

FORMULARIO ÚNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL

SOLICITUD DE:



Patente de invención



Patente de Modelo de Utilidad



Capítulo I



Capítulo II

2

SOLICITANTE
(71)

Nombre: **DSM N.V.**
Dirección: **Het Overloon 1,**
Nacionalidad o Domicilio: **6411 TE Heerlen,**
Países Bajos
Lugar de Constitución : **Países Bajos**
Teléfono: Fax:
E-mail

IDENTIFICACIÓN

C.C. ☐ NIT ☐

C.E. ☐ Otro ☐

Número

3

REPRESENTANTE
AP DERADO
(74)

Nombre: **JIMENA ESCOBAR URIBE**
Dirección: **Cra. 11A No. 94-76 (Of. 305)**
Teléfono: **6 162051/61** Fax: **6 161889**
E-mail: **escobaru@elsitio.net.co**

IDENTIFICACIÓN

C.C. ☒ NIT ☐

C.E. ☐ Otro ☐

Número **39.779.452 T.P 68228**

4

INVENTOR (ES)
(72)

Nombre: **VER ANEXOS**
Dirección:
Nacionalidad o domicilio:

5 PCT (86)

Solicitud Internacional No. PCT/NL01/00427 Fecha Mayo 31, 2001

Publicación Internacional No. WO 01/94296 A1 Fecha Diciembre 13, 2001

6 TITULO (54) PROCEDIMIENTO PARA LA PRODUCCIÓN DE LA OXIMA DE LA
CICLOHEXANONA.

6 Clasificación Internacional (51) C 07C 249/08

7 Prioridad

SI ☒ NO ☐

(33) País de Origen

EUROPA

EUROPA

(32) Fecha

Junio 5, 2000

Junio 5, 2000

(31) Número de Solicitud

00201970.1

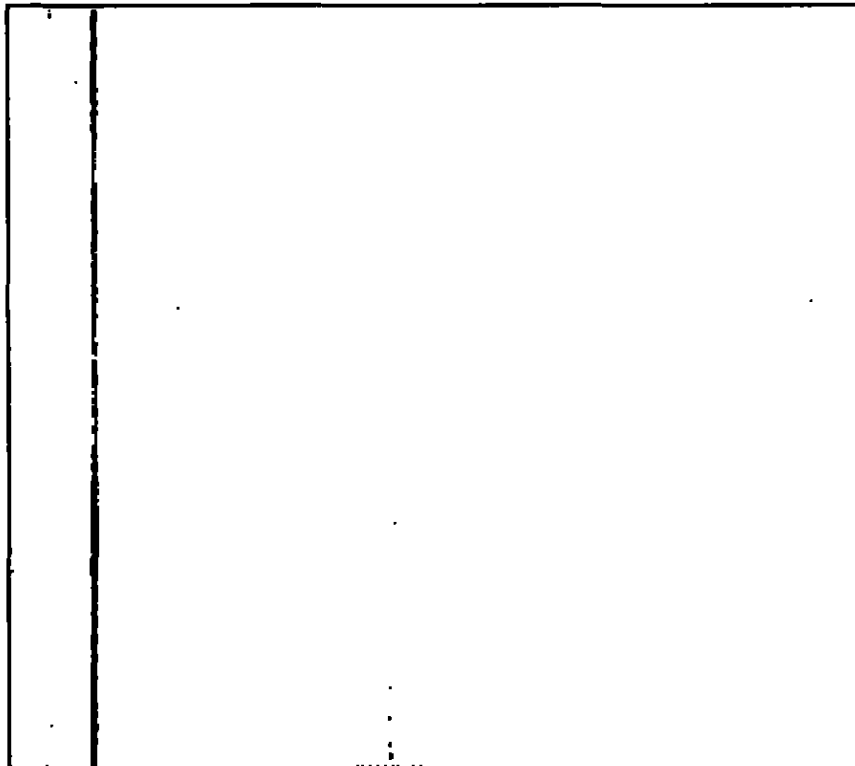
00201965.1

9 Comprobante de pago No. 02 - 79.307

Fecha : Noviembre 26, 2002

- ☐ Comprobante de pago de la tasa de presentación de la solicitud
- ☐ Documento que acredite la existencia y representación legal cuando el solicitante sea persona jurídica Prot. 17.794
- ☐ Poderes si fuere el caso Protocolo No. 17.794
- ☐ Documento de cesión del inventor al solicitante o a su causante
- ☐ Declaraciones
- ☐ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☐ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☐ Copia del examen preliminar internacional efectuado por la Autoridad Internacional de Examen Preliminar (IPEA).
- ☐ Traducción del examen preliminar internacional efectuado por la IPEA
- ☐ De ser el caso copia de contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas
- ☐ De ser el caso, certificado de depósito del material biológico
- ☐ Arte final 12 X 12 .
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☐ De ser el caso, modificaciones efectuadas a la solicitud internacional
- ☐ Otros

11 FIGURA CARACTERÍSTICA



12 Solicito la concesión de la patente

NOMBRE: JIMENA ESCOBAR URIBE

FIRMA: *Jimena Escobar*

C.C. 39.779.452 DE Usaquén T.P. 68.228

As. 2508/PCT

ANEXOS

INVENTORES

1.) **ARNO BENNEKER**
(6162 JD Geleen, Países Bajos);
2.) **HENK OEVERING**
(181 BR Elslloo, Países Bajos);
3.) **ALEX PIT**
(Evans, Georgia 30809, Estados Unidos de América);
4.) **PAULUS JOHANNES JACOBUS PIETERS**
(6181 KZ Stein, Países Bajos).

Solicito expresamente a nombre de la sociedad **DSM N.V.**, sociedad constituida de conformidad con las leyes de Países Bajos, domiciliada en Het Overloon 1, 6411 TE Heerlen, Países Bajos, el otorgamiento de Patente para la invención titulada **"PROCEDIMIENTO PARA LA PRODUCCIÓN DE LA OXIMA DE LA CICLOHEXANONA "**.

Clase: C 07


JIMENA ESCOBAR URIBE
C.C. 39.779.452 de Usaquen
T.P . 68.228

2408



4

Industria y Comercio
SUPERINTENDENCIA

SUPERINDUSTRIA Y COMERCIO
Radicacion : 02110469 00000000 Folios: 67
Fecha (MM): 2002-12-05 16:14:05
Tramite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTA
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 02 - 79,307
FECHA : NOVIEMBRE 26 DE 2002

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
ESCOBAR URIBE ASOCIADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	6513094	26/11/2002	5,171,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	1 TRANITES DE SOL. DE PATENTE DE IN	378,000.00
		TOTAL :	\$ 378,000.00

SON: TRESCIENTOS SETENTA Y OCHO MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

Carrera 13 No. 27-00 Pisos 5, 7 y 10
Conmutador 382 0840
Fax 350 5220
E-mail: info@sic.gov.co
www.sic.gov.co
Bogotá, D.C., Colombia

BIE

PCT REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference 20318WO
(if desired) (12 characters maximum)

PROCESS FOR THE PRODUCTION OF CYCLOHEXANONE OXIME

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

DSM N.V.
Het Overloon 1
6411 TE Heerlen (NL)

☐ This person is also inventor

Telephone No.

Facsimile No.

Teleprinter No.

State (that is, country) of nationality: NL

State (that is, country) of residence: NL

This person is applicant for the purposes of:

☐

all designated States

☐

all designated States except the United States of America

☒

the United States of America only

☐

the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

BENNEKER, Arno
Schrijnwerkersdreef 15
6162 JD Geleen, the Netherlands

This person is:

☐

applicant only

☒

applicant and inventor

☐

inventor only (if this check-box is marked, do not fill in below.)

State (that is, country) of nationality: NL

State (that is, country) of residence: NL

This person is applicant for the purposes of:

☐

all designated States

☐

all designated States except the United States of America

☒

the United States of America only

☐

the States indicated in the Supplemental Box

☒

Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☒

agent

☐

common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

VAN TOL - KOUTSTAAL, Charlotte Adeliene

DSM Patents & Trademarks
P.O. Box 9
6160 MA Geleen (NL)

Telephone No.

(+31)46-4767544

Facsimile No.

(+31)46-4761830

Teleprinter No.

☐

Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) OEVERING, Henk Burg. Eussenstraat 46 181 BR Elsloo, the Netherlands	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality NL	State (that is, country) of residence: NL
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) PIT, Alex 818 Walden Glen Court Evans, Georgia 30809, U.S.A.	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) PIETERS, Paulus Johannes Jacobus Eeckersteghe 14 6181 KZ Stein, the Netherlands	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality: NL	State (that is, country) of residence: NL
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.)
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.	

Box No.V DESIGNATION OF STATES

Mark the applicable check-boxes below; at least one must be marked.

The following designations are hereby made under Rule 4.9(a):

Regional Patent

- ☒ AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ EP European Patent: AT Austria, BE Belgium, CH & LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, TR Turkey, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | | |
|---|--|--|
| ☒ AE United Arab Emirates | ☒ GE Georgia | ☒ MW Malawi |
| ☒ AG Antigua and Barbuda | ☒ GH Ghana | ☒ MX Mexico |
| ☒ AL Albania | ☒ GM Gambia | ☒ MZ Mozambique |
| ☒ AM Armenia | ☒ HR Croatia | ☒ NO Norway |
| ☒ AT Austria | ☒ HU Hungary | ☒ NZ New Zealand |
| ☒ AU Australia | ☒ ID Indonesia | ☒ PL Poland |
| ☒ AZ Azerbaijan | ☒ IL Israel | ☒ PT Portugal |
| ☒ BA Bosnia and Herzegovina | ☒ IN India | ☒ RO Romania |
| | ☒ IS Iceland | ☒ RU Russian Federation |
| ☒ BB Barbados | ☒ JP Japan | |
| ☒ BG Bulgaria | ☒ KE Kenya | ☒ SD Sudan |
| ☒ BR Brazil | ☒ KG Kyrgyzstan | ☒ SE Sweden |
| ☒ BY Belarus | ☒ KP Democratic People's Republic of Korea | ☒ SG Singapore |
| ☒ BZ Belize | ☒ KR Republic of Korea | ☒ SI Slovenia |
| ☒ CA Canada | ☒ KZ Kazakhstan | ☒ SK Slovakia |
| ☒ CH & LI Switzerland and Liechtenstein | ☒ LC Saint Lucia | ☒ SL Sierra Leone |
| ☒ CN China | ☒ LK Sri Lanka | ☒ TJ Tajikistan |
| ☒ CO Colombia | ☒ LR Liberia | ☒ TM Turkmenistan |
| ☒ CR Costa Rica | ☒ LS Lesotho | ☒ TR Turkey |
| ☒ CU Cuba | ☒ LT Lithuania | ☒ TT Trinidad and Tobago |
| ☒ CZ Czech Republic | ☒ LU Luxembourg | ☒ TZ United Republic of Tanzania |
| ☒ DE Germany | ☒ LV Latvia | ☒ UA Ukraine |
| ☒ DK Denmark | ☒ MA Morocco | ☒ UG Uganda |
| ☒ DM Dominica | ☒ MD Republic of Moldova | ☒ US United States of America |
| ☒ DZ Algeria | | ☒ UZ Uzbekistan |
| ☒ EE Estonia | ☒ MG Madagascar | ☒ VN Viet Nam |
| ☒ ES Spain | ☒ MK The former Yugoslav Republic of Macedonia | ☒ YU Yugoslavia |
| ☒ FI Finland | ☒ MN Mongolia | ☒ ZA South Africa |
| ☒ GB United Kingdom | | ☒ ZW Zimbabwe |
| ☒ GD Grenada | | |

Check-boxes below reserved for designating States which have become party to the PCT after issuance of this sheet:

- ☒ EC Ecuador ☐ ☐
- ☐ ☐ ☐

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM

☐ Further priority claims are indicated in the Supplemental Box.

Filing Date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 5 June 2000 (05.06.00)	00201970.1		EP-NL	
item (2) 5 June 2000 (05.06.00)	00201985.1		EP-NL	
item (3)				

☐ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s)

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA)
(If two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA/

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)	Number	Country (or regional Office)
5 June 2000	00201970.1	EP-NL
5 June 2000	00201985.1	EP-NL

Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains^a the following number of sheets:

request : 4
description (excluding sequence listing part) :
claims :
abstract :
drawings :
sequence listing part of description :
Total number of sheets : _____

This international application is accompanied by the item(s) marked below:

- ☒ fee calculation sheet
- ☐ separate signed power of attorney
- ☒ copy of general power of attorney; reference number, if any:
- ☐ statement explaining lack of signature
- ☐ priority document(s) identified in Box No VI as item(s):
- ☐ translation of international application into (language):
- ☐ separate indications concerning deposited microorganism or other biological material
- ☐ nucleotide and/or amino acid sequence listing in computer readable form
- ☐ other (specify):

Figure of the drawings which should accompany the abstract:

Language of filing of the international application: English

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which she person signs (if such capacity is not obvious from reading the request).



G.A. van Tol - Koutstaal

For receiving Office use only		2. Drawings: ☐ received: ☐ not received:
1. Date of actual receipt of the purported international application:		
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid	

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

This sheet is not part of and does not count as a sheet of the international application.

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

Applicant's or agent's file reference 20318WO		International application No.	
Applicant DSM N.V.		Date stamp of the receiving Office	
CALCULATION OF PRESCRIBED FEES			
1. TRANSMITTAL FEE		110,-	T
2. SEARCH FEE International search to be carried out by (If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)		2082,-	S
3. INTERNATIONAL FEE Basic Fee The international application contains _____ sheets. first 30 sheets		901,-	b ₁
_____ remaining sheets x _____ additional amount =			b ₂
Add amounts entered at b ₁ and b ₂ and enter total at B		901,-	B
Designation Fees The international application contains 89 designations.			
6 x 193,- =		1158,-	D
number of designation fees payable (maximum 6) amount of designation fee			
Add amounts entered at B and D and enter total at I (Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)		2059,-	I
4. FEE FOR PRIORITY DOCUMENT (if applicable)			P
5. TOTAL FEES PAYABLE Add amounts entered at T, S, I and P, and enter total in the TOTAL box		4251,-	
☐ The designation fees are not paid at this time.		TOTAL	
MODE OF PAYMENT			
☒ authorization to charge deposit account (see below) ☐ bank draft ☐ coupons			
☐ cheque ☐ cash ☐ other (specify):			
☐ postal money order ☐ revenue stamps			
DEPOSIT ACCOUNT AUTHORIZATION (this mode of payment may not be available at all receiving Offices)			
The RO NL ☒ is hereby authorized to charge the total fees indicated above to my deposit account.			
☒ (this check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit) is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.			
☐ is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account.			
1500		31 May 2001	
Deposit Account No.		Date (day/month/year)	
Form PCT/RO/101 (Annex) (January 2001)		Signature G.A. van Tol - Koutstaal	

See Notes to the fee calculation sheet

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 December 2001 (13.12.2001)

PCT

(10) International Publication Number
WO 01/94296 A1

(51) International Patent Classification: C07C 249/06,
C01B 21/14

(74) Agent: VAN TOL-KOUTSTAAL, Charlotte, Adellene;
DSM Patents & Trademarks, P.O. Box 9, NL-6160 MA
Geleen (NL).

(21) International Application Number: PCT/NL01/00427

(22) International Filing Date: 31 May 2001 (31.05.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00201970.1 5 June 2000 (05.06.2000) EP
00201965.1 5 June 2000 (05.06.2000) EP

(71) Applicant (for all designated States except US): DSM N.V.
[NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(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, GR,
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, PL, PT, RO, RU, SD, SE, SG, SI, SK,
SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA,
ZW.

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

(72) Inventors; and

(75) Inventors/Applicants (for US only): BENNEKER, Arno
[NL/NL]; Schrijnwerkerdreef 15, NL-6162 JD Geleen
(NL). OEVERING, Henk [NL/NL]; Burg. Bussenstraat
46, NL-181 BR Bialoo (NL). PTT, Alex [US/US]; 818
Walden Glen Court, Evans, GA 30809 (US). PIETERS,
Paulus, Johannes, Jacobus [NL/NL]; Beckersteeghe 14,
NL-6181 KZ Stein (NL).

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: PROCESS FOR THE PRODUCTION OF CYCLOHEXANONE OXIME

(57) Abstract: The invention relates to a process for the production of cyclohexanone oxime in which a phosphate-containing aqueous reaction medium is cycled from a hydroxylammonium synthesis zone to a cyclohexanone oxime synthesis zone and back to the hydroxylammonium synthesis zone, in which hydroxylammonium synthesis zone hydroxylammonium is formed by catalytic reduction of nitrate with hydrogen, and in which cyclohexanone oxime synthesis zone hydroxylammonium is reacted with cyclohexanone to form cyclohexanone oxime, where the concentration hydroxylammonium in the aqueous reaction medium entering the cyclohexanone oxime synthesis zone is higher than 1.0 mol/l.

WO 01/94296 A1

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/NL 01/00427A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C249/08 C01B21/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data bases consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 138 750 A (STAMICARBON) 1 January 1969 (1969-01-01) claim 1; examples II, III	1-11
X	US 3 720 758 A (AGGENBACH P ET AL) 13 March 1973 (1973-03-13) example II	1-11
A	US 3 862 230 A (ELMENDORP JAN ET AL) 21 January 1975 (1975-01-21) claim 1; examples 11,16,17,21-23,30	1-11
A	US 3 997 607 A (DE ROOIJ ABRAHAM H) 14 December 1976 (1976-12-14) cited in the application	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw/doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

A document member of the same patent family

Date of the actual completion of the international search

24 July 2001

Date of mailing of the international search report

31/07/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5816 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Janus, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 01/00427

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1138750 A	01-01-1969	NL 6513426 A	17-04-1967
		BE 688260 A	14-04-1967
		CH 481888 A	30-11-1969
		DE 1272288 B	
		DK 117701 B	25-05-1970
		FR 1496435 A	22-12-1967
		IL 26663 A	17-09-1970
		NO 125629 B	09-10-1972
		SE 338985 B	27-09-1971
US 3720758 A	13-03-1973	NL 6914306 A	23-03-1971
		BE 756359 A	18-03-1971
		CA 934524 A	02-10-1973
		DE 2046198 A	01-04-1971
		FR 2062356 A	25-06-1971
		GB 1319347 A	06-06-1973
		JP 50017199 B	19-06-1975
US 3862230 A	21-01-1975	NL 6914308 A	23-03-1971
		AT 302995 B	15-10-1972
		BE 756360 A	18-03-1971
		BG 18603 A	25-02-1975
		CA 945999 A	23-04-1974
		CH 558339 A	31-01-1975
		CS 163223 B	29-08-1975
		DE 2046256 A	01-04-1971
		ES 383811 A	01-03-1973
		FR 2062945 A	02-07-1971
		GB 1279527 A	28-06-1972
		JP 48035255 B	26-10-1973
		PL 81358 A	30-08-1975
		RO 64371 A	15-07-1979
		SE 368822 B	22-07-1974
		ZA 7006279 A	27-05-1971
US 3997607 A	14-12-1976	NL 7405630 A	28-10-1975
		US 3940442 A	24-02-1976
		AR 202611 A	24-06-1975
		BE 828393 A	27-10-1975
		BR 7502549 A	03-03-1976
		CH 609335 A	28-02-1979
		CS 199266 B	31-07-1980
		DE 2518259 A	06-11-1975
		ES 436961 A	01-12-1976
		FR 2268794 A	21-11-1975
		GB 1506437 A	05-04-1978
		IT 1035465 B	20-10-1979
		JP 50154224 A	12-12-1975
		RO 73094 A	26-02-1982
		SU 586838 A	30-12-1977

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:
DSM PATENTS & TRADEMARKS
Attn. VAN TOL-KOUTSTAAL ...
P.O. BOX 9
NL-6160 MA Geleen
NETHERLANDS

135

Date of mailing
(day/month/year) 31/07/2001

Applicant's or agent's file reference
20318W0

FOR FURTHER ACTION See paragraphs 1 and 4 below

International application No.
PCT/NL 01/ 00427

International filing date
(day/month/year) 31/05/2001

Applicant
DSM N.V

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.
Filing of amendments and statement under Article 18:
The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Further action(s): The applicant is reminded of the following:

Shortly after 18 months from the priority date, the International application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the International application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority  European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Véronique Baillou
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NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 48.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 48.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. References to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PATENT CO-OPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 20318W0	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/NL 01/ 00427	International filing date (day/month/year) 31/05/2001	(Earliest) Priority Date (day/month/year) 05/06/2000
Applicant DSM N.V		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.
☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report
- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing :
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished
2. ☐ Certain claims were found unsearchable (See Box I).
3. ☐ Unity of invention is lacking (see Box II).
4. With regard to the title,
- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established by this Authority to read as follows:
5. With regard to the abstract,
- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.
6. The figure of the drawings to be published with the abstract is Figure No.
- ☐ as suggested by the applicant.
- ☐ because the applicant failed to suggest a figure.
- ☐ because this figure better characterizes the invention.
- ☒ None of the figures.

INTERNATI NAL SEARCH REP RT

International Application No

PCT/NL 01/00427

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C249/08 C01B21/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 138 750 A (STAMICARBON) 1 January 1969 (1969-01-01) claim 1; examples II,III	1-11
X	US 3 720 758 A (AGGENBACH P ET AL) 13 March 1973 (1973-03-13) example II	1-11
A	US 3 862 230 A (ELMENDORP JAN ET AL) 21 January 1975 (1975-01-21) claim 1; examples 11,16,17,21-23,30	1-11
A	US 3 997 607 A (DE ROOIJ ABRAHAM H) 14 December 1976 (1976-12-14) cited in the application	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *A* document member of the same patent family

Date of the actual completion of the international search

24 July 2001

Date of mailing of the international search report

31/07/2001

Name and mailing address of the ISA

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Fax: (+31-70) 340-3018

Authorized officer

Janus, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

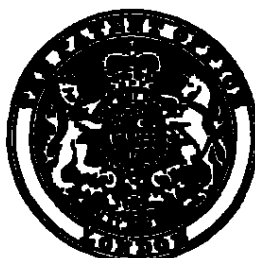
PCT/NL 01/00427

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1138750 A	01-01-1969	NL 6513426 A	17-04-1967
		BE 688260 A	14-04-1967
		CH 481888 A	30-11-1969
		DE 1272288 B	
		DK 117701 B	25-05-1970
		FR 1496435 A	22-12-1967
		IL 26663 A	17-09-1970
		NO 125629 B	09-10-1972
		SE 338985 B	27-09-1971
US 3720758 A	13-03-1973	NL 6914306 A	23-03-1971
		BE 756359 A	18-03-1971
		CA 934524 A	02-10-1973
		DE 2046198 A	01-04-1971
		FR 2062356 A	25-06-1971
		GB 1319347 A	06-06-1973
		JP 50017199 B	19-06-1975
US 3862230 A	21-01-1975	NL 6914308 A	23-03-1971
		AT 302995 B	15-10-1972
		BE 756360 A	18-03-1971
		BG 18603 A	25-02-1975
		CA 945999 A	23-04-1974
		CH 558339 A	31-01-1975
		CS 163223 B	29-08-1975
		DE 2046256 A	01-04-1971
		ES 383811 A	01-03-1973
		FR 2062945 A	02-07-1971
		GB 1279527 A	28-06-1972
		JP 48035255 B	26-10-1973
		PL 81358 A	30-08-1975
		RO 64371 A	15-07-1979
		SE 368822 B	22-07-1974
		ZA 7006279 A	27-05-1971
US 3997607 A	14-12-1976	NL 7405630 A	28-10-1975
		US 3940442 A	24-02-1976
		AR 202611 A	24-06-1975
		BE 828393 A	27-10-1975
		BR 7502549 A	03-03-1976
		CH 609335 A	28-02-1979
		CS 199266 B	31-07-1980
		DE 2518259 A	06-11-1975
		ES 436961 A	01-12-1976
		FR 2268794 A	21-11-1975
		GB 1506437 A	05-04-1978
		IT 1035465 B	20-10-1979
		JP 50154224 A	12-12-1975
		RO 73094 A	26-02-1982
		SU 586838 A	30-12-1977

PATENT SPECIFICATION

DRAWINGS ATTACHED

L138,750



L138,750

Date of Application and filing Complete Specification: 6 Oct., 1966.
No. 44743/66.
Application made in Netherlands (No. 6513 426) on 16 Oct., 1965.
Complete Specification Published: 1 Jan., 1969.
© Crown Copyright 1969.

