in the end product, with the problems discussed above.

European Patent Applications 0,142,448 and 0,143,100 describe processes for liquid/liquid extraction with a water-immiscible solvent in order to separate off
20 the salts formed during the hydrolysis of the HMTBN and discredit the evaporation process because of the production of a stronger colour and a higher oligomer content, a high energy consumption and difficulties during separation of the salts. Our process overcomes all of the
25 critical points in the said applications, because there is no increase in colour or in oligomers if the evaporation is carried out carefully at the temperatures specified in the process; the energy consumption is lower because a solvent/water azeotrope does not have to be
30 evaporated, as with our process, involving settling prior to evaporation, it is necessary only to evaporate the water contained in the organic phase. The process described in the present invention makes no use of any type of extraction process using a solvent in order to
35 improve the yield and/or the quality of the end product, as is the case in the abovementioned references; in fact, by virtue of a simple and inexpensive evaporation process a product is obtained which has equally good or even

5 better characteristics in respect of colour, odour and oligomer content. Moreover, the installation is less costly and less complex, and the risk of inflammable solvents during their transport, their storage and their handling is completely eliminated since our process uses aqueous solutions at all times.

10 US Patent 3,773,927 uses hydrochloric acid to hydrolyse HMTBN, improving the process described in US Patent 2,745,745, which uses sulphuric acid solutions as hydrolysis agent. Given that a HMTBA solution which is in a single phase is obtained by hydrolysis with hydrochloric acid, all of the ammonium chloride produced by the hydrolysis is in this phase; it follows that the subsequent separating processes are very difficult to
15 carry out with high yields, in view of the difficulties existing in dealing with suspensions of high viscosity; its industrial application would therefore appear not to be very viable. Moreover, we have been able to confirm that hydrochloric acid does not appear to be appropriate for carrying out the hydrolysis of the hydroxynitrile, in
20 view of the large amount of oligomers formed and in view of the strong coloration of the product. This makes it necessary to dilute it and to heat it to 90°C in the presence of hydrochloric acid, in order to hydrolyse the
25 oligomers formed.

US Patent 4,353,924 enables an aqueous solution of HMTBA to be obtained. However, the main property desired for the solution is that it should be free from corrosive properties with respect to steel surfaces.
30 Although partial neutralization of the hydrolysis mixture is envisaged, this neutralization is not imperatively carried out after the hydrolysis; it may be carried out after dehydration of the solution and before centrifuging, in order to separate the precipitated salt from the
35 mineral acid (ammonium chloride, ammonium sulphate, and the like), or after centrifuging, as the final step. On the basis of the brief text of this patent, it appears that a low yield from the recovery of the HMTBA may be

deduced. On the other hand, the neutralization conditions do not allow settling of the two phases, and the problem which this patent claims to solve appears to be irrelevant since it is necessary to stabilize the aqueous HMTBA solutions with small amounts of free mineral acid in order to prevent the formation of oligomers.

Thus, the process of the invention is advantageous compared with the known processes, both from the standpoint of the quality of the product obtained and with regard to the process economy; in fact, the recovery of the ammonium sulphate, the by-product exclusively present in the aqueous phase which is separated off by settling and in which the HMTBA concentration is low, is carried out in such a way that the recovery of the HMTBA as main product and of the ammonium sulphate as by-product is virtually quantitative.

The invention will now be illustrated by the following examples, which in no case have a limiting character.

EXAMPLE 1

200 g of 3-methylthiopropionaldehyde, together with 0.4 ml of pyridine, were introduced into a reactor provided with a thermostatic jacket, a stirrer, a thermometer and a dropping funnel. Keeping the temperature at 20°C by circulating glycol-containing water through the jacket of the reactor, 300 g of 20 % aqueous hydrocyanic acid solution were added, taking care that the said temperature is not exceeded during the addition of this acid. The temperature was then raised to 45°C and kept at this level for 15 minutes.

