



FORMULARIO ÚNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL

SOLICITUD DE:

1

☒

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: 8411 TE Heerlen,
Países Bajos

Lugar de Constitución : Países Bajos

Teléfono:

Fax:

E-mail

IDENTIFICACIÓN

C.C. ☐

NIT ☐

C.E. ☐

Otro ☐

Número

3

REPRESENTANTE
O APODERADO
(74)

Nombre: JIMENA ESCOBAR URIBE

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IDENTIFICACIÓN

C.C. ☒

NIT ☐

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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/NL01/00428

Fecha Mayo 31, 2001

Publicación Internacional No. WO 01/94297 A1

Fecha Diciembre 13, 2001

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

6 Clasificación Internacional (51) C 07C 249/00

7 Prioridad

(33) País de Origen

(32) Fecha

(31) Número de Solicitud

EUROPA

Junio 5, 2000

00201970.1

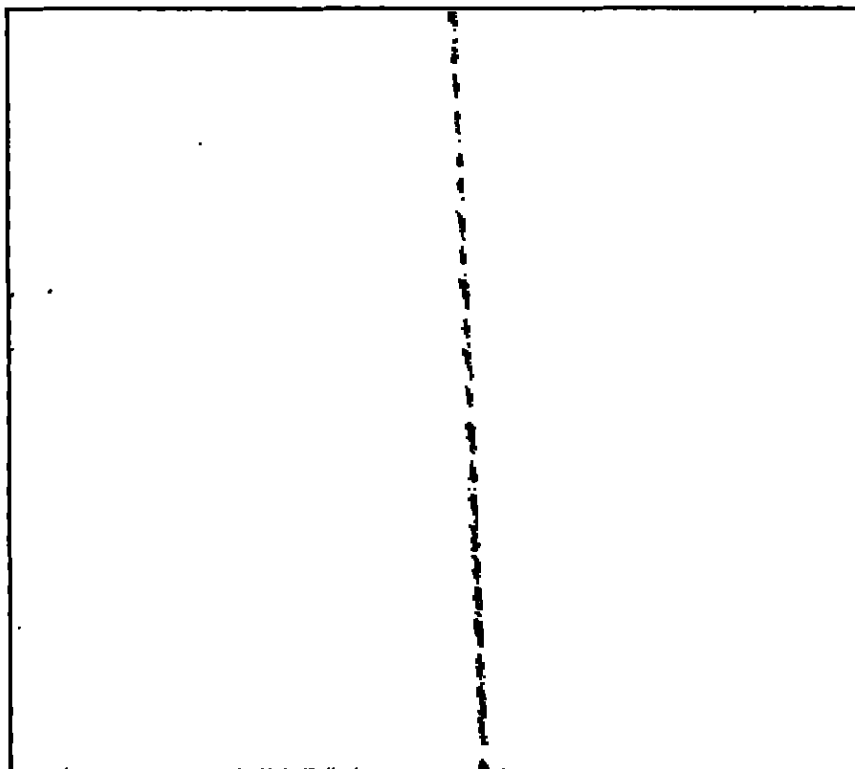
SI ☒ NO ☐

9 Comprobante de pago No. 02 - 76.462

Fecha Noviembre 15, 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 Uribe*

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

As. 2507/PCT

ANEXOS**INVENTORES**

- 1.) **MARC BLAAUW**
(6226 VZ Maastricht, Países Bajos);
- 2.) **ANTONIUS JACOBUS FRANCISCUS SIMONS**
(6163 HN Geleen, Países Bajos);
- 3.) **THEODORUS FRIEDERICH MARIA RIESTHUIS**
(6125 BZ Obbicht, Países Bajos);
- 4.) **ALEX PIT**
(Evans, Georgia 30809, Estados Unidos de América);
- 5.) **HENK OEVERING**
(6181 BR Elslloo, 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

2507



4

Industria y Comercio

SUPERINTENDENCIA

SUPERINDUSTRIA Y COMERCIO
Radicacion : 02110474 00000000 Folios: 50
Fecha (AMD): 2002-12-05 16:19:04
Tramite : 011 PCT-PATENT 379 FASE NACI 411 PRESENTA
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 02 - 76,462
FECHA : NOVIEMBRE 15 DE 2002

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
ESCOBAR URIBE ASOCIADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	7036701	14/11/2002	2,148,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
1		TRAMITES DE SOL. DE PATENTE DE IN	378,000.00
		TOTAL :	6 378,000.00

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

Already transmitted by fax on: 31.05.01

cc: A2C

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 3760WO
(if desired) (12 characters maximum)

MINUUT

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)

PCT

2001

Brecht Nr.

Amk 5529

☐ 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.)

BLAAUW, Marc
Habsburgerplein 29
6226 VZ Maastricht, 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 Adeline
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.

Form PCT/RO/101 (first sheet) (July 1998; reprint January 2001)

See Notes to the request form

1/601
Amk

M

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.) SIMONS, Antonius Jacobus Franciscus Mauritspark 24 6163 HN 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	
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.) RIESTHUIS, Theodorus Friederich Maria Karel van Bronkhorstlaan 32 6125 BZ Obbicht, 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.) OEVERING, Henk Burg. Eussenstraat 46 6181 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	
☐ 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.)

Sheet No...4..

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)				
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)(4)). 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)

5 June 2000

Number

00201970.1

Country (or regional Office)

EP-NL

Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following number of sheets:

request : 4

description (excluding sequence listing part) : 14

claims : 2

abstract : 1

drawings : 1

sequence listing part of description : 1

Total number of sheets : 22

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

1. ☒ fee calculation sheet
2. ☐ separate signed power of attorney
3. ☒ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☐ 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

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



C.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 1(2):		
5. International Searching Authority (if two or more are competent): 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

For receiving Office use only

Annex to the Request

Applicant's or agent's file reference 3760WO		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	2082,-	S
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.)		
3. INTERNATIONAL FEE		
Basic Fee		
The international application contains 22 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		
Designation Fees	901,-	B
The international application contains 89 designations.		
6	x 193,-	=
number of designation fees payable (maximum 6)	amount of designation fee	1158,-
Add amounts entered at B and D and enter total at I		
2059,- 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.)		
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,-		
TOTAL		
☐ The designation fees are not paid at this time.		
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 ROV 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)	Signature
		C.A. van Tol - Koutstaal

(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 01/94297 A1

- (51) International Patent Classification: C07C 249/08 (74) Agent: VAN TOL-KOUTSTAAL, Charlotte, Adellone; DSM Patents & Trademarks, P.O. Box 9, NL-6160 MA Geleen (NL).
- (21) International Application Number: PCT/NL01/00428
- (22) International Filing Date: 31 May 2001 (31.05.2001) (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 00201970.1 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).
- (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): BLAAUW, Marc [NL/NL]; Habsburgerplein 29, NL-6226 VZ Maastricht (NL). SIMONS, Antonius, Jacobus, Franciscus [NL/NL]; Mauritspark 24, NL-6163 HN Geleen (NL). RIESTHUIS, Theodorus, Friederich, Maria [NL/NL]; Karei van Bronkhorstlaan 32, NL-6125 BZ Obbicht (NL). PITT, Alex [US/US]; 818 Walden Glen Court, Evans, GA 30809 (US). OEVERING, Henk [NL/NL]; Burg, Eussenstraat 46, NL-6181 BR Elsloo (NL).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/94297 A1

(54) Title: PROCESS FOR THE PRODUCTION OF CYCLOHEXANONE OXIME

(57) Abstract: 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, wherein the phosphate concentration in the aqueous reaction medium entering the cyclohexanone oxime synthesis zone is higher than 3.0 mol/l.

INTERNATIONAL SEARCH REPORT

Inventor's Application No
PCT/NL 01/00428

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C249/08

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, BEILSTEIN Data, 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.
A	US 3 720 755 A (DUYVERMAN C ET AL) 13 March 1973 (1973-03-13) example 2	1-9
A	GB 1 284 515 A (STANICARBON N.V.) 9 August 1972 (1972-08-09) page 2, line 25 - line 40	1-9

☐ 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 doubt 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. 5818 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

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCTNOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:

DSM PATENTS & TRADEMARKS
Attn. Tol-Kolstaal van, C. A.
P.O. BOX 9
NL-6160 MA Geleen
NETHERLANDS

30 JUL 2001

EA

Reg.

13

13

4

Date of mailing
(day/month/year)

31/07/2001

Applicant's or agent's file reference

3760W0

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/NL 01/00428

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 19:

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 18 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 18 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,
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Authorized officer

Véronique Baillou

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 letter 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 46.1).