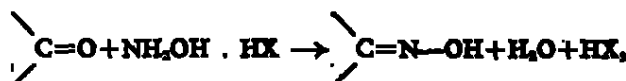
Index at acceptance:—C2 C2B36
Int. Cl.:—C 07 c 83/02

COMPLETE SPECIFICATION

Preparation of Oximes

5 We, STAMICARBON N.V., a Netherlands Limited Liability Company of 2 van der Maesenstraat, Heerlen, the Netherlands, 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:—

This invention relates to the preparation of oximes by reaction of a C₆—C₆—ketone particularly cyclohexanone, and a solution of a hydroxylammonium salt in water. 10
According to the reaction equation:



15 where

C=O represents the carbonyl group of the cyclic ketone and HX any given acid, it will be seen that the acid which is bound in the hydroxylammonium salt is liberated during the oxime formation. 20

A complete conversion of ketone into oxime can be achieved in a medium varying from weakly acid to neutral, and the acid liberated in the oxime formation being bound by addition of a neutralizing agent, usually gaseous ammonia or ammonia water. This technique results however in the formation of a salt. When hydroxylamine is introduced as hydroxylammonium sulphate, the salt thus produced is ammonium sulphate. 25 30

To reduce the production of salt in such reactions it has been proposed to carry out the reaction in a buffered medium, using a solution of a hydroxylammonium salt derived from a weak acid, the reaction mixture also containing a soluble salt of the said weak acid in such an amount that during the oxime formation this salt, together with the liberated acid, form a buffered reaction medium the pH of which is sufficiently high to allow the formation of oxime to proceed. 35 40

[Price 4s. 6d.]

Upon completion of the oxime formation and isolation of the oxime formed, the salt of the weak acid is separated from the solution, which insofar as the hydroxylammonium salt is concerned does not react further, and the separated salt fed back into the reaction medium in which the oxime formation takes place, while the remaining solution of the weak acid, which now has a low salt content, is used either in a hydroxylamine synthesis stage to convert hydroxylamine into hydroxylammonium salt, or for other acid-consuming purposes. 45 50

A process of this type has the disadvantage that the salt of the weak acid has to be repeatedly separated from the reacted solution, which is expensive. Another unattractive feature is the fact that it is economically necessary to recycle the isolated solid salt to the reaction medium. 55 60

It has now been found that in such buffered reaction processes the steps of isolating the salt from the reacted solution, and the recycling of this salt to the reaction medium, can be omitted if the ketone is dissolved in a water-immiscible i.e., water insoluble, or slightly water-miscible, organic solvent in which the oxime formed readily dissolves, and is brought into intimate counter-current con- 65 70

tact with an aqueous solution of a hydroxylammonium salt derived from a weak acid, which aqueous solution also contains an amount of a soluble salt of the weak acid which, together with the acid liberated in the oxime formation, forms the buffer medium.

The invention therefore consists of a process for the preparation of an oxime, which comprises contacting in a reaction zone in countercurrent flow a stream of a solution of a C_4-C_6 cyclic ketone in an organic solvent therefor, the said solvent being water-insoluble, or having a solubility in water of less than 0.1% by weight at 20°C, and which is a solvent also for the oxime reaction product; and a stream of an aqueous solution of the hydroxylammonium salt of an acid having a dissociation constant of from 2×10^{-4} to 10^{-6} , the said aqueous stream containing a further soluble salt of the said acid to provide, with free acid produced in the reaction zone, a buffered reaction medium; and withdrawing from the reaction zone a product stream of oxime dissolved in the said solvent therefor, and an aqueous stream containing free acid and the soluble salt thereof; separating solvent from the said product oxime; and recycling the solvent thus obtained to the said reaction zone.

Particularly suitable organic solvents for use in the process of the invention include inexpensive solvents such as toluene, benzene, methylcyclopentane and cyclohexane.

The weak acids to which the hydroxylamine is bound in the form of hydroxylamine salt in the aqueous starting solution must, while being sufficiently weak to produce, together with a salt derived from them, such a buffering effect that the pH is kept sufficiently high for making the oxime formation proceed also be sufficiently strong to be capable of forming the hydroxylammonium ion with dissolved hydroxylamine.

While theoretically these requirements are met by acids and acidic salts having a dissociation constant of 2×10^{-4} to 10^{-6} . However, in practice only the readily obtainable and consequently cheap, inorganic acids, such as phosphoric acid and ammonium or alkali-metal bisulphate, (which can be regarded as an acid), are in fact acceptable for this purpose. If the cyclic ketone is brought into countercurrent contact with the hydroxylammonium salt solution in the presence of the organic solvent, a relatively high degree of conversion of the ketone into the oxime is achieved even at very low pH-values, for example from 0 to 1.

In carrying out the oxime preparation according to the invention use may be made of the normal type of counterflow reactors, such as columns filled with packing bodies or rotating disc reactors, provided that the ketone-containing organic phase is sufficiently

finely distributed when it is contacted with the water phase containing the hydroxylammonium salt. A fine distribution can be promoted by pulsating the liquid flow.

The reaction can also be carried out as a counter-flow reaction in a system consisting of a number, e.g. 3 to 6, of series-connected reactors equipped with stirrers, each of these reactors also being provided with a liquid-liquid separator.

The starting solution containing the hydroxylammonium salt can be directly obtained in a hydroxylamine synthesis in which nitrate ions or NO are either electrolytically or with the aid of molecular hydrogen in the presence of a noble metal catalyst, reduced to hydroxylamine in a buffered acid medium. The aqueous solution which, so far as hydroxylamine is concerned, does not react further and has to be discharged during the oxime preparation can, after removal of traces of organic solvent and non-converted ketone, be recycled to such a hydroxylamine synthesis.

Owing to the presence of the organic solvent, the process according to the invention has the additional advantage that the oxime formed dissolves in the said solvent, while substances which are discharged together with this oxime if no organic solvent is present, such as the weak acid contained in the reaction mixture, are left in the aqueous phase. After the organic solvent has been separated off by distillation, an oxime is left, which can be processed into the corresponding lactam.

Two embodiments of the invention are hereinafter described and schematically illustrated in the accompanying drawings.

According to the embodiment shown in Figure 1, the oxime preparation is carried out in a counter-current reactor A, at one end of which the aqueous solution containing the hydroxylammonium salt of the acid together with a soluble salt of the weak acid, is supplied through conduit 1, while at the other end the cyclic ketone and the organic solvent are supplied through the conduits 2 and 3, respectively.

When these starting liquids flow in counter-current relationship through the reactor A, the ketone is converted into oxime, which dissolves in the organic solvent. The oxime-containing organic solvent is, (preferably after being washed with water or dilute ammonia to remove traces of acid salts from it), fed through conduit 4 to a rectifying column C provided with a heating spiral 5. The oxime thus separated is discharged from this rectifying column via conduit 6, while the evaporated solvent is, after being condensed, fed to an extraction plant B via conduit 7 to free the aqueous solution discharged from counter-flow reactor A via conduit 8, from any ketone and oxime still dissolved therein. The acid

aqueous solution thus obtained is discharged via conduit 9. Any solvent dissolved in this solution is recovered by stripping.

5 The embodiment shown in Figure II differs from that according to Figure I, in that the stream of organic solvent discharged from counter-flow reactor A, in which solvent non-converted ketone is still present, is, together with an amount of hydroxylammonium salt solution supplied via conduit 11, fed into an after-reaction vessel D provided with a stirrer 10 to convert the ketone still present into oxime at a pH which has been raised with the aid of an alkaline reagent supplied via conduit 12. The reaction mixture flows via conduit 13 into a liquid-liquid separator E, after which the supernatant layer (i.e. the organic solvent in which ketone is dissolved) is fed to column C, while the water layer 20 flows into counter-current reactor A via conduit 15.

The process according to Figure I can be used if a virtually complete conversion of ketone into oxime is directly achieved in counter-flow reactor A. The process according to Figure II may be applied if the conversion of ketone into oxime in counter-flow reactor A is incomplete.

30 The degree of conversion depends on the pH in the reaction medium and particularly on the pH of the reacted aqueous solution discharged from the counter-flow reactor via conduit 8. If the said pH is below about 0.5, further reaction at a raised pH will be required to achieve a virtually complete conversion of ketone into oxime.

35 In a preferred embodiment of the process according to the invention equimolecular amounts of ketone and hydroxylammonium salt are reacted per unit time. However, owing to the counter-flow circulation, a large excess of hydroxylammonium will be present with respect to ketone still to be converted when the hydroxylammonium salt solution enters the counter-flow reactor, which is favourable for achieving a satisfactory degree of conversion. The acid aqueous solution which, as far as hydroxylammonium salt is concerned, does not react further and has to be discharged from the system via conduit 9, can be advantageously fed to a hydroxylamine synthesis stage to serve as the reaction medium and to provide the acid required for binding the hydroxylamine formed as hydroxylammonium salt.

45 The following examples of the invention are provided:

EXAMPLE I

60 This is an example of the preparation of cyclohexanone oxime by reaction of a buffered hydroxylammonium phosphate solution and cyclohexanone in the presence of toluene.

Using the process according to Figure I, the following hydroxylammonium salt solution

was fed to counter-current reactor A via conduit 1, per unit time:

65 65 kmols of $\text{NH}_4\text{OH} \cdot \text{H}_2\text{PO}_4$,
97 kmols of $\text{NH}_4\text{H}_2\text{PO}_4$,
38 kmols of H_3PO_4 ,
191 kmols of NH_4NO_3 , and
3134 kmols of H_2O 70

The said solution was derived from a hydroxylamine synthesis stage in which nitrate ions, supplied in the form of 55% by weight of nitric acid, were reduced to hydroxylamine with the aid of hydrogen in a medium buffered with the aid of a combination of phosphate and phosphoric acid and in the presence of a platinum catalyst. The pH of the solution was 2.1. 75

A further solution of 65 kmols of cyclohexanone, and a toluene stream containing:

460 kmols of toluene,
9 kmols of cyclohexanone,
2 kmols of oxime and
5 kmols of H_2O . 80

were admitted to the said reactor A via the conduits 2 and 3, respectively.

The temperature in the reactor A was maintained at 78°C. 85

An oxime-containing toluene product stream was discharged from the reactor through conduit 4 to column C. The said product stream contained:

460 kmols of toluene,
65 kmols of oxime and
20 kmols of H_2O . 90

In column C, separation into oxime and toluene was effected. 65 kmols of oxime per unit time were discharged via conduit 6, while toluene (460 kmols) and water (20 kmols) were discharged to extraction column B via conduit 7. 100

An aqueous solution was discharged per unit time via conduit 8 to extraction column B containing:

191 kmols of NH_4NO_3 ,
97 kmols of $\text{NH}_4\text{H}_2\text{PO}_4$,
103 kmols of H_3PO_4 ,
9 kmols of cyclohexanone,
2 kmols of oxime and
3234 kmols of H_2O . 110

Which solution, as far as the hydroxylammonium salt is concerned, does not react further and which has a pH of 1.0. 115

After removal of toluene dissolved therein by stripping, the aqueous solution discharged from extraction column B had the following composition:

97 kmols of $\text{NH}_4\text{H}_2\text{PO}_4$,
191 kmols of NH_4NO_3 ,
103 kmols of H_3PO_4 , and
3249 kmols of H_2O . 120

This solution was recycled to the hydroxylamine synthesis stage to serve as the reaction medium in the reduction of nitric acid to hydroxylamine. 125

If, in contrast to the process according to the invention, cyclohexanone and a hydroxyl-

ammonium salt solution having the same composition as the one described in Example I is made to flow countercurrently in the absence of the organic solvent, an oxime-containing phase which comprises 1.25% by weight of cyclohexanone, 5.75% by weight of water and 0.63% by weight of phosphoric acid, will be obtained. This indicates that the oxime forming reaction has not proceeded to completion and that the oxime obtained still contains a considerable proportion of water, so that prior to its rearrangement to caprolactam, the oxime will either have to be dried or more SO_3 will have to be used in the said rearrangement. Moreover, the phosphoric acid in the reaction product is lost from the reaction.

A further disadvantage is that the water phase to be discharged will contain about 2.7% by weight of cyclohexanone. This non-converted cyclohexanone will have to be stripped from the solution and recycled to the oxime reactor.

EXAMPLE II

This is an example of the preparation of cyclohexanone oxime by reaction of cyclohexanone and a hydroxylammonium phosphate solution obtained by catalytic reduction of NO with the aid of hydrogen in a medium buffered with mono-ammonium phosphate and phosphoric acid.

Using again the process according to Figure I, the following hydroxylammonium salt solution was fed to reactor A via conduit 1, per unit time:

65 kmoles of $\text{NH}_2\text{OH} \cdot \text{H}_2\text{PO}_4$,
40 kmoles of $\text{N}_2\text{H}_4\text{PO}_4$,
25 kmoles of H_3PO_4 and
1000 kmoles of H_2O .

The said solution had a pH of 2.5, and was obtained by the catalytic reduction of NO with H in a medium buffered with ammonium phosphate and phosphoric acid.

65 kmoles of cyclohexanone and a toluene stream containing:

200 kmoles of toluene,
10 kmoles of cyclohexanone,
1 kmole of oxime and
5 kmoles of H_2O

were fed into the said reactor A via the conduits 2 and 3, respectively.

An oxime-containing toluene product stream consisting of 65 kmoles of oxime, 200 kmoles of toluene and 10 kmoles of H_2O , together forming an organic phase, were discharged from this reactor per unit time via conduit 4 and fed to column C, and therein separated into an oxime stream (65 kmoles) discharged as the product via conduit 6, and a toluene-water mixture (200 kmoles of toluene, 10 kmoles of water) discharged to extraction column B via conduit 7.

An aqueous phase containing 40 kmoles of $\text{NH}_4\text{H}_2\text{PO}_4$, 90 kmoles of H_3PO_4 , 10

kmoles of cyclohexanone, 1 kmole of oxime and 1060 kmoles of H_2O , and having a pH of 1.5, was discharged from reactor A to extraction column B, via conduit 8. The cyclohexanone and the oxime dissolved in the water phase were removed therefrom by extraction with the supplied toluene stream.

After removal of the dissolved toluene by stripping, the solution discharged via conduit 9 contained: 40 kmoles of $\text{NH}_4\text{H}_2\text{PO}_4$, 90 kmoles of H_3PO_4 and 1065 kmoles of H_2O . This solution can be used as the reaction medium in the catalytic reduction of NO to hydroxylamine with the aid of hydrogen, and can to this end be fed to such a hydroxylamine synthesis reactor.

EXAMPLE III

This is an example of the preparation of cyclohexanone oxime, starting from cyclohexanone and a hydroxylammonium sulphate solution buffered with the aid of ammonium sulphate and ammonium bisulphate.

Because of the higher acidity of the hydroxylammonium sulphate solution (pH=0-0.5) as compared with the hydroxylammonium salt solutions referred to in the two previous examples which had a pH of from 1 to 2, the reaction was carried out by the process according to Figure II.

The following solution was introduced via conduit 1 per unit time to one end of the reactor A,

80 kmoles of $\text{NH}_2\text{OH} \cdot \text{NH}_4\text{SO}_4$,
99.2 kmoles of NH_4HSO_4 ,
1.28 kmoles of $(\text{NH}_4)_2\text{SO}_4$,
10.4 kmoles of NH_4NO_3 ,
960 kmoles of H_2O .

The following solution was also introduced into the same end of reactor A via conduit 15.

1 kmole of $\text{NH}_2\text{OH} \cdot \text{NH}_4\text{SO}_4$,
44.12 kmoles of $(\text{NH}_4)_2\text{SO}_4$,
2.6 kmoles of NH_4NO_3 ,
379 kmoles of H_2O .

At the other end of reactor A, 100 kmoles of cyclohexanone, and a benzene stream containing 260 kmoles of benzene, 10 kmoles of cyclohexanone and 6 kmoles of H_2O , were supplied via the conduits 2 and 3, respectively.

A benzene stream containing 260 kmoles of benzene, 81 kmoles of oxime, 19 kmoles of cyclohexanone and 10 kmoles of H_2O was discharged from reactor A to the subsequent reactor D, to convert the cyclohexanone still present in the said benzene stream into oxime at a pH of 4.5 and a temperature of 60°C , together with hydroxylammonium salt solution supplied via conduit 11, the said salt solution having the composition:

20 kmoles of $\text{NH}_2\text{OH} \cdot \text{NH}_4\text{SO}_4$,
24.8 kmoles of NH_4HSO_4 ,
0.32 kmoles of $(\text{NH}_4)_2\text{SO}_4$,
2.6 kmoles of NH_4NO_3 .

A solution comprising 240 kmoles of H_2O

and 25.6% by weight of ammonia water, corresponding to 43.8 kmoles of NH_3 and 120 kmoles of H_2O , was supplied via conduit 12 to reactor D. The reaction mixture flowed from the said reactor D into the liquid-liquid separator E. The oxime-containing benzene layer, consisting of 100 kmoles of oxime, 10 kmoles of H_2O and 260 kmoles of benzene, was discharged from this separator and fed to column C, in which separation was effected between the oxime product (100 kmoles), which was discharged via conduit 6, and a benzene stream (260 kmoles of benzene and 10 kmoles of H_2O), which was discharged to extraction column B via conduit 7. The water layer formed in separator E was fed to reactor A via conduit 15.

The aqueous phase had a pH of about 0 and the composition

- 180.2 kmoles of NH_4HSO_4 ,
- 45.4 kmoles of $(\text{NH}_4)_2\text{SO}_4$,
- 13.0 kmoles of NH_4NO_3 ,
- 10.0 kmoles of cyclohexanone and
- 1416 kmoles of H_2O .

It was discharged from reactor A through conduit 8 and fed into extraction column B. Upon extraction therein by the benzene stream, followed by stripping off the dissolved benzene, an aqueous reaction solution was discharged through conduit 9 consisting of 180.2 kmoles of NH_4HSO_4 , 45.2 kmoles of $(\text{NH}_4)_2\text{SO}_4$, 13.0 kmoles of NH_4NO_3 and 1420 kmoles of H_2O .

Upon further neutralization with NH_3 , this solution can be processed into ammonium sulphate.

WHAT WE CLAIM IS:—

1. A process for the preparation of an oxime, which comprises contacting in a reaction zone in countercurrent flow a stream of a solution of a C_6 — C_8 cyclic ketone in an organic solvent therefor, the said solvent being water-insoluble, or having a solubility in water of less than 0.1% by weight at

20°C, and which is a solvent also for the oxime reaction product; and a stream of an aqueous solution of the hydroxylammonium salt of an acid having a dissociation constant of from 2×10^{-4} to 10^{-6} , the said aqueous stream containing a further soluble salt of the said acid to provide, with free acid produced in the reaction zone, a buffered reaction medium; and withdrawing from the reaction zone a product stream of oxime dissolved in the said solvent therefor, and an aqueous stream containing free acid and the soluble salt thereof; separating solvent from the said product oxime; and recycling the solvent thus obtained to the said reaction zone.

2. A process as claimed in Claim 1, in which the said weak acid is phosphoric acid, ammonium bisulphate or alkali-metal bisulphate.

3. A process as claimed in Claim 1 or Claim 2, in which the solvent recovered from the said product stream is contacted with the said aqueous stream from the reaction zone to extract residual ketone and/or oxime contained in said aqueous stream.

4. A process as claimed in Claim 3, in which the said hydroxylamine salt of a weak acid is obtained by reduction of nitrate ions or NO in a buffered solution comprising the said extracted aqueous stream.

5. A process as claimed in any of Claims 1 to 4, in which reaction in the reaction zone is effected with equimolecular streams of ketone and hydroxylammonium salt per unit time.

6. A process for the preparation of an oxime as claimed in Claim 1, substantially as hereinbefore described.

7. An oxime prepared by a process claimed in any of the preceding claims.

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Agents for the Applicants.

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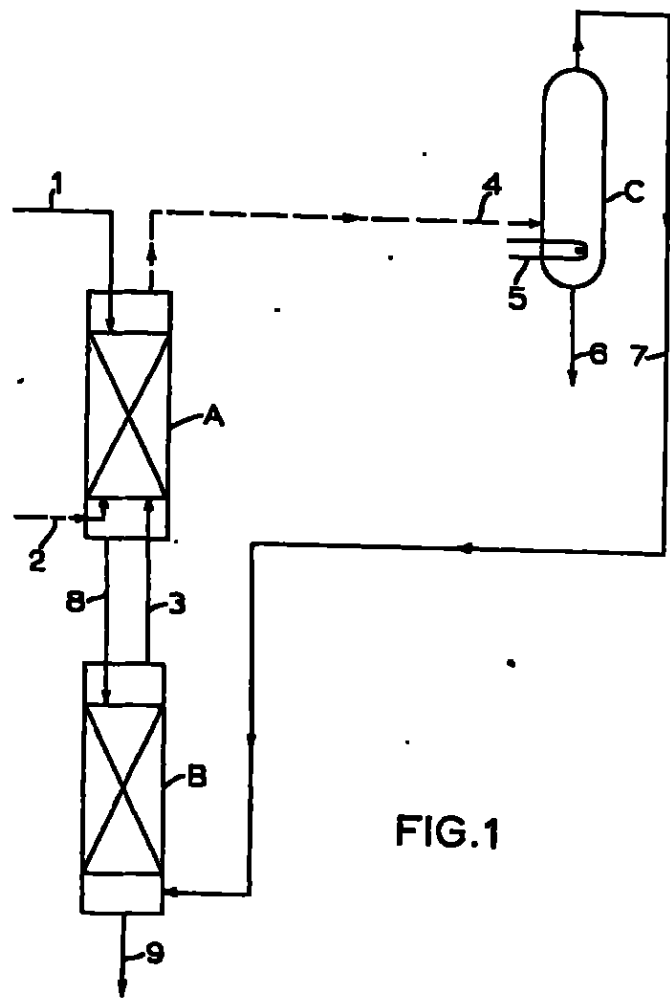


FIG.1

1138750 COMPLETE SPECIFICATION
 2 SHEETS *This drawing is a reproduction of
 the Original on a reduced scale
 Sheets 1 & 2*

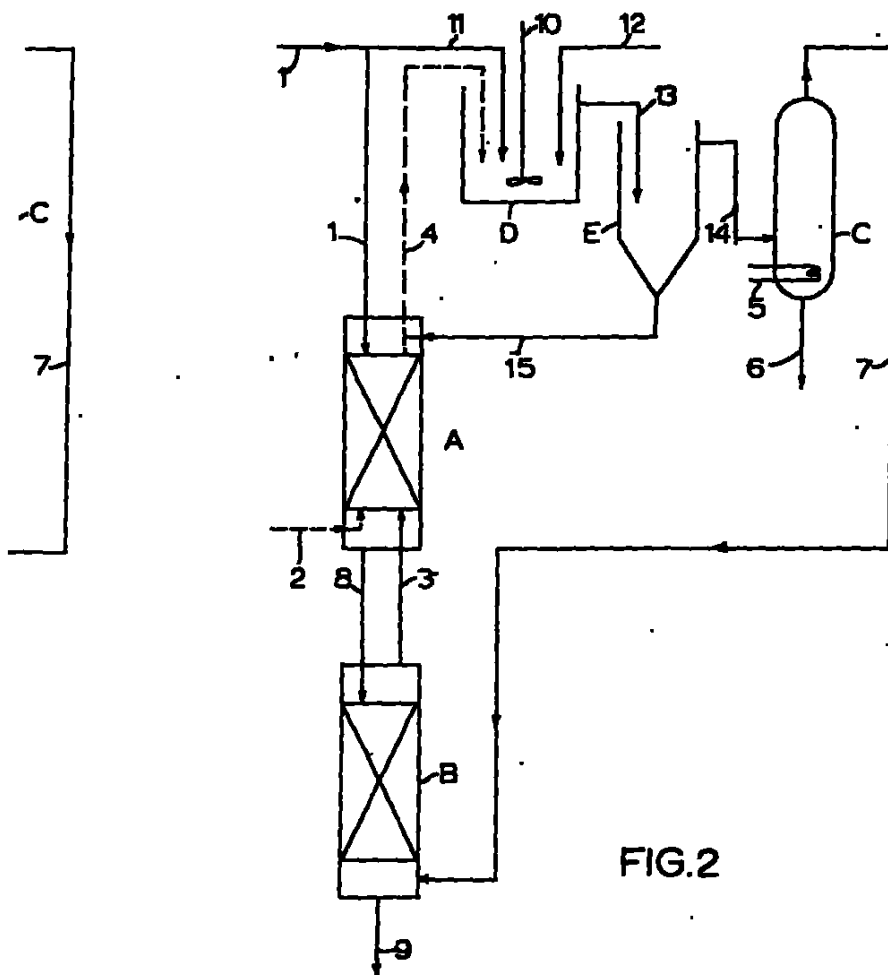


FIG.2

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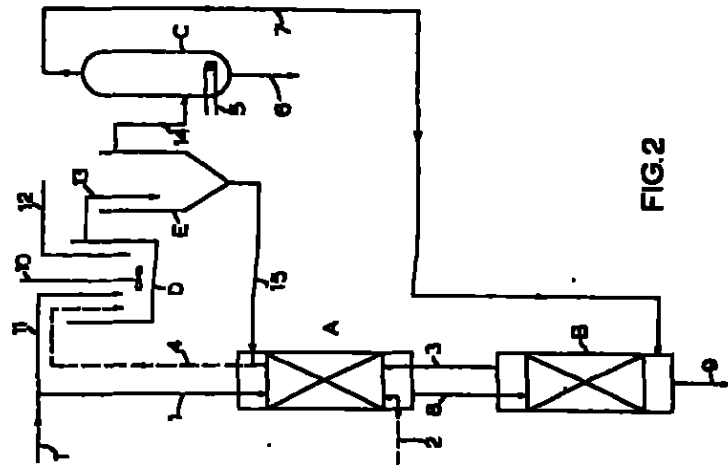