175 g of 98 % sulphuric acid were added to the same reactor, with vigorous stirring and using the highest possible rate of addition, watching, however, to ensure that the temperature of 50°C was not exceeded. After the addition of acid, the temperature was kept at 50°C for a further 30 minutes and the temperature was then raised rapidly to 90°C and kept at this level for 120 minutes, applying a slight vacuum to the reactor at

the same time. During this period 60 g of condensates were removed. When the hydrolysis reaction was complete, the sulphuric acid present in the reaction mixture was neutralized with ammonium hydroxide having a concentration of 25 % and the two phases formed were separated by settling out. The neutralization and settling temperature did not exceed 70°C.

The aqueous phase which had settled out was fed to a rotary evaporator where, owing to the application of vacuum, 266 g of water were evaporated and 231 g of ammonium sulphate were precipitated, which were recovered by filtering off. 52 g of mother liquors resulting from the filtration of the ammonium sulphate were retained for recycling to the reaction of Example 2 below (recycle 1).

The water present in the organic phase was removed by evaporation under vacuum and the ammonium sulphate suspension was filtered, thus yielding 117 g of cake and 287 g of HMTBA. The cake was dissolved in 233 g of water and retained for recycling into the reaction of Example 2 below (recycle 2). By analysis of the HMTBA obtained it was found that it contained 80 % by weight of HMTBA monomer, 12 % by weight of oligomers, 1.1 % of water and 0.8 % of sulphate ions. The HMTBA obtained was diluted and stabilized with water acidified with sulphuric acid, and a product was obtained which contained 88 % of HMTBA, 0.7 % of ammonium sulphate and 0.3 % of free sulphuric acid and had a coloration which, measured in degrees APHA, was less than 2000.

EXAMPLE 2

125 g of technical grade (98 %) 3-methylthiopropionaldehyde and 0.3 ml of pyridine, were introduced into a reactor fitted with a thermostatic jacket, a stirrer, a thermometer and a dropping funnel. While cooling the reactor to -10°C using glycol-containing water, 188 g of a 20 % aqueous hydrocyanic acid solution were added over a period of not less than 20 minutes. After this time had elapsed, the temperature of the reaction composition was raised to 45°C in the course of

10 minutes and the composition was kept at the said temperature for a further 30 minutes.

131 g of sulphuric acid having a concentration of 98 % were then added, while continuing to stir the mixture vigorously, and the mixture was cooled to 50°C in a continuous addition loop, where stirring of the mixture was maintained for a further 30 minutes. The acidified composition was then heated to 90°C and kept at the said temperature for 180 minutes, 32 g of water and volatile matter being removed during the first 60 minutes, by virtue of the application of vacuum to the reactor. For the remainder of the time the reactor was kept at boiling point under reflux at the cited temperature and under a slight vacuum. When the hydrolysis reaction was complete, recycles 1 and 2 were added and the sulphuric acid was then neutralized by adding a 25 % aqueous ammonia solution, while cooling so that the temperature did not rise above 70°C, and the two phases were allowed to separate out by settling, the said temperature being maintained. By means of settling, 414 g of aqueous phase containing 192 g of ammonium sulphate, which corresponds to 72 % of the total, and 381 g of organic phase, which contains the remainder of the ammonium sulphate and 198 g of HMTBA, which corresponds to 94 % of the total, were obtained.

Ammonium sulphate was precipitated from the aqueous phase by evaporation, under vacuum, of 90 % of the water present; after drying, 172 g of ammonium sulphate having a purity of more than 99.5 % were obtained, the recovery yield being higher than 99 %. The 52 g of mother liquors originating from the filtration of the suspension were recycled to the following reaction at the level of the mixing reactor and constitute the recycle from pipe (T) in the diagram of drawings.

By means of distillation under vacuum, the water was removed from the organic phase to dryness and 179 g of HMTBA with a purity of 98.5 % and 102 g of cake containing 73 % of ammonium sulphate and 27 % of HMTBA were

obtained. The said cake was dissolved using a small amount of water and recycled to the following reaction, at the level of the mixing reactor, for its recovery. This solution corresponds to the recycle from pipe (P) in the diagram of drawings. The HMTBA was adjusted with water acidified with sulphuric acid to give 200 g of a stable aqueous solution having a HMTBA concentration of 88 % by weight, a coloration of 1800 degrees APHA and a viscosity of 75 centistokes. By means of quantitative analysis specific for the HMTBA monomer in the end product, it was confirmed that it did not contain less than 80 % of this monomer.



