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PROVISIONAL SPECIFICATION

PREPARATION OF UNSYMMETRICAL DIMETHYL HYDRAZINE (UDMH) BY ELECTROLYTIC REDUCTION OF N-NITROSODIMETHYLAMINE (NDMA)

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT, (ACT XXI OF 1860)

The following Specification describes the nature of this Invention:

This is an invention by Handady Venkatakrishna Udupa, Kodethoor Shrivara Udupa, Poominathan Subbiah and Pachaimuthu Thirunavukkarasu, all Indians.

This invention relates to the preparation of unsymmetrical dimethyl hydrazine by electrolytic reduction of N-Nitrosodimethylamine.

Hitherto it has been proposed to prepare unsymmetrical dimethyl hydrazine by either catalytic high pressure hydrogenation of N-Nitrosodimethylamine or by the condensation of dimethylamine with chloramine.

This is open to objection that by such methods that preparation of catalyst and regeneration of the same is difficult and requires careful control of purity and pressure of hydrogen used for the hydrogenation. The yields obtained are also poor. Again in the case of conventional chemical and catalytic process, in addition to the required product UDMH, a portion of the starting material NDMA gets decomposed to dimethylamine which interferes in the isolation of pure UDMH. The object to this invention is to obviate these disadvantages by reducing the N-Nitrosodimethylamine in an aqueous acid medium. In the case of present electrolytic method the reduction is quantitative and no secondary product is formed.

To these ends, the invention broadly consists in reducing an aqueous solution of N-Nitrosodimethylamine in a supporting electrolyte of a mineral acid preferably sulphuric acid in an electrolytic cell. The diaphragm is an unglazed ceramic of cylindrical shape closed at one end. A rotating/stationary cathode of copper or lead is used. The catholyte is a mineral acid preferably sulphuric acid upto a strength of 30% (v/v) but preferably 10% (v/v) and the same acid is used as anolyte also. A lead strip is used as anode. The depolariser concentration from 1 to 15% but preferably 12% is used for the reduction. In the case of rotating electrode, the reduction is carried out at a current density upto 30 Amp/dm^2 but preferably at 20 Amp/dm^2 In the case of stationary cathode only very low current density of the order of 3 Amps/dm^2 was applied and, high current density (3 A/dm^2) could not be applied. The temperature can be upto 50°C but preferably between 30 to 35°C. The reduction is carried out to theoretical time corresponding to 4 F/mole of nitroso compound taken. The dimethyl hydrazine content in the catholyte is estimated after the reduction is completed and the solution is neutralised with NaoH and fractionally distilled to get an aqueous UDMH and this simplifies the product isolation.

The following typical examples are given to illustrate the invention:—

Example I

Catholyte	: 225 ml of 10% H_2SO_4
Anolyte	: 15 ml of 10% H_2SO_4
Cathode	: Rotating cylindrical lead (2·4 cm dia × 6 cm height) having a working surface area of 0·3 sq. dm.)
Anode	: Lead strip 2 cm × 10 cm × 0· 6 cm
N-Nitrosodimethylamine added	: 10 gms.
Current density	: 10 Amps/dm^2
Cell voltage	: 4 Volts
Temperature	: 30 to 35°C
Current efficiency	: 95%

Example II

Catholyte	: 225 ml of 10% H_2SO_4
Anolyte	: 15 ml of 10% H_2SO_4
Cathode	: Rotating cylindrical lead (2.4 cm dia × 6 cm height) having a working surface area of 0·3 dm^2
Anode	: Lead strip 2 cm × 10 cm × 0·6 cm
N-Nitrosodimethylamine	: 25 gms
Current density	: 20 Amps/dm^2
Cell voltage	: 5 Volts
Temperature	: 30 to 35°C
Current efficiency	: 90%

Example III

Catholyte	: 225 ml of 10% v/v H_2SO_4
Anolyte	: 15 ml of 10 v/v H_2SO_4
Cathode	: Rotating cylindrical type copper : 2.4 cm dia × 6 cm height working surface area 0·3 dm^2
Anode	: Lead 2 cm × 10 cm
Depolariser	
N-Nitrosodimethylamine added	: 10 gms
Current density	: 10 Amps/dm^2
Cell voltage	: 3.6 V
Temperature	: 30 to 35°C
Current efficiency	: 52%

At high current density (10 Amps/dm^2) the efficiency falls still lower (40%).

Though the current efficiency in rotating lead cathode is higher at 10 Amps/dm² than at 20 Amps/dm,² it is only marginal i.e. only 5% whereas the time taken to complete the electrolysis is reduced to 50% at 20 Amps/dm². In order to save the time high current density i.e. 20 Amps/dm² is preferred.

The following are among the main advantages of the invention:—

1. The electrochemical reduction of N-Nitrosodimethyamine could be conducted at atmospheric pressure without the use of any catalyst.

2. The use of rotating cathode permits employing high current density for the reduction.

3. The reduction is carried out completely and no secondary product is formed.

4. The isolation of the reduction product is simpler.

Dated this 3rd July, 1973.