FIG. 2

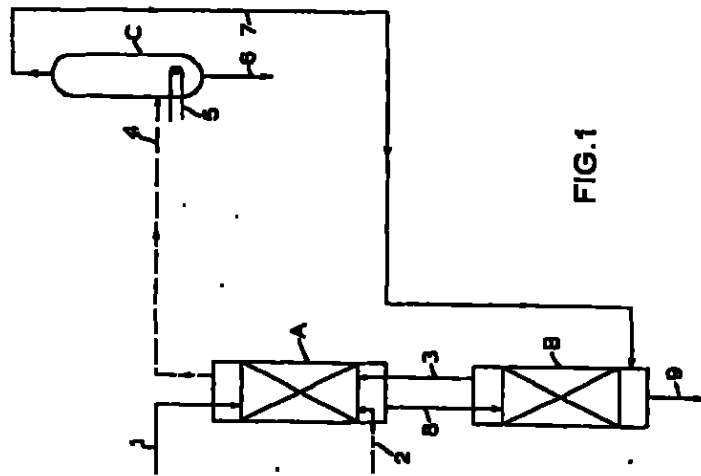


FIG. 1

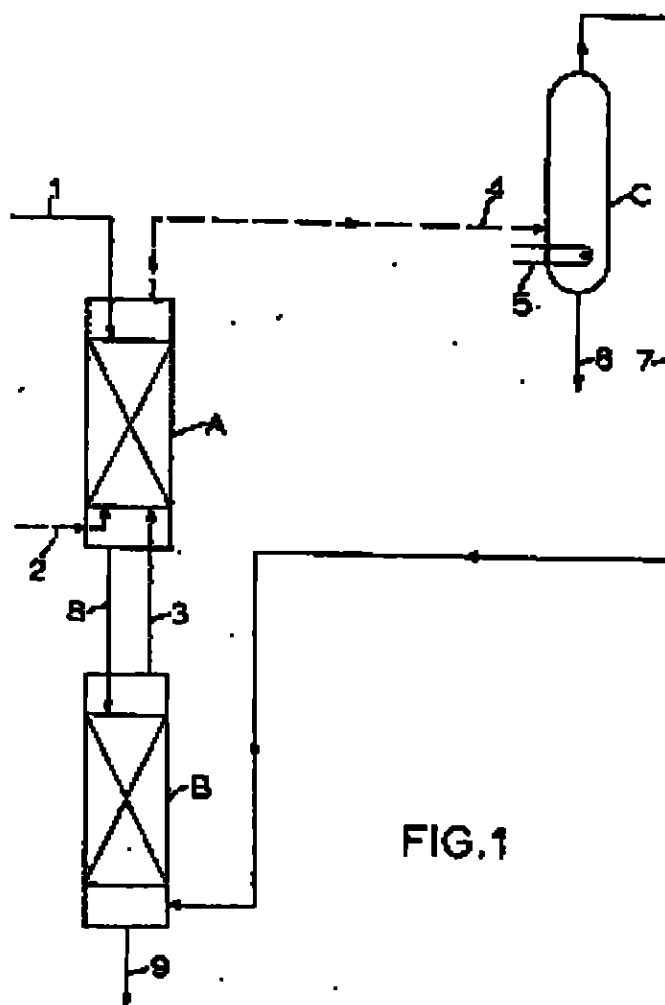


FIG.1

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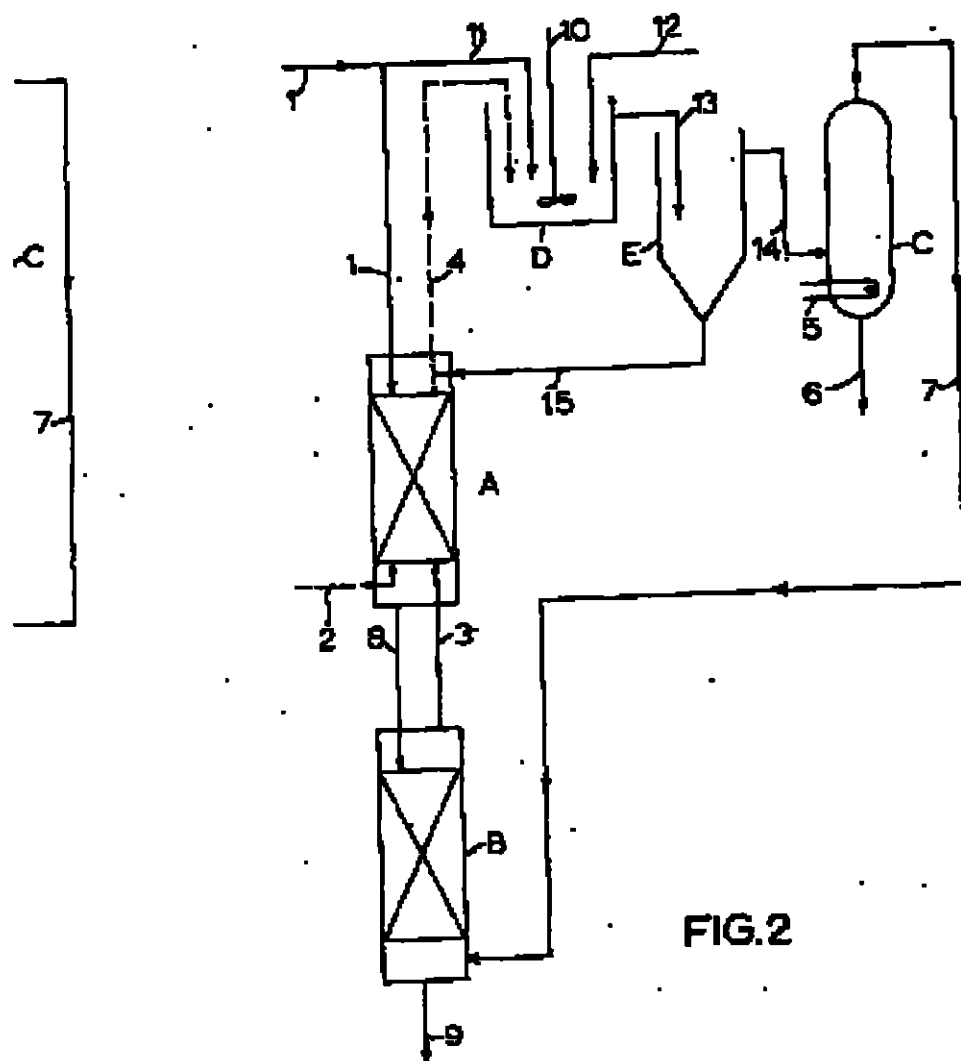
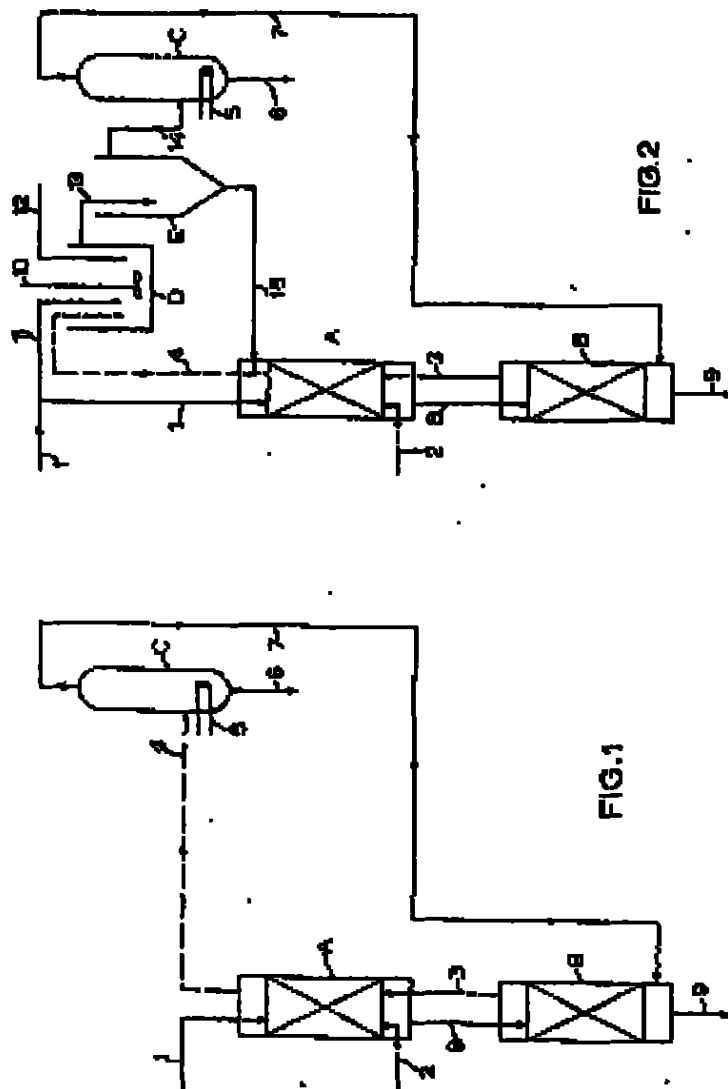


FIG.2

1136/50 COMPLETE SPECIFICATION
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20318 W2

United States Patent [19]

De Rooij et al.

111 3,720,758

[45] March 13, 1973

- [34] PROCESS FOR THE CONTINUOUS PREPARATION OF AN AQUEOUS SOLUTION OF A HYDROXYLAMMONIUM SALT**

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- [22] Filed: Sept. 21, 1970

- [21] Appl. No.: 73,905**

- [30] Foreign Application Priority Data**

Sep. 20, 1969 Netherlands 6914306

- [52] U.S. Cl.....423/388, 260/566 A, 423/545**

- [51] Int. CLC01c 1/24, C01c 1/00, C07c 131/10

- [58] **Field of Search**..23/190 A, 117, 119; 260/566 A

- [56] References Cited**
UNITED STATES PATENTS

3,416,886 12/1968 Capaul et al.23/117

FOREIGN PATENTS OR APPLICATIONS

1,138,750	1/1969	Great Britain.....	260/566 A
908,859	10/1962	Great Britain.....	23/119

908,859	10/1962	Great Britain.....	23/119
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Primary Examiner—Oscar R. Vertiz

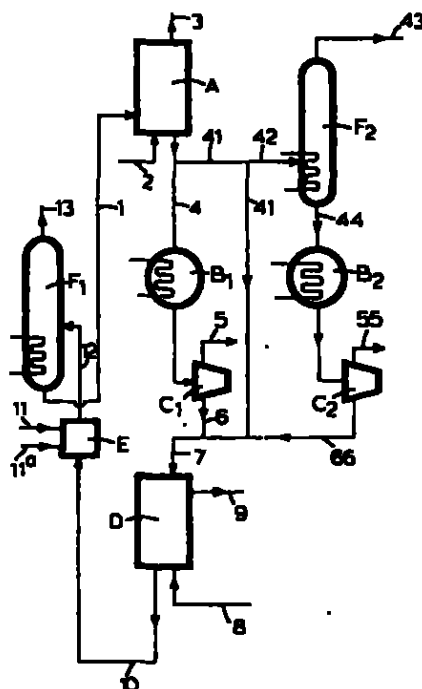
Assistant Examiner—Hoke S. Miller

Attorney—Cushman, Darby & Cushman

- [57]
- ABSTRACT**

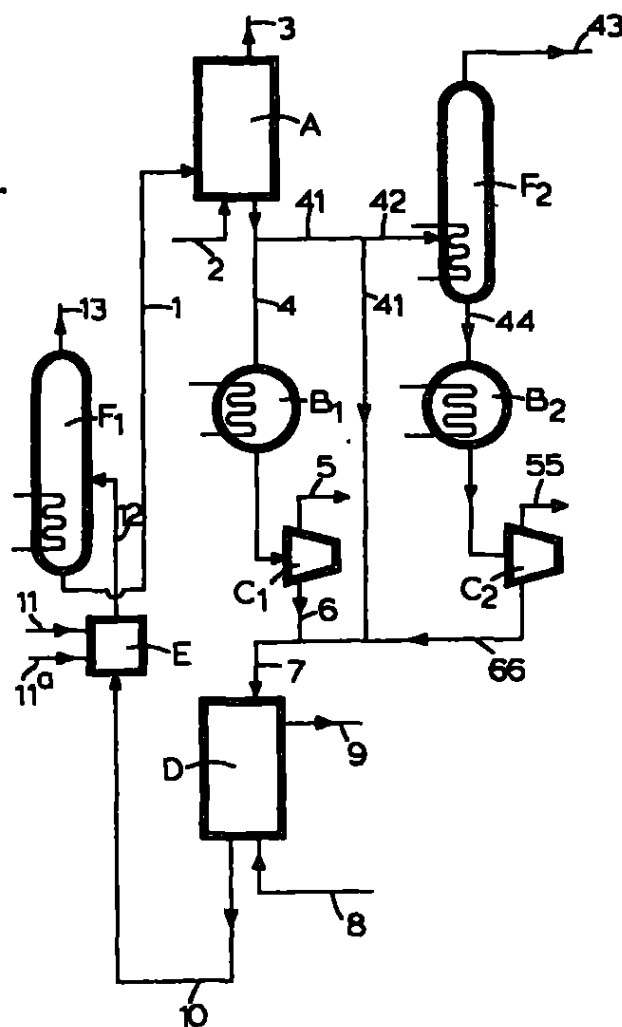
Hydroxylammonium salt solution prepared by catalytically reducing nitrate ions in aqueous solution using molecular hydrogen in a buffered reaction medium containing at least twice the number of sulphate ions as phosphate ions in which the ammonia produced as a by-product of the reaction is removed from the resulting solution as ammonium sulphate is disclosed.

5 Claims, 1 Drawing Figure



PATENTED MAR 13 1973

3,720,758



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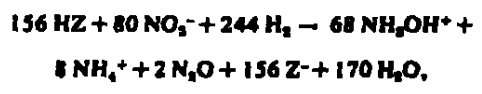
By
Cushman, Quirk & Cushman
ATTORNEYS

1
**PROCESS FOR THE CONTINUOUS PREPARATION
OF AN AQUEOUS SOLUTION OF A
HYDROXYLAMMONIUM SALT**

BACKGROUND OF THE INVENTION

This invention relates to an improved continuous process for the preparation of a hydroxylammonium salt in water by catalytic reduction of nitrate ions with the aid of molecular hydrogen in a medium buffered to a pH of 0 to 3, enabling the ammonia by-product formed in the hydroxylamine production to be separated from the solution in the form of the salt ammonium sulphate.

It is known that the catalytic reduction of nitrate ions is preferably carried out in the presence of a palladium catalyst, starting from make-up solutions which contain phosphoric acid or hydrogen sulphate in addition to relatively weak acids. Such a process is disclosed in U.S. Pat. No. 3,514,254. In this process reductions of nitrate ions to ammonium ions, nitrogen and nitrous oxide (N₂O) take place as secondary reactions. It has been found empirically that the chemical reactions taking place, if the process is carried out continuously at 25° C. with a palladium catalyst, can be represented approximately by the following gross equation, in which the formation of N₂ has been neglected:



where Z stands for the H₂PO₄ or the NH₄SO₄ radical.

This shows that the reduction of nitrate ions converts about 80 percent of the nitrate ions into hydroxylamine and about 10 percent of the nitrate ions into ammonia. This ammonia must be removed from the hydroxylamine-containing solution leaving the reactor, if the hydroxylamine synthesis is to be part of a circulation process which is linked with an oxime synthesis zone. In this manner a constantly circulating process liquid, that is the hydroxylamine-containing process liquid obtained from the above reduction, is fed to the oxime synthesis zone, where the hydroxylamine in the form of a salt is consumed with liberation of the acid with which the hydroxylamine formed the hydroxylammonium salt thereby producing the oxime which is recovered, whereupon an acid-containing process liquid is recirculated to the hydroxylamine synthesis zone, where said acid again binds hydroxylamine freshly formed in the hydroxylamine synthesis zone. An example of such a process is disclosed in copending application Ser. No. 73,907 filed concurrently herewith.

In considering ways in which to remove the undesired ammonia, it would seem apparent that to allow the ammonia formed as a by-product of the production of hydroxylamine to crystallize out in the form of an ammonia salt and then to separate the crystals from the solution would effectively remove the unwanted ammonia. In the case of a hydroxylamine synthesis, when conducted in a medium containing phosphoric acid, it would then be possible to separate the primary ammonium phosphate prior to evaporation and cooling.

It is, however, not attractive to recover the ammonium phosphate in this manner, not only because it is present only in small quantities, but also because a quantity of relatively expensive pure phosphoric acid, which should be pure because it is intended for use in a

2

catalytic process, is removed from the reaction mixture in the form of an ammonium salt. The phosphoric acid so removed in the form of primary ammonium phosphate has only the practical value of a fertilizer, such as the value of P₂O₅ in fertilizers containing ammonium phosphate, which are prepared with less expensive and less pure phosphoric acid. Moreover, in the rearrangement of cyclohexanone oxime to caprolactam, the ultimate commercial object of oxime production, a large quantity of ammonium sulphate is liberated, so that also in the hydroxylamine synthesis it would be preferable to recover ammonium sulphate as a by-product rather than the primary ammonium phosphate, or ammonium nitrate.

Apparently, it would therefore seem more attractive to carry out the hydroxylamine synthesis in a reaction medium which contains ammonium sulphate and ammonium hydrogen sulphate, so that the ammonium which is formed as a by-product of the hydroxylamine production could, indeed, be separated out from the reaction mixture in the form of ammonium sulphate rather than as ammonium phosphate.

However, it has been observed that such a hydroxylamine synthesis method wherein ammonium sulphate is recovered has the disadvantage that the catalyst customarily employed in the art, palladium, is less active and less selective in a reaction medium containing only ammonium sulphate and ammonium hydrogen sulphate than in a reaction medium containing only alkali metal or ammonium dihydrogen phosphate and phosphoric acid. It is for this reason that the method of using phosphate ions in the reaction medium is preferred. Furthermore, the subsequent oxime synthesis will also be carried out preferably with the aid of a solution containing hydroxylammonium dihydrogen phosphate rather than with a solution containing only hydroxylammonium-ammonium sulphate, in view of the more favorable pH conditions attendant with the use of hydroxylammonium dihydrogen phosphate permitting a higher efficiency.

DETAILED DESCRIPTION OF THE INVENTION

It has now been found that the ammonium ions formed as a by-product can also be separated out of the hydroxylamine synthesis reaction mixture as ammonium sulphate in a highly effective manner if the hydroxylamine synthesis is carried out in a reaction medium which contains both phosphoric acid, (or ammonium or alkali metal dihydrogen phosphate, as the case may be,) and sulphates, if said reaction medium contains a quantity of ammonium sulphate such that the molar (ΣSO₄)/ΣPO₄ ratio is at least 2. In this ratio ΣSO₄ represents the sum of all SO₄ radicals present in the reaction mixture, whether or not bound in the form of salts and ΣPO₄ represents the sum of all PO₄ radicals present in the reaction mixture, whether or not bound in the form of salts. In other words, sulphate ions are present in the reaction mixture in an amount at least twice as great as the phosphate ions.

In such a reaction medium having the desired SO₄/PO₄ ratio both the activity and selectivity of the palladium catalyst are still very satisfactory, while ammonium sulphate and not primary ammonium phosphate will crystallize out of the hydroxylammonium salt solution upon cooling, or evaporation and cooling.

It has also been found that when using a hydroxylammonium salt solution which, in addition to PO_4 , also contains SO_4 in the above ratio, the pH conditions in the subsequent oxime synthesis are more suitable than in a corresponding oxime synthesis when using a hydroxylammonium salt solution which contains only the sulphate ions.

Another advantage is that due to the relatively high sulphate content of the hydroxylamine-containing circulating liquid when practicing the present invention, the oxime synthesis can be carried out more economically by reacting the cyclohexanone to be converted to the corresponding amine with the aqueous hydroxylamine solution in counter-currents and thereby avoiding the usual application of a non-water-miscible or poorly water-miscible organic solvent for cyclohexanone and cyclohexanone oxime. Expensive solvent recovery procedures known in the art are thus obviated. Such a method has been disclosed in copending application Ser. No. 73,906 filed concurrently herewith, the disclosure of which is hereby incorporated by reference.

The crystallization point of the reaction mixture directly affects the facility of ammonium sulphate removal. If the hydroxylamine synthesis solution obtained under the usual process conditions (having a pH of about 1.5-2) has a high crystallization point, for instance, about 60 °C, ammonium sulphate can be separated out by simple cooling and at a suitable molar (XSO_4)/(XPO_4) ratio of about 2. However, if the solution has a lower crystallization point, for example, of about 45 °C, then either the solution must first be concentrated and then cooled, or the molar (XSO_4)/(XPO_4) ratio has to be considerably higher than 2 to allow ammonium sulphate to be separated out. Thus the best separation of ammonium sulphate is attained using solutions having crystallization points from about 45° to 60 °C; however crystallization points may vary in wide ranges, as for example from about 20° to 90 °C. However, the crystallization point of the resulting solution need not be a limiting factor, for the solution can easily be concentrated, as hereinafter described, and the ammonium sulphate removed from the concentrated solution.

It is also possible both to maintain a much higher (XSO_4)/(XPO_4) ratio and to concentrate the solution before cooling, especially if ammonium sulphate is to be crystallized out of a solution with a particularly low crystallization point, for example of about 20° - 30 °C. The resulting hydroxylammonium phosphate solution is suitable as such to be converted, by reaction with cyclohexanone, directly to cyclohexanone oxime e.g. according to the process described in U.S. Pat. No. 3,429,920, the disclosure of which is hereby incorporated by reference.

Reaction parameters are well known for this synthesis and are disclosed in U.S. Pat. No. 3,514,254, the disclosure of which is hereby incorporated by reference. The catalyst concentration, temperature and pressure of the reaction may vary widely without rendering the reaction impossible or causing the resulting hydroxylamine to decompose. For instance, the catalyst may range from 0.001 - 0.1 gram of a noble metal per gram of nitrate. The temperature may be maintained between the freezing point and about 125° C.; however the ambient or slightly higher (20°-60° C.) tempera-

tures are preferred. The pressure may be atmospheric, but a pressure of 5 atm. is commercially attractive. Operation outside these preferred ranges does not affect the principles of the invention but generally will only add to the cost of the process.

One embodiment of the process according to the invention is shown schematically in the accompanying drawing.