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. Reference 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 COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 3760W0	FOR FURTHER ACTION see Notification of Transmitted of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/NL 01/ 00428	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.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 01/00428

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07C249/08		
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, BEILSTEIN Data, 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.
A	US 3 720 755 A (DUYVERMAN C ET AL) 13 March 1973 (1973-03-13) example 2	1-9
A	GB 1 284 515 A (STAMICARBON N.V.) 9 August 1972 (1972-08-09) page 2, line 25 - line 40	1-9
☐ 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. 'Z' 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. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3018		Authorized officer Janus, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 01/00428

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3720755 A	13-03-1973	NL 7004350 A	28-09-1971
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United States Patent (19)
Duyverman et al.

(11) **3,720,755**
(45) **March 13, 1973**

[54] **PROCESS FOR PREPARING A
SOLUTION CONTAINING HYDROXYL
AMMONIUM PHOSPHATE**

[75] **Inventors:** Coenraad J. Duyverman, Sittard;
Marthin J. Gorgels, Stein both of
Netherlands

[73] **Assignee:** Stamlecarbon N.V., Heerlen, Nether-
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[22] **Filed:** March 26, 1971

[21] **Appl. No.:** 128,495

[30] **Foreign Application Priority Data**
May 24, 1971 Netherlands7004350

[52] **U.S. Cl.**.....423/307, 423/321
[51] **Int. Cl.**....C01b 15/16, C01b 25/26, C01b 25/16
[58] **Field of Search** ...23/107, 165 B, 190 H; 210/36,
210/40, 41; 252/472

[56] **References Cited**

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826,089	7/1906	Day	252/472 X

Primary Examiner—Oscar R. Ventiz
Assistant Examiner—Gregory A. Heller
Attorney—Cushman, Darby & Cushman

[57] **ABSTRACT**

A process for preparing a solution of hydroxylam-
monium phosphate which includes catalytic reduction
of nitrate ions in an aqueous solution containing
phosphoric acid using molecular hydrogen.

In order to maintain the activity of the catalyst the
phosphoric acid to be fed to the synthesis zone is first
freed of heavy metal contaminants by contacting the
phosphoric acid for a sufficient time with hydrogen
and an absorbent consisting of a metal of the platinum
group.

4 Claims, No Drawings

PROCESS FOR PREPARING A SOLUTION CONTAINING HYDROXYL AMMONIUM PHOSPHATE

The present invention relates to the preparation of a solution of hydroxylammonium phosphate by catalytic reduction of nitrate ions in an aqueous solution containing phosphoric acid using molecular hydrogen.

The reduction is effected by means of a noble-metal catalyst, such as palladium, platinum or rhodium, whether or not on a carrier.

The influence of contaminants on the catalytic activity of metal catalysts of the platinum metal group can be favorable, but more likely is very unfavorable. It is advantageous, therefore, to start with as pure as possible starting materials, to which, if necessary, certain amounts of the elements which raise the activity of the catalyst can be added.

Rock phosphate ore from which phosphoric acid is synthesized is composed not only of calcium oxide and phosphorus pentoxide, but also generally contains considerable quantities of contaminants, the most important of which are Al_2O_3 , Fe_2O_3 , SiO_2 , sulphate and fluoride. In addition, the rock phosphate ore may also contain small quantities of one or more of the following elements As, Ba, Be, B, Cd, Ca, Cr, Cu, J, Pb, Mn, Mo, Ni, rare earths, Rb, Se, Ag, Sr, Sn, Ti, U, V, Zn and Zr, usually in the form of oxides or salts. These contaminants appear in the phosphoric acid prepared from the rock phosphate, whether the phosphoric acid is prepared by the electric furnace method or by the wet process using sulfuric acid. These contaminants are present in only small amounts in the order of parts per million (ppm).

The process according to the present invention provides a method of removing traces of contaminants of dissolved elements, especially heavy metals, from solutions wherein the contaminants occur in such small quantities that they cannot be successfully removed by prior art methods such as cathodic precipitation using a mercury surface as cathode.

According to the invention the contaminants are removed from the contaminated solution by suspending a finely divided metal of the platinum group in the solution and, subsequently, bubbling hydrogen through the solution for some time, or by suspending the metal of the platinum group in a solution already saturated with hydrogen. The various heavy metal contaminants which are present in the dissolved state in the contaminated solution precipitate on the finely divided, highly noble metal.

The temperature and pressure at which the process of the present invention is accomplished can be varied between wide limits. The temperature may lie between the point of solidification of the contaminated solution and the temperature at which the solution exhibits a boiling-like phenomena. Elevation of the temperature increases the speed of purification.

The pressure may be subatmospheric, atmospheric as well as superatmospheric. A higher hydrogen pressure has a favorable influence on the rate at which the purification reaction takes place.

Metals of the platinum group which can be used in the process of this invention include platinum, palladium, ruthenium, rhodium, osmium and iridium. The purification reaction will proceed more efficiently if the

metal catalyst has a large external surface, such as metal 'black', metallic sponge, or if it is finely divided on a carrier material with a large specific surface. The carrier material must be resistant to the medium to be purified. Several acceptable carriers are, for instance, graphite, active carbon or silica gel ('aerosil').

It is believed that the heavy-metal ions present in the contaminated solution to be treated are reduced under the influence of the platinum metal-hydrogen combination and thus deposit on the platinum metal mass.

In addition to removing heavy-metal ions, the process of this invention removes several from contaminated solutions by adsorbing them on the platinum metal mass. Examples of such contaminants that can be removed by the process of this invention are Pb, Cu, Mo, As, Sb, S, Hg, J, Sn, Ti, Cd, Ga, Ge, In.

The invention will be further described with reference to the following examples in which solutions of phosphoric acid or a solution of phosphates were treated according to the process of the invention. The purified solutions were tested for their suitability in the catalytic reduction of nitric acid with molecular hydrogen in the presence of a palladium-containing catalyst. In the examples, purification was generally effected at room temperature, in a vessel provided with a stirrer, so that the hydrogen bubbled through the solution in a finely divided state. The rate of hydrogen feed was about 5-10 N liters of H_2 /hour/liter of liquid.

Finely divided palladium supported on carbon was suspended in the solution as the hydrogen was passed through. The time of treatment took one or more hours. The particles of palladium supported on the carbon were then separated from the liquid by means of a filter or centrifuge. Subsequently, the liquid was tested at room temperature, 25°C, for its suitability for use in the catalytic reduction of nitric acid to hydroxylamine with the aid of molecular hydrogen using a palladium on carbon catalyst suspended in the reaction medium.

The hydrogen used in the catalytic reduction of nitric acid to hydroxylamine was fed to the reaction vessel through a flow meter. The reaction mixture consisted of, at the beginning of each example, 100 ml of a solution containing 2.69 moles per liter of H_2PO_4 , 2.1 moles per liter of NaOH and 2.65 moles per liter of $NaNO_3$, 300 mg of 5 weight % Pd supported on active carbon and 0.26 mg of GeO_2 were suspended in the solution. The hydrogen absorption during the reaction was determined as a function of the time. On completion of the test, the quantities of hydroxylamine and ammonia formed were determined. The hydrogen consumption and the ratio of the hydroxylamine/ammonia produced are measures of the suitability of the starting phosphoric acid or the solutions prepared therefrom. The suitability phosphoric acid was qualified as follows:

bad—The phosphoric acids rated bad contained excessive poisons and would be unsuitable in commercial practice. The activity of the catalyst system under the test conditions, even when GeO_2 was added as activator, remained low, i.e. less than 13 g. of NH_2OH per g. of palladium per hour, while further, the selectivity, i.e., the molar ratio between HN_2OH formed and NH_3 formed was smaller than 10:1.

moderate—The activity of the catalyst solution was relatively low under the test conditions. Produc-

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tion of 13-20 g. of NH₄OH per g. of palladium per hour was obtained, while the addition of GeO₂ as activator resulted only a small increase in activity. The solutions rated moderate would still be unsuitable in commercial practice.

good—The activity was relatively low under the test conditions. Production of 13-20 g. of NH₄OH per g. of palladium per hour was obtained, addition of GeO₂ as activator led to a considerable increased activity, i.e. 20-25 g. of NH₄OH per g. of palladium per hour.

very good—The activity, after addition of GeO₂, was maximum, i.e. more than 25 g. of hydroxylamine per g. of palladium per hour, while also, the selectivity was high, i.e., such that the molar ratio between NH₄OH formed and NH₃ formed is greater than 10:1.

