



(86) Date de dépôt PCT/PCT Filing Date: 2002/09/26

(87) Date publication PCT/PCT Publication Date: 2003/04/03

(45) Date de délivrance/Issue Date: 2010/04/06

(85) Entrée phase nationale/National Entry: 2004/03/25

(86) N° demande PCT/PCT Application No.: NO 2002/000344

(87) N° publication PCT/PCT Publication No.: 2003/027018

(30) Priorité/Priority: 2001/09/27 (NO20014699)

(51) Cl.Int./Int.Cl. *C01C 1/02* (2006.01),
C01B 17/74 (2006.01), *C01B 17/90* (2006.01),
C01C 1/242 (2006.01)

(72) Inventeur/Inventor:
HANSEN, TORD, NO

(73) Propriétaire/Owner:
SILICA TECH ANS, NO

(74) Agent: OGILVY RENAULT LLP/S.E.N.C.R.L., S.R.L.

(54) Titre : DECOMPOSITION PAR VOIE CHIMIQUE ET THERMIQUE DU SULFATE D'AMMONIUM EN AMMONIAC ET
ACIDE SULFURIQUE

(54) Title: CHEMICAL AND THERMAL DECOMPOSITION OF AMMONIUM SULPHATE INTO AMMONIA AND
SULPHURIC ACID

(57) **Abrégé/Abstract:**

A method is described for manufacturing ammonia and sulphuric acid by decomposition of ammonium sulphate by a chemical and thermal handling process. The method concerns mixing of ammonium sulphate with concentrated sulphuric acid, where the mixture is heated to a temperature above 235 °C, whereby ammonium sulphate is melted, and thereafter by heating the mixture to above 280 °C but below the boiling point of concentrated sulphuric acid. It is hereby achieved to decompose ammonium sulphate into ammonia gas and sulphuric acid liquid simultaneously, where the produced sulphuric acid during the reaction time is mixed ideally with the concentrated sulphuric acid from the initial basis mixture.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 April 2003 (03.04.2003)

PCT

(10) International Publication Number
WO 03/027018 A1

(51) International Patent Classification⁷: **C01C 1/02**,
C01B 17/90 // C01C 1/242

(21) International Application Number: PCT/NO2/00344

(22) International Filing Date:
26 September 2002 (26.09.2002)

(25) Filing Language: Norwegian

(26) Publication Language: English

(30) Priority Data:
20014699 27 September 2001 (27.09.2001) NO

(71) Applicant (for all designated States except US): **SILICA
TECH ANS** [NO/NO]; Ole Johan Aulie, P.O. Box 165,
N-1313 Vøyenenga (NO).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **HANSEN, Tord**
[NO/NO]; Vakåsveien 52, N-1395 Hvalstad (NO).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,

CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii)) for all designations
- of inventorship (Rule 4.17(iv)) for US only

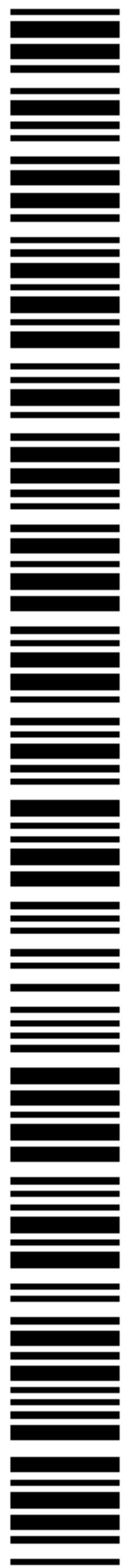
Published:

- with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: CHEMICAL AND THERMAL DECOMPOSITION OF AMMONIUM SULPHATE INTO AMMONIA AND SUL-
PHURIC ACID

(57) Abstract: A method is described for manufacturing ammonia and sulphuric acid by decomposition of ammonium sulphate by a chemical and thermal handling process. The method concerns mixing of ammonium sulphate with concentrated sulphuric acid, where the mixture is heated to a temperature above 235 °C, whereby ammonium sulphate is melted, and thereafter by heating the mixture to above 280 °C but below the boiling point of concentrated sulphuric acid. It is hereby achieved to decompose ammonium sulphate into ammonia gas and sulphuric acid liquid simultaneously, where the produced sulphuric acid during the reaction time is mixed ideally with the concentrated sulphuric acid from the initial basis mixture.



WO 03/027018 A1

Chemical and thermal decomposition of ammonium sulphate into ammonia and sulphuric acid

Description of invention

The present invention relates to a method for decomposition of ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) into ammonia (NH_3) and sulphuric acid (H_2SO_4) by chemical and thermal treatment.

Ammonium sulphate falls out as a by-product from several different chemical processes. Ammonium sulphate was earlier used as a fertilizer component, but is later substituted by ammonium nitrate for this purpose. Ammonium sulphate is still to a certain extent used as a fertilizer component in some developing countries. However is ammonium sulphate in most processing cases considered to be an undesired by-product with limited marketing possibilities.

Ammoniumsulphate is a water soluble crystalline product with a melting point at 235°C . At temperatures above 280°C ammonium sulphate decomposes into ammonia, sulphur trioxide and nitrogenous gases.