In this drawing, A is the hydroxylamine synthesis reactor, to which the phosphoric acid solution containing the nitrate and sulphate ions is fed through a pipe 1. These nitrate ions are reduced by means of hydrogen supplied through a pipe 2; the waste gases are discharged through a pipe 3 and the hydroxylammonium salt solution thus produced containing ammonium sulphate and alkali metal or ammonium dihydrogen phosphate is fed, through a pipe 4, to a cooler B1, where the solution becomes supersaturated in ammonium sulphate. A suspension of ammonium sulphate crystals is fed from the cooler B1 to a separator C1, for instance a centrifuge, where the ammonium sulphate crystals are separated from the mother liquor containing the hydroxylammonium salt. The crystals leave the system through a pipe 5; the mother liquor is fed, through piping 6-7, to an oxime synthesis reactor D, where, combining with cyclohexanone supplied through a pipe 8, it forms the oxime, which leaves the system through a pipe 9.

A solution virtually exhausted in hydroxylammonium salt is fed through a pipe 10 to a mixing vessel E, which further receives nitric acid through a pipe 11 and sulphuric acid through a pipe 11a, whereupon the mixture is fed, through a pipe 12, to an evaporator F1. In this evaporator the reaction water formed during the hydroxylamine synthesis and the oxime synthesis, and the water introduced with the nitric acid, is evaporated, to be discharged through a pipe 13, while a solution suitable for use in the hydroxylamine synthesis is fed from the evaporator F1 to the hydroxylamine synthesis reactor A through pipe 1.

Instead of supplying make-up nitric acid, it is also possible to introduce nitric vapors through pipe 11, so that nitric acid is formed in situ in the mixing vessel E, which in this case should of course be an absorption column (not shown).

If the solution leaving reactor A has such a concentration that ammonium sulphate cannot be separated from it by simple cooling, a certain portion of this solution may first be split off, then concentrated, and the required quantity of ammonium sulphate separated from the concentrated solution.

With this alternative method, the hydroxylammonium salt solution obtained in reactor A is carried off through a pipe 41; part of this solution is fed, through a pipe 42, to an evaporator F2, water vapor is discharged through a pipe 43, and the concentrated solution is fed, through a pipe 44 to a cooler B2, from where a suspension of crystals is fed to a centrifuge C2, where it is separated into crystals which are carried off through a pipe 55, and mother liquor, which is carried off through a pipe 66 and added to the solution flowing through pipe 41, to be fed, through pipe 7, to the oxime synthesis reactor D.

With the process represented in the embodiment of the invention shown in the drawing, ammonium

sulphate crystals are separated from the solution flowing from the hydroxylamine synthesis reactor A to the oxime synthesis reactor D. These ammonium sulphate crystals could also be separated from the solution flowing from the oxime synthesis reactor D to the hydroxylamine synthesis reactor A. However, preference is given to the process shown in the drawing, because here the solution is not yet diluted with the reaction water formed in the oxime synthesis reactor, so that the $(\text{NH}_4)_2\text{SO}_4$ crystals will form more readily and are therefore more easily removed.

The present invention is also illustrated by the following examples with reference to the drawing in which, unless otherwise indicated, all parts and percentages are by weight.

Example I describes a solution from which ammonium sulphate crystallizes out immediately upon cooling; example II describes a solution which must first be concentrated before the formation of ammonium sulphate crystals which are subsequently recovered on cooling.

EXAMPLE I

A hydroxylamine salt solution is prepared and continuously fed into reactor A, with the aid of a palladium-loaded activated carbon catalyst and a molar excess of molecular hydrogen representing about 900 moles, from a solution having the following molar composition: 85 H_3PO_4 , 85 NH_4HSO_4 , 140 NH_4NO_3 , 125 $(\text{NH}_4)_2\text{SO}_4$ and 1545 H_2O . The reaction mixture is retained for 0.5 hours in reactor A at a pH of about 1.5-2 and a temperature of 80 °C. The hydroxylamine salt solution thus obtained has the following molar composition: 30 H_3PO_4 , 70 NH_4NO_3 , 210 $(\text{NH}_4)_2\text{SO}_4$, 55 $\text{NH}_2\text{OHH}_2\text{PO}_4$ and 1,800 H_2O and a crystallization temperature of about 60 °C. Gaseous components, mainly hydrogen, the remainder nitrogen and nitrogen oxides were discharged through waste gas conduit 3. The entire quantity of hydroxylamine salt solution produced is cooled in cooler B1 to about 30 °C.

An amount of 7.5 moles of $(\text{NH}_4)_2\text{SO}_4$ crystallizes out of this solution. The crystallized $(\text{NH}_4)_2\text{SO}_4$ is separated from the hydroxylamine salt solution by means of a centrifuge C1. In the oxime synthesis reactor D cyclohexanone oxime is prepared as described in copending application Ser. No. 73,906 filed concurrently herewith by addition of 55 moles of cyclohexanone. After removal of 55 moles of the oxime, nitric acid and sulphuric acid are added, in mixer E, to the hydroxylamine-free solution thus obtained. The quantity of nitric acid added is equivalent to the quantity previously converted in reactor A namely 70 moles, and is conveniently in the form of a 55 percent-by-weight aqueous solution of nitric acid, and 7.5 moles of sulphuric acid is also added in the form of a 95 percent-by-weight aqueous solution of the acid, which is also equivalent to the quantity of $(\text{NH}_4)_2\text{SO}_4$ crystals previously separated from the circulating liquid.

In an evaporator F1 the reaction water is removed from the circulating liquid and the volume thereof is reduced, whereupon the resulting solution, suitable for the hydroxylamine synthesis, is fed back to reactor A for further hydroxylamine synthesis.

EXAMPLE II

A hydroxylamine salt solution is prepared in reactor A, in a similar manner as in example I, with the aid of a palladium-loaded activated carbon catalyst and hydrogen, from a solution having the following molar composition: 100 H_3PO_4 , 100 NH_4HSO_4 , 100 NH_4NO_3 , 100 $(\text{NH}_4)_2\text{SO}_4$ and 1,700 H_2O . The reaction mixture is retained in reactor A for a period of 0.5 hours at 60 °C. at a pH of 1.5 - 2 in the presence of 988 moles of molecular hydrogen. The hydroxylamine salt solution thus obtained has the following molar composition: 44 H_3PO_4 , 22 NH_4NO_3 , 191 $(\text{NH}_4)_2\text{SO}_4$, 56 $\text{NH}_2\text{OHH}_2\text{PO}_4$, 9 $\text{NH}_2\text{OHNH}_2\text{SO}_4$ and 1,869 H_2O and a crystallization temperature of about 45 °C.

From a portion of the above reaction mixture 127 moles of water is evaporated in evaporator F2. The concentrated solution has the following molar composition: 12 H_3PO_4 , 6 NH_4NO_3 , 52 $(\text{NH}_4)_2\text{SO}_4$, 15 $\text{NH}_2\text{OHH}_2\text{PO}_4$, 2 $\text{NH}_2\text{OHNH}_2\text{SO}_4$ and 378 H_2O , and a crystallization temperature of about 55 °C. The solution is then cooled in a cooler-crystallizer B2 to about 30 °C, as a result of which 6.5 moles of $(\text{NH}_4)_2\text{SO}_4$ crystallize out. The crystals are separated from the hydroxylamine-containing solution in centrifuge C2. The part-stream thus obtained is now added to and mixed with the main stream, and cyclohexanone oxime is prepared by adding 65 moles of cyclohexanone to the solution containing hydroxylamine. The oxime formation proceeds substantially as described in British Pat. No. 1,138,750; 65 moles of the oxime are recovered.

Nitric and sulphuric acid are added to the solution exhausted in hydroxylamine which leaves the oxime synthesis reactor D. In mixer E 78 moles of HNO_3 are added, conveniently in the form of a 55 percent-by-weight aqueous solution of the acid, this quantity equivalent to the quantity previously converted in the hydroxylamine synthesis reactor, and 6.5 moles of sulphuric acid, in the form of a 95 percent-by-weight aqueous solution of the acid, which is equivalent to the quantity previously separated in the form of $(\text{NH}_4)_2\text{SO}_4$ crystals. In an evaporator F1 the reaction water and the quantity of water added with the nitric and sulphuric acids is removed from the circulating liquid, whereupon a suitable starting solution for the hydroxylamine synthesis is fed back to the synthesis reactor A.

We claim:

1. In a continuous process for the preparation of an aqueous solution containing hydroxylammonium salt in a reaction zone, wherein nitrate ions in an acidic aqueous reaction medium buffered to a pH of 0-3 in said reaction zone are reduced by molecular hydrogen in the presence of a catalyst at a temperature above at least the freezing point of the reaction medium with the formation of ammonium ions as a by-product of said process, the improvement wherein both sulphate and phosphate ions are present in said reaction medium, the molar ratio of said sulphate ions and phosphate ions present expressed as:

$$(\Sigma \text{SO}_4)/(\Sigma \text{PO}_4)$$

is at least 2, and

said ammonium ions thus formed and present in said aqueous solution containing hydroxylammonium salt are separated therefrom in the form of solid ammonium sulphate.

2. A continuous process for the preparation of an aqueous solution containing hydroxylammonium salt in a reaction zone A wherein nitrate ions in an acidic aqueous reaction medium buffered to a pH of 0-3 in said reaction zone are reduced by molecular hydrogen in the presence of a catalyst at a temperature above at least the freezing point of the reaction medium with the formation of ammonium ions as a by-product of said process, the process including both sulphate and phosphate ions present in said reaction medium, the molar ratio of said sulphate ions and phosphate ions present expressed as:

$$(\Sigma \text{SO}_4)/(\Sigma \text{PO}_4)$$

is at least 2, and said ammonium ions thus formed and present in said aqueous solution containing hydroxylammonium salt are separated therefrom in the form of solid ammonium sulphate, said reaction zone A for the preparation of hydroxylammonium salt is in fluid communication with a reaction zone B for the synthesis of cyclohexanone oxime,

in said reaction zone B cyclohexanone is continuously contacted in counter current with an aqueous solution comprising said hydroxylammonium salt, and a circulating aqueous solution passes from reaction

zone A to reaction zone B and returns to reaction zone A, wherein:

- said circulating aqueous solution is enriched in hydroxylammonium salt in reaction zone A and conducted to reaction zone B,
- said hydroxylammonium salt, when reacted with cyclohexanone, is decomposed into cyclohexanone oxime and an acid in reaction zone B,
- said acid produced in step (b) together with said circulating liquid is returned to reaction zone A where it is again enriched in hydroxylammonium salt,

the improvement wherein said ammonium ions formed as a by-product of the hydroxylammonium salt synthesis are continuously separated from said circulating liquid in the form of ammonium sulphate crystals.

3. The process of claim 2 wherein said ammonium sulphate crystals are separated from that portion of said circulating liquid flowing to reaction zone B for the synthesis of cyclohexanone oxime.

4. The process of claim 1 wherein said separation of ammonium sulphate is effected by cooling said aqueous solution containing the hydroxylammonium salt.

5. The process of claim 4 wherein said aqueous solution is concentrated by evaporation before cooling.

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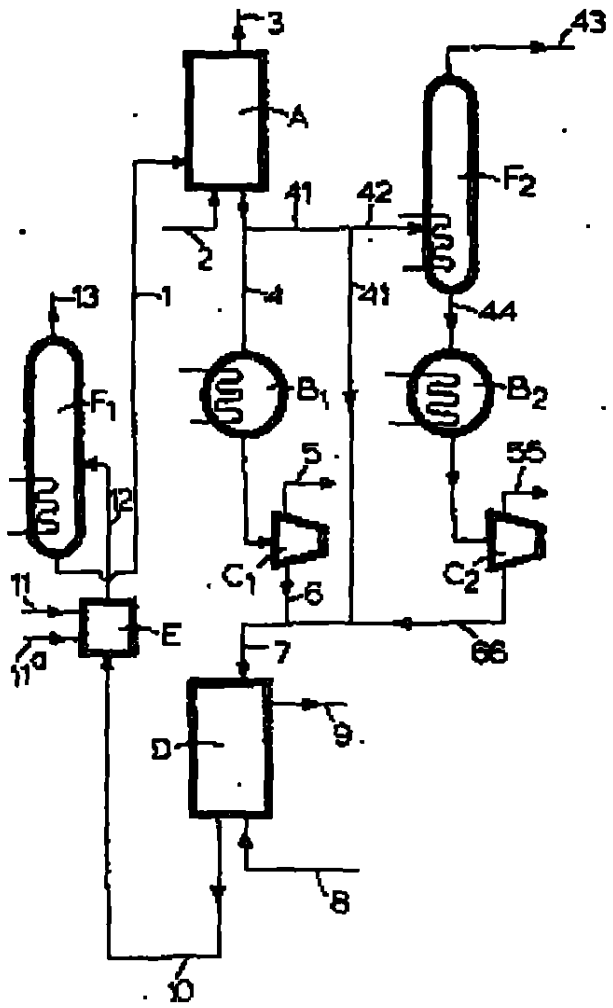
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abstract

United States Patent [19]
De Rooij et al.

[11] **3,862,230**
[45] **Jan. 21, 1975**

- [54] **CONTINUOUS PREPARATION OF CYCLOHEXANONE OXIME**
- [75] **Inventors:** Abraham H. De Rooij, Geleen; Jan Elmendorp, Brunssum, both of Netherlands
- [73] **Assignee:** Stankarbon N.V., Heerlen, Netherlands
- [22] **Filed:** Dec. 7, 1973
- [21] **Appl. No.:** 422,712
- Related U.S. Application Data**
- [63] **Continuation of Ser. No. 73,906, Sept. 21, 1970, abandoned.**
- Foreign Application Priority Data**
- Sept. 20, 1969 Netherlands..... 6914308
- [52] **U.S. Cl.**..... 260/566 A
- [51] **Int. Cl.**..... C07c 131/04
- [58] **Field of Search**..... 260/566 A

[56] **References Cited**
FOREIGN PATENTS OR APPLICATIONS
1,138,750 0/1969 Great Britain..... 260/566 A

Primary Examiner—Bernard Helfin
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Attorney, Agent, or Firm—Cushman, Darby & Cushman

[57] **ABSTRACT**
A process for the continuous preparation of an oxime from cyclohexanone and an aqueous buffered solution of a hydroxylammonium salt together with free phosphoric acid, phosphates, nitrates, and optionally sulphates all in controlled amounts and without the use of an organic solvent is disclosed. The resulting aqueous reaction mixture contains a manageable amount of unreacted cyclohexanone which is subsequently recovered and recirculated.

1 Claim, No Drawings

CONTINUOUS PREPARATION OF CYCLOHEXANONE OXIME

This is a continuation, of application Ser. No. 73,906 filed Sept. 21, 1970, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to an improved process for the continuous preparation of cyclohexanone oxime, in which cyclohexanone is reacted with a counter-current of a buffered aqueous solution of hydroxylammonium salt derived from a relatively weak acid, such as phosphoric acid, ammonium hydrogen sulphate or an alkali hydrogen sulphate.

It has already been proposed in British Pat. No. 1,138,750 to carry out such a process in the presence of a non-water-miscible or poorly water-miscible organic solvent for cyclohexanone and the cyclohexanone oxime product, which, together with the cyclohexanone, flows in counter-current to the aqueous solution of the hydroxylammonium salt on the one hand, a pure solution of the oxime in the solvent is then obtained, and on the other hand only a small amount of cyclohexanone remains dissolved in the solution leaving the reactor, which is virtually exhausted in hydroxylammonium salt. In this manner the hydroxylammonium salt is efficiently used. A further advantage of the organic solvent process is its flexibility with respect to the temperature conditions; operational temperatures below the solidification point of the oxime formed are not objectionable, the possibility of solid matter being deposited and clogging the equipment is obviated since the oxime is kept in solution in the organic solvent.

Moreover, in the absence of an organic solvent there is a risk of cyclohexanone and the cyclohexanone oxime thus formed being attacked by the acid reaction medium, which becomes increasingly acidic as additional hydroxylammonium salt is consumed. When the process is practiced using an organic solvent, attack is possible only at the interface between the organic solvent and the more or less acidic aqueous solution containing the hydroxylammonium salt, thereby the risk of attack by the acid reaction medium is considerably reduced.

However, attendant with the above advantages is the disadvantage of the cost of separation of the oxime from the solvent by distillation. If no organic solvent were used in the continuous preparation of the oxime, this cost of distillation could admittedly be saved, but only at the expense of the other above-mentioned advantages. Also, the additional cost of stripping the unreacted cyclohexanone from the aqueous solution virtually exhausted in hydroxylammonium salt that has remained behind is a consideration when an organic solvent is not used.

DESCRIPTION OF THE INVENTION

It has now been found that a cyclohexanone oxime of sufficient purity, comparable to that produced using an organic solvent, can also be obtained in a continuous process without the use of an organic solvent when the process is carried out such that the contact time between the aqueous solution containing the hydroxylammonium salt and the cyclohexanone flowing in counter-current does not exceed a total contact time of 6 minutes. Indeed, the process of the present invention is even more economical than a similar process using an

organic solvent provided that the composition of the aqueous solution starting material containing the hydroxylammonium salt is selected such that no more than 0.9 ton of cyclohexanone per ton of cyclohexanone oxime produced remains dissolved in the effluent solution and need be recovered therefrom.

The time of contact between the aqueous solution containing hydroxylammonium salt whether or not other dissolved substances are present and the cyclohexanone is actually the residence time in minutes in the reaction zone R which is equal to the reaction volume V divided by the sum of the feeds to the synthesis zone or reactor Σf of the aqueous solution containing hydroxylammonium salt and the cyclohexanone, measured in parts by volume per unit time. This relationship is represented by the equation:

$$R = V/\Sigma f$$

With a longer contact time than 6 minutes, the risk of attack by the acid reaction medium attended by formation of unwanted by-product increases. Notwithstanding the above, with a longer contact time of for example 30 minutes, an oxime of reasonable quality can still be obtained. However, in that case it should be taken into account that the cost of purifying the caprolactam, the ultimate product obtained from the rearrangement of the cyclohexanone oxime, may increase. Thus operation using a contact time in excess of about 6 minutes does not affect the principles of the invention but generally will only add to the cost of the process.

The quantity of cyclohexanone to be recovered from the reaction mixture per kg of oxime produced depends only in part on the solubility of the cyclohexanone in the effluent aqueous solution exhausted in hydroxylammonium salt. Another factor which plays a role in the quantity of cyclohexanone recovered is the composition of the starting solution containing hydroxylammonium salt. More particularly, the concentration of hydroxylammonium salt and the concentration of other components dissolved in the starting hydroxylammonium salt solution affect the quantity of cyclohexanone, in tons per ton of oxime produced, remaining behind in the aqueous solution exhausted in hydroxylammonium salt. Therefore, the higher the concentration of dissolved substances in the original solution containing hydroxylammonium salt, the smaller the quantity of cyclohexanone to be recovered will be.

In the known process, as discussed in U.S. Pat. No. 3,514,254, the disclosure of which is hereby incorporated by reference, of preparing a hydroxylammonium salt solution by catalytic reduction of nitrate ions in a reaction medium buffered with phosphate phosphoric acid, the hydroxylammonium dihydrogen phosphate solution produced always contains the primary alkali and/or ammonium salts of phosphoric acid and ammonium nitrate in addition to free phosphoric acid.

In order to maintain the activity of the catalyst in the reduction reaction, it is desirable, on the one hand, to use a minimum nitrate content of 0.7 mole per kilogram of solution. However, on the other hand, this content cannot be increased indefinitely, since a high concentration of nitrate in the reaction solution will affect the solubility of the other components. Therefore, in practice the concentration of ammonium salts will not exceed 4 moles per kg of solution. Since the preparation of hydroxylamine by catalytic reduction of nitrate ions with phosphate and phosphoric acid in a buffered

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solution is generally carried out at a pH of 1.3 - 2.0, measured with a pH meter, at a temperature of about 20° to 90 °C, the ratio between phosphate and phosphoric acid is in practice within certain limits, for instance, of about 2 to 3, so that only the concentrations of dissolved phosphate and phosphoric acid can be varied.

It has now been found possible to meet the condition that the quantity of cyclohexanone remaining behind in and to be recovered from the effluent aqueous solution of the oxime synthesis should not exceed 0.9 per kg of oxime produced, by maintaining the concentration of hydroxylammonium salt and the concentration of dissolved phosphate and phosphoric acid present in the starting solution above certain values. Moreover, the presence of other salts, particularly sulphates, has been found to have a very favorable effect, in that these salts considerably reduce the quantity of cyclohexanone to be recovered. For, it has been discovered that, if the starting solution is a hydroxylammonium salt solution which, in addition to the hydroxylammonium dihydrogen phosphate and at least 0.7 mole/kg of nitrate, contains free phosphoric acid and alkali or ammonium salts of phosphoric acid, and, if desired, the corresponding salts of sulphuric acid, and if the solution has a pH, measured with a pH meter of 1.3 to 2.0, the quantity of cyclohexanone remaining behind in the effluent exhausted aqueous solution can be kept from exceeding 0.9 kg of oxime. This maximum desired cyclohexanone content will be controlled provided that care is taken that the hydroxylammonium salt content of the starting solution is equal to or higher than 0.5 mole/kg solution, and that the sum of the concentrations of dissolved phosphoric acid, phosphates, and sulphates, if present (which sum will hereinafter be written as ΣPO_4 and $\Sigma\text{PO}_4 + \text{SO}_4$, respectively), does not exceed 1 mole/kg of solution.

The higher the concentration of the hydroxylammonium salt and the higher the concentration of ΣPO_4 or $\Sigma\text{PO}_4 + \text{SO}_4$ in the starting solution, the smaller the quantity of cyclohexanone to be recovered from the effluent solution exhausted in hydroxylammonium salt. Of course it is desirable to maintain the quantity of unreacted cyclohexanone as low as possible in order to increase efficiency of the reaction and decrease cyclohexanone recovery costs.

For instance, the quantity of cyclohexanone to be recovered per kg of oxime produced is less than 0.5 kg if the hydroxylammonium salt content of the starting solution is about 0.7 mole/kg and $\Sigma\text{PO}_4 = 2.0$ moles/kg. Particularly advantageous is the presence of dissolved sulphate in the starting solution. In the presence of, for instance, 1.75 moles of sulphate/kg of solution in addition to 1 mole of $[\text{PO}_4]$ /kg, at a hydroxylammonium salt content of 0.66 mole/kg, the quantity of cyclohexanone to be recovered is 0.09 kg per kg of oxime produced. The use of a favorable ratio of SO_4 to PO_4 in the synthesis of the hydroxylammonium salt is described in copending application Ser. No. 73,905 filed Sept. 21, 1970, the disclosure of which is hereby incorporated by reference.

The oxime production according to the present invention can be carried out in normal counter-current reactors, such as packed columns, sieve-plate, or so-called "rotating-disc" reactors, in which the organic phase, the cyclohexanone, and the aqueous solution containing the hydroxylamine are in contact with each

other in fine dispersion. If required, an even finer dispersion can be obtained by pulsating the liquid streams. Pressure within the reaction zone varies with the reactor used; however, while pressures with the range of about 1 to 20 atm. are particularly effective, higher pressures may be used.

The oxime synthesis reaction can also be conveniently carried out in a number of reactors, for example three to six reactors arranged in series and equipped with stirrers, each reactor being provided with a liquid/liquid separator, and the cyclohexanone being continuously fed to one end and the aqueous hydroxylammonium salt solution continuously supplied to the other end of the battery of reactors.

One embodiment of the invention is shown schematically in the accompanying drawing. According to this embodiment, the oxime preparation is carried out in a counter-current reactor A, the top and bottom ends of which are widened to function as liquid/liquid separators. The organic phase, that is the cyclohexanone, is fed to the bottom of the reactor through a pipe 1, the heavier water phase is fed to the top of the column through a pipe 2.

In the top of column A the oxime formed separates from the water phase. A sufficiently high temperature is maintained here of about 80° to 120 °C which is above the solidification point of the watercontaining oxime in order to keep the oxime in the molten condition. An operational pH of about 0.3 to 1.0 is maintained. The oxime phase, which still contains about 1 to 2 percent by weight of non-converted cyclohexanone, is fed, through a pipe 3, to a secondary stirred reactor B, to which are fed also a small amount of solution containing hydroxylammonium salt, through a pipe 22, and an alkaline reagent, preferably ammonia, through a pipe 4, in such a quantity that the pH in the secondary reactor is maintained at a value of approximately 4.5.