Three different samples of phosphoric acid, differing in origin, were used in the examples. The samples being indicated as acid A, B and C respectively.

The following table shows the contaminants contained in these samples in mg per liter of the 85 weight % H₃PO solutions.

Elements	Acid A	Acid B	Acid C
Cd	3	1	1
Pb	7	3	2
Cu	1	0.5	0.5
Sh	1	unknown	unknown
As	0.5	unknown	unknown
Al	5	unknown	unknown
Fe	9	1	5
Mo	0.5	unknown	unknown
Sn	10	4	1
Suitability	Moderate	Moderate	Good

EXAMPLE 1

In 1 kg of each of the phosphoric acids A, B and C, 10 g. of 0.5 weight % Pd on active carbon (total of 50 mg of Pd) was suspended and hydrogen was passed through the suspension at a rate of 5 N liters per hour for 10 hours. The temperature was maintained at about 25°C. The palladium-carbon particles were then separated from the phosphoric acids and the resulting phosphoric acid solutions were tested for suitability in the catalytic reduction of nitric acid to hydroxylamine with molecular hydrogen. In all three cases, the suitability was found to have become 'very good' as a result of the treatment.

The amount of contaminants in the phosphoric acid solutions was drastically reduced by the treatment according to this invention. The data for acid A showed that after the treatment, the Pb content had decreased from 7 mg to 0.4 mg, the Cu content from 1 mg to less than 0.2 mg and Sn to less than 0.5 mg/l.

EXAMPLE 2

Demineralized water and sodium hydroxide were used to prepare a buffer solution of each of the non-purified acids A and C. These solutions contained 2.69 moles of H₃PO₄ and 2.1 moles of NaOH per liter. The suitability of these buffered phosphoric acid solutions in the catalytic syntheses of hydroxylamine ranged from moderate to good.

After these buffered phosphoric acid solutions were treated in accordance with the present invention by suspending 2.5 g. of 0.5 weight % palladium on carbon

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per 1 liter of the phosphoric acid and passing through hydrogen at 25°C for 10 hours, the suitability of the two buffered acid solutions in the catalytic synthesis of hydroxylamine was very good.

EXAMPLE 3

Hydrogen was passed through 1 kg of phosphoric acid A for 16 hours with 6 g. of palladium black being suspended in the phosphoric acid solution instead of palladium suspended on active carbon as in example 1.

The phosphoric acid after being separated from the palladium black was used in the catalytic synthesis of hydroxylamine and the suitability was very good.

EXAMPLE 4

To determine the approximate minimum quantity of the platinum group metal to be suspended in the acid solutions to be treated, samples of the buffered phosphoric acid A of example 2 were treated with hydrogen at 25°C for 16 hours with the buffered solutions containing various quantities of the platinum group metal. In the following table, the suitability of the treated buffered acid solutions in the hydroxylamine synthesis is given with the corresponding quantity of adsorbent (palladium 0.5 percent by weight) suspended in the buffered acid solution during the treatment thereof according to the invention.

Quantity of palladium adsorbent in grams per kg of buffer solution	Suitability of acid solution in the Catalytic synthesis of hydroxylamine
0	moderate
0.5	moderate
1.5	good
2	very good
2.5	very good

As can be seen from the above table, suspending as little as 1.5 grams of the palladium adsorbent (containing 0.5 percent palladium by weight) in the acid solution and bubbling hydrogen therethrough results in considerable increase in the suitability of the acid solution for further use in the catalytic synthesis of hydroxylamine.

EXAMPLE 5

The influence of duration of treatment of the solutions in example 4 was determined by treating 1 kg samples of phosphoric acid A with 10 g. of adsorbent (0.5 weight % Pd on carbon) at 25°C for various periods of time. The results are shown in the following table:

Contact time in hours	Suitability of the treated acid solution in the catalytic synthesis of hydroxylamine
0	moderate
1	good
5	very good
72	very good

As can be seen, as little as 1 hour duration of treatment resulted in greatly improved suitability of the acid solution for further use in the catalytic synthesis of hydroxylamine.

The degree of distribution of the metal from the platinum group on the carbon or other carrier mass also has an influence on the effectiveness of the process

according to the present invention. If, for instance, when 5 weight % Pd on carbon was used as adsorbent, it was found possible to treat 1.5 kg of phosphoric acid A with 1 g. of adsorbent and obtain an improvement in the acid's suitability for further use in the catalytic synthesis of hydroxylamine to the qualification very good. However, if, instead of 1 g. of 5 weight % Pd on carbon, the palladium-equivalent quantity of 10 g. of 0.5 weight % Pd on carbon was used in the treatment, it was found possible to improve 2 kg of phosphoric acid A to the same level of suitability.

It was also found that the quantity of carrier material such as active carbon had no influence whatever on the effectiveness of the process according to the present invention. When the treatment was performed using 1 g of 5 weight percent palladium on carbon with an additional 9 g of active carbon, the result obtained was essentially the same as obtained without the additional 9 g. of active carbon.

EXAMPLE 6

To show the influence of an increase in temperature on the process of the present invention, 2 samples of phosphoric acid A of 1 kg each were contacted with hydrogen having 10 g of 0.5 weight % Pd on active carbon suspended therein, at temperatures of 60° C and 25 respectively. After a treatment of 1 hour, the suitability for further use in the catalytic synthesis of hydroxylamine of the phosphoric acid solution being treated at 60° C was very good. The phosphoric acid solution treated at 25° C required a 5 hour period to obtain the same increase in suitability.

In the process of the present invention, the treatment with hydrogen and a metal or combination of metals from the platinum group is essential. Treatment with platinum group metals such as Ru, Rh, Os, Ir and Pt, or a combination of said metals, in the presence of hydrogen leads to similar favorable results in relation to the suitability of phosphoric acid for the hydroxylamine synthesis as shown above when using palladium as shown in the following example.

EXAMPLE 7

Hydrogen was passed through a sample of phosphoric acid A containing an adsorption mass consisting of 1 weight percent platinum on active carbon, at 25° C for 16 hours. A quantity of 10 g. of adsorption mass per kg of 85 weight percent phosphoric acid was used.

After removing the adsorption mass from the phosphoric acid solution, it was found that the suitability of the phosphoric acid in the catalytic synthesis of hydroxylamine was very good. However, when silver on

a carbon carrier was used instead of platinum on a carbon carrier, no improvement in quality of the phosphoric acid solution was obtained.

In the above examples, the treatment of the phosphoric acid was always effected in a reaction vessel provided with a stirrer, which was used to keep the adsorbent in suspension, as well as to divide the hydrogen into fine bubbles.

Of course, it is also possible to operate without mechanically stirring the solution and to keep the adsorbent suspended by the hydrogen stream. The acid can also be treated in a column with the acid or the solution to be purified and the hydrogen being contacted in either counter-current or in co-current fashion over a bed of the platinum group metal containing adsorbent. To avoid excessive resistance in such a column, the adsorbent should be present in the form of small lumps, granules, tablets, etc. The treatment may also be effected, continuously, in a reaction vessel provided with filter candles to retain the adsorbent.

If the adsorbent should appear to become inactive or insufficiently active due to adsorption of large amounts of the contaminants, it can be regenerated, for instance, by desorption with solvents that take up the contaminants. In the case of an adsorbent consisting of a platinum metal on carbon, the carbon will, preferably, be burned off, the remaining metal oxide be dissolved and, subsequently, this solution used for the preparation of new adsorbent.

What is claimed is:

1. In a process for producing a solution of hydroxylammonium phosphate comprising catalytically reducing nitrate ions in an aqueous solution and in the presence of molecular hydrogen and phosphoric acid,

the improvement comprising removing heavy-metal contaminants from the phosphoric acid, prior to introduction into the hydroxylammonium phosphate production process, by (i) contacting the phosphoric acid containing heavy-metal contaminants with hydrogen and an adsorbent consisting essentially of a metal of the platinum group, thereby reducing the heavy metal contaminants and absorbing the heavy-metal contaminants on the adsorbent; and (ii) separating the adsorbent from the thus purified phosphoric acid.

2. A process according to claim 1, in which the phosphoric acid is a partially neutralized solution.

3. A process according to claim 1, in which the phosphoric acid is contacted with the hydrogen and the adsorbent for at least 1 hour at a temperature of from about 25° C to 60° C.