CLAIMS

1. Process for preparing aqueous solutions of 2-hydroxy-4-methylthiobutyric acid (hereinafter designated HMTBA) resulting from the hydrolysis reaction, in
5 a single stage, of 2-hydroxy-4-methylthiobutyronitrile with sulphuric acid, characterised in that the following operations are carried out:

a) neutralising the acidic mixture resulting from the hydrolysis reaction and the recyclings with ammonium
10 hydroxide (NH_4OH), so as to form two phases, an organic phase containing a predominant proportion of HMTBA and a secondary proportion of ammonium sulphate, and an aqueous phase containing a predominant proportion of ammonium sulphate and a secondary proportion of HMTBA;

15 b) separating the two phases;

c) precipitating the ammonium sulphate from the aqueous phase by evaporation of water, at atmospheric or reduced pressure, and then separating off the said ammonium sulphate by filtration and/or centrifuging, and
20 recycling the resulting liquid, which contains unprecipitated ammonium sulphate and dissolved HMTBA, to the neutralisation reactor;

d) concentrating the organic phase by evaporation of the water present in this phase in order to obtain an
25 HMTBA suspension which contains a residual portion of ammonium sulphate;

e) separating the suspension resulting from the previous operation, by centrifuging and/or settling, in order to obtain an HMTBA which is virtually free from
30 ammonium sulphate and an impure ammonium sulphate cake containing HMTBA;

f) dissolving in water the impure ammonium sulphate cake obtained in the previous operation and recycling the resulting solution to the neutralisation
35 reactor; and

g) diluting with water the HMTBA obtained in step e) and, if appropriate, stabilising it with a small quantity of sulphuric acid.



2. Process according to Claim 1, characterised in that the ammonium hydroxide used in the neutralisation operation (a) has a concentration of 20-35 % by weight and, optionally, is obtained by injecting gaseous NH_3 into the hydrolysis reaction mixture.
3. Process according to Claim 1 or 2, characterised in that the temperature of the mixture is controlled during the neutralisation to ensure that it does not exceed a value of approximately 70°C .
4. Process according to one of Claims 1 to 3, characterised in that, in operation (d), the proportion of water in the organic phase is adjusted to a value of 0.5-1 % by weight by evaporation under reduced pressure.
5. Process according to one of Claims 1 to 4, characterised in that the ammonium sulphate produced in operation (c) is recovered, after separating off and drying, as a by-product virtually free from HMTBA.