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COMPLETE SPECIFICATION
(SEE SECTION 10)

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the registration of Societies Act (Act XXI of 1860)

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:

This is an invention by HANDADY VENKATAKRISHNA UDUPA, KODETHOOR SHRIVARA UDUPA, POOMINATHAN SUBBIAN and PACHAIMUTHU THIRUNAVUKKARASU, all of the Central Electrochemical Research Institute, Karaikudi-6, India, Tamil Nadu, all Indian citizens.

The invention relates to the preparation of unsymmetrical dimethyl hydrazine by electrolytic reduction of N-nitrosodimethylamine. Unsymmetrical dimethyl hydrazine is an important liquid propellant used in space research.

Hitherto it has been proposed to prepare unsymmetrical dimethyl hydrazine by either catalytic high pressure hydrogenation of N-nitrosodimethylamine or by the condensation of dimethylamine with chloramine.

The objection to the hitherto known process is that by such methods the preparation of catalyst and regeneration of the same is difficult and requires careful control of purity and pressure of hydrogen used for the hydrogenation. The yields obtained are also poor. Again in the case of conventional chemical and catalytic process, in addition to the required product UDMH, a portion of the starting material NDMA gets decomposed to dimethylamine which interferes in the isolation of pure UDMH.

The main object of this invention is to obviate these disadvantages by electrolytically reducing the N-nitrosodimethylamine in an aqueous acid medium, so that the reduction is almost quantitative and no secondary product is formed.

The invention broadly consists in electrolytically reducing an aqueous solution of N-nitrosodimethylamine in a supporting electrolyte of a mineral acid preferably sulphuric acid. A rotating/stationary cathode of copper or lead is used for the reduction.

As a result of the invention, it is possible to reduce N-nitrosodimethylamine in almost quantitative yield without any secondary product being formed.

The present invention consists of a process which comprises in electrolytically reducing an aqueous solution of N-nitrosodimethylamine in a supporting electrolyte of a mineral acid preferably sulphuric acid using a rotating/stationary cathode of lead or copper, anode of lead or lead alloy and employing diaphragm of unglazed porous ceramic or blue asbestos cloth supported on a wooden frame. Thus, a cylindrical unglazed ceramic porous pot closed at one end or blue asbestos cloth supported on a wooden frame is used as diaphragm. As a result of this invention, the reduction of N-nitrosodimethylamine is achieved in almost quantitative yield without any secondary product.

Block type flow sheet for the process is given in Fig. 1 of the accompanying drawing. The invention broadly consits in electrolytically reducing an aqueous solution of N-nitrosodimethylamine in a supporting electrolyte of a mineral acid preferably sulphuric acid. The electrolytic cell is charged with the supporting electrolyte of sulphuric acid upto 30% (v/v) (Sp. gr. 1.31) but preferably 10% (v/v) (Sp. gr. 1.10) containing N-nitrosodimethylamine of concentration from 1 to 15% but preferably of 12% (catholyte). The anolyte is dilute sulphuric acid upto 30% strength but preferably 10% separated from the catholyte by means of a diaphragm of either unglazed porous ceramic or blue asbestos cloth supported on a wooden frame. In the case of rotating cathode, the reduction is carried out at a current density upto 30 amp/sq. dm. but preferably at 20 Amp/sq. dm. In the case of stationary cathode only very low current density of the order of 3 amp/sq. dm. is applied and high current density (more than 3 amp/sq. dm.) could not be applied. The temperature can be upto 50°C but preferably between 30 to 35°C. The reduction is carried out to theoretical time corresponding to 4 F/mole of nitroso compound taken. The dimethyl hydrazne content in the catholyte is estimated after the reduction is completed and the solution is neutralised with NaOH solution and distilled to get an aquesous UDMH.

The following examples are given to illustrate the invention:

Example I

Cathode	Rotating cylindrical lead (2, 4 cm dia × 6 cm ht); Area 0·3 sq. dm.
Anode	Lead strip 2 cm × 10 cm × 0·6 cm.
Current	3 amps
Cell voltage	4 volts
Catholyte	225 ml of 10% H_2SO_4 (v/v)
Anolyte	15 ml of 10% H_2SO_4 (v/v)
N-nitrosodimethylamine added	10 gms
Current density	10 amp/sq. dm.
Temperature	30 to 35°C
Current efficiency	95% :

Example II

Cathode	Rotating cylindrical lead—area 6·75 sq. dm.
Current	100 amps
Cell voltage	4·5 to 5·0 volts
Catholyte	10·4 litres of 10% (v/v) aqueous H_2SO_4
Anolyte	3 litres of 10% (v/v) aquesous H_2SO_4
N-Nitrosodimethylamine added	1066 gms
Anode	Lead (perforated cylindrical) area 11.0 sq. dm.
Temperature	40—45°C
Dimethylhydrazine estimated	850 gms
Current efficiency	94·8%

The following are the main advantages of the invention:

(a) The electrochemical reduction of N-nitrosodimethylamine could be conducted at atmospheric pressure without the use of any catalyst.

(b) The use of rotating cathode permits employing high current density for the reduction.