4. A process according to claim 1, in which the adsorbent is palladium supported on activated carbon.

* * * * *

376040

PATENT SPECIFICATION

(11) 1284515

1284515

DRAWINGS ATTACHED

- (21) Application No. 21606/71 (22) Filed 19 April 1971
- (31) Convention Application No. 7 001 906 (32) Filed 11 Feb. 1970 in
- (33) Netherlands (NL)
- (45) Complete Specification published 9 Aug. 1972
- (51) International Classification C07C 131/04
- (52) Index at acceptance
C2C 221 225 227 22Y 30Y 346 709 711 719 MV



(54) IMPROVED CYCLIC PROCESS FOR PREPARING AND WORKING UP A HYDROXYLAMMONIUM SALT SOLUTION

(71) 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 an improved recycle process for the preparation and processing of a hydroxylammonium salt solution in a cyclohexanone oxime synthesis, and to apparatus when used for carrying out the improved process.

Hydroxylammonium salts are used in the preparation of oximes from ketones, in particular in the preparation of cyclohexanone oxime from cyclohexanone.

In a known recycle process an acidic buffered aqueous reaction medium containing buffer acids or acidic salts, for example phosphoric acid and bisulphate and buffer salts derived from these acids, is recycled through a hydroxylammonium salt synthesis zone wherein nitrate ions are catalytically reduced with molecular hydrogen to hydroxylamine, and through an oximation zone. The make-up for the nitrate ions consumed, usually about 60 wt. % nitric acid solution, is added to the recycling aqueous reaction medium before it passes into the hydroxylammonium salt synthesis zone.

The hydroxylamine reacts with free buffer acid to form the corresponding hydroxylammonium salt and the resulting solution containing hydroxylammonium salt is passed to the oximation zone, where the hydroxylammonium salt reacts with a ketone to form the corresponding oxime, with liberation of acid.

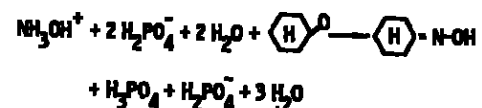
After the oxime has been separated from the aqueous reaction medium it is again recycled to the hydroxylammonium salt synthesis zone.

For example, if the hydroxylamine synthesis is based on a solution containing phosphoric acid and nitrate, the chemical reactions occurring during the successive operations can be represented by the following equations:

1) Formation of hydroxylammonium salt:



2) Formation of cyclohexanone oxime starting from cyclohexanone:



3) Make-up in the form of HNO₃ for nitrate ions consumed after separation of the oxime formed:

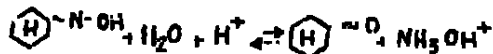


After the HNO₃ has been added, the resulting solution, after removal of the water formed in the reaction and also introduced with the make-up nitric acid, has theoretically the same composition as the initial solution used for the hydroxylammonium salt formation.

The catalyst used for the reduction of the nitrate ions is a palladium catalyst, generally from 5% to 20% by weight palladium on a carrier material, e.g. carbon or alumina. The activity of this catalyst is adversely affected if the catalyst contracts organic substances, for example the ketone that is to be converted into the oxime and the resulting oxime itself.

To prevent the catalyst from being poisoned, the recycled reaction medium, before entering the hydroxylamine synthesis zone, has to be substantially liberated from the ketone and oxime dissolved in it. In practice the aqueous liquid discharged from the oxime synthesis zone is for this purpose freed of any cyclohexanone and cyclohexanone oxime by a stripping process.

In this stripping process the ketone is distilled off as such, but the oxime will first be hydrolyzed according to the reaction equation.



Depending on the temperature, an equilibrium will slowly develop in the liquid to be stripped off, but an oxime residue will be left, which residue is carried along by the bottom product of the stripping column.

In order not to poison the catalyst, this oxime residue must be removed from the recycling liquid or be rendered harmless, for instance by an oxidation or decomposition process after make-up by nitric acid or nitric oxide and nitrous oxide gases.

According to the invention, the hydrolysis-equilibrium between oxime and the corresponding ketone is shifted much farther to the right by removing the hydroxylamine evolved during the hydrolysis by the use of nitric oxide and nitrous oxide gases according to the equation:



The invention provides a recycle process for the production of cyclohexanone oxime in which a buffered aqueous reaction medium with an acid reaction, which contains nitrate ions or nitric oxide and nitrous oxide and phosphoric acid and/or bisulphate, is recycled between a hydroxylamine synthesis zone and a cyclohexanone oxime synthesis zone, and in the hydroxylamine synthesis zone nitrate ions or nitric oxide and nitrous oxide are reduced with molecular hydrogen in the presence of a noble metal catalyst to hydroxylamine, which hydroxylamine is consumed in the oxime synthesis zone, and the cyclohexanone oxime is separated from the aqueous reaction liquid, whereafter this aqueous reaction liquid, before being returned to the hydroxylamine synthesis zone, is substantially freed of remaining cyclohexanone and cyclohexanone oxime in a stripping process and fresh nitrate ions or nitric oxide and nitrous oxide required for the hydroxylamine synthesis are supplied, in which the recycling liquid is contacted with nitric oxide and nitrous oxide at an elevated temperature in a contacting zone before the said stripping process, and an oxime-impoverished, cyclohexanone-enriched recycle liquid obtained therefrom is subjected to the said stripping process.

An embodiment of the invention is hereinafter described and illustrated in the accompanying drawing, which is a diagrammatic representation of apparatus used therein.

Referring to the drawing A and B represent the hydroxylamine synthesis zone and the oxime synthesis zone respectively.

Hydrogen is introduced to zone A, filled with a palladium catalyst, through line 1. Unreacted hydrogen and possibly other off-gases are discharged from zone A through line 2. Zone A is supplied with recycling reaction medium through line 12, and the medium, enriched with hydroxylamine, is transferred from zone A to oxime synthesis zone B through line 3.

The ketone to be converted, possibly with a solvent, for example toluene, is added to zone B through line 4 and produced oxime, possibly with the solvent, is removed from the system through line 5. The recycling liquid, now impoverished in hydroxylamine but still containing traces of ketone or oxime, is introduced into column F through line 6. In this column oxime is hydrolyzed into ketone according to the invention with the aid of nitric oxide and nitrous oxide supplied through line 11 via valve 11b. The recycling liquid is then passed into stripping column C through line 16. Ketone in vaporous condition and water vapour are passed to condensed D as overheads.

5 A water-ketone azeotrope condenses and flows to separating vessel E, and ketone
 is returned therefrom through line 8 to oxime synthesis zone B, whilst part of the
 water flows back through line 9 into the top section of column C and the remainder
 is drained. Condenser D is cooled with cooling water flowing through cooling pipes
 14, whilst stripping column C is supplied with heat by heating coils 13. The recycling
 liquid is then introduced into absorption column G through line 10, and nitric oxide
 and nitrous oxide gases are supplied thereto through line 11 via valve 11a and are
 absorbed in the recycling liquid to form nitric acid *in situ* which is passed to the
 10 hydroxylamine synthesis zone through line 12. Non-absorbed gases leave the system
 through line 15.

Instead of forming nitric acid *in situ*, nitric acid make-up may be applied to the
 recycling liquid directly, absorption column G being then not required.

15 The quantities of the gases supplied to the columns can be controlled by means
 of valves 11a and 11b, or if desired supplied into column F directly. It is not necessary
 that column F is an absorption column. Any reaction vessel in which the circulation
 liquid is adequately contacted with the gases may be used.

20 By way of illustration the accompanying table shows the amounts of oxime and
 ketone present in the various stages of the cycle of the process with reference to the
 indicating numerals of the accompanying drawing together with the quantities, and
 the compositions in the various stages are expressed in gram-moles.

25 From the table it is to be seen that the carbon content is significantly larger than
 would correspond with the oxime and ketone contents. The reason is that in the pro-
 cess some ketone or oxime is always oxidized into organic compounds, e.g. adipic acid,
 which have no detrimental influence on the activity of the catalyst however. Ultimately
 such organic compounds are oxidized into H₂O and CO₂ and/or are discharged from
 the cycle with the oxime produced.