From the secondary reactor B the reaction mixture flows, through a pipe 5, to the liquid/liquid separator C, where the molten oxime produced is separated from the water phase and carried off through a pipe 6. This oxime can be rearranged to caprolactam as disclosed, for example, in U.S. Pat. No. 2,769,000 after having been washed with water to remove impurities if necessary.

The water phase discharged from the bottom of separator C is fed to the top of column A through a pipe 7. In the base of column A a water phase virtually exhausted in hydroxylammonium salt is collected, in which, for example, 1-6 percent by weight of cyclohexanone has remained behind. This water phase is fed, through a pipe 8, to the top of a stripping column D, where the cyclohexanone dissolved in the water phase is stripped off by heating, for example with steam supplied through a pipe 9. The top product, a cyclohexanone-water azeotrope, is condensed in a condenser E. The condensate flows into a separator F, from which the top layer of cyclohexanone is fed back to the reactor A through a pipe 10; the cyclohexanone-free water phase is discharged from the bottom of the stripping column D through a pipe 11.

Said water phase may be recirculated from pipe 11 to a hydroxylammonium salt synthesis zone (not shown), to serve as reaction medium therein, in which case the hydroxylamine thus formed reacts with the acid present in the water phase previously removed

from the hydroxylammonium salt to form the hydroxylammonium salt, whereupon the hydroxylammonium salt solution thus obtained is recirculated to the oxime synthesis reactor A through pipe 2. A suitable process for preparing a solution containing hydroxylammonium salt is described in U.S. Pat. No. 3,514,254, the disclosure of which is hereby incorporated by reference.

The process according to the invention will be elucidated by means of the following working examples. In these examples, the starting solutions containing hydroxylammonium salt differ one from the other in composition, in that different compositions of make-up solution are supplied to a hydroxylammonium salt synthesis zone. In the following examples the solution containing the hydroxylammonium salt is prepared according to the process disclosed in U.S. Pat. No. 3,514,254.

The data given in these examples and the results obtained have been listed in the following table.

order not to work precisely on this border line, the ΣPO_4 content will have to be higher than 1, as is illustrated by examples 7 and 13 in comparison with example 1.

Excellent results are obtained if a large quantity of salt is present in solution. In that case, the content of cyclohexanone remaining behind, and hence the quantity of cyclohexanone to be recovered, is greatly reduced, as will be confirmed by comparing examples 26 and 29 with example 13.

We claim:

1. A process for the continuous preparation of cyclohexanone oxime which comprises:

a. reacting in the absence of an organic solvent cyclohexanone in an oxime synthesis zone with a counter-current of a buffered aqueous solution containing hydroxylamine having a pH of about 1.3 - 2.0 and comprising:

	Composition of the feed to the hydroxylamine synthesis, moles						Hydroxylammonium salt solution obtained (Process stream 2)			Cyclohexanone content of exhausted aqueous solution, g by weight	Cyclohexanone to be recuperated, kg per kg of oxime
Example	H ₃ PO ₄	HNO ₃	NH ₄ NO ₃	H ₂ SO ₄	(NH ₄) ₂ SO ₄	H ₂ O	NH ₄ OH ⁺ , moles/kg	PO ₄ , moles/kg	PO ₄ +SO ₄ , moles/kg	Process stream 2	Process stream 10
1	100	80	100	—	—	4,250	0.68	1.0	1.0	6.2	0.81
2	125	60	145	—	—	5,400	0.545	1.0	1.0	5.6	0.91
3	150	40	190	—	—	6,500	0.455	1.0	1.0	5.2	1.01
4	175	20	235	—	—	7,670	0.39	1.0	1.0	4.9	1.11
5	200	—	280	—	—	8,850	0.34	1.0	1.0	4.6	1.21
6	100	80	80	—	—	3,330	0.85	1.25	1.25	6.0	0.63
7	125	60	120	—	—	4,100	0.68	1.25	1.25	5.5	0.72
8	150	40	160	—	—	4,970	0.565	1.25	1.25	4.9	0.77
9	175	20	200	—	—	5,835	0.485	1.25	1.25	4.5	0.82
10	200	—	240	—	—	6,700	0.425	1.25	1.25	4.2	0.87
11	100	80	67	—	—	3,550	1.02	1.5	1.5	5.9	0.51
12	125	60	103	—	—	3,250	0.815	1.5	1.5	5.0	0.54
13	150	40	140	—	—	3,950	0.68	1.5	1.5	4.4	0.57
14	175	20	177	—	—	4,650	0.58	1.5	1.5	4.0	0.61
15	200	—	213	—	—	5,350	0.51	1.5	1.5	3.8	0.66
16	100	80	50	—	—	1,710	1.36	2.0	2.0	5.8	0.38
17	125	60	83	—	—	2,300	1.09	2.0	2.0	4.6	0.37
18	150	40	115	—	—	2,680	0.905	2.0	2.0	3.9	0.38
19	175	20	148	—	—	3,160	0.775	2.0	2.0	3.4	0.39
20	200	—	180	—	—	3,640	0.68	2.0	2.0	3.1	0.40
21	100	80	40	—	—	1,200	1.70	2.5	2.5	5.7	0.30
22	125	60	70	—	—	1,560	1.36	2.5	2.5	4.3	0.28
23	150	40	100	—	—	1,910	1.18	2.5	2.5	3.4	0.26
24	175	20	130	—	—	2,260	0.97	2.5	2.5	2.9	0.26
25	200	—	160	—	—	2,620	0.85	2.5	2.5	2.6	0.27
26	100	—	200	44	130	3,000	0.665	1.0	2.75	0.3	0.99
27	125	—	275	37.5	37.5	3,000	0.70	1.25	3.0	1.9	0.91
28	125	—	295	37.5	112.5	3,000	0.625	1.25	2.75	1.1	0.20
29	200	—	200	—	75	3,000	0.68	1.0	1.75	1.3	0.20
30	125	—	135	30	10	1,500	1.24	2.4	3.0	1.59	0.11

From the foregoing examples it is apparent that if the solutions containing hydroxylammonium salt are free of sulphate and have a hydroxylammonium salt content below 0.5 mole, the quantity of non-converted cyclohexanone to be recovered exceeds the value of 0.9 kg per kg of oxime produced (see examples 3, 4 and 5), and as a consequence the process, while operable, can no longer compete with the oxime preparation using a non-water-miscible or poorly water-miscible organic solvent.

Border-line cases in which the quantity of unreacted cyclohexanone is near the 0.9 kg limit are those examples (examples 1 and 2) in which, although the hydroxylammonium salt content is higher than 0.5 mole/kg, the concentration of ΣPO_4 is just equal to unity. In

hydroxylammonium dihydrogen phosphate present in an amount at least equal to about 0.5 mole per kilogram of said solution,

ammonium nitrate, nitric acid or mixtures thereof present in an amount of at least about 0.7 moles per kilogram of said solution,

phosphoric acid and a compound selected from the class consisting of alkali salts of phosphoric acid, ammonium salts of phosphoric acid and mixtures thereof, the total concentration of phosphoric acid and said salt when dissolved is at least equal to about 1 mole per kilogram of said solution, and a member selected from the class consisting of alkali salts of sulphuric acid, ammonium salts of sulphuric acid and mixtures thereof; the contact time

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being the residence time of the respective fluids in the oxime synthesis zone as expressed by the general equation:

$R = V/\Sigma f$

wherein R is the residence time in the synthesis zone in minutes, V is the reaction volume, and Σf is the sum of the feeds to the synthesis zone measured in parts by

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volume per unit of time, and R does not exceed 6;

b. separating the oxime from the reaction mixture; and

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c. discharging from said oxime synthesis zone a solution virtually exhausted in hydroxylamine and containing not more than about 0.9 kg of unreacted cyclohexanone per kg. of oxime produced.

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United States Patent [19]
de Rooij

[11] **3,997,607**
[45] **Dec. 14, 1976**

[54] **RECYCLING PROCESS FOR THE
PREPARATION OF CYCLOHEXANONE
OXIME**

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[22] **Filed:** Apr. 24, 1975

[21] **Appl. No.:** 571,396

Related U.S. Application Data

[63] Continuation-in-part of Ser. Nos. 542,045, Jan. 17,
1975, and Ser. No. 564,085, April 1, 1975, said Ser.
No. 542,045, is a continuation-in-part of Ser. No.
95,389, Dec. 4, 1970, and Ser. No. 95,318, Dec. 4,
1970, said Ser. No. 564,085, is a continuation-in-part
of Ser. No. 422,711, Dec. 7, 1973, and Ser. No.
422,713, Dec. 7, 1973.

[30] **Foreign Application Priority Data**

Apr. 26, 1974 Netherlands 7405630

[52] **U.S. Cl.** 260/566 A

[51] **Int. Cl.³** C07C 131/04

[58] **Field of Search** 260/566 A

[56] **References Cited**
FOREIGN PATENTS OR APPLICATIONS

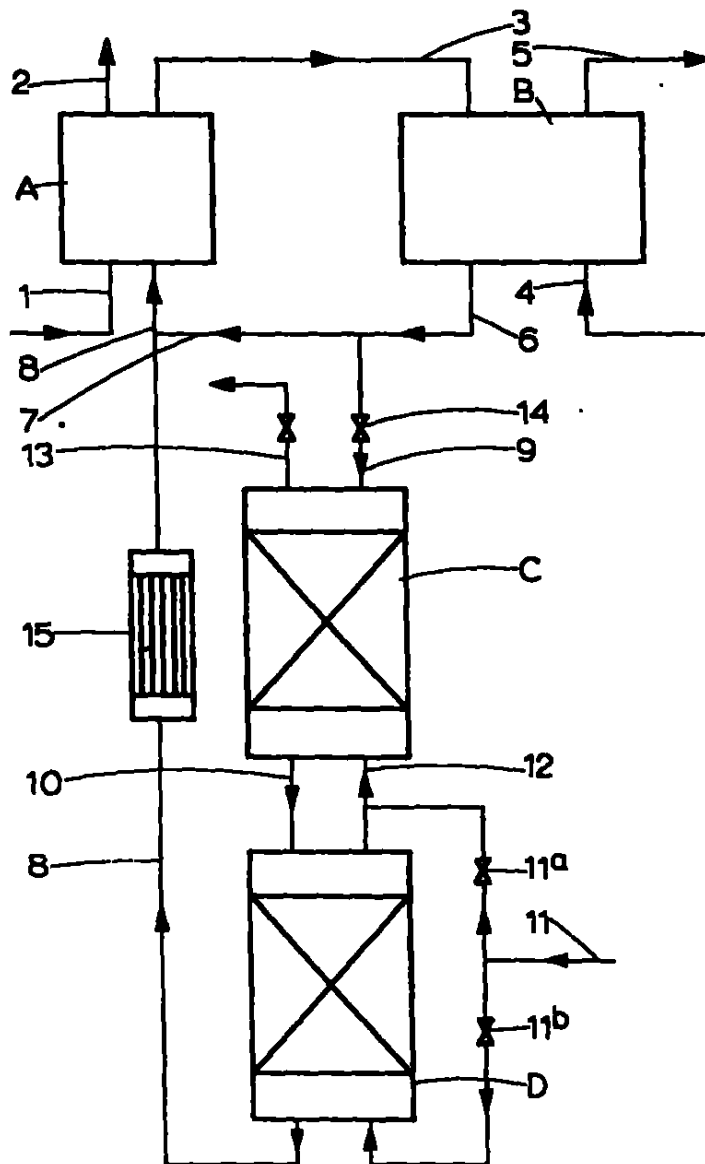
441,674	6/1972	Australia	260/566 A
944,362	3/1974	Canada	260/566 A
1,283,894	8/1972	United Kingdom	260/566
1,283,496	7/1972	United Kingdom	260/566 A

Primary Examiner—Gerald A. Schwartz
Attorney, Agent, or Firm—Cushman, Darby &
Cushman

[57] **ABSTRACT**

An improved cyclic process for producing cyclohexa-
none oxime is provided wherein the circulating reac-
tion medium is subjected to a heat treatment, at a tem-
perature of at least 120° C in the presence of nitrous
gases, and at an absolute pressure of over 1 atmo-
sphere, as it circulates between the oxime synthesis
zone and the hydroxylamines synthesis zone. Cyclohex-
anone oxime is a valuable commercial commodity e.g.
for the preparation of nylon-6 via ϵ -caprolactam.

8 Claims, 1 Drawing Figure



3,997,607

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RECYCLING PROCESS FOR THE PREPARATION OF CYCLOHEXANONE OXIME

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part application of Ser. No. 542,045, filed Jan. 17, 1975, which is relied upon and incorporated herein by reference. This application is also a continuation-in-part application of U.S. Pat. Application, Ser. No. 564,085, filed Apr. 1, 1975 in the name of the inventor for IMPROVED CYCLIC PROCESS FOR PREPARING AND WORKING UP A HYDROXYL-AMMONIUM SALT SOLUTION, which is also relied upon and incorporated herein by reference. Said U.S. Pat. Application Ser. No. 542,045 (filed Jan. 17, 1975) is in turn a continuation-in-part application of both U.S. Pat. Applications Ser. No. 95,389 and Ser. No. 95,318, both filed on Dec. 4, 1970. U.S. Pat. Application Ser. No. 564,085, filed Apr. 1, 1975, in the name of the inventor, for IMPROVED CYCLIC PROCESS FOR PREPARING AND WORKING UP A HYDROXYL-AMMONIUM SALT SOLUTION, is a continuation-in-part application of (a) Ser. No. 422,711, filed Dec. 7, 1973, which in turn is a Rule 60 application of Ser. No. 114,172, filed Feb. 10, 1971 and now abandoned, and (b) Ser. No. 422,713, filed Dec. 7, 1973, which is in turn is a Rule 60 application of Ser. No. 114,171, filed Feb. 10, 1971, now abandoned.

BACKGROUND OF THE INVENTION

The invention relates to a cyclic process for the preparation of cyclohexanone oxime from cyclohexanone and a hydroxyl-ammonium salt which includes the steps of preparing a solution of the required hydroxyl-ammonium salt and of reacting the hydroxyl-ammonium salt with cyclohexanone.

British Patent Specification No. 1,283,894 discloses a process wherein a buffered aqueous reaction medium showing an acid reaction is recycled between (1) a zone for the synthesis of hydroxyl-ammonium ions by means of molecular hydrogen, and (2) a zone for the synthesis of cyclohexanone oxime, in which the resulting hydroxyl ammonium ions react with cyclohexanone to form cyclohexanone oxime. In this process the buffering action of the reaction medium is due to the presence of buffer acids and salts thereof, in the reaction medium, e.g., phosphoric acid and/or bisulphate as a buffer acid with a phosphate and/or sulphate, respectively, as a buffer salt.

Before the recycled aqueous reaction medium is passed into the zone for the synthesis of hydroxyl-ammonium salt, it is enriched with the required nitrate ions either by addition of nitric acid or by absorption of nitrous gases in the aqueous reaction medium, in which instance nitric acid is formed in situ.

The catalyst used for the reduction of the nitrate ions is, for instance palladium or a palladium-platinum alloy, and the catalyst support is, for instance, carbon or aluminum oxide. The carrier is loaded with catalyst so that the supporting material contains, e.g., 5-20% by weight of catalyst.

The aforementioned reference discloses that the activity of such a catalyst is adversely affected if the catalyst is contaminated with organic substances, such as the cyclohexanone to be converted or the cyclohexanone oxime product. To overcome this problem, the

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reference teaches reducing the total content of dissolved ketone and oxime in the recycling liquid to a value of at most 0.02% by weight by heating the recycling liquid at a temperature of at least 50° C in the presence of nitrous gases, before the recycling liquid is passed into the zone for the synthesis of the hydroxyl-ammonium salt. The required amount of nitrous gases can then be adjusted by adding nitrous gases or an alkali nitrite to the recycling liquid.

This known process for lowering the ketone and oxime content has the following drawbacks:

1. A large amount of recycling liquid per ton of final product must be subjected to said heat-treatment.

2. If an ammonium salt is used as a buffer salt in the recycling liquid, the ammonium-ion content may become too low, because the known reaction of ammonium ions with nitrous gases with simultaneous formation of nitrogen at a temperature of over about 40° C appears to proceed at least equally as quickly as the reaction in which the catalyst poisons are rendered harmless.

3. As any hydroxyl-ammonium salt present during the heat-treatment may decompose, the overall process efficiency in using an excess amount of hydroxyl-ammonium salt in order to obtain cyclohexanone oxime with the lowest possible cyclohexanone content is not always controllable.

SUMMARY OF THE INVENTION

It has now been found that the above drawbacks can be obviated, and yet the activity and selectivity of the catalyst can be retained, by heating and recycling liquid partly and/or periodically at a temperature of at least 120° C and under pressure in contact with nitrous gases, before it is passed into the zone for the synthesis of hydroxyl-ammonium salt. If the heat treatment is applied to only part of the recycling liquid, e.g. 10%, at atmospheric pressure and at a lower temperature, e.g. 50°-80° C, (1) the desired effect of the improvement of the invention is not realized, and (2) reduction of the activity and selectivity of the catalyst to a considerable extent, apparently, occurs. Examination of this adverse effect on the catalyst disclosed that the cyclohexanone oxime still contained in the untreated part of the recycling liquid is reduced to cyclohexylamine, which, when subjected to a heat treatment at a temperature of below 120° C, decomposes and is converted into catalyst poisons.

The relation between the temperature of the heat treatment in question and the cyclohexylamine content of an aqueous solution that is comparable to the recycling liquid is apparent from the results of a number of experiments at various temperatures, which are compiled in the table below. In each experiment nitrous gases (obtained by mixing 28 parts by volume of nitrogen monoxide and 72 parts by volume of air) were passed through 1500 grams of aqueous solution for about 2 hours at the rate of 7 liters per minute. The aqueous solution was contained in an autoclave under autogenous pressure (based on atmospheric pressure at room temperature) and contained 1 mole of orthophosphoric acid, 1.1 moles of mono-ammonium phosphate, 2 moles of ammonium nitrate, and 0.4 gram of cyclohexyl amine per kilogram at the start of each experiment. The amount of nitrous gases passed through was considerably larger than was required for the decomposition of the ammonium ions according to the reaction:



in which the required nitrogen dioxide was formed by oxidation of the nitrogen monoxide with the oxygen of the air in the nitrous gases used.

Table

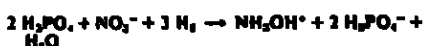
Temp. in °C	cyclohexyl amine and catalyst poisons formed therefrom, in % of original amount of cyclohexyl amine	% of original amount of cyclohexyl amine converted into dicarboxylic acids	% of original amount of cyclohexyl amine discharged as carbon dioxide
40	98	2	0
60	94	4.5	1.5
80	85	14	1
100	53	36	11
110	20	60	20
125	0	65	35
150	0	55	45

As appears from the table, the cyclohexyl amine has completely decomposed at the temperatures 125° and 150° C. The carbon dioxide formed from the cyclohexyl amine is discharged as a gas, while the dicarboxylic acids formed from the cyclohexyl amine, together with the cyclohexanone oxime, are removed from the recycling liquid by extraction. Thus, it is an object of the invention to remove from the reaction medium those organic substances which will contaminate the catalyst employed to reduce the nitrate ions.

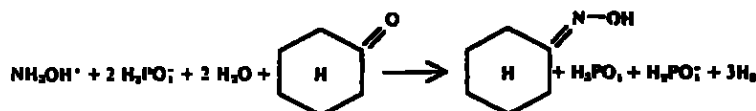
DETAILED DESCRIPTION OF THE INVENTION

The chemical reactions taking place during the successive steps of the process for the preparation of cyclohexanone oxime wherein the reaction medium comprises a solution containing phosphoric acid, are as follows:

1. formation of hydroxyl-ammonium salt in the hydroxyl-ammonium salt synthesis zone:



2. formation of cyclohexanone oxime in the oximation zone:



3. make-up, in the form of HNO₃, of nitrate ions consumed, after the oxime formed has been separated from the reaction mixture:



The cyclic process for the preparation of oximes from hydroxylamine of a hydroxyl-ammonium salt is carried out in an acidic, buffered, aqueous reaction medium containing buffer acids such as phosphoric acid, bisulfate or buffer salts derived from these acids and mixtures thereof. The reaction medium is circulated between a hydroxyl-ammonium salt synthesis zone, where nitrate ions, which have been added to the reaction medium, are catalytically reduced with molecular H₂ to hydroxylamine, and an oximation zone where a ketone is added to react with the hydroxyl-

ammonium salt to produce an oxime. The nitrate ions consumed in the hydroxyl-ammonium synthesis zone are added to the circulating reaction medium just before the reaction medium is introduced into the hydroxyl-ammonium salt synthesis zone. The nitrate ions are generally added in the form of nitric acid of approx-

imately 60 weight percent.

The nitrate ions in the hydroxylamine synthesis zone are first converted into hydroxylamine which in turn reacts with the available buffer acid in the reaction medium, forming the corresponding hydroxyl-ammonium salt. The resulting solution obtained, containing hydroxyl-ammonium salt, is withdrawn from the hydroxylamine synthesis zone and circulated to the oximation zone, where the hydroxyl-ammonium salt, together with a ketone, which is also fed to the oximation zone, forms the corresponding oxime, with liberation of acid. The oxime is removed from the oxime synthesis zone. The reaction medium withdrawn from the oxidation zone contains small amounts of oxime and ketone. This aqueous reaction medium is then returned to the hydroxylamine synthesis zone.

Following the make-up of HNO₃, a solution is again available which, after removal of both the water formed by the reaction and the water introduced with the nitric acid make-up, will, theoretically, have the same composition as the initial solution used for the formation of hydroxyl-ammonium salt. This solution is then circulated back to the hydroxylamine synthesis zone. The reduction of the nitrate ions in the hydroxyl-

amine synthesis zone is accomplished in the presence of a catalyst; usually a palladium catalyst is used although a palladium-platinum alloy catalyst can be used.

The palladium is suspended on a carrier material of carbon or aluminum oxide. The carrier material is usually loaded to a desired degree, for instance, 5-20 weight percent of palladium, based on the carrier.

Organic substances, such as the ketone which is to be converted into oxime, and the resulting oxime itself, have an adverse effect on the activity of the catalyst if allowed to come into contact with the catalyst. To prevent the catalyst from being poisoned by these compounds, the circulating reaction medium must be purged of the ketone and oxime contaminants prior to its entering the hydroxylamine synthesis zone. The ketone and oxime content of the reaction medium should preferably be reduced to a value of not more

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than 0.02% by weight before the reaction medium is recirculated to the hydroxylamine synthesis zone.

The invention is directed to a cyclic process for undertaking those three reactions. The cyclic process of the invention is directed to an improvement in a process which comprises recycling an acidic aqueous buffer reaction medium which contains an ammonium salt as the buffer salt from a zone in which the step of catalytically reducing nitrate ions to hydroxyl-ammonium ions (the acid salt of hydroxylamine) is undertaken to a zone in which said hydroxyl ammonium ions react with cyclohexanone to form cyclohexanone oxime, wherein the required amount of nitrate (ions) and cyclohexanone are fed to the respective zones and wherein cyclohexanone oxime is discharged from the zone in which it is produced. The improvement of the invention comprises heating at least a portion of that liquid which is recycled between the two aforementioned zones to a temperature of at least 120° C, at an absolute pressure which is greater than one pressure absolute and in the presence of nitrous gases, wherein heating is undertaken after the liquid has been discharged from the zone in which cyclohexanone oxime is synthesized and before the liquid is fed into that zone in which hydroxyl-ammonium salt is produced. This heating step can be undertaken periodically in the continuous process of recycling said liquid.

The temperature in the hydroxylamine synthesis zone ranges from about 40° to about 100° C, while the temperature in the oxime synthesis zone ranges from 40° to 90° C. These two zones may be maintained at atmospheric, sub-atmospheric or at elevated pressures.