(c) The reduction is carried out completely and no secondary product is formed.

(d) The isolation of the reduction product is simpler than the commercial process.

We claim:—

(1) A process for the preparation of unsymmetrical dimethyl hydrazine which consists in electrolytically reducing an aqueous solution of N-nitrosodimethylamine in a supporting electrolyte of a mineral acid preferably sulphuric acid using a rotating/stationary cathode of lead or copper, anode of lead or lead alloy and employing diaphragm of unglazed porous ceramic or blue asbestos cloth supported on a wooden frame.

(2) A process as claimed in Claim 1 wherein the reduction is carried out at a current density upto 30amps/sq.dm but preferably at 20 amp/sq. dm. in the case of rotating cathode and upto 3 amp/sq. dm. in the case of stationary cathodes.

(3) A process as claimed in Claim 1 wherein the reduction is carried out at temperatures upto 50°C but preferably between 30 to 35°C.

(4) A process for the prepartion of unsymmetrical dimethyl hydrazine substantially as hereinbefrore described.

Dated this 14th day of June, 1974.

PATENTS OFFICER,
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COMPLETE SPECIFICATION

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Nº OF SHEETS .- 1
SHEET Nº :-1.

No. 1601/Cal/73 No 139949

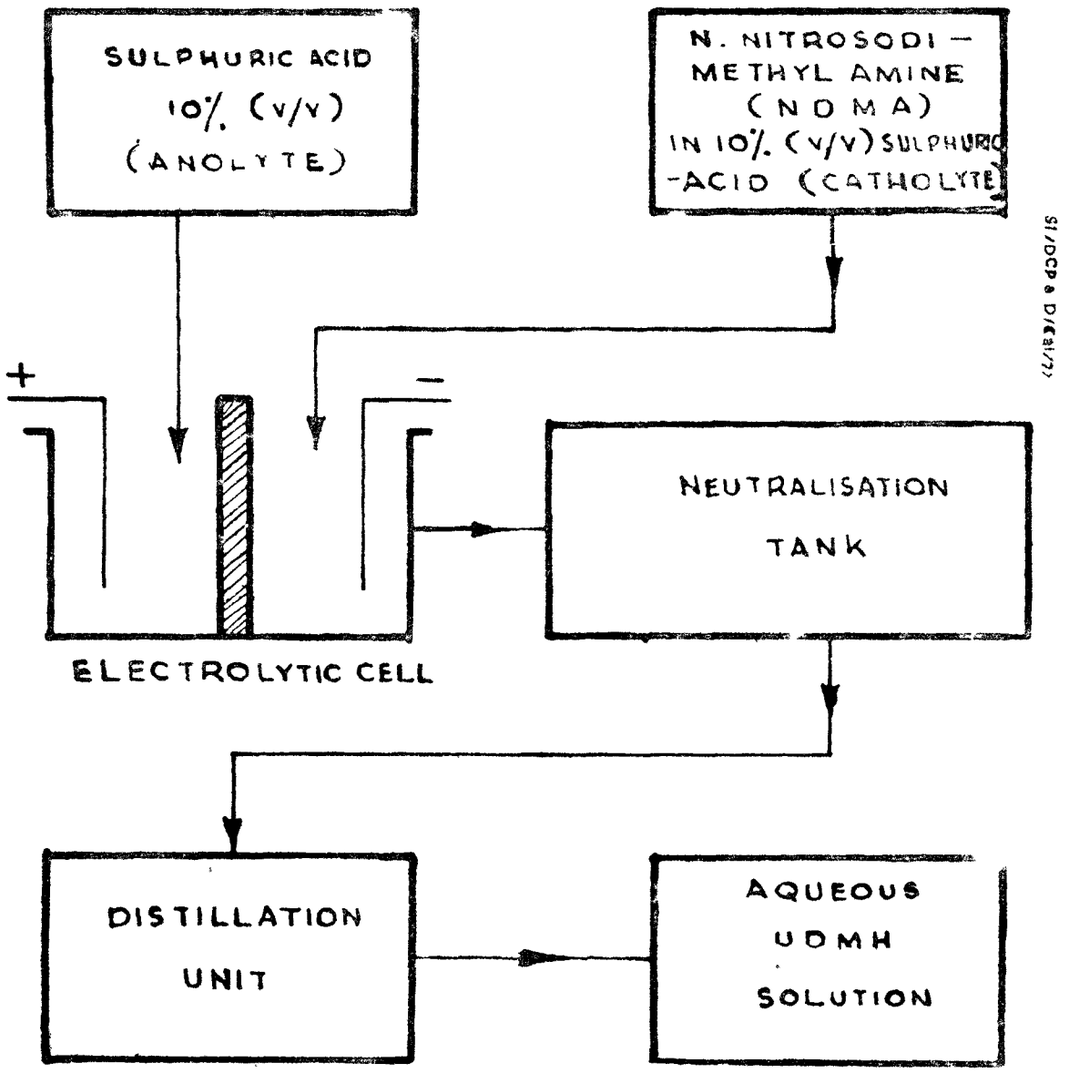

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FIG.- 1.

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