Process stage reference no	H ₂ PO ₄	NH ₄ H PO ₄	NH ₄ NO ₃	H ₂ O	Oxime	Cyclo- hexanone	NO NO ₂	N ₂	O ₂	N ₂ O	C
6	112	88	195	3238	0 50	—	—	—	—	—	5 2
16	113 5	86 5	196 5	3232	—	0 50	—	—	—	—	4 2
10	113 5	86 5	196 5	3224	—	—	—	—	—	—	1 2
12	200	—	275	3000	—	—	—	—	—	—	1 0
11	—	—	—	—	—	—	88 5	708	88 5	—	—
via 11b							2	16	2	—	—
15							—	732	73 1	0 5	1 2
7				3		0 50					3 0

As an alternative to the process specifically described with reference to the accom-
panying drawing the process of the invention may be applied to similar processes
wherein instead of nitrate ions nitric oxide and nitrous oxide is reduced to hydroxyl
amine with the aid of a platinum catalyst by means of molecular hydrogen whereby
poisoning of the platinum catalyst is avoided

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WHAT WE CLAIM IS:—

1. A recycle process for the production of cyclohexanone oxime in which a buffered aqueous reaction medium with an acid reaction which contains nitrate ions or nitric oxide and nitrous oxide, and phosphoric acid and/or bisulphate, is recycled between a hydroxylamine synthesis zone and a cyclohexanone oxime synthesis zone, and in the hydroxylamine synthesis zone nitrate ions or nitric oxide and nitrous oxide are reduced with molecular hydrogen in the presence of a noble metal catalyst to hydroxylamine, which hydroxylamine is consumed in the oxime synthesis zone, and the cyclohexanone oxime is separated from the aqueous reaction liquid, whereafter this aqueous reaction liquid, before being returned to the hydroxylamine synthesis zone, is substantially freed of remaining cyclohexanone and cyclohexanone oxime in a stripping process and fresh nitrate ions or nitric oxide and nitrous oxide required for the hydroxylamine synthesis are supplied, in which the recycling liquid is contacted with nitric oxide and nitrous oxide gases at an elevated temperature in a contacting zone before the said stripping process, and an oxime-impooverished cyclohexanone-enriched recycle liquid obtained therefrom is subjected to the said stripping process.
2. A recycle process according to Claim 1, substantially as hereinbefore described.
3. Apparatus when used in the process according to Claim 1, substantially as hereinbefore described and illustrated in the accompanying drawing.

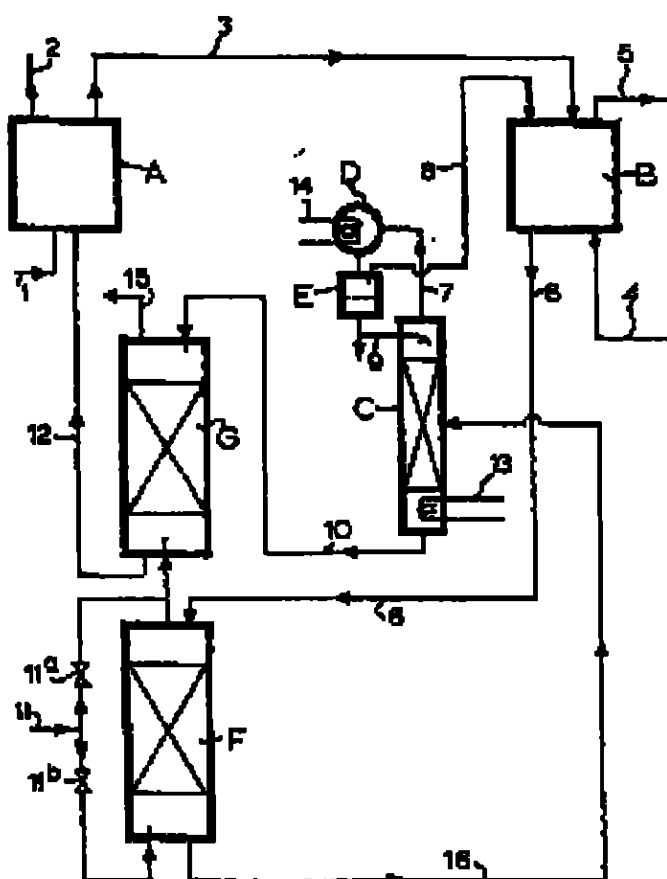
HYDE & HEIDE & O'DONNELL,
 47, Victoria Street, London SW1H 0BS
 Chartered Patent Agents,
 Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
 Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
 which copies may be obtained.

1294515 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale



cc^v AIC

The demand must be filed directly with the competent International Preliminary Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:
IPEA/EPN

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only

Identification of IPEA		Date of receipt of DEMAND	
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference 3760WO	
International application No. PCT/NL01/00428	International filing date (day/month/year) 31 May 2001 (31.05.01)	(Earliest) Priority date (day/month/year) 5 June 2000 (05.06.00)	
Title of invention PROCESS FOR THE PRODUCTION OF CYCLOHEXANONE OXIME			
Box No. II APPLICANT(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.) DSM N.V. Het Overloon 1 6411 TE Heerlen the Netherlands		Telephone No. Facsimile No. Teleprinter No. Applicant's registration No. with the Office	
State (that is, country) of nationality: NL		State (that is, country) of residence: NL	
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.) BLAAUW, Marc Habsburgerplein 29 6226 VZ Maastricht the Netherlands		State (that is, country) of nationality: NL State (that is, country) of residence: NL	
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.) SIMONS, Antonius Jacobus Franciscus Mauritspark 24 6163 HN Geleen the Netherlands		State (that is, country) of nationality: NL State (that is, country) of residence: NL	
☒ Further applicants are indicated on a continuation sheet.			

17/12/01
Abx

R

Continuation of Box No. II APPLICANT(S)

If none of the following sub-boxes is used, this sheet should not be included in the demand.

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.)

RIESTHUIS, Theodorus Friederich Maria
Karel van Bronkhorstlaan 32
6125 BZ Obbicht
the Netherlands

State (that is, country) of nationality: NL

State (that is, country) of residence: NL

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.)*

PIT, Alex
818 Walden Glen Court
Evans, Georgia 30809, U.S.A.

State (that is, country) of nationality: US

State (that is, country) of residence: US

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.)

OEVERING, Henk
Burg. Eussenstraat 46
181 BR Elsloo,
the Netherlands

State (that is, country) of nationality: NL

State (that is, country) of residence: NL

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.)*

State (that is, country) of nationality:

State (that is, country) of residence:

Further applicants are indicated on another continuation sheet.

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCEThe following person is ☐ agent ☒ common representativeAnd ☐ has been appointed earlier and represents the applicant(s) also for international preliminary examination.☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.☒ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.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.)*DAUTZENBERG, Jozef Marie Andreas
DSM Patents & Trademarks
Office Geleen
P.O. Box 9
6160 MA Geleen (NL)

Telephone No.

(+31)46-4761790

Facsimile No.

(+31)46-4761830

Teleprinter No.

Applicant's registration No. with the Office



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.

Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION**Statement concerning amendments:***

1. The applicant wishes the international preliminary examination to start on the basis of:

☒ the international application as originally filedthe description ☐ as originally filed☐ as amended under Article 34the claims ☐ as originally filed☐ as amended under Article 19 (together with any accompanying statement)☐ as amended under Article 34the drawings ☐ as originally filed☐ as amended under Article 342. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination:☒ which is the language in which the international application was filed.☐ which is the language of a translation furnished for the purposes of international search.☐ which is the language of publication of the international application.☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination**Box No. V ELECTION OF STATES**

The applicant hereby elects all eligible States (that is, all States which have been designated and which are bound by Chapter II of the PCT)

excluding the following States which the applicant wishes not to elect:

Sheet No. 4

International application No.

PCT/NL01/00428

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purpose of international preliminary examination:

- | | | |
|--|---|--------|
| 1. translation of international application | : | sheets |
| 2. amendments under Article 34 | : | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | sheets |
| 5. letter | : | sheets |
| 6. other (specify) | : | sheets |

For International Preliminary Examining Authority use only

received not received

☐	☐
☐	☐
☐	☐
☐	☐
☐	☐
☐	☐

The demand is also accompanied by the item(s) marked below:

- | | |
|--|--|
| 1. ☒ fee calculation sheet | 5. ☐ statement explaining lack of signature |
| 2. ☐ original separate power of attorney | 6. ☐ sequence listing in computer readable form |
| 3. ☐ original general power of attorney | 7. ☐ other (specify): |
| 4. ☐ copy of general power of attorney; reference number, if any: | |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

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


Dts. J.M.A. Dautzenberg
(Procuratiehouder)

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):

- | | |
|--|--|
| 3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. | ☐ The applicant has been informed accordingly |
| 4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5. | |
| 5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82. | |

For International Bureau use only

Demand received from IPEA on:

CHAPTER II

PCT

FEE CALCULATION SHEET

Annex to the Demand

International application No. PCT/NL01/00428	For International Preliminary Examining Authority use only													
Applicant's or agent's file reference 3760WO	Date stamp of the IPEA													
Applicant DSM N.V. et al														
CALCULATION OF PRESCRIBED FEES 1. Preliminary examination fee EUR 1533 P 2. Handling fee (<i>Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.</i>) EUR 147 H 3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box EUR 1680 TOTAL														
MODE OF PAYMENT <table style="width: 100%;"> <tr> <td style="width: 40%;">☒ authorization to charge deposit account with the IPEA (see below)</td> <td style="width: 20%;">☐</td> <td style="width: 40%;">cash</td> </tr> <tr> <td>☐ cheque</td> <td>☐</td> <td>revenue stamps</td> </tr> <tr> <td>☐ postal money order</td> <td>☐</td> <td>coupons</td> </tr> <tr> <td>☐ bank draft</td> <td>☐</td> <td>other (specify):</td> </tr> </table>			☒ authorization to charge deposit account with the IPEA (see below)	☐	cash	☐ cheque	☐	revenue stamps	☐ postal money order	☐	coupons	☐ bank draft	☐	other (specify):
☒ authorization to charge deposit account with the IPEA (see below)	☐	cash												
☐ cheque	☐	revenue stamps												
☐ postal money order	☐	coupons												
☐ bank draft	☐	other (specify):												
AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT (This mode of payment may not be available at all IPEAs) <table style="width: 100%;"> <tr> <td style="width: 50%; vertical-align: top;"> ☒ Authorization to charge the total fees indicated above. ☒ (<i>This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit</i>) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above. </td> <td style="width: 50%; vertical-align: top;"> IPEA/ EP Deposit Account No.: 2809 0052 Date: 17 December 2001 Name: Drs. J.M.A. Dautzenberg Signature: </td> </tr> </table>			☒ Authorization to charge the total fees indicated above. ☒ (<i>This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit</i>) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.	IPEA/ EP Deposit Account No.: 2809 0052 Date: 17 December 2001 Name: Drs. J.M.A. Dautzenberg Signature:										
☒ Authorization to charge the total fees indicated above. ☒ (<i>This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit</i>) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.	IPEA/ EP Deposit Account No.: 2809 0052 Date: 17 December 2001 Name: Drs. J.M.A. Dautzenberg Signature:													

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

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

13 FEB 2002
BA Reg. 2297

NOTIFICATION OF TRANSMITTAL OF
INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing (day/month/year)		08/02/2002
Applicant's or agent's file reference 3760WO		IMPORTANT NOTIFICATION
International application No. PCT/NL 01/ 00428	International filing date (day/month/year) 31/05/2001	Priority date (day/month/year) 05/06/2000
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.

Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer PITTORRU R Tel. (+49-89) 2399 2828
---	---



PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 3760W0	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NL 01/ 00428	International filing date (day/month/year) 31/05/2001	Priority date (day/month/year) 05/06/2000
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 <u>2</u> 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 consists 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 05/02/2002
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer JONES M H Tel. (+49-89) 2399 2828 

Form PCT/IPEA/409 (cover sheet) (July 1998)

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/NL 01/ 00428

I. Basis of report

1. The basis of international preliminary examination report 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).

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

3. To the extent that the international preliminary examination has been carried out (see item III above), the following is pointed out (Article 35 (2) and (3) (b) and Rule 70.7 and 70.8 (ii) PCT):

In light of the documents cited in the international search report, it is considered that the invention as claimed in the independent claims meets the criteria mentioned in Article 33 (1) PCT, i.e. it appears to be novel, to involve an inventive step and to be industrially applicable.

TRATAD DE COOPERACION EN MATERIA DE PATENTES

PCT

INFORME EXAMEN PRELIMINAR INTERNACIONAL (PCT artículo 36 y regla 70)

Referencia del solicitante o agente 3760WO	PARA PROSEGUIR Ver notificación de la transmisión del examen preliminar internacional (formato PCT/IPEA/416)	
No. Solicitud Internacional PCT/NL 01/00428	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 2 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; citas 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 05/02/2002
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 JONES M H Teléfono: +49 89 2399 2828

INFORME DEL EXAMEN PRELIMINAR INTERNACIONAL

Solicitud internacional No. PCT/NL 01/00428

I. BASE DEL INFORME

1. La base de este Informe del examen preliminar internacional es la solicitud como fue presentada originalmente.

III. El no-establecimiento de opinión en relación con la novedad, nivel inventivo y aplicación industrial

2. La pregunta de si la presente invención reivindicada aparenta ser novedosa, si tiene altura inventiva, o es aplicable industrialmente no ha sido objeto del examen preliminar internacional en relación con las reivindicaciones que no han sido buscadas (Art. 17(2) (a) o (3) y Regla 66.1 (a) PCT); ver también el informe de búsqueda internacional en relación con:

2.1 Solicitudes que contienen una pluralidad de reivindicaciones independientes (generalmente no más de 1 reivindicación independiente en la misma categoría es necesaria); Art. 6 PCT);

2.2 Materia que no fue objeto de búsqueda (Art. 17 (2) (a), Regla 66.1 (e) PCT).

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

3. Si se llevare a cabo el examen preliminar internacional (ver el ítem III mencionado anteriormente), se señala lo siguiente (Art. 35 (2) y (3) (b) y Regla 70.7 y 70.8 (II) PCT):

A la luz de los documentos citados en el informe de búsqueda internacional, se considera que la invención como es definida en por lo menos algunas de las reivindicaciones no aparenta cumplir los criterios mencionados en el Artículo 33 (1) PCT, esto es, no aparenta ser novedosa, tener nivel inventivo ni ser aplicable industrialmente.

**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.

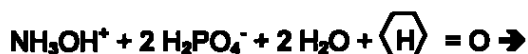
Las oximas pueden ser producidas en un procedimiento en el cual un medio de reacción acuoso, tamponado, que contiene ácidos o sales ácidas tampón, por ejemplo tampones de fosfato, y las sales tampón derivadas de estos ácidos, se recircula de modo continuo entre una zona de síntesis de hidroxilamonio, en la cual los iones nitrato se reducen catalíticamente con hidrógeno molecular hasta hidroxilamonio, y una zona de oximación en la que una cetona, por ejemplo, ciclohexanona, se convierte en una oxima. Antes de que se haga pasar el medio de reacción acuoso a la zona de síntesis de hidroxilamonio, dicho medio puede ser 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 una cetona, por ejemplo, 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 HNO_3 para compensar el agotamiento de la fuente de iones nitrato después de la separación de la oxima formada



El catalizador usado en la reducción de los iones nitrato es generalmente paladio y/o platino sobre un material soporte de carbono o alúmina, estando cargado el material soporte con una cantidad de 1 a 25 % en peso de paladio y/o platino. La actividad del catalizador se ve afectada de modo adverso por la presencia de contaminantes orgánicos, tales como la cetona y la oxima, en la corriente de recirculación.

Se han desarrollado una serie de técnicas para resolver este problema de la corriente de recirculación que contiene altas cantidades de contaminantes que intoxican o saturan el catalizador. El documento US-A-3.940.442 describe que la saturación del catalizador se evita calentando el medio de reacción acuoso que está siendo recirculado desde la zona de síntesis de la oxima de la ciclohexanona hasta la zona de síntesis del hidroxilamonio a una temperatura elevada en el intervalo de 50 °C a 106 °C. Los documentos GB-A-1.283.894 y US-A-3.997.807 describen que el tratamiento por calor del medio de reacción acuoso en presencia de ácido nitroso, los respectivos gases nitrosos reducen la extensión de la saturación del catalizador.

Se ha encontrado ahora 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 hidroxilamonio.

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 fosfato en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 3,0 mol/l. La invención proporciona también 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 fosfato en el medio de reacción acuoso que entra

en la zona de síntesis de la oxima de la ciclohexanona es mayor que 3,0 mol/l.

Usando el procedimiento según la invención es posible disminuir la cantidad de contaminantes orgánicos que saturan el catalizador, en particular la ciclohexanona y/o la oxima de la ciclohexanona, residuales, que entran en la zona de síntesis del hidroxilammonio en circunstancias posteriores iguales. Según la invención, es posible también omitir las etapas de separación de los contaminantes orgánicos o disminuir la amplitud a la que se llevan a cabo estas etapas, por ejemplo, usando un equipo más pequeño, con el aumento de la concentración de fosfato evitando o recortando el aumento de la cantidad de los contaminantes orgánicos que entran en la zona de síntesis del hidroxilammonio. Según la invención, es posible también aumentar la concentración de hidroxilammonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona, con el aumento de la concentración de fosfato evitando o suavizando un aumento de la cantidad de los contaminantes orgánicos que entran en la zona de síntesis del hidroxilammonio.