Within the different process combinations where ammonium sulphate is formed, are sulphuric acid and ammonia in most cases involved as input materials. Under these conditions there will be favorable both of environmental and economical reasons, to decompose ammoniumsulphate into ammonia and sulphuric acid in order to recirculate the input materials of the process, or to obtain saleable products.

There are a some known methodes concerning decomposition of ammonium sulphate descibed in the following documents:

- (1) Chemical Abstracts, Vol 65 (1966), Acc.Nr. 70990, Zh. Neorgan.Chim.,1966, 11(7), 1673-8 (Russia)
- (2) DE 1151492

(3) DE 1160421

The above listed documents describes methodes where ammonium sulphate by thermal treatment and complete decomposition forms gases of NH_3 , H_2O and SO_3/SO_2 at temperatures above 350°C . The german patent publications describes further a process involving coke, coal or charcoal as reduction materials under oxygen free conditions where it is achieved to obtain SO_2 based sulphuric acid in water solution and where ammonia is seperated out in a circuit with ammoniumhydrogen sulphate and potassium sulphate.

The present invention concerns a method for manufacturing of ammonia gas (NH_3) and sulphuric acid (H_2SO_4) characterized wherein ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) is mixed with concentrated sulphuric acid, and by heating the mixture to a temperature above 235°C , whereby ammonium sulphate is melted, and thereafter by heating the mixture to above 280°C but below the boiling point of concentrated sulphuric acid (290°C - 320°), by which ammonium sulphate is decomposed into ammonia gas and sulphuric acid liquid simultaneously, and where the produced sulphuric acid during the reaction time is mixed ideally with the concentrated sulphuric acid from the initial basis mixture.

By this method it is achieved to decompose ammonium sulphate to a fully extent into ammonia gas and sulphuric acid liquid, where the ammonia gas during processing is evaporated and separated out from a restsolution consisting of sulphuric acid.

An example of manufacturing proceedure is given as follows.

Example

The basis material consisting of 3-5 mm $\varnothing$ crystalline ammonium sulphate, is mixed with 95-97% concentrated sulphuric acid in a reactor at a weight ratio of ammonium sulphate/sulphuric acid = 1/2 .

The reactor is heated up to approx. 250°C whereby ammonium sulphate melts out in a separate liquid phase above the concentrated sulphuric acid. The reactor is thereafter heated upto 285°C whereby ammonium sulphate is decomposed. During decomposition of ammonium sulphate, the ammonia gas formed is evacuated out at the top of the reactor and thereafter cooled down and stored in a separate tank. The rest product from the decomposition consisting of concentrated sulphuric acid mixes ideally with the initial sulphuric acid from the basis mixture. After completed reaction, corresponding to approx. 1 hour, the sulphuric acid in the reactor is transferred to a separate intermediate tank for delution with a limited amount of water in order to regulate the acid concentration to about 95-97%. The produced amount of sulphuric acid from the ammonium sulphate decomposition is then transferred to a separate storage tank, while the remaining part of the sulphuric acid is cooled down to about 250°C and thereafter circulated back to the reactor in a repeating production cycle for decomposition of new ammonium sulphate rawmaterial.

Additional comments to known methodes

The present invention differs from known methodes by which ammonium sulphate in crystal form is melted in a liquid consisting of concentrated sulphuric acid (95-97%) at a temperature of approx. 250°C, i.e. above the melting point of ammonium sulphate corresponding to 235°C. The melted ammonium sulphate is then floating as a separate layer upon the underlying concentrated sulphuric acid. By raising the temperature to 285°C, i.e. above the temperature of ammonium sulphate decomposition corresponding to 280°C, but below the boiling point of concentrated sulphuric acid corresponding to 290°C- 320°C, it is then achieved to evaporate ammonia gas (NH₃) separatly while the rest part of the ammonium sulphate consisting of 100% concentrated sulphuric acid (H₂SO₄) is mixed ideally with the concentrated sulphuric acid from the initial basis mixture. It is hereby achieved to decompose ammonium sulphate directly to ammonia gas and sulphuric acid liquid.

This method is of substantial difference from other known methodes where ammonium sulphate first is decomposed to gases consisting of NH₃, H₂O, SO₃ and subsequent SO₂, at temperatures above 350°C, and where the mixture of gases by a sequence of following processes are converted to ammonia and sulphuric acid.

Claims

We claim:

1. A method for manufacturing of ammonia gas (NH_3) and sulphuric acid (H_2SO_4) *characterized* wherein ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) is mixed with concentrated sulphuric acid, and by heating the mixture to a temperature above 235°C , whereby ammonium sulphate is melted, and thereafter by heating the mixture to above 280°C but below the boiling point of concentrated sulphuric acid, by which ammonium sulphate is decomposed into ammonia gas and sulphuric acid liquid simultaneously, and where the produced sulphuric acid during the reaction time is mixed ideally with the concentrated sulphuric acid from the initial basis mixture.
2. The method of claim 1, *characterized* wherein the weight ratio ammonium-sulphate/sulphuric-acid is between approx. 2.0 – 0.1 and where the melting temperature of ammoniumsulphate is kept between approx. 240°C - 270°C and where the decomposition temperature is kept at approx. 285°C .