The heat treatment according to the invention may be carried out at various temperatures over 120° C. The heat treatment, in accordance with the invention, is undertaken at elevated pressure. The elevated pressure is chosen, in relation to the temperature of the heat treatment, to maintain the recycled liquid in the liquid state. As the temperature chosen for heat treatment increases, it is obvious that correspondingly higher pressures will have to be used in order to keep the recycling liquid to be treated in the liquid state. For practical purposes it suffices to use temperatures not exceeding 175° C. At temperatures between 120° and 175° C the required pressure varies between about 1.1 and about 7 atmospheres gauge.

Periodic treatment of the whole volume of the recycling liquid in the process according to the invention has the drawback that the required composition of the total recycling liquid is changed intermittently, which renders undertaking the recycling of the liquid through the two zones in a continuous way more complex. Thus, preferably part of the recycling liquid is always subjected to the heat treatment; e.g. 4-20% of the total recycling liquid. Suitably, an amount of 5-12% of the total recycling liquid is subjected to the heat treatment of the invention.

During the heat treatment according to the invention, the recycling liquid should be contacted with nitrous gases. The terminology "nitrous gases" here denotes gas containing nitrogen dioxide, in which the nitrogen dioxide can be formed in situ, e.g. from nitrogen monoxide and oxygen, and in which also an inert gas, such as, e.g., nitrogen, may be present. The nitrogen dioxide can optionally be admixed with nitrogen monoxide. Preferably nitrous gases which contain 0.4 - 2.5 moles of nitrogen monoxide per mole of nitrogen dioxide are employed. A mixture of this type can be

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obtained by known methods by catalytic combustion of ammonia with air or by reaction of the acid, e.g. the acid recycling liquid, with an alkali nitrite.

The amount of nitrous gases which is contacted with the recycling liquid to be treated should naturally be greater than the amount consumed in the decomposition of the ammonium ions according to the above-mentioned reaction equation. Very suitable results can be obtained in practice if the partial nitrous pressure (sum of partial pressures of nitrogen dioxide and nitrogen monoxide) has a value which is higher than the nitrous-gas pressure of nitric acid at a temperature corresponding to the temperature at which the heat treatment is effected. At temperatures ranging between 120° and 175° C, this nitrous-gas pressure exceeds 0.15 atmosphere.

An embodiment of the process according to the invention is shown in a simplified way in the Drawing.

DESCRIPTION OF THE DRAWING

In this FIGURE, A and B denote the zone for the synthesis of hydroxyl-ammonium salt and the zone for the synthesis of cyclohexanone oxime, respectively. Hydrogen is fed through conduit 1 to zone A, in which a catalyst containing palladium is suspended in the reaction medium. Hydrogen that has not reacted and other vent gases, if any, are removed through conduit 2. Through conduit 3, zone A is fed with the recycled reaction medium, which, after being enriched with hydroxyl-ammonium salt, is passed into zone B for the synthesis of cyclohexanone oxime through conduit 3. Cyclohexanone, which can optionally be dissolved in an organic solvent which is a solvent for cyclohexanone and cyclohexanone oxime (e.g. toluene, benzene, xylenes, cyclohexane and methylcyclopentane), is fed to zone B through conduit 4, while the resulting cyclohexanone oxime, optionally in solution in the organic solvent, is discharged through conduit 5. The recycling liquid is returned to the zone A for the synthesis of hydroxylamine through conduits 6, 7 and 8.

A part flow of the recycling process liquor is passed into a column C by way of control valve 14 and a conduit 9, and subsequently returned to the zone A for the synthesis of hydroxyl amine by way of conduit 10, reaction vessel D, a condensor 15, and conduit 8. Nitrous gases are fed to the system through conduit 11. The greater part of the amount of nitrous gases fed in are passed through valve 11a and conduit 12 into absorption column C, where they are absorbed at a comparatively low temperature, e.g. 40°-60° C with simultaneous formation of nitric acid. The remaining part of the amount of nitrous gases supplied through conduit 11 is passed, via valve 11b, into reaction vessel D, which is kept at an absolute pressure of at least 1 atmosphere and a temperature of over 120° C, e.g. 120°-175° C, and where the decomposition of the compounds that are poisonous to the catalyst is effected by the presence of nitrous gases. The amount of nitrous gases to be fed to the column C and the reaction vessel D can be controlled in a simple way by adjustment of the valves 11a and 11b. If so desired, the nitrous gases to be introduced into reaction vessel D may be absorbed separately, at a temperature below 60° C, in liquid from absorption column C, and the liquid enriched with nitrous gases which is so obtained be passed into the reaction vessel D. This vessel may then be designed to have a smaller size.

It is also possible to feed the total amount of nitrous gases to reaction vessel D. The amount of nitrous gases will then have to be such that a sufficiently large amount flows from reaction vessel D through conduit 12 to absorption column C in order to form the required amount of nitric acid. Non-absorbed gases are discharged through reducing valve 13.

The reaction products formed in reaction vessel D are mainly monocarboxylic and dicarboxylic acids which have no poisonous effect on the catalyst. The content of these compounds in the recycling liquid remains at a low level, as these compounds are largely removed through conduit 5 together with the cyclohexanone oxime formed. The invention is further elucidated by the following example.

EXAMPLE

In the continuous preparation of cyclohexanone oxime according to the diagram shown in the FIGURE, in which the catalyst used in zone A was palladium on coal with 10% by weight of palladium, the composition of the liquid flowing through conduit 6 (at the rate of 16.7 kilograms per hour) was:

$\text{H}_3\text{PO}_4 = 1.13$ moles per kilogram

$\text{NH}_4\text{H}_2\text{PO}_4 = 1.01$ moles per kilogram

$\text{NH}_4\text{NO}_3 = 1.39$ moles per kilogram

$(\text{NH}_4\text{OH})_2\text{PO}_4 = 0.02$ mole per kilogram

$\text{H}_2\text{O} = 36.55$ moles per kilogram

The total amount of organic compounds contained in this liquid as impurities was 400 parts by weight per million, calculated as carbon. Of the total amount, 1 p.p.m. related to cyclohexanone oxime, 17 p.p.m. to cyclohexylamine, 80 p.p.m. to carboxylic acids, and 302 p.p.m. to unknown amine compounds.

An amount of about 6% of the liquid flow through conduit 6 was passed into absorption column C through control valve 14 and conduit 9, and subsequently into reaction vessel D by way of conduit 10. Through conduit 11 and the opened valve 11b, 740 liters/h of nitrous gases were passed into reaction vessel D and, subsequently, through conduit 12, into absorption column C. The gas supplied through conduit 11 had an absolute pressure of 6-7 atmospheres and its composition was:

5.2% by volume of NO

5.1% by volume of NO_2

10% by volume of O_2

79.9% by volume of N_2

The temperature in reaction vessel D was kept at 125° C by means of steam heating (not shown). The temperature in absorption column C was kept at about 40° C by means of a cooler (not shown). The absolute pressure in columns D and C was 6-7 atmospheres. The vent gas discharged through reducing valve 13 had the composition:

0.1% by volume of NO

0.005% by volume of N_2O

6.1% by volume of O_2

6.2% by volume of H_2O

87.6% by volume of N_2

The liquid discharged from reaction vessel D through conduit 8 contained:

$\text{H}_2\text{O} = 23$ moles per kilogram

$\text{HNO}_3 = 6.15$ moles per kilogram

$\text{H}_3\text{PO}_4 = 1.01$ moles per kilogram

In addition, this liquid contained 260 p.p.m. of organic compounds (calculated as carbon), 258 p.p.m. of which in the form of harmless carboxylic acids. Cyclo-

hexanone oxime and cyclohexylamine could no longer be detected in this liquid.

What is claimed is:

1. In a cyclic process for producing cyclohexanone oxime, comprising recycling an acidic buffered aqueous reaction medium containing an ammonium salt as a buffer salt between a zone (A) for the synthesis of hydroxyl-ammonium salt, in which zone hydroxyl-ammonium ions are formed by catalytic reduction of nitrate ions and a zone (B) for the synthesis of cyclohexanone oxime, in which zone the resulting hydroxyl-ammonium ions react with cyclohexanone to form cyclohexanone oxime; wherein nitrate ions and cyclohexanone are fed to zones A and B, respectively, and wherein cyclohexanone oxime is discharged from zone (B); and wherein the said recycled reaction medium is treated after leaving zone (B) and before it is fed back into zone (A) to remove residual amounts of cyclohexanone and cyclohexanone oxime, the improvement consisting of heating at least a portion of said recycled liquid at a temperature of at least 120° C, in the presence of nitrous gases, and at an absolute pressure of over 1 atmosphere, after said recycled liquid has been discharged from zone (B) and before it is fed to the zone for the synthesis of hydroxyl-ammonium salt (A).

2. The process according to claim 1, wherein 5 to 12% of the recycling liquid is subjected to said heat treatment, continuously.

3. In a cyclic process for producing cyclohexanone oxime, comprising recycling an acidic buffered aqueous reaction medium containing an ammonium salt as a buffer salt between a zone (A) for the synthesis of hydroxyl-ammonium salt, in which zone hydroxyl-ammonium ions are formed by catalytic reduction of nitrate ions and a zone (B) for the synthesis of cyclohexanone oxime, in which zone the resulting hydroxyl-ammonium ions react with cyclohexanone to form cyclohexanone oxime; wherein nitrate ions and cyclohexanone are fed to zones A and B, respectively, and wherein cyclohexanone oxime is discharged from zone (B); and wherein the said recycled reaction medium is treated after leaving zone (B) and before it is fed back into zone (A) to remove residual amounts of cyclohexanone and cyclohexanone oxime, the improvement consisting of heating at least a portion of said recycled liquid periodically at a temperature of at least 120° C, in the presence of nitrous gases, and at an absolute pressure of over 1 atmosphere, after said recycled liquid has been discharged from zone (B) and before it is fed to the zone for the synthesis of hydroxyl-ammonium salt (A).

4. The process according to claim 1, wherein said nitrous gases comprise a nitrogen dioxide and nitrogen monoxide, wherein said nitrogen monoxide is present in an amount ranging from between 0.4 to 2.5 moles per mole of nitrogen dioxide.

5. The process according to claim 1, wherein only a portion of said recycled liquid is subjected to said heating step.

6. The process according to claim 5, wherein 20% of said recycling liquid is subjected to the heating step.

7. The process according to claim 5, wherein said heating step is undertaken periodically in the continuous process of recycling said liquid.

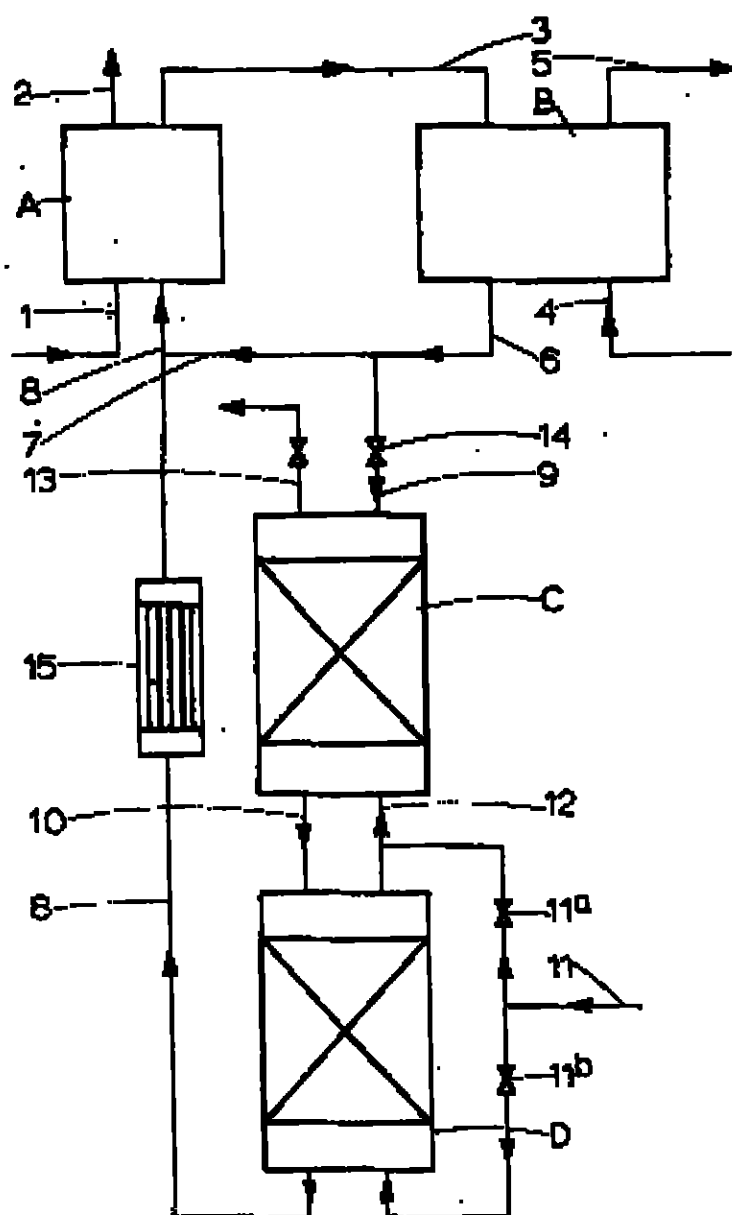
8. The process according to claim 3, wherein the whole volume of the recycling liquid is subjected to said heating step.

* * * * *

U.S. Patent

Dec. 14, 1976

3,997,607



PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

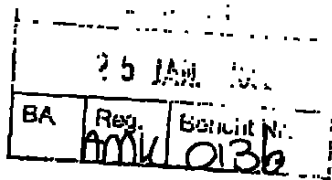
PCT

To:

DAUTZENBERG, Joseph M. A.
DSM PATENTS & TRADEMARKS
P.O. BOX 9
NL-6160 MA Geleen
PAYS-BAS

WRITTEN OPINION

(PCT Rule 66)



Date of mailing
(day/month/year)

23/01/2002

Applicant's or agent's file reference

20318WO/PO/

REPLY DUE

within 2 / 00 months/days
from the above date of mailing

International application No.

PCT/NL 01/ 00427

International filing date (day/month/year)

31/05/2001

Priority date (day/month/year)

05/06/2000

International Patent Classification (IPC) or both national classification and IPC

C07C249/08

Applicant

DSM N.V et al.

1. This written opinion is the first drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also For an additional opportunity to submit amendments, see Rule 66.4. For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4b. For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 05/10/2002

Name and mailing address of the IPEA/



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Examiner

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WRITTEN OPINION

International application No. PCT/NL 01/ 00427

I. Basis of the opinion

1. The basis of this written opinion is the application as originally filed.

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

2. The question of whether the claimed invention appears to be novel, to involve an inventive step, or to be industrially applicable has not been and will not be the subject of the international preliminary examination (Article 34 (4) (a) (i) (ii) PCT; see also international search report) in respect of:
 - 2.1 Applications having an unnecessary plurality of independent claims (generally not more than 1 independent claim in the same category is necessary; Article 6 PCT);
 - 2.2 unsearched subject-matter (Article 17 (2) (a), Rule 66.1 (e) PCT), e.g.
 - 2.2.1 claimed subject-matter under Rule 39.1 PCT,
 - 2.2.2 applications where the description, the claims, or the drawings fail to comply with the prescribed requirements to such an extent that no meaningful search could have been carried out;
 - 2.3 claimed subject-matter under Rule 67.1 PCT.

V. Reasoned statement under Rule 66.2(a)(II) with regard to novelty, inventive step or industrial applicability

3. To the extent that the international preliminary examination has been carried out (see item III above), the following is pointed out:

In light of the documents cited in the international search report, it is considered that the invention as claimed in at least one of the independent claims does not appear to meet the criteria mentioned in Article 33 (1) PCT, i.e. does not appear to be novel and/or to involve an inventive step.

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4. If amendments are filed, the Applicant must comply with the requirements of Rule 66.8 PCT and indicate the basis in the originally filed application of the amendments made (Article 34 (2) (b) PCT) otherwise these amendments will not be taken into consideration for the establishment of international preliminary examination. The attention of the applicant is drawn to the fact that if the application contains an unjustified plurality of independent claims no examination of any of the claims will be carried out.

PATENT COOPERATION TREATY

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

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18 APR. 2002

Patent Nr.
7335

PCT

WRITTEN OPINION

(PCT Rule 66)

Applicant's or agent's file reference 20318WO/POI		Date of mailing (day/month/year) 18.04.2002
International application No. PCT/NL01/00427	International filing date (day/month/year) 31/05/2001	Priority date (day/month/year) 05/06/2000
International Patent Classification (IPC) or both national classification and IPC C07C249/08		
Applicant DSM N.V et al.		

- This written opinion is the first drawn up by this International Preliminary Examining Authority.
- This opinion contains indications relating to the following items:
 - ☒ Basis of the opinion
 - ☐ Priority
 - ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - ☐ Lack of unity of invention
 - ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - ☐ Certain document cited
 - ☐ Certain defects in the international application
 - ☐ Certain observations on the international application
- The applicant is hereby invited to reply to this opinion.

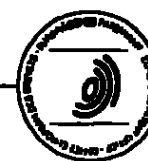
When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4. For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis. For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.
- The final date by which the international preliminary examination report must be established according to Rule 66.2 is: 05/10/2002.

Name and mailing address of the international preliminary examining authority:  European Patent Office D-80288 Munich Tel. +49 89 2399 - 0 Tx: 523856 epmu d Fax: +49 89 2399 - 4465	Authorized officer / Examiner Janus, S Formalities officer (incl. extension of time limits) Roche, S Telephone No. +49 89 2399 8031
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WRITTEN OPINION

International application No. PCT/NL01/00427

I. Basis of the opinion

1. With regard to the elements of the international application (Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed"):

Description, pages:

1-16 as originally filed

Claims, No.:

1-11 as originally filed

Drawings, sheets:

1/1 as originally filed

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

WRITTEN OPINION

International application No. **PCT/NL01/00427**

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):
(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Rule 66.2(a)(II) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement
- | | | |
|-------------------------------|--------|------|
| Novelty (N) | Claims | 1-10 |
| Inventive step (IS) | Claims | 11 |
| Industrial applicability (IA) | Claims | |
2. Citations and explanations
see separate sheet

- 1.1 GB-A-1,138,750 (D1) discloses (see claim 1) a continuous process for the preparation of cyclohexanone oxime from cyclohexanone and hydroxylammonium in an organic solvent, wherein the aqueous hydroxylammonium is present in a phosphate buffer solution. In examples II and III, a solution comprising much more than 1 mole/l of hydroxylammonium is fed in the reaction zone.

This prior process is considered to anticipate the subject-matter of present claims 1-10 (Art. 33.2 PCT).

- 1.2 US-A-3,720,758 (D2) discloses a process for the preparation of concentrated aqueous hydroxylammonium solutions to be used in known processes, such as that of D1 (see in particular example II which refers back to D1 and also relates to a feed hydroxylammonium solution with a concentration above 1 mol/l).

Claims 1-10 are therefore regarded as lacking novelty over D2 as well (Art. 33.2 PCT).

2. Claim 11 is novel over D1 and D2, but only due to the fact that the hydroxylammonium concentration in the aqueous stream leaving the reaction zone is not indicated in D1/D2, reason for which it has been assumed that this compound could not be detected in these prior processes. Therefore, the processes of these documents are regarded as superior in performance over that of claim 11, reason for which inventive step cannot be acknowledged for this subject-matter (Art. 33.3 PCT).

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

DAUTZENBERG, Joseph M. A.
DSM Patents & Trademarks
P.O. BOX 9
NL-6180 MA Geleen
PAYS-BAS

DSM P&T		
17 SEP. 2002		
BA	Rec.	Bericht Nr. 6222

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing (day/month/year)	13.09.2002
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Applicant's or agent's file reference 20318WO/PO/
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IMPORTANT NOTIFICATION

International application No. PCT/NL01/00427

International filing date (day/month/year) 31/05/2001
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Priority date (day/month/year) 05/06/2000
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Applicant DSM N.V et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the International application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

For the purpose of deciding whether the claimed invention is patentable or not, the elected Offices may apply criteria additional to or different from the criteria on which the international preliminary examination report is based (see Articles 27(5), 33(5)). Additional criteria may include e.g. exemptions from patentability and the requirements of enabling disclosure and of clarity and support of claims.

Name and mailing address of the IPEA/  European Patent Office D-80288 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465

Authorized officer Roche, S Tel. +49 89 2399-8031	
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 20318WO/PO/		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NL01/00427	International filing date (day/month/year) 31/05/2001	Priority date (day/month/year) 05/08/2000	
International Patent Classification (IPC) or national classification and IPC C07C249/08			
Applicant DSM N.V et al.			
1. This International preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of 4 sheets, including this cover sheet. ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT). These annexes consist of a total of sheets.			
3. This report contains indications relating to the following items: - I ☒ Basis of the report - II ☐ Priority - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability - IV ☐ Lack of unity of invention - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement - VI ☐ Certain documents cited - VII ☐ Certain defects in the international application - VIII ☐ Certain observations on the international application			
Date of submission of the demand 18/12/2001		Date of completion of this report 13.09.2002	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523655 epmu d Fax: +49 89 2399 - 4485		Authorized officer Janus, S Telephone No. +49 89 2399 8333 	

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL01/00427

I. Basis of the report

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17):* Description, pages:

1-16 as originally filed

Claims, No.:

1-11 as originally filed

Drawings, sheets:

1/1 as originally filed

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/NL01/00427**

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):
(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	11
	No:	Claims	1-10
Inventive step (IS)	Yes:	Claims	
	No:	Claims	11
Industrial applicability (IA)	Yes:	Claims	1-11
	No:	Claims	

2. Citations and explanations
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NL01/00427

- 1.1 GB-A-1,138,750 (D1) discloses (see claim 1) a continuous process for the preparation of cyclohexanone oxime from cyclohexanone and hydroxylammonium in an organic solvent, wherein the aqueous hydroxylammonium is present in a phosphate buffer solution. In examples II and III, a solution comprising much more than 1 mole/l of hydroxylammonium is fed in the reaction zone.

This prior process is considered to anticipate the subject-matter of present claims 1-10 (Art. 33.2 PCT).

- 1.2 US-A-3,720,758 (D2) discloses a process for the preparation of concentrated aqueous hydroxylammonium solutions to be used in known processes, such as that of D1 (see in particular example II which refers back to D1 and also relates to a feed hydroxylammonium solution with a concentration above 1 mol/l).

Claims 1-10 are therefore regarded as lacking novelty over D2 as well (Art. 33.2 PCT).

2. Claim 11 is novel over D1 and D2, but only due to the fact that the hydroxylammonium concentration in the aqueous stream leaving the reaction zone is not indicated in D1/D2, reason for which it has been assumed that this compound could not be detected in these prior processes. Therefore, the processes of these documents are regarded as superior in performance over that of claim 11, reason for which inventive step cannot be acknowledged for this subject-matter (Art. 33.3 PCT).

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TRATADO DE COOPERACION EN MATERIA DE PATENTES

PCT

INF RME EXAMEN PRELIMINAR INTERNACIONAL

(PCT artículo 36 y regla 70)

Referencia del solicitante o agente 20318WO/PO/	PARA PROSEGUIR Ver notificación de la transmisión del examen preliminar internacional (formato PCT/IPEA/416)	
No. Solicitud Internacional PCT/NL01/00427	Fecha de presentación internacional (día/mes/año) 31/05/2001	Fecha de prioridad (día/mes/año) 05/06/2000
Clasificación Internacional de Patentes (IPC) o clasificación nacional e IPC C07C249/08		
Solicitante DSM N.V et al.		

1. Este examen preliminar internacional ha sido preparado por esta Autoridad encargada del Examen Preliminar Internacional y es transmitida al solicitante de acuerdo con el artículo 36.
2. Este INFORME consiste de un total de 4 páginas, incluyendo esta hoja.

Este informe también está acompañado por ANEXOS, esto es hojas de la descripción, reivindicaciones y/o dibujos, los cuales han sido modificados y son la base para este informe y/o hojas que contienen rectificaciones presentadas ante esta Autoridad (ver Regla 70.16 y Sección 607 de las Instrucciones Administrativas bajo el PCT).

Estos anexos consisten en un total de ___ hojas.