Según la invención, 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 3,0 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, 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 3,3 mol/l, más preferiblemente mayor que 3,4 mol/l, particularmente mayor que 3,5 mol/l, más particularmente mayor que 3,7 mol/l. El aumento de la concentración de fosfato da como resultado una disminución adicional de la concentración de los contaminantes orgánicos que salen de la zona de síntesis de la oxima de la ciclohexanona. No hay un límite superior específico para la concentración de fosfato. 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.

No hay un límite inferior específico para la concentración de hidroxilammonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclo-

hexanona. 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 0,8 mol/l. Es ventajoso un aumento de la concentración de hidroxilamonio, ya que entonces se puede aumentar la conversión del hidroxilamonio en la zona de síntesis de la oxima de la ciclohexanona. Además, la cantidad de la oxima de la ciclohexanona producida por unidad de tiempo se puede aumentar aumentando la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona. 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 1,0 mol/l, más preferiblemente mayor que 1,1 mol/l, particularmente mayor que 1,2 mol/l, más particularmente mayor que 1,4 mol/l, y muy preferiblemente mayor que 1,6 mol/l. 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.

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 el medio de reacción acuoso que sale de la zona de síntesis de la oxima de la ciclohexanona. El procedimiento según la invención, tiene la ventaja de que con él este efecto se suaviza o se evita.

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, y muy preferiblemente mayor que 2,4, donde $c(\text{fosfato})$ representa la concentración de fosfato (en mol/l) y $c(\text{NH}_2\text{OH}^+)$ representa la concentración de hidroxilamonio (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 hidroxilamonio 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 $c(\text{fosfato})/c(\text{NH}_3\text{OH}^+)$ es menor que 10.

En la zona de síntesis de la oxima de la ciclohexanona, se hace reaccionar el hidroxilammonio para formar la oxima de la ciclohexanona. Preferiblemente, el medio de reacción acuoso y la ciclohexanona se ponen en contacto en un flujo contracorriente. Es preferible, que la ciclohexanona, el disolvente orgánico y el medio de reacción acuoso se pongan en contacto en la zona de síntesis de la oxima de la ciclohexanona y que un medio orgánico que comprende el disolvente orgánico y la oxima de la ciclohexanona sea separado de la zona de síntesis de la oxima de la ciclohexanona. Esto es un modo muy efectivo de separar la oxima de la ciclohexanona del medio de reacción acuoso. Un procedimiento adecuado en el que se usa un disolvente orgánico, es por ejemplo el descrito en el documento GB-A-1.138.750. Muy 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. 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. Un aumento de 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 tiene la ventaja de que la separación del disolvente orgánico de la oxima de la ciclohexanona, por ejemplo en un proceso de destilación, se puede realizar usando menos energía. 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. Se puede alcanzar un aumento de la concentración de la oxima de la ciclohexanona, por ejemplo, reduciendo el caudal del disolvente en la zona de síntesis de la oxima con relación al caudal de la ciclohexanona en la zona de síntesis de la oxima. 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.

Se ha encontrado en esta invención que un aumento de 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 puede dar como resultado un aumento de la concentración de contaminantes orgánicos en el medio de reacción acuoso que sale de la zona de síntesis del hidroxilamonio. El procedimiento según la invención, tiene la ventaja de que con él este efecto se suaviza o se evita.

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 6, más preferiblemente entre 1,5 y 4.

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 con el fin de reducir la cantidad de contaminantes orgánicos residuales, 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, se pone en contacto con un disolvente orgánico en una zona de extracción. El disolvente orgánico usado en la zona de extracción es preferiblemente el mismo que el disolvente orgánico usado en la zona de síntesis de la oxima de la ciclohexanona. 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. 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 hace funcionar 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. Preferiblemente, el contenido conjunto de la ciclohexanona y la oxima de la ciclohexanona en el medio de reacción acuoso que sale de la zona de extracción es menor que 0,2 % en peso (2000 ppm), 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 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 hidroxilammonio 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).

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 hidroxilammonio. 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.

5 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 40-65 °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
10 en la zona de síntesis del hidroxilamonio, está entre 0,5 y 6, 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
15 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

20 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 y B representan la zona de síntesis del hidroxilamonio y la zona de síntesis de la oxima de la ciclohexanona, respectivamente.
25 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
30 la zona B de síntesis de la oxima de la ciclohexanona a través de la línea 3. La concentración de fosfato en el medio de reacción acuoso que se pasa desde la zona A de síntesis del hidroxilamonio a la zona B de síntesis de la oxima de la ciclohexanona, es mayor que 3,0 mol/l. La ciclohexanona a ser convertida, se añade en un disolvente orgánico a la zona B de síntesis de la oxima a través de la línea 4. La ciclohexanona
35 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 síntesis de la oxima, 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 síntesis de la oxima, el contenido de hidroxilamonio del medio de reacción acuoso ha sido reducido 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.

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 tempe-

ratura de 55 °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:

1,30 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$

1,38 mol de $\text{NH}_4\text{H}_2\text{PO}_4$

5 0,365 mol de H_3PO_4

1,73 mol de NH_4NO_3

41,5 mol de H_2O

y se añadió de forma continua a la zona B de síntesis de la oxima de la ciclohexanona (una columna con empaquetamiento, pulsada, funcionando a 55 °C), junto con ciclohexanona y tolueno. La relación molar del hidroxilammonio añadido a la zona de síntesis de la oxima de la ciclohexanona por unidad de tiempo frente a la ciclohexanona añadida a la zona de síntesis de la oxima de la ciclohexanona por unidad de tiempo, esto es la relación hidroxilammonio (en mol/s)/ciclohexanona (en mol/s) fue 0,95. Sustancialmente todo el hidroxilammonio había reaccionado para formar la oxima de la ciclohexanona. La oxima de la ciclohexanona disuelta en tolueno se separó de la zona de síntesis del hidroxilammonio, siendo la concentración de 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.

El medio de reacción acuoso que sale de la zona C de extracción contenía 123 ppm (0,0123 % en peso) de compuestos orgánicos residuales (ciclohexanona + la oxima de la ciclohexanona).

Ejemplo 2

25 En este ejemplo todas las condiciones son las mismas del ejemplo 1, excepto que el medio de reacción acuoso que sale de la zona A de síntesis del hidroxilammonio y entra en la zona B de síntesis de la oxima de la ciclohexanona tenía la siguiente composición:

1,30 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$

30 1,38 mol de $\text{NH}_4\text{H}_2\text{PO}_4$

0,665 mol de H_3PO_4

1,73 mol de NH_4NO_3

39,9 mol de H_2O

El medio de reacción acuoso que sale de la zona C de extracción contenía 43 ppm de compuestos orgánicos residuales (ciclohexanona + la oxima de la ciclohexanona).

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 de síntesis del hidroxilamonio y entra en la zona B de síntesis de la oxima de la ciclohexanona tenía

5 la siguiente composición:

1,50 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$

1,45 mol de $\text{NH}_4\text{H}_2\text{PO}_4$

0,39 mol de H_3PO_4

1,65 mol de NH_4NO_3

10 39,8 mol de H_2O

El medio de reacción acuoso que sale de la zona C de extracción contenía 218 ppm de compuestos orgánicos residuales (ciclohexanona + la oxima de la ciclohexanona).

Ejemplo 4

15 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 de síntesis del hidroxilamonio y entra en la zona B de síntesis de la oxima de la ciclohexanona tenía la siguiente composición:

1,5 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$

20 1,45 mol de $\text{NH}_4\text{H}_2\text{PO}_4$

0,80 mol de H_3PO_4

1,65 mol de NH_4NO_3

37,8 mol de H_2O

25 El medio de reacción acuoso que sale de la zona C de extracción contenía 42 ppm de compuestos orgánicos residuales (ciclohexanona + la oxima de la ciclohexanona).

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 de síntesis del hidroxilamonio y entra en la zona B de síntesis de la oxima de la ciclohexanona tenía la siguiente composición:

1,50 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$

1,45 mol de $\text{NH}_4\text{H}_2\text{PO}_4$

0,93 mol de H_3PO_4

35 1,65 mol de NH_4NO_3

36,9 mol de H_2O

El medio de reacción acuoso que sale de la zona C de extracción contenía 24 ppm de compuestos orgánicos residuales (ciclohexanona + la oxima de la ciclohexanona).