As printed

Patentansprüche

1. Verfahren zur Herstellung wäßriger Lösungen der 2-Hydroxy-4-methylthio-buttersäure (im folgenden als AHMTB bezeichnet), die der Hydrolysereaktion in einer einzigen Stufe von 2-Hydroxy-4-methylthio-butyronitril mit Schwefelsäure entstammt, gekennzeichnet durch die Durchführung der folgenden Maßnahmen:
 - (a) Neutralisation des der Hydrolysereaktion und den Recyclisierungen entstammenden, sauren Gemisches mit Ammoniumhydroxid (NH_4OH), derart, daß zwei Phasen gebildet werden, eine organische Phase, die einen Hauptanteil an AHMTB und einen Nebenanteil an Ammoniumsulfat enthält, und eine wäßrige Phase, die einen Hauptanteil an Ammoniumsulfat und einen Nebenanteil an AHMTB enthält;
 - (b) die Trennung der beiden Phasen;
 - (c) die Ausfällung von Ammoniumsulfat aus der wäßrigen Phase durch Verdampfen von Wasser bei atmosphärischem oder vermindertem Druck, hiernach die Abtrennung des Ammoniumsulfats durch Filtrieren und/oder Zentrifugation und das Recyclisieren zu dem Neutralisationsreaktor der resultierenden Flüssigkeit, die nicht-ausgefälltes Ammoniumsulfat und gelöstes AHMTB enthält;
 - (d) das Einengen der organischen Phase durch kontinuierliches Verdampfen des Wassers in dieser Phase, um eine Suspension von AHMTB zu erhalten, die einen verbliebenen Ammoniumsulfat-Anteil enthält;
 - (e) das Abtrennen durch Zentrifugieren und/oder Dekantieren der der vorhergehenden Maßnahme entstammenden Suspension, um ein AHMTB, das von Ammoniumsulfat praktisch frei ist, und einen unreinen AHMTB enthaltenden Ammoniumsulfatkuchen zu erhalten;
 - (f) die Auflösung des bei der vorhergehenden Maßnahme erhaltenen Kuchens von unreinem Ammoniumsulfat in Wasser und das Recyclisieren der resultierenden Lösung zu dem Neutralisationsreaktor; und
 - (g) das Verdünnen der in Stufe (e) erhaltenen AHMTB mit Wasser und gegebenenfalls die Stabilisierung mit einer geringen Menge Schwefelsäure.
2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das bei der Neutralisationsmaßnahme (a) verwendete Ammoniumhydroxid eine Konzentration von 20 bis 35 Gew.% besitzt und gegebenenfalls durch Einspritzung von gasförmigem NH_3 in das Hydrolysereaktionsgemisch erhalten wird.
3. Verfahren gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß man während der Neutralisation die Temperatur des Gemisches kontrolliert, damit sie nicht den Wert von etwa 70°C überschreitet.
4. Verfahren gemäß einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß bei der Stufe (d) der Anteil des Wassers in der organischen Phase auf einen Wert von 0,5 bis 1 Gew.% durch Verdampfen unter vermindertem Druck gebracht wird.
5. Verfahren gemäß einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das bei der Maßnahme (c)



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gebildete Ammoniumsulfat nach Abtrennen und Trocknen als praktisch von AHMTB freies Nebenprodukt wiederverwertet wird.

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Claims

1. Process for preparing aqueous solutions of 2-hydroxy-4-methylthiobutyric acid (hereinafter designated HMTBA) resulting from the hydrolysis reaction, in a single stage, of 2-hydroxy-4-methylthiobutyronitrile with sulphuric acid, characterised in that the following operations are carried out:
 - a) neutralising the acidic mixture resulting from the hydrolysis reaction and the recyclings with ammonium hydroxide (NH_4OH), so as to form two phases, an organic phase containing a predominant proportion of HMTBA and a secondary proportion of ammonium sulphate, and an aqueous phase containing a predominant proportion of ammonium sulphate and a secondary proportion of HMTBA;
 - b) separating the two phases;
 - c) precipitating the ammonium sulphate from the aqueous phase by evaporation of water, at atmospheric or reduced pressure, and then separating off the said ammonium sulphate by filtration and/or centrifuging, and recycling the resulting liquid, which contains unprecipitated ammonium sulphate and dissolved HMTBA, to the neutralisation reactor;
 - d) concentrating the organic phase by evaporation of the water present in this phase in order to obtain an HMTBA suspension which contains a residual portion of ammonium sulphate;
 - e) separating the suspension resulting from the previous operation, by centrifuging and/or settling, in order to obtain an HMTBA which is virtually free from ammonium sulphate and an impure ammonium sulphate cake containing HMTBA;
 - f) dissolving in water the impure ammonium sulphate cake obtained in the previous operation and recycling the resulting solution to the neutralisation reactor; and
 - g) diluting with water the HMTBA obtained in step e) and, if appropriate, stabilising it with a small quantity of sulphuric acid.
2. Process according to Claim 1, characterised in that the ammonium hydroxide used in the neutralisation operation (a) has a concentration of 20-35 % by weight and, optionally, is obtained by injecting gaseous NH_3 into the hydrolysis reaction mixture.
3. Process according to Claim 1 or 2, characterised in that the temperature of the mixture is controlled during the neutralisation to ensure that it does not exceed a value of approximately 70°C.
4. Process according to one of Claims 1 to 3, characterised in that, in operation (d), the proportion of water in the organic phase is adjusted to a value of 0.5-1 % by weight by evaporation under reduced pressure.
5. Process according to one of Claims 1 to 4, characterised in that the ammonium sulphate produced in operation (c) is recovered, after separating off and drying, as a by-product virtually free from HMTBA.