3. Este informe contiene indicaciones que se relacionan con los siguientes puntos:
 - I. ☒ Base del Informe
 - II. ☐ Prioridad
 - III. ☐ El no-establecimiento de opinión en relación con la novedad, nivel inventivo y aplicación industrial
 - IV. ☐ Falta de unidad de invención
 - V. ☒ Declaración motivada bajo el Art. 35(2) con relación a la novedad, nivel inventivo o aplicación industrial; citaciones y explicaciones que soportan dicha declaración
 - VI. ☐ Ciertos documentos citados
 - VII. ☐ Ciertos defectos en la solicitud internacional
 - VIII. ☐ Ciertas observaciones en la solicitud internacional

Fecha de presentación de la demanda 18/12/2001	Fecha en que se completó este informe 13.09.2002
Nombre y dirección de la autoridad encargada del examen preliminar internacional: Oficina de Patentes Europea D-80298 Munich Tel. +49 89 2399-0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Oficial autorizado JANUS, S Teléfono: +49 89 2399 8333

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**INFORME DEL EXAMEN
PRELIMINAR INTERNACIONAL**

Solicitud internacional No. PCT/NL01/00427

I. BASE DEL INFORME

1. En relación con los elementos de la solicitud internacional (las hojas de reemplazo que han sido suministradas a la oficina receptora como respuesta a la invitación bajo el artículo 14 serán referidas como "presentadas originalmente" y no están anexas a este Informe debido a que no contienen modificaciones (Regla 70.16 y 70.17)):

CAPITULO DESCRIPTIVO, PAGINAS:

1-16 Como fueron presentadas originalmente

REIVINDICACIONES, No.:

1-11 Como fueron presentadas originalmente

DIBUJOS, HOJAS:

1/1 Como fueron presentadas originalmente

2. En relación con el idioma, todos los elementos marcados anteriormente fueron suministrados a esta Autoridad en el idioma en que la solicitud internacional fue presentada, a menos que se indique lo contrario bajo este punto.

Estos elementos fueron suministrados o estaban disponibles para esta autoridad en el siguiente idioma, el cual es:

☐ El idioma de la traducción aportada a efectos de la búsqueda internacional (bajo la Regla 23.1(b))

☐ El idioma de publicación de la solicitud internacional (bajo la Regla 48.3(b))

☐ El idioma de la traducción suministrada para efecto del examen preliminar internacional (bajo la Regla 55.2 y/o 55.3)

3. Respecto a cualquier secuencia nucleótido y/o aminoácido revelado en la solicitud internacional, el examen preliminar internacional fue llevado a cabo con base en la lista de secuencias:

☐ Contenidas en la solicitud internacional de forma escrita

☐ Presentadas junto con la solicitud internacional en forma legible por computador

☐ Aportada posteriormente a esta Autoridad en forma escrita

☐ Suministrada posteriormente a esta Autoridad en forma legible por computador

☐ La declaración de que la lista de secuencias aportada posteriormente en forma escrita no va más allá que lo revelado en la solicitud internacional como fue presentada.

☐ La declaración de que la información inscrita en forma legible por computador es idéntica a la lista de secuencias en forma escrita aportada.

4. Las modificaciones han resultado en la cancelación de:

☐ El capítulo descriptivo páginas:

☐ Las reivindicaciones Nos.:

☐ Los dibujos hojas:

INFORME DEL EXAMEN
PRELIMINAR INTERNACIONAL

Solicitud internacional No. PCT/NL01/00427

5. ____ Este informe ha sido establecido como si (algunas de) las modificaciones no hubieran sido efectuadas debido a que se ha considerado que van más allá de lo reivindicado mediante la solicitud internacional.

(A cualquier hoja de reemplazo que contenga dichas modificaciones debe hacerse referencia bajo el punto 1 y ser anexada a este informe)

6. Observaciones adicionales, si necesarias:

V. Declaración motivada, bajo el Art. 35(2) con relación a la novedad, nivel inventivo o aplicación industrial; citas y explicaciones que sustentan dicha declaración

1. Declaración

Novedad

SI: Reivindicaciones 11

NO: Reivindicaciones 1-10

Nivel inventivo

SI: Reivindicaciones

NO: Reivindicaciones 11

Aplicación industrial

SI: Reivindicaciones 1-11

NO: Reivindicaciones

2. Citas y explicaciones

Ver hoja anexa

**INFORME DEL EXAMEN
PRELIMINAR INTERNACIONAL**

Solicitud internacional No. PCT/NL01/00427

- 49
- 1.1 GB-A-1,138,750 (D1) revela (ver reivindicación 1) un proceso continuo para la preparación de la oxima ciclohexanona de ciclohexanona e hidroxilammonio en un solvente orgánico, en donde el hidroxilammonio acuoso está presente en una solución amortiguadora de fosfato. En los ejemplos II y III, una solución que comprende mucho más que 1 mol/l de hidroxilammonio es suministrado a la zona de reacción.

El proceso de esta anterioridad se considera como una anticipación de la materia de las reivindicaciones 1-10 de la presente solicitud de patente (Art. 33.2 PCT).

- 1.2 US-A-3,720,758 (D2) revela un proceso para la preparación de soluciones hidroxilammonio acuoso concentradas para ser utilizadas en procesos conocidos, tal como el de D1 (ver especialmente el ejemplo II el cual hace referencia a D1 y también se relaciona a una solución hidroxilammonio suministrada con una concentración superior a 1 mol/l).

2. La reivindicación 11 es novedosa al ser comparada con D1 y D2, pero únicamente debido al hecho que la concentración hidroxilammonio en la corriente acuosa que deja la zona de reacción no es indicada en D1 ni D2, razón por la cual se ha asumido que este compuesto no podría detectarse en los procesos de estas anterioridades. Por lo tanto, los procesos de estos documentos son considerados como superiores en cuanto a su desempeño al compararse con la reivindicación 11, razón por la cual no se reconoce que haya nivel inventivo sobre esta materia (Art. 33.3 PCT).

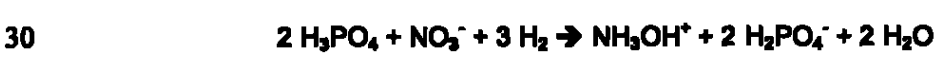
PROCEDIMIENTO PARA LA PRODUCCIÓN DE LA OXIMA DE LA CICLOHEXANONA

La invención se refiere a un procedimiento para la producción de la oxima de la ciclohexanona, en el cual un medio de reacción acuoso que contiene fosfato se somete a un ciclo de operaciones desde una zona de síntesis de hidroxilamonio hasta una zona de síntesis de la oxima de la ciclohexanona y retorno a la zona de síntesis del hidroxilamonio, en cuya zona de síntesis del hidroxilamonio se forma el hidroxilamonio por reducción catalítica de nitrato con hidrógeno, y en cuya zona de síntesis de la oxima de la ciclohexanona se hace reaccionar el hidroxilamonio con ciclohexanona en presencia de un disolvente orgánico para formar la oxima de la ciclohexanona.

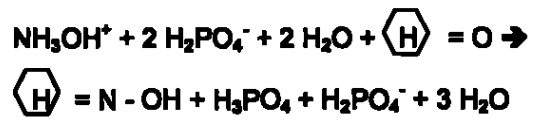
Tal procedimiento es conocido a partir del documento US-A-3.997.607 que describe un procedimiento para la producción de la oxima de la ciclohexanona, en el cual un medio de reacción acuoso, tamponado, que contiene ácidos o sales ácidas tampón, por ejemplo tampones de fosfato, se recircula de modo continuo entre una zona de síntesis de hidroxilamonio, en la cual los iones nitrato se reducen catalíticamente con hidrógeno molecular hasta hidroxilamonio, y una zona de oximación en la que la ciclohexanona, se convierte en la oxima de la ciclohexanona. Antes de que se haga pasar el medio de reacción acuoso a la zona de síntesis de hidroxilamonio, dicho medio es enriquecido con los iones nitrato necesarios por medio de la adición de ácido nítrico o por absorción de gases nitrosos en el medio de reacción acuoso en cuyo caso el ácido nítrico se forma *in situ*. Después de haber sido enriquecido en hidroxilamonio en la zona de síntesis del hidroxilamonio, se hace pasar el medio de reacción acuoso a la zona de síntesis de la oxima, en la que el hidroxilamonio reacciona con la ciclohexanona, formando la correspondiente oxima. Se puede separar entonces la oxima del medio de reacción acuoso, el cual se recircula a la zona de síntesis del hidroxilamonio.

Las reacciones químicas netas que tienen lugar durante el procedimiento se pueden representar por las siguientes ecuaciones:

1) Preparación del hidroxilamonio:



2) Preparación de la oxima:



3) Suministro de HNO₃ para compensar el agotamiento de la fuente de iones nitrato después de la separación de la oxima formada



En el procedimiento del documento US-A-3.997.607, el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona contiene hidroxilamonio sin convertir. Se ha descrito que el hidroxilamonio presente en el medio
5 de reacción acuoso se puede descomponer cuando el medio de reacción acuoso se somete a un tratamiento por calor en presencia de gases nitrosos a temperaturas elevadas. En el procedimiento del documento US-A-3.997.607, el tratamiento por calor se realiza para separar los contaminantes orgánicos del medio de reacción acuoso.

En un procedimiento de recirculación, es posible a menudo recircular los reactantes sin convertir, en cuyo caso una conversión incompleta no dará como resultado una pérdida de reactantes. Sin embargo, se ha encontrado en esta invención, que incluso sin el tratamiento por calor descrito en US-A-3.997.607, tiene lugar una descomposición del hidroxilamonio en el medio de reacción acuoso que se recircula desde la zona de síntesis de la oxima de la ciclohexanona hasta la zona de síntesis del hidroxilamonio. Se encuentra que la descomposición tiene lugar particularmente después de
10 15 la adición de ácido nítrico al medio de reacción acuoso o durante la formación de ácido nítrico por absorción de gases nitrosos en el medio de reacción acuoso.

Se ha encontrado en esta invención que la cantidad de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formada en la zona de síntesis del hidroxilamonio, disminuye al aumentar la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona.
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Por tanto, la invención proporciona un procedimiento para la producción de la oxima de la ciclohexanona, en el cual un medio de reacción acuoso que contiene fosfato se somete a un ciclo de operaciones desde una zona de síntesis de hidroxilamonio hasta una zona de síntesis de la oxima de la ciclohexanona y retorno a la zona de síntesis del hidroxilamonio, en cuya zona de síntesis del hidroxilamonio se forma el hidroxilamonio por reducción catalítica de nitrato con hidrógeno, y en cuya zona de síntesis de la oxima de la ciclohexanona se hace reaccionar el hidroxilamonio con ciclohexanona en presencia de un disolvente orgánico para formar la oxima de la ciclohexanona, caracterizado porque la concentración de hidroxilamonio en el medio de
25 30 reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 1,0 mol/l.

Según la invención, sólo se pierden pequeñas cantidades de hidroxilamonio a causa de la descomposición por la cantidad de hidroxilamonio formada en la zona de síntesis del hidroxilamonio (y por la cantidad de la oxima de la ciclohexanona formada
35

en la zona síntesis de la oxima de la ciclohexanona). Además se puede alcanzar una alta conversión del hidroxilamonio en la oxima de la ciclohexanona.

Según la invención, la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 1,0 mol/l. Preferiblemente, la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 1,1 mol/l, más preferiblemente, mayor que 1,2 mol/l, más preferiblemente mayor que 1,4 mol/l, y en particular mayor que 1,6 mol/l. El aumento de la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona tiene la ventaja de que la cantidad de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formada en la zona de síntesis de hidroxilamonio (y por la cantidad de la oxima de la ciclohexanona formada en la zona de síntesis de la oxima de la ciclohexanona) disminuya. Además, se aumenta la conversión del hidroxilamonio. Un aumento de la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona se puede alcanzar, por ejemplo, aumentando el tiempo de residencia en la zona de síntesis del hidroxilamonio y/o aumentando la concentración de nitrato en el medio de reacción acuoso que entra en la zona de síntesis del hidroxilamonio. No hay un límite superior específico para la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona. Generalmente, la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona está por debajo de 2,5 mol/l.

Preferiblemente, la concentración de hidroxilamonio en el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona es menor que 0,1 mol/l, más preferiblemente menor que 0,08 mol/l, en particular menor que 0,05 mol/l. La concentración de hidroxilamonio en el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona es generalmente mayor que 0,005 mol/l, en particular mayor que 0,01 mol/l. Preferiblemente la conversión del hidroxilamonio es mayor que 90 %, más preferiblemente mayor que 95 %. Como se usa aquí la conversión se define como $(c(\text{NH}_2\text{OH}^+)_{\text{entrada}} - c(\text{NH}_2\text{OH}^+)_{\text{salida}}) / c(\text{NH}_2\text{OH}^+)_{\text{entrada}} \times 100 \%$, donde $c(\text{NH}_2\text{OH}^+)_{\text{entrada}}$ representa la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona y $c(\text{NH}_2\text{OH}^+)_{\text{salida}}$ representa la concentración de hidroxilamonio en el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona.

En la zona de síntesis de la oxima de la ciclohexanona, se hace reaccionar el

hidroxilammonio con ciclohexanona en presencia de un disolvente orgánico para formar la oxima de la ciclohexanona. Típicamente, el disolvente orgánico y la ciclohexanona se añaden a la zona de síntesis de la oxima de la ciclohexanona, y un medio orgánico que comprende el disolvente orgánico y la oxima de la ciclohexanona se separa de la zona de síntesis de la oxima de la ciclohexanona. Preferiblemente, el medio de reacción acuoso y una corriente que comprende la ciclohexanona y el disolvente orgánico, se ponen en contacto en un flujo contracorriente. Un procedimiento adecuado, es por ejemplo el descrito en el documento GB-A-1.138.750. Se puede hacer uso de tipos conocidos de reactores contracorriente, tales como por ejemplo, las columnas pulsadas llenas con partículas de empaquetamiento o reactores de disco rotatorio. También es posible usar un sistema que comprende un número, por ejemplo 3 a 6, de reactores conectados en serie equipados con agitadores, estando también provistos cada uno de estos reactores de un separador líquido-líquido. Se puede usar cualquier disolvente orgánico en el que se puedan disolver la ciclohexanona y la oxima de la ciclohexanona, tal como por ejemplo alcoholes, cetonas, ésteres, éteres, hidrocarburos, y sus mezclas. Preferiblemente, el disolvente orgánico tiene una solubilidad en agua menor que 0,1 % en peso a 20 °C. Preferiblemente, el disolvente orgánico se selecciona del grupo constituido por benceno, tolueno, xileno, metilciclopentano, ciclohexano y sus mezclas. Muy preferiblemente, el disolvente orgánico es tolueno. Preferiblemente, la ciclohexanona se disuelve en el disolvente orgánico.

No hay un límite inferior específico para la concentración de la oxima de la ciclohexanona en el medio orgánico que sale de la zona de síntesis de la oxima de la ciclohexanona. Generalmente, la concentración de la oxima de la ciclohexanona en el medio orgánico que sale de la zona de síntesis de la oxima de la ciclohexanona es mayor que 5 % en peso. Preferiblemente, la concentración de la oxima de la ciclohexanona en el medio orgánico que sale de la zona de síntesis de la oxima de la ciclohexanona es mayor que 25 % en peso, más preferiblemente mayor que 30 % en peso, particularmente mayor que 35 % en peso, más particularmente mayor que 38 % en peso. El aumento de la concentración de la ciclohexanona en el medio orgánico que sale de la zona de síntesis de la oxima es un modo efectivo de separar cantidades mayores de la oxima de la ciclohexanona desde la zona de síntesis de la oxima de la ciclohexanona. Generalmente, la concentración de la oxima de la ciclohexanona en el medio orgánico que sale de la zona de síntesis de la oxima de la ciclohexanona es menor que 95 % en peso, preferiblemente menor que 80 % en peso, más preferiblemente menor que 60 % en peso. Todas las concentraciones de la oxima de la ciclohexanona en el medio orgánico se dan con relación a la suma del peso de la oxima de

la ciclohexanona más el disolvente orgánico.

La zona de síntesis de la oxima de la ciclohexanona puede hacerse funcionar a una temperatura que varía desde 40 a 150 °C y a presión atmosférica, sub-atmosférica o elevada, preferiblemente entre 0,05 y 0,5 MPa, más preferiblemente entre 0,1 y 0,2 MPa y muy preferiblemente entre 0,1 y 0,15 MPa. Preferiblemente, el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona tiene un pH entre 1 y 8, más preferiblemente entre 1,5 y 4.

En una realización preferida, la zona de síntesis de la oxima de la ciclohexanona comprende una zona de reacción en la que se hace reaccionar el hidroxilammonio con ciclohexanona para formar la oxima de la ciclohexanona, mediante poner en contacto el medio de reacción acuoso y la corriente que comprende la ciclohexanona y el disolvente orgánico en un flujo contracorriente, y una zona de extracción en la que se ponen en contacto el medio de reacción acuoso y un disolvente orgánico, preferiblemente en un flujo contracorriente, siendo añadido a la zona de reacción el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona, y siendo añadido a la zona de extracción el medio de reacción acuoso que sale de la zona de reacción. Esta realización tiene la ventaja de que los compuestos orgánicos residuales que tienen un efecto adverso sobre la actividad del catalizador, en particular la ciclohexanona y la oxima de la ciclohexanona, se separan del medio de reacción acuoso que sale de la zona de reacción. Preferiblemente, se añade ciclohexanona a la zona de síntesis de la oxima, entre la zona de reacción y la zona de extracción. Preferiblemente, el disolvente orgánico que sale de la zona de extracción se añade a la zona de reacción. Preferiblemente, se añade ciclohexanona a la zona de síntesis de la oxima de la ciclohexanona en el disolvente orgánico que entra en la zona de extracción. Se puede hacer uso de tipos conocidos de extractores, tales como por ejemplo, una columna de extracción, o uno o más reactores equipados con agitadores, opcionalmente conectados en serie, estando provistos también cada uno de estos reactores de un separador líquido-líquido. Preferiblemente, se usa una columna pulsada llena con partículas de empaquetamiento. Se hacen funcionar la zona de reacción y la zona de extracción preferiblemente a una temperatura que varía de 40 a 150 °C y a presión atmosférica, sub-atmosférica o elevada, preferiblemente entre 0,05 y 0,5 MPa, más preferiblemente entre 0,1 y 0,2 MPa y muy preferiblemente entre 0,1 y 0,15 MPa. Se puede hacer uso de tipos conocidos de extractores, tales como por ejemplo, las columnas de extracción, preferiblemente columnas pulsadas llenas con partículas de empaquetamiento, o uno o más reactores equipados con agitadores, opcionalmente conectados en serie, estando provistos también cada uno de estos reactores de un

separador líquido-líquido. Preferiblemente, el disolvente orgánico tiene una solubilidad en agua menor que 0,1 % en peso a 20 °C. Preferiblemente, el disolvente orgánico se selecciona del grupo constituido por benceno, tolueno, xileno, metilciclopentano, ciclohexano y sus mezclas. Muy preferiblemente, el disolvente orgánico es tolueno. Las condiciones de operación para la zona de reacción y la zona de extracción no son necesariamente las mismas. Preferiblemente, se usa el mismo disolvente en la zona de reacción y en la zona de extracción. Preferiblemente, el contenido conjunto de la ciclohexanona y de la oxima de la ciclohexanona en el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona es menor que 0,2 % en peso (2000 ppm), preferiblemente menor que 0,1 % en peso, más preferiblemente menor que 0,05 % en peso, particularmente menor que 0,02 % en peso, más particularmente menor que 0,01 % en peso, y muy preferiblemente menor que 0,005 % en peso (con relación al peso del medio de reacción acuoso).

Preferiblemente, el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona se somete a una o más etapas de separación antes de entrar en la zona de síntesis del hidroxilamonio para reducir la cantidad de contaminantes orgánicos, en particular ciclohexanona y la oxima de la ciclohexanona. Preferiblemente, el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona o que sale de la zona de extracción se somete a destilación para conseguir una disminución adicional de los contaminantes orgánicos. Se puede usar, por ejemplo, el procedimiento de destilación descrito en el documento US-A-3.940.442. Es preferible que el contenido conjunto de la ciclohexanona y la oxima de la ciclohexanona en el medio de reacción acuoso que entra en la zona de síntesis del hidroxilamonio no sea mayor que 0,02 % en peso (200 ppm), más preferiblemente no mayor que 0,005 % en peso, particularmente no mayor que 0,002 % en peso, más particularmente no mayor que 0,001 % en peso, y muy preferiblemente no mayor que 0,0002 % en peso (con relación al peso del medio de reacción acuoso).

Se ha encontrado en esta invención que un aumento de la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona puede dar como resultado un aumento de la concentración de contaminantes orgánicos, en particular ciclohexanona y la oxima de la ciclohexanona, en el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona. Estos contaminantes orgánicos pueden ser separados, por ejemplo, usando uno o más de los procedimientos de separación descritos anteriormente.

Se ha encontrado en esta invención que un aumento de la concentración de fosfato en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de

la ciclohexanona da como resultado una disminución de la concentración de los contaminantes orgánicos en el medio de reacción acuoso que se recircula desde la zona de síntesis de la oxima de la ciclohexanona hasta la zona de síntesis del hidroxilammonio. Generalmente, la concentración de fosfato en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 2,0 mol/l, preferiblemente mayor que 2,5 mol/l, más preferiblemente mayor que 3,0 mol/l, particularmente mayor que 3,3 mol/l, más particularmente mayor que 3,5 mol/l, y muy preferiblemente mayor que 3,7 mol/l. El aumento de la concentración de fosfato tiene la ventaja de que el efecto del aumento de la concentración de hidroxilammonio sobre la concentración de los contaminantes orgánicos en el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona se suaviza o se evita. Preferiblemente, la concentración de fosfato se elige de tal modo que no aparezca cristalización, lo que depende, entre otros, de la temperatura y de la concentración de otros componentes en el medio de reacción acuoso. Generalmente, la concentración de fosfato en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es menor que 8 mol/l, preferiblemente menor que 5 mol/l, más preferiblemente menor que 4,5 mol/l. Como se usa aquí, la concentración de fosfato indica la suma de la concentración de todos los fosfatos, sin distinción de la forma en que están presentes, expresada en moles por litro del medio de reacción acuoso. Preferiblemente, los fosfatos están presentes como PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , H_3PO_4 , sales de PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , y/o sus combinaciones. Preferiblemente, en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona, la relación $c(\text{fosfato})/c(\text{NH}_2\text{OH}^+)$ es mayor que 2,0, más preferiblemente mayor que 2,1, particularmente mayor que 2,2, más particularmente mayor que 2,3, donde $c(\text{fosfato})$ representa la concentración de fosfato (en mol/l) y $c(\text{NH}_2\text{OH}^+)$ representa la concentración de hidroxilammonio (en mol/l). Es ventajoso un aumento de esta relación, ya que éste da como resultado una disminución de la cantidad de contaminantes orgánicos que entran en la zona de síntesis del hidroxilammonio en circunstancias posteriores iguales. No hay un límite superior específico para la relación. Si la relación es demasiado alta, el procedimiento puede llegar a ser menos interesante desde un punto de vista económico. En general la relación $c(\text{fosfato})/c(\text{NH}_2\text{OH}^+)$ es menor que 10.

Se ha encontrado en esta invención que una disminución de la relación molar de (hidroxilammonio añadido a la zona de síntesis de la oxima de la ciclohexanona por unidad de tiempo)/(ciclohexanona añadida a la zona de síntesis de la oxima de la ciclohexanona por unidad de tiempo) da como resultado una disminución de la concentración de los contaminantes orgánicos en el medio de reacción acuoso que sale de la

zona de síntesis del hidroxilamonio. Preferiblemente, la relación f_h/f_c es menor que 1,00, donde f_h representa la cantidad molar de hidroxilamonio añadida a la zona de síntesis de la oxima de la ciclohexanona por unidad de tiempo (en moles por unidad de tiempo), y f_c representa la cantidad molar de ciclohexanona añadida a la zona de síntesis de la oxima de la ciclohexanona por unidad de tiempo (en moles por unidad de tiempo). Preferiblemente, la relación f_h/f_c es $< 0,99$, más preferiblemente menor que 0,98, particularmente menor que 0,97, y más particularmente menor que 0,96. La disminución de la relación tiene la ventaja de que el efecto del aumento de la concentración de hidroxilamonio sobre la concentración de los contaminantes orgánicos en el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona se suaviza o se evita. Esta disminución de las relaciones tiene como resultado una disminución adicional de la concentración de los contaminantes orgánicos en el medio de reacción acuoso que se recircula desde la zona de síntesis de la oxima de la ciclohexanona hasta la zona de síntesis del hidroxilamonio. No hay ningún límite inferior específico para la relación f_h/f_c . Generalmente, f_h/f_c es $> 0,5$, preferiblemente f_h/f_c es $> 0,7$, más preferiblemente f_h/f_c es $> 0,8$. La relación f_h/f_c deseada se puede obtener de diferentes modos. Es posible, por ejemplo, disminuir la relación aumentando el caudal de la ciclohexanona que se añade a la zona de síntesis de la oxima de la ciclohexanona con relación al caudal del medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona. Es posible también, disminuir la relación disminuyendo la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona.