Ejemplo 6

- 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 de síntesis del hidroxilamonio y entra en la zona B de síntesis de la oxima de la ciclohexanona tenía la siguiente composición:

- 1,60 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$
 10 1,45 mol de $\text{NH}_4\text{H}_2\text{PO}_4$
 0,30 mol de H_3PO_4
 1,65 mol de NH_4NO_3
 39,6 mol de H_2O

- El medio de reacción acuoso que sale de la zona C de extracción contenía 277
 15 ppm de compuestos orgánicos residuales (ciclohexanona + la oxima de la ciclohexanona).

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 de síntesis del hidroxilamonio y entra en la zona B de síntesis de la oxima de la ciclohexanona tenía la siguiente composición:

- 1,8 mol de $\text{NH}_3\text{OH}\cdot\text{H}_2\text{PO}_4$
 1,45 mol de $\text{NH}_4\text{H}_2\text{PO}_4$
 0,88 mol de H_3PO_4
 25 1,65 mol de NH_4NO_3
 36,4 mol de H_2O

El medio de reacción acuoso que sale de la zona C de extracción contenía 26 ppm de compuestos orgánicos residuales (ciclohexanona + la oxima de la ciclohexanona).

- 30 En la tabla se da un resumen de los ejemplos 1 a 7, indicando la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona (en mol/l para el medio de reacción acuoso que tiene una densidad de 1,25 mol/l), la concentración de fosfato en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona (en mol/l) y la concentración de compuestos orgánicos residuales (ciclohexanona + la oxima de la ciclohexanona) en el medio de reacción acuoso que sale de la zona de extracción.
- 35

Los ejemplos demuestran que un aumento de la concentración de fosfato da como resultado una disminución de la concentración de compuestos orgánicos residuales en circunstancias posteriores iguales (por ejemplo, a concentración constante de hidroxilamonio). Los ejemplos demuestran también que un aumento de la concentración de compuestos orgánicos residuales como resultado de un aumento de la concentración de hidroxilamonio se evita o se suaviza al aumentar la concentración de fosfato.

Tabla: Resumen de los resultados de los ejemplos 1 a 7

Ejemplo	Concentración de hidroxilamonio (mol/l)	Concentración de fosfato (mol/l)	Concentración de compuestos orgánicos residuales (ppm)
1	1,3	3,04	123
2	1,3	3,34	43
3	1,5	3,34	218
4	1,5	3,75	42
5	1,5	3,88	24
6	1,6	3,35	277
7	1,6	3,93	26

En el texto anterior se han ilustrado y descrito realizaciones particulares de esta 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 fosfato en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 3,0 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 fosfato en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 3,0 mol/l.

3. El procedimiento según la reivindicación 1 o la reivindicación 2, caracterizado porque 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 3,3 mol/l, preferiblemente mayor que 3,5 mol/l, más preferiblemente mayor que 3,7 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 0,8 mol/l.

5. El procedimiento según la reivindicación 4, caracterizado porque la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima, es mayor que 1,0 mol/l.

6. El procedimiento según la reivindicación 5, caracterizado porque la concentración de hidroxilamonio en el medio de reacción acuoso que entra en la zona de síntesis de la oxima, es mayor que 1,2 mol/l, preferiblemente mayor que 1,4 mol/l, y más preferiblemente mayor que 1,6 mol/l.

7. El procedimiento según una cualquiera de las reivindicaciones 1 a 6, caracterizado porque 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 $> 2,0$, donde $c(\text{fosfato})$

representa la concentración de fosfato (en mol/l) y $c(\text{NH}_3\text{OH}^+)$ representa la concentración de hidroxilamonio (en mol/l).

8. El procedimiento según la reivindicación 7, caracterizado porque en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona, la relación $c(\text{fosfato})/c(\text{NH}_3\text{OH}^+)$ es $> 2,1$.

9. El procedimiento según una cualquiera de las reivindicaciones 1 a 8, caracterizado porque la ciclohexanona, el disolvente orgánico y el medio de reacción acuoso se ponen en contacto en la zona de síntesis de la oxima de la ciclohexanona y porque 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.

10. El procedimiento según la reivindicación 9, 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.

11. El procedimiento según la reivindicación 9 o la reivindicación 10, 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 5 % en peso.

12. El procedimiento según la reivindicación 11, 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.

RESUMEN

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 fosfato en el medio de reacción acuoso que entra en la zona de síntesis de la oxima de la ciclohexanona es mayor que 3,0 mol/l.

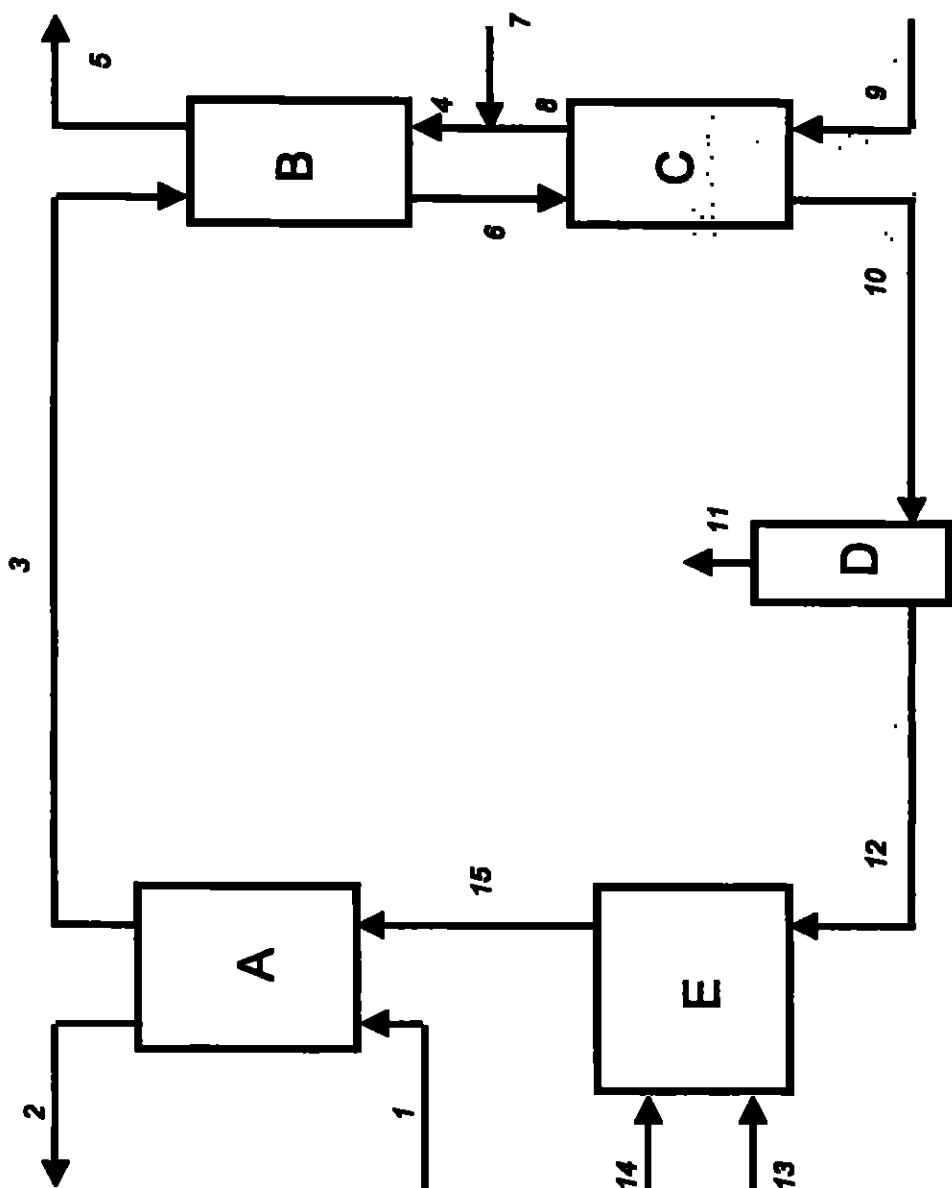


FIG. 1

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
PATENTE DE INVENCION	()	()
MODELO DE UTILIDAD	()	()
Indicación de que se solicita la concesion de una patente	()	()
Datos de identificación del solicitante o de la persona que se presenta la solicitud	()	()
Descripción de la invencion.	()	()
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 solicitante o de la persona que presenta La solicitud	()	()
Representación gráfica del esquema de trazado	()	()
Comprobante de pago de las tasas establecidas	()	()
COMPLETA ()	INCOMPLETA ()	()

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