Generalmente, el medio de reacción acuoso es un medio de reacción ácido, tamponado. El medio de reacción acuoso puede contener amonio (NH_4^+), por ejemplo, formado como un producto secundario en la síntesis del hidroxilamonio. Preferiblemente, en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona, la relación $c(\text{NH}_4^+)/c(\text{fosfato})$ está entre 0,1 y 3, más preferiblemente entre 0,2 y 2, y muy preferiblemente entre 0,5 y 1,5, donde $c(\text{NH}_4^+)$ representa la concentración de NH_4^+ en mol/l y $c(\text{fosfato})$ representa la concentración de fosfato en mol/l.

Generalmente, el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona contiene nitrato (NO_3^-). Preferiblemente, en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona, la relación $c(\text{NO}_3^-)/c(\text{fosfato})$ está entre 0,05 y 1, más preferiblemente entre 0,1 y 0,5, donde $c(\text{NO}_3^-)$ representa la concentración de NO_3^- en mol/l y $c(\text{fosfato})$ representa la concentración de fosfato en mol/l.

En la zona de síntesis de hidroxilamonio, el hidroxilamonio se forma por la reducción catalítica del nitrato con hidrógeno. La zona de síntesis del hidroxilamonio, puede hacerse funcionar a una temperatura que varía de 20 a 100 °C, preferiblemente 30-90 °C, más preferiblemente 40-85 °C, y a presión atmosférica, sub-atmosférica o elevada, preferiblemente entre 0,1 y 5 MPa, más preferiblemente entre 0,3 y 3 MPa y en particular entre 0,5 y 2 MPa (presión parcial de hidrógeno). Preferiblemente, el pH en la zona de síntesis del hidroxilamonio, está entre 0,5 y 8, más preferiblemente entre 1 y 4. El catalizador empleado en esta zona está generalmente presente en un intervalo entre 1 a 25 % en peso, preferiblemente entre 5 a 15 % en peso de un metal precioso, con relación al peso total del soporte más el catalizador. Preferiblemente, el catalizador es un catalizador que contiene paladio, por ejemplo un catalizador que contiene paladio o un catalizador que contiene paladio-platino, presente sobre un soporte, tal como un soporte de carbono o alúmina. Generalmente, el catalizador está presente en la zona de síntesis de hidroxilamonio en una cantidad de 0,2-5 % en peso con relación al peso del líquido total que está en el recipiente(s) del reactor de hidroxilamonio.

Breve descripción del dibujo

La Figura 1 es un diagrama esquemático de una realización del procedimiento según la presente invención.

Descripción de una realización

Con relación a la Figura 1, A representa la zona de síntesis del hidroxilamonio. Se usa una zona de síntesis de la oxima de la ciclohexanona que comprende la zona B de reacción y la zona C de extracción. A la zona A, que contiene el catalizador, se añade hidrógeno a través de la línea 1; se descarga el hidrógeno sin reaccionar, con cualquier otro gas, a través de la línea 2. El medio de reacción acuoso, que contiene, entre otros, fosfato, se añade a la zona A a través de la línea 15 y después de haber sido enriquecido en hidroxilamonio (también en amonio como un sub-producto) en la zona de síntesis del hidroxilamonio, se pasa a la zona B de reacción a través de la línea 3. La concentración de hidroxilamonio en el medio de reacción acuoso que se pasa desde la zona A a la zona B, es mayor que 1,0 mol/l. La ciclohexanona a ser convertida, se añade en un disolvente orgánico a la zona B de reacción a través de la línea 4. La ciclohexanona se introduce en el disolvente orgánico a través de la línea 7. La parte mayor de la oxima de la ciclohexanona producida y disuelta en el disolvente orgánico, se separa del sistema a través de la línea 5.

Después de salir de la zona B de reacción, el medio de reacción acuoso se pasa a la zona C de extracción a través de la línea 6. Después de salir de la zona B de reacción, el contenido de hidroxilamonio del medio de reacción acuoso ha sido reduci-

do por la reacción y contiene pequeñas cantidades de ciclohexanona y de oxima de la ciclohexanona contaminantes. El disolvente orgánico entra en la zona C de extracción a través de la línea 9. Dentro de la zona C de extracción, se separa una adicional oxima de la ciclohexanona del medio de reacción acuoso y se elimina de la zona C en el disolvente orgánico a través de la línea 8. En la zona C de extracción, se reducen los contaminantes orgánicos residuales (ciclohexanona + la oxima de la ciclohexanona) del medio de reacción acuoso.

El medio de reacción acuoso sale de la zona C de extracción a través de la línea 10 que pasa el medio de reacción acuoso hasta una columna D de destilación para una operación de separación. En esta columna, se hidroliza la oxima de la ciclohexanona a ciclohexanona, y la ciclohexanona así formada junto con la ciclohexanona que ya estaba presente, se descarga con otros materiales orgánicos y agua (por ejemplo como una mezcla azeotrópica) a través de la línea 11. El medio de reacción acuoso que está recirculando en el sistema pasa después a través de la línea 12 a la zona E. En la zona E, se produce ácido nítrico. Preferiblemente, el ácido nítrico se produce, en la zona E o después de ella, haciendo reaccionar el aire añadido a través de la línea 13 con amoníaco añadido a través de la línea 14 y con agua procedente del medio de reacción acuoso. También es posible suministrar directamente ácido nítrico al medio de reacción acuoso en lugar de producir el ácido nítrico. Con ello, se aumenta el nivel de nitrato en el medio inorgánico de la zona E. En la zona E, los iones amonio, por ejemplo formados como un sub-producto en la síntesis del hidroxilamonio, se pueden convertir por medio de gases que contienen óxidos de nitrógeno. Sin embargo, también se pueden usar otros métodos para la separación de los iones amonio. Después, el medio de reacción acuoso completa el ciclo volviendo a la zona A de síntesis del hidroxilamonio a través de la línea 15. El proceso se realiza de forma continua.

Los siguientes ejemplos específicos deben ser considerados como meramente ilustrativos y no limitantes del resto de la descripción.

EJEMPLOS 1-7

En todos los ejemplos, se usó la realización que se ilustra en la Figura 1.

30 Ejemplo 1

En la zona A de síntesis del hidroxilamonio (que contiene un catalizador (Pd al 8 % en peso y Pt al 2 % en peso, sobre soporte de carbono), funcionando a una temperatura de 50 °C a una presión de 1 MPa (presión parcial de hidrógeno)) se produjo, por unidad de tiempo, un medio de reacción acuoso que tiene la siguiente composición:

1,00 mol de $\text{NH}_2\text{OH} \cdot \text{H}_2\text{PO}_4$

1,14 mol de $\text{NH}_4\text{H}_2\text{PO}_4$

0,74 mol de H_3PO_4

1,78 mol de NH_4NO_3

43,0 mol de H_2O

5 y se añadió de forma continua (a través de la línea 3) a la zona B de reacción (una columna con empaquetamiento, pulsada, funcionando a 55 °C), junto con ciclohexanona (suministrada a través de la línea 7) y tolueno (suministrado a través de la línea 9). La relación molar f_i/f_c fue 0,95. Un medio orgánico que comprende la oxima de la ciclohexanona disuelta en tolueno se separó de la zona de síntesis del hidroxilamonio (a través de la línea 5), siendo la concentración de la oxima de la ciclohexanona del 38 % en peso (con relación a la suma de los pesos del tolueno + la oxima de la ciclohexanona). El medio de reacción acuoso que sale de la zona B, se añadió a la zona C de extracción (una columna con empaquetamiento, pulsada, funcionando a 70 °C), junto con tolueno.

15 El medio de reacción acuoso que sale de la zona C de extracción contenía 0,0475 mol/l de hidroxilamonio. Siguiendo la formación *in situ* de ácido nítrico por absorción de gases nitrosos en la planta E del ácido nítrico, no se encontró hidroxilamonio en el medio de reacción acuoso que entra en la zona A. La cantidad molar de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formado en la zona de síntesis del hidroxilamonio fue 4,75 %.

Ejemplo 2

En este ejemplo todas las condiciones son las mismas del ejemplo 1 (incluyendo la relación molar f_i/f_c y la concentración de la oxima de la ciclohexanona en el medio orgánico), excepto que el medio de reacción acuoso que sale de la zona A y entra en la zona B tenía la siguiente composición:

1,25 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$

1,25 mol de $\text{NH}_4\text{H}_2\text{PO}_4$

0,75 mol de H_3PO_4

1,75 mol de NH_4NO_3

30 40,5 mol de H_2O

El medio de reacción acuoso que sale de la zona C de extracción contenía 0,0438 mol/l de hidroxilamonio. Siguiendo la formación *in situ* de ácido nítrico por absorción de gases nitrosos en la planta E del ácido nítrico, no se encontró hidroxilamonio en el medio de reacción acuoso que entra en la zona A. La cantidad molar de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formado en la zona de síntesis del hidroxilamonio fue 3,50 %.

Ejemplo 3

En este ejemplo todas las condiciones son las mismas de los ejemplos anteriores, excepto que el medio de reacción acuoso que sale de la zona A y entra en la zona B tenía la siguiente composición:

- 5 1,33 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$
- 1,18 mol de $\text{NH}_4\text{H}_2\text{PO}_4$
- 0,71 mol de H_3PO_4
- 1,70 mol de NH_4NO_3
- 40,9 mol de H_2O

- 10 El medio de reacción acuoso que sale de la zona C de extracción contenía 0,0438 mol/l de hidroxilamonio. Siguiendo la formación *in situ* de ácido nítrico por absorción de gases nitrosos en la planta E del ácido nítrico, no se encontró hidroxilamonio en el medio de reacción acuoso que entra en la zona A. La cantidad molar de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formado en la zona de síntesis del hidroxilamonio fue 3,30 %.
- 15

Ejemplo 4

En este ejemplo todas las condiciones son las mismas de los ejemplos anteriores, excepto que el medio de reacción acuoso que sale de la zona A y entra en la zona B tenía la siguiente composición:

- 20 1,44 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$
- 1,18 mol de $\text{NH}_4\text{H}_2\text{PO}_4$
- 0,71 mol de H_3PO_4
- 1,88 mol de NH_4NO_3
- 39,3 mol de H_2O

- 25 El medio de reacción acuoso que sale de la zona C de extracción contenía 0,0463 mol/l de hidroxilamonio. Siguiendo la formación *in situ* de ácido nítrico por absorción de gases nitrosos en la planta E del ácido nítrico, no se encontró hidroxilamonio en el medio de reacción acuoso que entra en la zona A. La cantidad molar de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formado en la zona de síntesis del hidroxilamonio fue 3,22 %.
- 30

Ejemplo 5

En este ejemplo todas las condiciones son las mismas de los ejemplos anteriores, excepto que el medio de reacción acuoso que sale de la zona A y entra en la zona B tenía la siguiente composición:

- 35 1,48 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$
- 1,64 mol de $\text{NH}_4\text{H}_2\text{PO}_4$

0,69 mol de H_3PO_4
 1,41 mol de NH_4NO_3
 38,3 mol de H_2O

El medio de reacción acuoso que sale de la zona C de extracción contenía
 5 0,0375 mol/l de hidroxilamonio. Siguiendo la formación *in situ* de ácido nítrico por absorción de gases nitrosos en la planta E del ácido nítrico, no se encontró hidroxilamonio en el medio de reacción acuoso que entra en la zona A. La cantidad molar de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formado en la zona de síntesis del hidroxilamonio fue 2,54 %.

10 Ejemplo 6

En este ejemplo todas las condiciones son las mismas de los ejemplos anteriores, excepto que el medio de reacción acuoso que sale de la zona A y entra en la zona B tenía la siguiente composición:

15 1,54 mol de $NH_3OH.H_2PO_4$
 1,63 mol de $NH_4H_2PO_4$
 0,71 mol de H_3PO_4
 1,63 mol de NH_4NO_3
 37,2 mol de H_2O

El medio de reacción acuoso que sale de la zona C de extracción contenía
 20 0,0188 mol/l de hidroxilamonio. Siguiendo la formación *in situ* de ácido nítrico por absorción de gases nitrosos en la planta E del ácido nítrico, no se encontró hidroxilamonio en el medio de reacción acuoso que entra en la zona A. La cantidad molar de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formado en la zona de síntesis del hidroxilamonio fue 1,22 %.

25 Ejemplo 7

En este ejemplo todas las condiciones son las mismas de los ejemplos anteriores, excepto que el medio de reacción acuoso que sale de la zona A y entra en la zona B tenía la siguiente composición:

30 1,63 mol de $NH_3OH.H_2PO_4$
 1,65 mol de $NH_4H_2PO_4$
 0,70 mol de H_3PO_4
 1,51 mol de NH_4NO_3
 38,5 mol de H_2O

El medio de reacción acuoso que sale de la zona C de extracción contenía
 35 0,0163 mol/l de hidroxilamonio. Siguiendo la formación *in situ* de ácido nítrico por absorción de gases nitrosos en la planta E del ácido nítrico, no se encontró hidroxilamo-

nio en el medio de reacción acuoso que entra en la zona A. La cantidad molar de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formado en la zona de síntesis del hidroxilamonio fue 1,00 %.

5 Los resultados de los ejemplos 1 a 7 se han resumido en la tabla 1, que muestra la cantidad molar de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formado en la zona de síntesis del hidroxilamonio (en %) y la conversión del hidroxilamonio. Se demuestra que un aumento de la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona da como resultado una disminución de la cantidad molar
10 de hidroxilamonio perdida a causa de la descomposición por la cantidad de hidroxilamonio formado en la zona de síntesis del hidroxilamonio y un aumento de la conversión del hidroxilamonio.

Ejemplo	$c(\text{NH}_2\text{OH}^+)$ _{entrada} (mol/l)	$c(\text{NH}_2\text{OH}^+)$ _{salida} (mol/l)	Conversión de NH_2OH^+ (%)	Pérdida de NH_2OH^+ (%)
1	1,00	0,0475	95,25	4,75
2	1,25	0,0438	96,5	3,50
3	1,33	0,0438	96,7	3,30
4	1,44	0,0463	96,78	3,22
5	1,48	0,0375	97,46	2,54
6	1,54	0,0188	98,78	1,22
7	1,63	0,0163	99,0	1,00

En el texto anterior se han ilustrado y descrito realizaciones particulares de esta
15 invención. Sin embargo, los expertos en la técnica pueden entender que se pueden hacer diferentes modificaciones, sin separarse del espíritu y alcance de la invención. Por tanto, la interpretación de esta invención no debe limitarse más que por las reivindicaciones adjuntas.

REIVINDICACIONES

1. Un procedimiento para la producción de la oxima de la ciclohexanona, en el cual un medio de reacción acuoso que contiene fosfato se somete a un ciclo de operaciones desde una zona de síntesis de hidroxilamonio hasta una zona de síntesis de la oxima de la ciclohexanona y retorno a la zona de síntesis del hidroxilamonio, en cuya zona de síntesis del hidroxilamonio se forma el hidroxilamonio por reducción catalítica de nitrato con hidrógeno, y en cuya zona de síntesis de la oxima de la ciclohexanona se hace reaccionar el hidroxilamonio con ciclohexanona en presencia de un disolvente orgánico para formar la oxima de la ciclohexanona, caracterizado porque la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 1,0 mol/l.

2. Un procedimiento para la producción de la oxima de la ciclohexanona, en el cual un medio de reacción acuoso que contiene hidroxilamonio, fosfato y nitrato se añade a una zona de síntesis de la oxima de la ciclohexanona, en la que el hidroxilamonio se hace reaccionar con ciclohexanona en presencia de un disolvente orgánico para formar la oxima de la ciclohexanona, caracterizado porque la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 1,0 mol/l.

3. El procedimiento según la reivindicación 1 o la reivindicación 2, caracterizado porque la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 1,2 mol/l.

4. El procedimiento según una cualquiera de las reivindicaciones 1 a 3, caracterizado porque la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona, es mayor que 1,4 mol/l.

5. El procedimiento según una cualquiera de las reivindicaciones 1 a 4, caracterizado porque la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona, es mayor que 1,6 mol/l.

6. El procedimiento según una cualquiera de las reivindicaciones 1 a 5, caracterizado porque el medio de reacción acuoso y una corriente que comprende la ciclohexanona y el disolvente orgánico, se ponen en contacto en un flujo contracorriente.

7. El procedimiento según una cualquiera de las reivindicaciones 1 a 6, caracterizado porque el disolvente orgánico y la ciclohexanona se añaden a la zona de síntesis de la oxima de la ciclohexanona, y un medio orgánico que comprende el disolvente orgánico y la ciclohexanona, se separa de la zona de síntesis de la oxima de la ciclohexanona, siendo la concentración de la oxima de la ciclohexanona en el medio orgánico mayor que 5 % en peso.

8. El procedimiento según la reivindicación 7, caracterizado porque la concentración de la oxima de la ciclohexanona en el medio orgánico que sale de la zona de síntesis de la oxima de la ciclohexanona es mayor que 25 % en peso.

5 9. El procedimiento según una cualquiera de las reivindicaciones 1 a 8, caracterizado porque el disolvente orgánico se selecciona del grupo constituido por benceno, tolueno, xileno, metilciclopentano, ciclohexano y sus mezclas.

10. El procedimiento según una cualquiera de las reivindicaciones 1 a 9, caracterizado porque la concentración de hidroxilammonio en el medio de reacción acuoso que sale la zona de síntesis de la oxima de la ciclohexanona, es menor que 0,1 mol/l.

10 11. El procedimiento según la reivindicación 10, caracterizado porque la concentración de hidroxilammonio en el medio de reacción acuoso que sale la zona de síntesis de la oxima de la ciclohexanona está entre 0,01 y 0,05 mol/l.

RESUMEN

La invención se refiere a un procedimiento para la producción de la oxima de la ciclohexanona, en el cual un medio de reacción acuoso que contiene fosfato se somete a un ciclo de operaciones desde una zona de síntesis de hidroxilamonio hasta una zona de síntesis de la oxima de la ciclohexanona y retorno a la zona de síntesis del hidroxilamonio, en cuya zona de síntesis del hidroxilamonio se forma el hidroxilamonio por reducción catalítica de nitrato con hidrógeno, y en cuya zona de síntesis de la oxima de la ciclohexanona se hace reaccionar el hidroxilamonio con ciclohexanona para formar la oxima de la ciclohexanona, en el que la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 1,0 mol/l.

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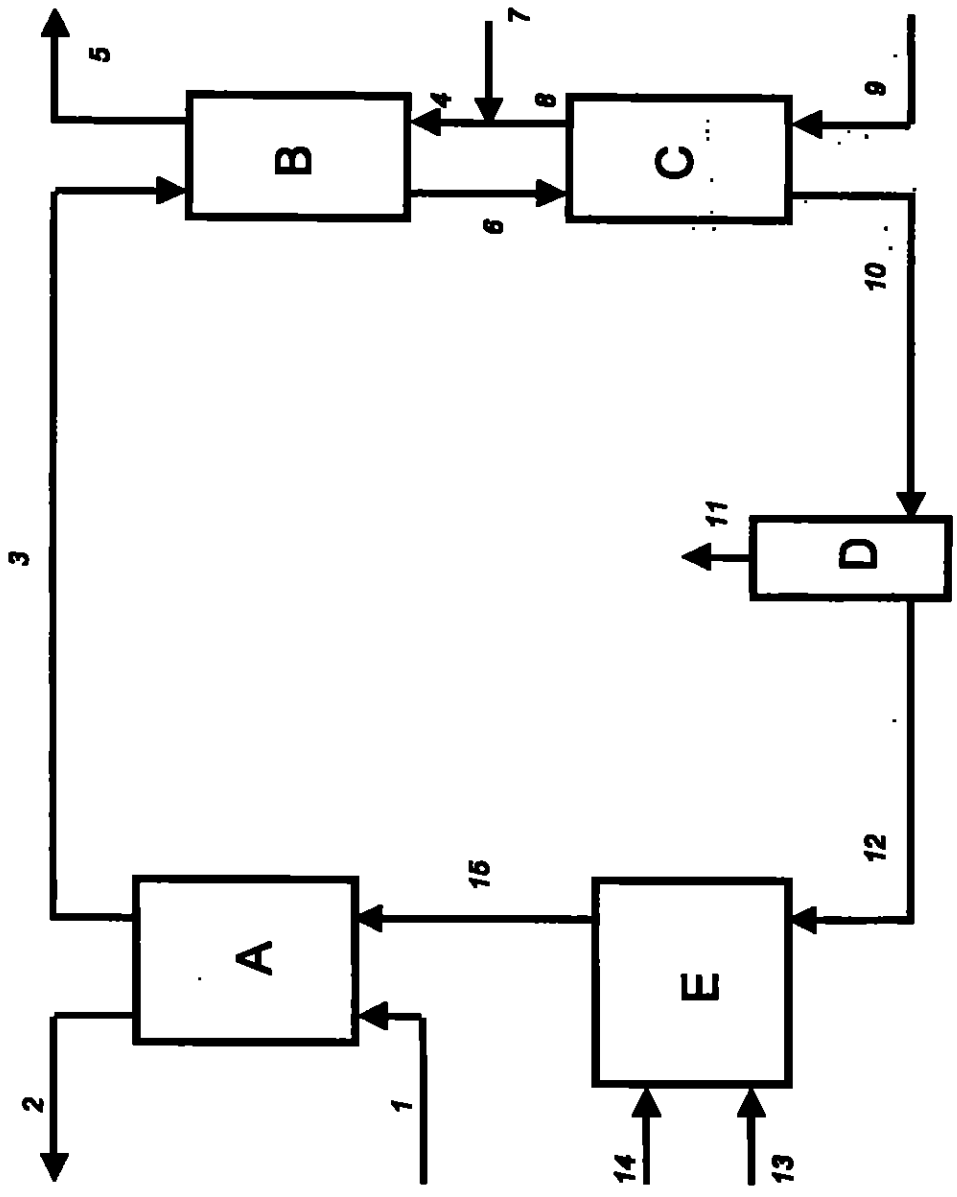


FIG. 1

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
PATENTE DE INVENCION	()	()
MODELO DE UTILIDAD	()	()
- Indicación de que se solicita la concesión de una patente.	()	()
- Datos de identificación del solicitante o de la persona que se presenta la solicitud.	()	()
- Descripción de la invención.	()	()
- Dibujos de ser estos pertinentes.	()	()
- Comprobante de Pago de las tasas establecidas.	()	()
COMPLETA ()	INCOMPLETA ()	()
DISEÑO INDUSTRIAL ()		
- Indicación de que se solicita el registro de Diseño Industrial	()	()
- Datos de identificación del solicitante o de la persona que presenta la solicitud.	()	()
- Representación gráfica y fotográfica del Diseño Industrial o muestra del Material que incorpora el diseño.	()	()
- Comprobante de pago de las tasas establecidas	()	()
COMPLETA ()	INCOMPLETA ()	()
ESQUEMA DE TRAZADO ()		
- Indicación de que solicita el registro de un Esquema de trazado.	()	()
- Datos de identificación del solcitante o de la persona que presenta La solicitud.	()	()
- Representación gráfica del esquema de trazado	()	()
- Comprobante de pago de las tasas establecidas.	()	()
COMPLETA ()	INCOMPLETA ()	()

Firma Responsable: *Edwar*

05-12-2002.

Fecha: