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SOLICITUD

PATENTE DE INVENCION

21 EXPEDIENTE No.

04-21423

54 TITULO PROCESO PARA DESTILAR A PRESION REDUCIDA UN PRODUCTO ALCALINO DE
CAPROLACTAMA

51 CLASIFICACION INTERNACIONAL C07D 223/10

71 SOLICITANTE DSM IP Asocio B V,

DOMICILIO HEERLEN, HOLANDA

74 APODERADO JIMENA ESCOBAR URIBE

22 BOGOTA, D C, MARZO 7, 2004

SS

FORMULARIO ÚNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL

SOLICITUD DE:

1

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Patente de Invención

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Patente de Modelo de Utilidad

☐

Capítulo I

☒

Capítulo II

2

SOLICITANTE
(71)

Nombre: **DSM IP Assets B.V.**
Dirección: Het Overloon 1, NL-6411 TE
Nacionalidad o Domicilio: Heerlen, Holanda
Lugar de Constitución: Holanda
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C.C. ☐ NIT ☐
C.E. ☐ Otro ☐
Número

3

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AP DERADO
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4

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Dirección:
Nacionalidad o domicilio:

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7 Clasificación Internacional (51) C07D 223/10

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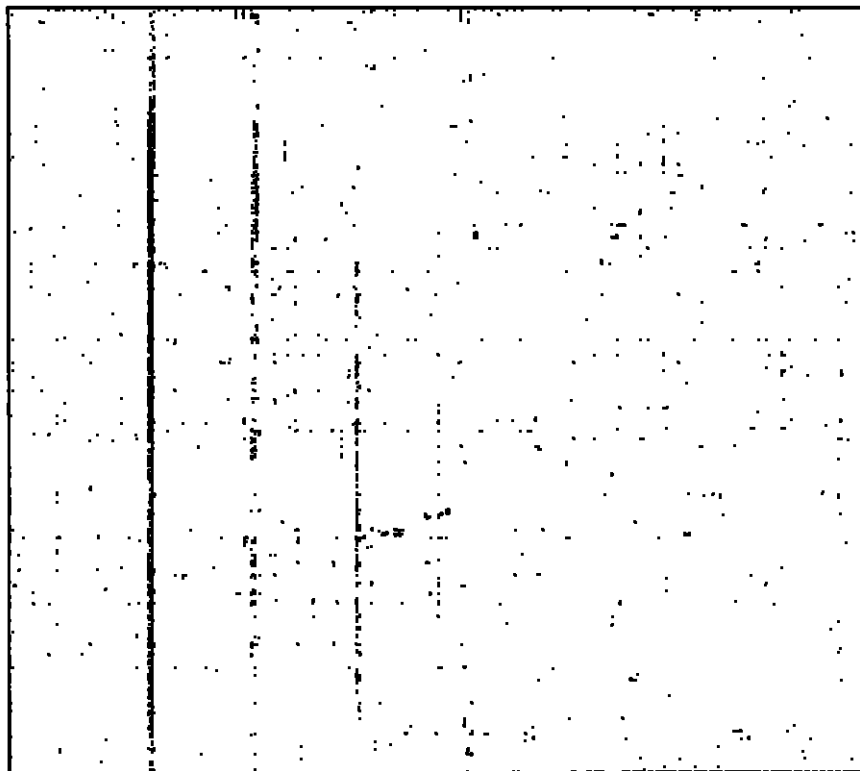
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9 Comprobante de pago No. 04 - 15.043 Fecha Febrero 25, 2004

- ☐ 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
- ☐ Poderes si fuere el caso
- ☐ 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 * Notificación de la inscripción de un cambio.

11 FIGURA CARACTERÍSTICA



12 Solicito la concesión de la patente

NOMBRE: JIMENA ESCOBAR URIBE

FIRMA: *Jimena Uribe*

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

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***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
ESCOBAR URIBE ASOCIADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	9706081	25/02/2004	6,928,700.00

***** CONCEPTO *****

CANT. RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN	422,000.00
	TOTAL :	422,000.00

SON: CUATROCIENTOS VEINTIDOS MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

ANEXOS

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- 6.) **MOSTERT, Eelco**
(Ambachtsstraat 28, NL-6411 LP Heerlen, Holanda).

Solicito expresamente a nombre de la sociedad **DSM IP Assets B.V.**, sociedad constituida de conformidad con las leyes de Holanda, domiciliada en Het Overloon 1, NL-6411 TE, Heerlen, Holanda, el otorgamiento de Patente para la invención titulada "PROCESO PARA DESTILAR A PRESIÓN REDUCIDA UN PRODUCTO ALCALINO DE CAPROLACTAMA".

Clase: CO7D 223/10


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

POWER OF ATTORNEY

The undersigned
acting on behalf of and representing
DSM IP ASSETS B.V.
domiciled at Het Overloon 1, 6411 TE Heerlen, The
Netherlands
hereby appoints
JIMENA ESCOBAR-URIBE and/or **IGNACIO
ESCOBAR-URIBE**
domiciled at Bogota, Colombia
CARRERA 11 A No. 94-76 OF. 305-306

as our true and legal attorneys with the necessary
powers: 1. to apply to the administrative, judicial and
police authorities of the Republic of Colombia, in any
instance or appeal, for obtaining registration of patents,
utility models, industrial designs, commercial ensigns
and names, trademarks, domain names, copyrights and
neighbouring rights, plant varieties, health licenses as
well as their assignments, extensions, renewals,
changes of name and domicile; 2. to prepare, apply for,
obtain, execute and register contracts, licenses,
authorizations and registrations of any kind; 3. to
intervene as plaintiffs or defendants, in any instance or
appeal, before any judge, court, tribunal, corporation,
public officer or authority in any judicial, administrative
or police action, such as: actions dealing with
commercial ensigns and names; oppositions against
trademark registrations; caducity and nullity actions;
recovery actions, actions arising from obtainment and
working of license agreements; actions dealing with
unfair competition; criminal actions; actions claiming
indemnity for damages, complaints or remarks on all
sort of industrial property matters; the performance of
precautionary measures, and in any other similar
action, measure or appeal related to industrial property
matters, copyrights and neighbouring rights and
obtainment of plant varieties rights. To this effect, we
hereby authorize them to file applications, make
descriptions, amendments, protests, declarations,
oppositions, cancellations, appeals and claims; to pay
taxes, quotas and fines as provided by law; to waive or
abandon granted rights or rights in process of being
granted, to receive all kind of documents and securities;
to issue the respective releases and, in general to take,
before said authorities, pertinent steps to the above-
mentioned purposes and take all measures they may
deem advisable to protect our interests, with all other
necessary legal faculties, and we hereby declare as
good and valid whatever the attorneys should do to our
benefit.

This power comprises the authority to ratify or confirm
on our behalf any action, as well as the faculty of
receiving, desisting, transacting, compromising,
conciliating, substituting and revoking substitutions,
taking notifications and appointing judicial or extra-
judicial attorneys.

Signed at Heerlen
on 27 May 2003



Emil Rudolf Antonius MATULEWICZ, proxy-holder

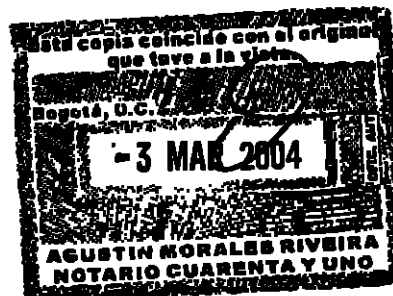
DOCUMENTO DE PODER

El suscrito
obrando en nombre y representación de con
DSM IP ASSETS B.V.
domicilio en Het Overloon 1, 6411 TE Heerlen,
Holanda
 nombra a
JIMENA ESCOBAR-URIBE y/o **IGNACIO ESCOBAR-
URIBE**
domiciliados en Bogotá, Colombia
CARRERA 11 A No. 94-76 OF. 305-306

apoderados verdaderos y legales con poder especial,
amplio y suficiente: 1. para recabar de las oficinas y
autoridades colombianas administrativas, judiciales y
de policía en cualquier instancia o recurso, la obtención
de patentes de invención, modelos de utilidad, diseños
industriales, registro de marcas, nombres de dominio,
registro de derechos de autor y derechos conexos,
registro de variedades vegetales, depósito de nombres
comerciales y enseñanzas, registros sanitarios, así como
sus traspasos, prórrogas, renovaciones, cambios de
nombre y de domicilio; 2. elaborar, tramitar, solicitar,
obtener, realizar, ejecutar y registrar contratos,
licencias, autorizaciones y registros de cualesquiera
clase; 3. intervenir como demandante o como
demandado en cualquier instancia y recurso, y ante
cualquier juez, entidad, corporación, funcionario público
o autoridad en acciones judiciales, administrativas y de
policía, tales como acciones derivadas del nombre o
enseña comerciales; observaciones u oposición a
registro de marcas; acciones de caducidad y nulidad;
acciones reivindicatorias; acciones derivadas de la
obtención o explotación de licencias; acciones de
competencia desleal; demandas penales y civiles;
acciones de indemnización de perjuicios, reclamos u
observaciones a cualquier asunto sobre propiedad
industrial; el ejercicio de medidas cautelares y
cualesquiera otras acciones, medidas o recursos
similares relacionados con la propiedad industrial, los
derechos de autor y derechos conexos y los derechos
de obtentor de variedades vegetales. A este efecto, los
facultamos para elevar solicitudes, formular
descripciones, enmiendas, protestas, declaraciones,
oposiciones, cancelaciones, apelaciones y reclamos;
pagar impuestos, cuotas y gravámenes prescritos por
la ley; renunciar o desistir a derechos concedidos o en
curso de concesión; recibir toda clase de documentos y
valores dando el descargo respectivo, y, en general,
para dar ante dichas autoridades todos los pasos
necesarios al efecto indicado y tomar todas las
medidas que creyeren conducentes al resguardo de
nuestros intereses, con todas las demás facultades
necesarias y por este documento desde ahora
declaramos válido y bueno todo cuanto los apoderados
hicieren en nuestro beneficio.

Este poder comprende la facultad de ratificar o
confirmar en nuestro nombre lo actuado, así como la
facultad de desistir, transigir, comprometer, conciliar,
sustituir y revocar sustituciones, recibir notificaciones y
nominar apoderados judiciales o extrajudiciales.

Firmado en Heerlen
en 27 May 2003

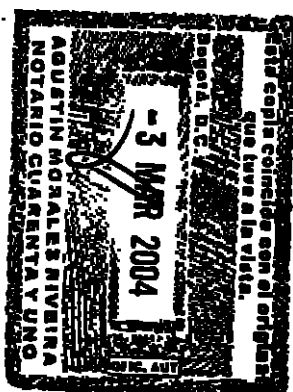
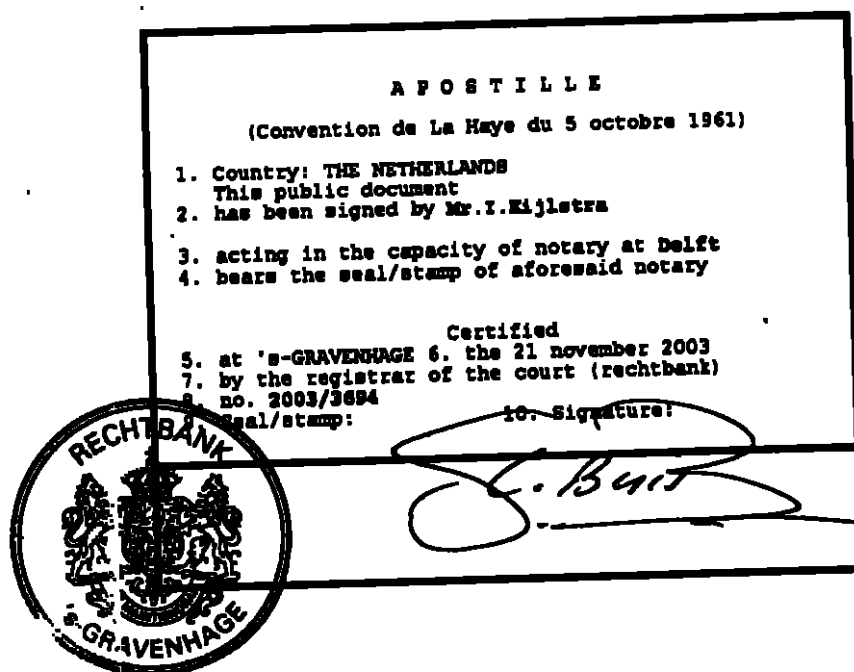


I, the undersigned, hereby certify that DSM IP Assets B.V. with full address at Het Overloon 1, 6411 TE Heerlen, The Netherlands, was at the day the foregoing instrument was signed, duly organized, registered and existing under the Laws of The Netherlands, and that Mr. Emil Rudolf Antonius MATULEWICZ, who signed the foregoing instrument, was at that day a lawful representative of the Corporation, and duly authorized to sign the documents relating to trademarks, including this Certificate, Power of Attorney and other documents concerning the recordation of certain rights and changes thereof, on behalf of the Corporation.

Delft, The Netherlands, by me
Izaak Kijlstra, LL.M., Notary,
practising at Delft, The Netherlands



on this 17th day of November. 2003



BOGOTA D.C. DICIEMBRE 12, 2003

**TRADUCCIÓN OFICIAL LEGALIZACIÓN PODER DE
DSM IP ASSETS B.V. A JIMENA ESCOBAR-URIBE y/o IGNACIO ESCOBAR-URIBE**

NOTA DE TRADUCCIÓN) SE TRATA DE UN PODER DE FECHA MAYO 27, 2003, CONFERIDO POR DSM IP ASSETS B.V. A JIMENA ESCOBAR-URIBE Y/O IGNACIO ESCOBAR-URIBE. ESTE PODER ESTA EN IDIOMAS INGLES Y CASTELLANO.

YO, EL SUSCRITO CON EL PRESENTE CERTIFICO QUE DSM IP ASSETS B.V. CON DIRECCIÓN COMPLETA EN HET OVERLOON 1, 8411 TE HEERLEN, PAISES BAJOS, ESTABA PARA EL DIA EN QUE EL ANTERIOR INSTRUMENTO FUE FIRMADO, DEBIDAMENTE ORGANIZADA, REGISTRADA Y EXISTIENDO BAJO LAS LEYES DE LOS PAISES BAJOS, Y QUE EL SR. EMIL RUDOLF ANTONIUS MATULEWICZ, QUIEN FIRMO EL ANTERIOR DOCUMENTO, ERA EN ESE DIA EL REPRESENTANTE LEGAL DE LA CORPORACIÓN, Y DEBIDAMENTE AUTORIZADO PARA FIRMAR LOS DOCUMENTOS RELACIONADOS CON NOMBRES COMERCIALES, INCLUYENDO ESTE CERTIFICADO, PODER, Y OTROS DOCUMENTOS CONCERNIENTES AL REGISTRO DE CIERTOS DERECHOS Y CAMBIOS EN LOS MISMOS, EN NOMBRE DE LA CORPORACIÓN.

DELFT, PAISES BAJOS, POR MI,
ISAAC KIJLSTRA, LL.M. NOTARIO
EJERCIENDO EN DELFT, LOS PAISES BAJOS

HOY NOVIEMBRE 17, 2003

(SELLO) Mr. I. KIJLSTRA, NOTARIO DELFT.

APOSTILLE

(Convención de la Haya, Octubre 5, 1961)

1. PAIS: LOS PAISES BAJOS
ESTE DOCUMENTO PUBLICO
2. HA SIDO FIRMADO POR MR. I. KIJLSTRA
3. ACTUANDO EN SU CALIDAD DE NOTARIO EN DELFT



02. CONT. TRADUCCIÓN OFICIAL LEGALIZACIÓN PODER DE
DSM IP ASSETS B.V. A JIMENA ESCOBAR-URIBE y/o IGNACIO ESCOBAR-URIBE

4. LLEVA EL SELLO/ESTAMPILLA DEL MENCIONADO NOTARIO

CERTIFICADO

5. EN 'S-GRAVENHAGE.

6. EL 21 NOVIEMBRE 2003

7. POR EL REGISTRADOR DE LA CORTE (RECHTBANK)

8. NR. 2003/3694

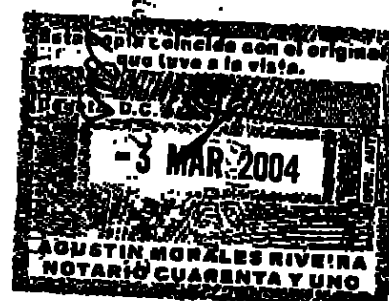
10. FIRMA (HAY UNA FIRMA)

(SELLO) RECHTBANK, 'S-GRAVENHAGE

Fidel Murcia
FIDEL ANTONIO MURCIA MURCIA
Traductor e Interprete Oficial
Resolución No. 488/04 Ministerio de Justicia



Fidel Murcia



RESUMEN

La invención se refiere a un proceso para destilar a presión reducida un producto de caprolactama alcalino, dicho producto de caprolactama alcalino comprende (i) caprolactama, (ii) impurezas orgánicas, y (iii) una o más bases seleccionadas del grupo que consiste en hidróxidos alcalinos y amino caproato alcalino, caracterizado por que la alcalinidad del producto de caprolactama alcalino es menor que 5 meq por Kg de caprolactama.

PROCESO PARA DESTILAR A PRESION REDUCIDA UN PRODUCTO
ALCALINO DE CAPROLACTAMA

La presente invención se refiere a un proceso para purificar caprolactama, el cual comprende destilación a presión reducida de un producto de caprolactama alcalino.

La producción de caprolactama generalmente comprende la preparación del producto de caprolactama, e.g., mediante rearreglo de Beckmann, seguida de la purificación del producto de caprolactama para obtener un producto de caprolactama grado polimerizable. La purificación puede incluir destilación del producto de caprolactama a presión reducida en presencia de una base, e.g., un hidróxido alcalino o un amino caproato alcalino. Se mencionan amplios intervalos para la cantidad de base adicionada. En DD-A-202870 se describe un proceso en el cual el producto de caprolactama se purifica por destilación bajo presión reducida después de la adición de 0.05% a 1.0 % de una sal alcalina del ácido capróico al producto de caprolactama a ser purificado. En US-A-3, 839, 324, se describe un proceso en el cual la caprolactama se somete a destilación alcalina a vacío, en el que el hidróxido de sodio está presente entre 0.05 – 0.5 % en peso. En US-A-5, 496, 941 se describe un proceso en el que la caprolactama se destila en presencia de una base, la cantidad de base añadida se escoge por regla del

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0.05 al 0.9 % en moles con base en la caprolactama. En US-A-4, 457, 807 se describe un proceso en el cual caprolactma no tratada que contiene 0.2 mg de NaOH sólido por gramo de caprolactama (5 mmol de NaOH por Kg de caprolactama) se suministra a la columna de rectificación donde se efectúa la rectificación a presión reducida.

Se ha encontrado ahora, que la calidad de la caprolactama purificada, e.g., expresada por el número PAN, está influenciada por la alcalinidad del producto de caprolactama a ser destilado, en particular, se ha encontrado que el número PAN disminuye cuando la alcalinidad del producto alcalino de caprolactma se disminuye por debajo de 5 meq por Kg de caprolactama. Se encontró que la ocurrencia de fluctuaciones indeseadas en la calidad, e.g., que resultan de la oxidación de la caprolactma durante la destilación, disminuyen cuando la alcalinidad se aumenta por encima de 0 meq por Kg de caprolactama.

En consecuencia la invención proporciona un proceso para purificar caprolactama, el cual comprende destilación a presión reducida de un producto de caprolactama alcalino, dicho producto de caprolactama alcalino comprende (i) caprolactama, (ii) impurezas, (iii) una o más bases seleccionadas del grupo que consiste de hidróxidos alcalinos y amino caproatos alcalinos, caracterizados porque la alcalinidad del producto de caprolactama alcalino es menor que 5 meq (5 mili-equivalentes) por Kg de caprolactama.

Como se usa aquí, la alcalinidad se refiere a la alcalinidad a 25 °C determinada por titulación (después que se diluye el producto de caprolactama alcalino con agua de pH= 5.7 para obtener una solución que contiene 15 % en peso de caprolactama) con solución de HCl 0.01 N hasta un pH de 5.7, por lo tanto:

$$\text{Alcalinidad} = \frac{V \cdot t}{a} \cdot 1000 / 0.15$$

Donde:

V = mL de solución de HCl adicionados

t = molaridad de la solución de HCl (=0.01)

a = peso de la muestra (g)

El proceso de acuerdo con la invención produce una caprolactama purificada que tiene una alta calidad, en particular un bajo número PAN (determinado de acuerdo con la ISO DIS 8660 – Plásticos- Determinación del índice de permanganato de la caprolactama- método Espectrométrico, revisión de la primera edición (ISO 8660; 1988). Mas aún se obtiene un bajo valor de extinción (determinado de acuerdo con la ISO 7059 -caprolactama para uso industrial- Determinación de la absorbancia a una longitud de onda de 290 nm)

Preferiblemente la alcalinidad del producto de caprolactama alcalino es menor que 4.5 meq por Kg de producto de caprolactama alcalino, más preferiblemente menor

que 4.0 meq por Kg, en particular menor que 3.0 meq por Kg, más en particular menor que 2.0 meq por Kg. Esta además disminuye el número PAN.

Preferiblemente la alcalinidad del producto de caprolactama alcalino es mayor que 0.05 meq por Kg de producto de caprolactama alcalino, más preferiblemente mayor que 0.10 meq por Kg, en particular mayor que 0.15 meq por kg. Incrementando la alcalinidad hasta los valores anteriores, se mejora la estabilidad, i.e., la sensibilidad para la ocurrencia de fluctuaciones indeseadas en la calidad.

Como se usa aquí los valores mencionados para la alcalinidad y concentraciones en el producto de caprolactama alcalino se refieren a los valores de alcalinidad del producto de caprolactama alcalino a ser destilada, o sea cuando el producto de caprolactama alcalino se alimenta a la zona de destilación, i.e., la zona en la cual se efectúa la destilación, los valores mencionados para la alcalinidad y otras concentraciones en el producto de caprolactama alcalino se refieren a los valores en el producto de caprolactama alcalino, entrando a la zona de destilación.

El producto de caprolactama alcalino comprende caprolactama. Típicamente, el producto de caprolactama alcalino comprende del 95 al 99 % en peso de caprolactma, en particular al menos el 97 % en peso de caprolactama, más en particular al menos el 98 % en peso de caprolactama (relativo al peso total del producto de caprolactma alcalina).

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Las impurezas pueden ser impurezas orgánicas, e.g., impurezas orgánicas de bajo punto de ebullición (que tienen un punto de ebullición más bajo que el de la caprolactama) y/o impurezas de alto punto de ebullición (que tienen un punto de ebullición más alto que el de la caprolactama).

El producto de caprolactama alcalino puede incluir agua. Preferiblemente, el producto de caprolactama alcalino comprende menos del 5 % en peso, más preferiblemente menos del 3 % en peso, en particular menos del 2 % en peso, más en particular menos del 1 % en peso (relativo al peso del producto de caprolactama alcalino). Una muy baja cantidad de agua tiene la ventaja que permite crear y mantener más fácilmente una presión reducida, durante la destilación.

El producto de caprolactama alcalino comprende una o más bases seleccionadas del grupo que consiste de hidróxidos alcalinos y aminocaproatos alcalinos. Preferiblemente, una o más bases se seleccionan del grupo que consiste de hidróxido de sodio, aminocaproato de sodio, hidróxido de potasio, aminocaproato de potasio, más preferiblemente se selecciona del grupo que consiste de hidróxido de sodio y aminocaproato de sodio. Preferiblemente al menos el 75 % en moles, más preferiblemente al menos el 85 % en moles, en particular al menos el 95 % en moles, más en particular sustancialmente toda de dichas una o más bases es aminocaproato alcalino. Incrementar las cantidades relativas de aminocaproato tiene la ventaja que disminuye la ocurrencia de polimerización

durante la destilación. La formación de oligómeros y polímeros es desventajosa ya que produce obstrucciones en el equipo de destilación. Sobre todo se pierde caprolactama. Los porcentajes anteriores se dan en relación a la cantidad total molar de dichas una o más bases.

El proceso de acuerdo con la invención, es preferiblemente un proceso para la purificación del producto de caprolactama, dicho producto de caprolactama comprende (i) caprolactama, (ii) impurezas; en donde dicho proceso comprende la adición de una o más de las bases a dicho producto de caprolactama, para obtener el producto de caprolactama alcalino. Preferiblemente el hidróxido alcalino se adiciona como una solución acuosa del hidróxido alcalino. Típicamente el producto de caprolactama comprende del 15 al 99 % en peso de caprolactama, en particular al menos el 50% en peso de caprolactama, más en particular al menos el 75 % en peso de caprolactama. Típicamente, el producto de caprolactama es un producto de caprolactama acuosa que contiene agua. Típicamente la suma de la cantidad de agua y caprolactama y agua en el producto de caprolactama es preferiblemente al menos del 95 % en peso, en particular al menos el 87 % en peso, más en particular al menos el 98 % en peso. Estos porcentajes se dan en relación al peso total del producto de caprolactama. En una formulación de la invención, el producto de caprolactama tiene una acidez de entre 0 y 5 meq por Kg de caprolactama, es neutro, o tiene una alcalinidad de entre 0 y 5 meq por Kg de caprolactama. En esta formulación el producto de caprolactama alcalino se puede producir mediante la adición de muy pequeñas cantidades de dichas una o más

bases. Esto produce una caprolactama purificada que tiene una buena calidad, expresada mediante el número PAN y una buena estabilidad. Como se usa aquí la acidez se refiere a la acidez a 25 °C determinada por titulación (después de diluir el producto de caprolactama alcalino con agua de pH = 5.7 para obtener una solución que contiene el 15 % en peso de caprolactama) con una solución de NaOH 0.01 N hasta pH 5.7, por lo tanto,

$$\text{Acidez} = \frac{V \cdot t}{a} \cdot 1000 / 0.15$$

Donde:

V = mL de solución de NaOH adicionados

t = molaridad de la solución de NaOH (=0.01)

a = peso de la muestra (g)

Preferiblemente, el producto de caprolactama es neutro o tiene una alcalinidad de entre 0 y 5 meq por Kg de caprolactama. En una formulación el proceso comprende la adición de entre 0.05 a 10 mmol de una o más bases por Kg de caprolactama, preferiblemente entre 0.05 y 5.0 mmol por Kg, más preferiblemente entre 0.10 y 4.5 mmol por Kg, en particular entre 0.15 y 3.0 mmol por Kg, más en particular entre 0.20 y 2.0, mucho más preferiblemente menor que 1.0 mmol por Kg de caprolactama. Preferiblemente la cantidad de base adicionada se disminuye cuando el producto de caprolactama es menos ácido / más alcalino. En una formulación, el producto de caprolactama alcalino se obtiene directamente

después de la adición de una o más bases, y el producto de caprolactama alcalino se puede destilar sin más etapas previas a dicha destilación. En otra formulación el producto alcalino obtenido que sigue a la adición, se somete a una o más etapas de purificación, e.g., a una etapa en la cual se separa el agua del producto alcalino para obtener el producto de caprolactama alcalino a ser destilado.

En una formulación preferida, el proceso incluye la adición del hidróxido alcalino al producto de caprolactama, formando un producto alcalino y haciendo reaccionar al menos parte de dicho hidróxido alcalino, en el producto alcalino, para formar aminocaproato alcalino antes de la destilación. Esto tiene la ventaja que el aminocaproato alcalino se puede formar sin que se necesite un equipo separado para preparar dicho aminocaproato alcalino. En esta formulación, el hidróxido alcalino se agrega preferiblemente al producto de caprolactama que contiene al menos 3 % en peso de agua, más preferiblemente al menos 5 % en peso de agua (relativo al peso total del producto de caprolactama). Los hidróxidos alcalinos se pueden convertir ventajosamente para formar aminocaproatos durante la etapa de separación de agua.

El proceso de acuerdo con la invención puede ser un proceso por lotes o un proceso continuo. Preferiblemente el proceso es un proceso continuo.

El producto de caprolactama para el cual se pueden adicionar dichas una o más bases, se puede obtener por varios caminos, e.g., rearreglo de Beckmann. Se

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puede hacer un rearrreglo de Beckmann sobre la ciclohexanona-oxima en presencia de ácido sulfúrico u oleum, produciendo una mezcla de rearrreglo de Beckmann. Una base, preferiblemente amoníaco, se puede adicionar a la mezcla de rearrreglo de Beckmann, produciendo una mezcla de rearrreglo de Beckmann neutralizada. En una formulación de la invención la preparación del producto de caprolactama incluye, (a) recuperar de la mezcla de rearrreglo de Beckmann neutralizada, por extracción con un solvente orgánico, un producto orgánico que comprende el solvente orgánico y la caprolactama, (b) recuperar de dicho producto orgánico, por extracción con agua o por evaporación del solvente orgánico en presencia de agua, un producto de caprolactama acuosa. Seguido de su recuperación del producto orgánico, el producto de caprolactama acuosa, preferiblemente se hidrogena en presencia de un catalizador para hidrogenación. En el caso que el producto de caprolactama acuosa se recupere del producto orgánico por evaporación del solvente orgánico en presencia de agua, el producto orgánico preferiblemente se lava con agua o con solución acuosa alcalina antes de dicha evaporación. En el caso que el producto de caprolactama acuosa se recupere del producto orgánico por extracción con agua, el producto de caprolactama acuosa preferiblemente se somete a un intercambiador iónico antes de la hidrogenación. Preferiblemente dichas una o más bases se adicionan al producto de caprolactama acuosa después de la etapa de hidrogenación.

La destilación se puede llevar a cabo en cualquier zona adecuada de destilación, por ejemplo en una columna de destilación. La destilación se efectúa a presión

reducida. Preferiblemente la destilación se efectúa a una presión menor que 50 kPa, más preferiblemente menor que 20 kPa, en particular menor que 10 kPa. Preferiblemente, la temperatura está entre 100 y 200 °C, más preferiblemente entre 110 y 180 °C. Estas temperaturas se refieren a las temperaturas en el fondo de la columna de destilación en la cual se efectúa la destilación. Típicamente la destilación incluye separación de las impurezas orgánicas de bajo punto de ebullición (que tienen un punto de ebullición más bajo que el de la caprolactama) del producto de caprolactama alcalino y/o separación de impurezas orgánicas de alto punto de ebullición (que tienen un punto de ebullición más alto que el de la caprolactama) del producto de caprolactama alcalino. Preferiblemente, la destilación incluye una primera etapa, en la que se sacan del producto de caprolactama alcalino, como producto de cabeza las impurezas de bajo punto de ebullición mientras que se deja como producto de fondo el producto de caprolactama alcalino que contiene las impurezas de alto punto de ebullición, y una segunda etapa en la que se recupera la caprolactama purificada como producto de cabeza y se separan las impurezas de alto punto de ebullición como producto de fondo.

Preferiblemente la caprolactama es ϵ -caprolactama.

La invención se elucida con los siguientes ejemplos, sin embargo no se limita a los mismos.

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En todos los ejemplos las especificaciones dadas, se determinaron como sigue:

PAN: ISO DIS 8660 –Plásticos- Determinación del índice de permanganato de la caprolactama- método Espectrométrico, revisión de la primera edición ISO 8660; 1988,

E₂₉₀. ISO 7059- Caprolactama para uso industrial- determinación de la absorbancia a una longitud de onda de 290 nm,

Bases Volátiles (VB): ISO 8661- caprolactma para uso industrial- determinación del contenido de bases volátiles- método por titulación después de la destilación.

Alcalinidad: Titulación con solución acuosa de ácido clorhídrico 0.01 M.

Ejemplo 1

En un proceso continuo para la producción de caprolactma pura, se produjo continuamente una corriente de producto de caprolactama por rearreglo de Beckmann de la ciclohexanona-oxima en presencia de oleum, se neutralizó la mezcla de rearreglo de Beckmann con amoníaco, la caprolactama se separó mediante técnicas de extracción de la mezcla neutralizada de rearreglo de Beckmann. Dicha corriente fue sometida a una serie de etapas de purificación que incluyen purificación con un intercambiador iónico, hidrogenación y una primera

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separación de agua. La corriente resultante de producto de caprolactama contiene cerca del 85 % en peso de caprolactama y cerca del 15 % de agua e impurezas y tiene las siguientes especificaciones (PAN 2.6, $E_{290} = 0.32$, VB = 0.44 meq / Kg, alcalinidad = 0.02 meq / Kg). A esta corriente se le adicionaron continuamente 4.80 mmol de NaOH por Kg de caprolactama (como solución acuosa al 15 %).

La corriente resultante de producto de caprolactama alcalino se separa del agua en una serie de evaporadores, la temperatura en los evaporadores varía entre 80 y 125 °C, el tiempo total de residencia en y entre los evaporadores fue de 3 horas. Como resultado se obtuvo un producto de caprolactama alcalino que contiene cerca del 0.5 % en peso de agua. En dicho producto de caprolactama alcalino al menos el 90 % de la base adicionada parece haber reaccionado para formar aminocaproato de sodio. El producto de caprolactama alcalino (alcalinidad 4.83 meq / Kg) que sale de la serie de evaporadores se destiló a presión reducida en dos etapas. En la primera etapa las impurezas de bajo punto de ebullición y el agua se separaron en una columna de destilación a una temperatura (en el fondo) de 175 °C y una presión de 5.2 kPa, siendo el tiempo de residencia algunos minutos. En la segunda etapa se separaron las impurezas de alto punto de ebullición en una columna de destilación a una temperatura (en el fondo) de 133 °C y una presión de 1.2 kPa, siendo el tiempo de residencia una hora. Las especificaciones de la caprolactama purificada se indican en la tabla 1.

Ejemplos II-VII

Se repitió el ejemplo I con la diferencia que se adicionaron distintas cantidades de NaOH, dando como resultado distintos valores para la alcalinidad de lo alimentado a la primera etapa de destilación (destilación a 175 °C). Las especificaciones de la caprolactama obtenida después de la destilación se indican en la tabla 1.

Tabla 1

Ejemplo	NaOH adicionado	Alcalinidad alimentada En la primera etapa de Destilación (175 °C)	PAN	E ₂₈₀	VB	Alcalinidad
Nr	mmol de NaOH/Kg Caprolactama	meq OH ⁻ / Kg			meq OH ⁻ / Kg	meq OH ⁻ / Kg
I	4.80	4.83	3.71	0.14	0.16	0.012
II	2.90	2.92	3.60	0.13	0.14	0.015
III	1.25	1.29	3.54	0.13	0.11	0.017
IV	0.90	0.95	2.88	0.11	0.12	0.013
V	0.75	0.78	2.89	0.12	0.18	0.012
VI	0.60	0.65	2.59	0.12	0.12	0.011
VII	0.50	0.55	1.15	0.06	0.11	0.024
VIII	0.30	0.32	1.28	0.07	0.17	0.023

Estos ejemplos muestran que el número PAN se disminuye sin afectar las otras propiedades de la caprolactama, si la cantidad de NaOH adicionada y consecuentemente la alcalinidad del producto de caprolactama alcalino se disminuye. Por otra parte la extinción disminuye con la disminución de la cantidad de NaOH adicionado.

REIVINDICACIONES

1. Proceso para destilar a presión reducida un producto de caprolactama alcalino, dicho producto de caprolactama alcalino comprende (i) caprolactama, (ii) impurezas orgánicas, y (iii) una o más bases seleccionadas del grupo que consiste de hidróxidos alcalinos y amino caproatos alcalinos, caracterizado por que la alcalinidad del producto de caprolactama alcalino es menor que 5 meq. Por Kg de caprolactama.
2. Un proceso de acuerdo con la reivindicación 1, en el cual la alcalinidad del producto de caprolactama alcalino está entre 0.10 y 3 meq por Kg de caprolactama.
3. Un proceso de acuerdo con la reivindicación 2, en el cual la alcalinidad del producto de caprolactama alcalino está entre 0.15 y 2 meq por Kg de caprolactama.
4. Un proceso de acuerdo con las reivindicaciones 1 a 3, en el cual dicha una o mas bases son seleccionadas del grupo que consiste de hidróxido de sodio, amino caproato de sodio, hidróxido de potasio, amino caproato de potasio.

5. Un proceso de acuerdo con cualquiera de las reivindicaciones 1 a 3, en el cual al menos el 75 % en moles de dicha una o más bases es amino caproato alcalino.
6. Un proceso de acuerdo con cualquiera de las reivindicaciones 1 a 5, el cual dicho producto de caprolactama alcalino comprende al menos 95 % en peso de caprolactama.
7. Un proceso de acuerdo con cualquiera de las reivindicaciones 1 a 6 para la purificación del producto de caprolactama, dicho producto de caprolactama comprende (i) caprolactama y (ii) impurezas, en el cual dicho proceso comprende la adición de una o mas bases seleccionadas del grupo que consiste en un hidróxido alcalino y de un amino caproato alcalino a dicho producto de caprolactama en una cantidad como para producir el producto de caprolactama alcalino.
8. Un proceso de acuerdo con la reivindicación 7, en el cual el producto de caprolactama tiene una acidez de entre 0 y 5 meq por Kg de caprolactama, es neutro, o tiene una alcalinidad de entre 0 y 5 meq por Kg de caprolactama.

9. Un proceso de acuerdo con la reivindicación 7 o la reivindicación 8, en el cual el proceso involucra la adición de dicha una o más bases a dicho producto de caprolactama en una cantidad menor que 10 mmol por Kg de caprolactama.
10. Un proceso de acuerdo con la reivindicación 9, en el cual el proceso involucra la adición a dicho producto de caprolactama de entre 0.10 y 5 mmol de dicha una o más bases por Kg de caprolactama.
11. Un proceso de acuerdo con la reivindicación 10, en el cual el proceso involucra la adición a dicho producto de caprolactama de entre 0.15 y 3 mmol de dicha una o más bases por Kg de caprolactama.
12. Un proceso de acuerdo con cualquiera de las reivindicaciones 7 a 11, en el cual el producto de caprolactama comprende al menos 15 % en peso de caprolactama.
13. Un proceso de acuerdo con la reivindicación 12, en el cual el producto de caprolactama comprende agua y la suma de las cantidades de agua y caprolactama en el producto de caprolactama es al menos del 95 % en peso.

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14. Un proceso de acuerdo con cualquiera de las reivindicaciones 7 a 13, en el cual el proceso involucra la adición del hidróxido alcalino a dicho producto de caprolactama produciendo un producto alcalino, y convirtiendo al menos parte de dicho hidróxido alcalino en el producto alcalino para formar el amino caproato alcalino antes de dicha destilación.
15. Un proceso de acuerdo con cualquiera de las reivindicaciones 1 a 14, en el cual la caprolactama es obtenida por un reareglo Beckmann.
16. Un proceso de acuerdo con cualquiera de las reivindicaciones 1 a 15, en el cual el proceso involucra la destilación del producto de caprolactama a una temperatura entre 100 y 200°C.
17. Un proceso de acuerdo con cualquiera de las reivindicaciones 1 a 16, en el cual el proceso involucra la destilación del producto de caprolactama a una presión menor que 10 kPa.
18. Un proceso de acuerdo con cualquiera de las reivindicaciones 1 a 17, en el cual dicha destilación incluye la separación de las impurezas de bajo punto

de ebullición del producto de caprolactama alcalino y/o la separación de las impurezas de alto punto de ebullición del producto de caprolactama alcalino.

19. Un proceso de acuerdo con la reivindicación 18, en el cual dicha destilación incluye en una primer etapa, la separación como un producto de cabeza de las impurezas de bajo punto de ebullición del producto de caprolactama alcalino, mientras se deja el producto de caprolactma alcalino que contiene impurezas de alto punto de ebullición como un producto de fondo y en una segunda etapa se separan las impurezas de alto punto de ebullición del producto de fondo y se recupera la caprolactama como un producto de cabeza.

20. Un proceso de acuerdo con cualquiera de las reivindicaciones 1 a 19, en el cual el proceso es un proceso continuo.

PCT
REQUEST

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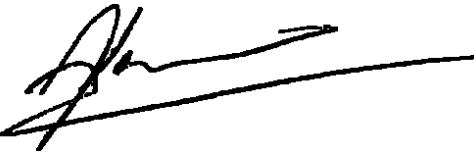
Box No. I TITLE OF INVENTION process for distilling alkaline caprolactam product at reduced pressure	
Box No. II APPLICANT ☐ This person is also inventor	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name 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 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
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	
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This international application contains: (a) the following number of sheets in paper form: request (including declaration sheets) : 5 description (excluding sequence listing part) : 8 claims : 3 abstract : 1 drawings : _____ Sub-total number of sheets : 17 Sequence listing part of description (actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (b) below) : _____ Total number of sheets : 17 (b) sequence listing part of description filed in computer readable form (i) ☐ only (under Section 801(a)(i)) (ii) ☐ in addition to being filed in paper form (under Section 801(a)(ii)) Type and number of carriers (diskette, CD-ROM, CR-R or other) on which the Sequence listing part is contained (additional copies to be indicated under item 9(ii), in right column) :	This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item): 1. ☒ fee calculation sheet : _____ 2. ☐ original separate power of attorney : _____ 3. ☐ original general power of attorney : _____ 4. ☒ copy of the general power of attorney; reference number, if any: : _____ 5. ☐ statement explaining lack of signature : _____ 6. ☐ priority document(s) identified in Box No. VI as item(s): : _____ 7. ☐ translation of international application into (language): : _____ 8. ☐ separate indications concerning deposited microorganism or other biological material : _____ 9. ☐ sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CR-R or other)) (i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application) : _____ (ii) ☐ (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter : _____ (iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing part mentioned in left column : _____ 10. ☐ other (specify): : _____	Number of items
Figure of the drawings which should be accompany the abstract:	Language of filing of the international application: English	
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Box No. VI

PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application:* regional Office	International application: receiving Office
item (1) 27 August 2001 (27/08/2001)	01203217.3	EP		
item (2) 27 August 2001 (27/08/2001)	01203215.7	EP		
item (3) 27 August 2001 (27/08/2001)	01203214.0	EP		
item (4)				
item (5)				

☐ Further priority claims are indicated in the Supplemental Box.

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 this International application is the receiving Office) identified above as:

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INTERNATIONAL SEARCHING AUTHORITY

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Box No. VIII

DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

		Number of declarations
☐ Box No. VIII (i)	Declaration as to the identity of the inventor	:
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☐ Box No. VIII (iv)	Declaration of inventorship (only for the purposes of the designation of the United States of America)	:
☐ Box No. VIII (v)	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	:

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(54) Title: PROCESS FOR DISTILLING ALKALINE CAPROLACTAM PRODUCT AT REDUCED PRESSURE

(57) Abstract: The invention relates to a process for distilling alkaline caprolactam product at reduced pressure, said alkaline caprolactam product comprising (i) caprolactam, (ii) organic impurities, and (iii) one or more bases selected from the group consisting of alkali hydroxide and alkali amino caproate, characterized in that the alkalinity of the alkaline caprolactam product is less than 5 meq. per kg of caprolactam.

PROCESS FOR DISTILLING ALKALINE CAPROLACTAM PRODUCT
AT REDUCED PRESSURE

The invention relates to a process for purifying caprolactam, which process involves distilling alkaline caprolactam product at reduced pressure.

The production of caprolactam generally involves the preparation of caprolactam product, e.g. by Beckmann rearrangement, followed by purification of the caprolactam product to obtain polymerizable grade caprolactam product. The purification can include distillation of the caprolactam product at reduced pressure in the presence of a base, e.g. alkali hydroxide or an alkali amino caproate. Large ranges are mentioned for the amount of added base. DD-A-202870 describes a process in which caprolactam product is purified by distillation under reduced pressure after addition of 0.05 to 1.0 % of the alkali salt of caproic acid to the caprolactam product to be purified. US-A-3,839,324 describes a process in which caprolactam is subjected to an alkaline distillation in vacuo, wherein sodium hydroxide is present as 0.05 –0.5 percent by weight. US-A-5,496,941 describes a process wherein caprolactam is distilled in the presence of a base, the amount of added base as a rule being chosen from 0.05 to 0.9 mol.% based on caprolactam. US-A-4,457,807 describes a process in which untreated caprolactam containing 0.2 mg of solid NaOH per gram of caprolactam (5 mmol NaOH per kg of caprolactam) is supplied to a rectification column wherein rectification is effected under reduced pressure.

It is now found that the quality of the purified caprolactam, e.g. as expressed by the PAN number, is influenced by the alkalinity of the caprolactam product to be distilled. In particular, the PAN number is found to decrease when the alkalinity of the alkaline caprolactam product is decreased to below 5 meq. per kg of caprolactam. The occurrence of undesired fluctuation in quality, e.g. resulting from the oxidation of caprolactam during distillation, is found to decrease when the alkalinity is increased to above 0 meq. per kg of caprolactam.

Accordingly the invention provides a process for purifying caprolactam, which process involves distilling alkaline caprolactam product at reduced pressure, said alkaline caprolactam product comprising (i) caprolactam, (ii) impurities, and (iii) one or more bases selected from the group consisting of alkali hydroxide and alkali amino

caproate, characterized in that the alkalinity of the alkaline caprolactam product is less than 5 meq. (5 milli equivalent) per kg of caprolactam.

As used herein alkalinity refers to the alkalinity at a temperature of 25 °C as determined by titration (after diluting the alkaline caprolactam product with water of pH = 5.7 to obtain a solution containing 15 wt.% caprolactam) with a 0.01 N HCl solution to a pH of 5.7, whereby

$$\text{alkalinity} = \frac{v * t}{a * 0.15} * 1000$$

10 Where:

v = ml of HCl solution added
 t = molarity of HCl solution (=0.01)
 a = weight of sample (g)

15 The process according to the invention results in purified caprolactam having a high quality, in particular a low PAN number (as determined in accordance with ISO DIS 8660-Plastics-Determination of permanganate index of caprolactame-Spectrometric method, revision of first edition (ISO 8660; 1988)). Moreover a low value for the extinction (as determined in accordance with ISO 7059 - caprolactam for industrial use- Determination of absorbance at a wavelength of 290 nm) is obtained.

20 Preferably, the alkalinity of the alkaline caprolactam product is lower than 4.5 meq. per kg of alkaline caprolactam product, more preferably lower than 4.0 meq. per kg, in particular lower than 3.0 meq. per kg, more in particular lower than 2.0 meq. per kg. This further decreases the PAN number.

25 Preferably, the alkalinity of the alkaline caprolactam product is higher than 0.05 meq. per kg of alkaline caprolactam product, more preferably higher than 0.10 meq. per kg, in particular higher than 0.15 meq. per kg. Increasing the alkalinity to above these values improves the stability, i.e. the sensitivity to occurrence of undesired fluctuations in quality.

30 As used herein the values mentioned for the alkalinity and concentrations in the alkaline caprolactam product refer to the values of the alkaline caprolactam product to be distilled. viz. when the alkaline caprolactam product is fed to a distillation zone, i.e. the zone in which the distillation is effected, the mentioned values for alkalinity and other

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concentrations in the alkaline caprolactam product refer to the values in the alkaline caprolactam product entering the distillation zone.

5 The alkaline caprolactam product comprises caprolactam. Typically, the alkaline caprolactam product comprises 95 to 99.9 wt.% of caprolactam, in particular at least 97 wt.% of caprolactam, more in particular at least 98 wt.% of caprolactam (relative to the weight of alkaline caprolactam product).

The impurities may be any organic impurities, e.g. low-boiling organic impurities (having a lower boiling point than caprolactam) and/or high-boiling organic impurities (having a higher boiling point than caprolactam).

10 The alkaline caprolactam product may include water. Preferably, the alkaline caprolactam product comprises less than 5 wt.%, more preferably less than 3 wt.%, in particular less than 2 wt.%, more in particular less than 1 wt.% (relative to the weight of alkaline caprolactam product). A lower amount of water has the advantage that a reduced pressure is easier to create and maintain during distilling.

15 The alkaline caprolactam product comprises one or more bases selected from the group consisting of alkali hydroxide and alkali amino caproate. Preferably the one or more bases are selected from the group consisting of sodium hydroxide, sodium amino caproate, potassium hydroxide, and potassium amino caproate, more preferably selected from the group consisting of sodium hydroxide and sodium amino caproate. Preferably, at
20 least 75 mol.%, more preferably at least 85 mol.%, in particular at least 95 mol.%, more in particular substantially all of said one or more bases is alkali amino caproate. Increasing the relative amounts of alkali amino caproate has the advantage that the occurrence of polymerization during the distillation is lessened. The formation of oligomers and polymers is disadvantageous since it may result fouling of the distillation equipment. Moreover
25 caprolactam is lost. The above percentages are given relative to the total molar quantity of said one or more bases.

The process according to the invention is preferably a process for the purification of caprolactam product, said caprolactam product comprising (i) caprolactam and (ii) impurities, wherein said process comprises adding one or more of the bases to
30 said caprolactam product to yield the alkaline caprolactam product. Preferably, the alkali hydroxide is added as an aqueous solution of alkali hydroxide.

Typically, the caprolactam product comprises 15 to 99.9 wt.% of caprolactam, in particular at least 50 wt.% of caprolactam, more in particular at least 75 wt.% of caprolactam. Typically, the caprolactam product is aqueous caprolactam product comprising water. Typically the sum quantity of water and caprolactam and water in the caprolactam product is preferably at least 95 wt.%, in particular at least 97 wt.%, more in particular at least 98 wt.%. These percentages are given relative to the weight of the caprolactam product. In one embodiment of the invention, the caprolactam product has an acidity of between 0 and 5 meq. per kg caprolactam, is neutral, or has an alkalinity of between 0 and 5 meq. per kg caprolactam. In this embodiment the alkaline caprolactam product can be prepared by adding very small amounts of said one or more bases. This results in purified caprolactam having a good quality, as expressed by the PAN number, and a good stability. As used herein acidity refers to the acidity at a temperature of 25 °C as determined by titration (after diluting the alkaline caprolactam product with water of pH = 5.7 to obtain a solution containing 15 wt.% caprolactam) with a 0.01 N NaOH solution to a pH of 5.7, whereby

$$\text{acidity} = \frac{v * t}{a * 0.15} * 1000$$

Where:

- 20 v = ml of NaOH solution added
 t = molarity of NaOH solution (=0.01)
 a = weight of sample (g)

Preferably, the caprolactam product is neutral or has an alkalinity of between 0 and 5 meq. per kg of caprolactam. In an embodiment, the process comprises adding between 0.05 and 10 mmol of the one or more bases per kg caprolactam, preferably between 0.05 and 5.0 mmol per kg, more preferably between 0.10 and 4.5 mmol per kg, in particular between 0.15 and 3.0 mmol per kg, more in particular between 0.20 and 2.0, most preferably less than 1.0 mmol per kg caprolactam. Preferably, the amount of added base is decreased when the caprolactam product is less acidic/more alkaline. In an embodiment, the alkaline caprolactam product is directly obtained after addition of the one or more bases, and the alkaline caprolactam product may be distilled without further steps prior to said distilling. In another embodiment, alkaline product

obtained following the addition is subjected to one or more purification steps, e.g. to a step in which water is separated from the alkaline product, to obtain the alkaline caprolactam product to be distilled.

In a preferred embodiment, the process involves adding alkali hydroxide to the caprolactam product, yielding an alkaline product, and reacting at least part of said alkali hydroxide in the alkaline product to form alkali amino caproate prior to the distilling. This has the advantage that the alkali amino caproate can be formed without needing separate equipment for preparing said alkali amino caproate. In this embodiment, the alkali hydroxide is preferably added to caprolactam product comprising at least 3 wt.% water, more preferably at least 5 wt.% of water (relative to the total weight of the caprolactam product). Alkali hydroxide may advantageously be converted to form alkali amino caproate during a water separation step.

The process according to the invention may be a batch process or a continuous process. Preferably, the process is a continuous process.

The caprolactam product to which said one or more bases may be added may be obtained in various ways, e.g. by Beckmann rearrangement. A Beckmann rearrangement of cyclohexanone oxime may be effected in the presence of sulphuric acid or oleum, resulting in a Beckmann rearrangement mixture. A base, preferably ammonia, may be added to the Beckmann rearrangement mixture, resulting in a neutralized Beckmann rearrangement mixture. In an embodiment of the invention the preparation of the caprolactam product includes, (a) recovering from a neutralized Beckmann rearrangement mixture, by extraction with an organic solvent, an organic product comprising the organic solvent and caprolactam, (b) recovering from said organic product, by extraction with water or by evaporation of the organic solvent in the presence of water, an aqueous caprolactam product. Following its recovery from the organic product, the aqueous caprolactam product is preferably hydrogenated in the presence of a hydrogenation catalyst. In the event that the aqueous caprolactam product is recovered from the organic product by evaporation of the organic solvent in the presence of water, the organic product is preferably washed with water or with an alkaline aqueous solution prior to said evaporation. In the event that the aqueous caprolactam product is recovered from the organic product by extraction with water, the aqueous caprolactam product is preferably subjected to an ion exchanger prior

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to hydrogenation. Preferably said one or more bases are added to the aqueous caprolactam product after a hydrogenation step.

The distillation may be carried out in any suitable distillation zone, for instance a distillation column. The distillation is effected at reduced pressure. Preferably the distillation is effected at a pressure of less than 50 kPa, more preferably less than 20 kPa, in particular less than 10 kPa. Preferably, the temperature is between 100 and 200°C, more preferably between 110 and 180 °C. These temperatures refer to the temperature in the bottom of the distillation column in which the distillation is effected. Typically, the distilling includes separating low-boiling organic impurities (having a lower boiling point than caprolactam) from the alkaline caprolactam product and/or separating organic high-boiling impurities (having a higher boiling point than caprolactam) from the alkaline caprolactam product. Preferably, the distilling includes, in a first step, separating out as a top product low-boiling impurities from the alkaline caprolactam product while leaving alkaline caprolactam product containing high-boiling impurities as a bottom product, and, in a second step, separating out high-boiling impurities from the bottom product, and recovering purified caprolactam as a top product.

Preferably, the caprolactam is ϵ -caprolactam

The invention will now be elucidated with reference to the following examples without, however, being limited thereto.

In all examples the specifications given were determined as follows:

PAN: ISO DIS 8660-Plastics-Determination of permanganate index of caprolactam-Spectrometric method, revision of first edition ISO 8660; 1988,

E₂₉₀: ISO 7059 - caprolactam for industrial use- determination of absorbance at a wavelength of 290 nm,

Volatile bases (VB) ISO 8661 - Caprolactam for industrial use - Determination of volatile bases content - Titrimetric method after distillation.

Alkalinity: titration with an aqueous solution of 0.01 M hydrochloric acid.

Example 1

In a continuous process for the production of pure caprolactam, a stream of caprolactam product was continuously produced by Beckmann rearrangement of cyclohexanone oxime in the presence of oleum, neutralizing the Beckmann rearrangement

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mixture with ammonia, separating caprolactam from the neutralized Beckmann rearrangement by extraction techniques. Said stream was subjected to a series of purification steps including purification with an ion exchanger, hydrogenation and a first dewatering. The resulting stream of caprolactam product contained about 85 wt. % caprolactam, about 15 wt. % water, and impurities, and had the following specifications (PAN = 2.6, E_{280} = 0.32, VB = 0.44 meq/kg, alkalinity = 0.02 meq/kg). To this stream was continuously added 4.80 mmol NaOH per kg of caprolactam (as 15% aqueous solution). The resulting stream of alkaline caprolactam product was dewatered in a series of evaporators, the temperatures in the evaporators varying between 80 and 125 °C. The total residence time in and between the evaporators was 3 hours. As a result alkaline caprolactam product was obtained containing about 0.5 wt. % water. In said alkaline caprolactam product at least 90% added base appeared to have been reacted to form sodium amino caproate. The alkaline caprolactam product (alkalinity 4.83 meq/kg) leaving the series of evaporators was distilled in two steps under reduced pressure. In the first step low-boiling impurities and water were separated in a distillation column, at (bottom) temperature of 175 °C, and a pressure of 5.2 kPa, the residence time being several minutes. In the second step high-boiling impurities were separated in a distillation column at a (bottom) temperature of 133 °C, a pressure of 1.2 kPa, the residence time being 1 hour. The specifications of the resulting purified caprolactam are indicated in table 1.

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Examples II-VIII

Example I was repeated with the difference that different amounts of NaOH were added, resulting in different values for the alkalinity of the feed of the first distillation step (distillation at 175 °C). The specifications of the caprolactam obtained after distillation are indicated in table 1.

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Table 1

Example	Added NaOH	Alkalinity feed First distillation (175 °C) step	PAN	E ₂₉₀	VB	Alkalinity
Nr.	mmol NaOH /kg capr	meq OH-/kg			meq OH-/kg	meq OH-/kg
I	4.80	4.83	3.71	0.14	0.16	0.012
II	2.90	2.92	3.60	0.13	0.14	0.015
III	1.25	1.29	3.54	0.13	0.11	0.017
IV	0.90	0.95	2.88	0.11	0.12	0.013
V	0.75	0.78	2.89	0.12	0.18	0.012
VI	0.60	0.65	2.59	0.12	0.12	0.011
VII	0.50	0.55	1.15	0.08	0.11	0.024
VIII	0.30	0.32	1.26	0.07	0.17	0.023

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These examples show that the PAN number is decreased without impairing the other properties of the caprolactam, if the amount of added NaOH and, consequently, the alkalinity the alkaline caprolactam product is decreased. Moreover the extinction decreases with decreasing amount of added NaOH.

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CLAIMS

- 5 1. Process for distilling alkaline caprolactam product at reduced pressure, said alkaline caprolactam product comprising (i) caprolactam, (ii) organic impurities, and (iii) one or more bases selected from the group consisting of alkali hydroxide and alkali amino caproate, characterized in that the alkalinity of the alkaline caprolactam product is less than 5 meq. per kg of caprolactam.
- 10 2. Process according to claim 1, wherein the alkalinity of the alkaline caprolactam product is between 0.10 and 3 meq. per kg of caprolactam.
3. Process according to claim 2, wherein the alkalinity of the alkaline caprolactam product is between 0.15 and 2 meq. per kg of caprolactam.
- 15 4. Process according to any one of claims 1 to 3, wherein said one or more bases are selected from the group consisting of sodium hydroxide, sodium amino caproate, potassium hydroxide, potassium amino caproate.
5. Process according to any one of claims 1 to 3, wherein at least 75 mol.% of said one or more bases is alkali amino caproate.
6. Process according to any one of claims 1 to 5, wherein said alkaline caprolactam product comprises at least 95 wt.% of caprolactam.
- 20 7. Process according to any one of claims 1 to 6 for the purification of caprolactam product, said caprolactam product comprising (i) caprolactam and (ii) impurities, wherein said process comprises adding one or more bases selected from the group consisting of alkali hydroxide and alkali amino caproate to said caprolactam product in an amount so as to yield the alkaline caprolactam
- 25 product.
8. Process according to claim 7, wherein the caprolactam product has an acidity of between 0 and 5 meq. per kg of caprolactam, is neutral, or has an alkalinity of between 0 and 5 meq. per kg of caprolactam.
- 30 9. Process according to claim 7 or claim 8, wherein the process involves adding said one or more bases to said caprolactam product in an amount of less than 10 mmol per kg caprolactam.

10. Process according to claim 9, wherein the process involves adding to said caprolactam product between 0.10 and 5 mmol of said one or more bases per kg of caprolactam.
- 5 11. Process according to claim 10, wherein the process involves adding to said caprolactam product between 0.15 and 3 mmol of said one or more bases per kg of caprolactam.
12. Process according to any one of claims 7 to 11, wherein the caprolactam product comprises at least 15 wt.% of caprolactam.
- 10 13. Process according to claim 12, wherein the caprolactam product comprises water and the sum quantity of water and caprolactam in the caprolactam product is at least 95 wt.%.
14. Process according to any one of claims 7 to 13, wherein the process involves adding alkali hydroxide to said caprolactam product yielding an alkaline product, and converting at least part of said alkali hydroxide in the alkaline product to form alkali amino caproate prior to said distilling.
- 15 15. Process according to any one of claims 1 to 14, wherein the caprolactam is obtained by a Beckmann rearrangement.
16. Process according to any one of claims 1 to 15, wherein the process involves distilling the alkaline caprolactam product at a temperature between 100 and 20 200 °C.
17. Process according to any one of claims 1 to 16, wherein the process involves distilling the alkaline caprolactam product at a pressure of less than 10 kPa.
18. Process according to any one of claims 1 to 17, wherein said distilling includes separating out low-boiling impurities from the alkaline caprolactam product and/or separating out high-boiling impurities from the alkaline caprolactam product.
- 25 19. Process according to claim 18, wherein said distilling includes, in a first step, separating out as a top product low-boiling impurities from the alkaline caprolactam product while leaving alkaline caprolactam product containing high-boiling impurities as a bottom product, and, in a second step, separating out high-boiling impurities from the bottom product, and recovering caprolactam as a top product.
- 30

20. Process according to any one of claims 1 to 19, wherein the process is a continuous process.

PATENT COOPERATION TREATY

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From the INTERNATIONAL BUREAU

PCT

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To:

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P.O. Box 9
NL-6160 MA Geleen
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Amk 5709

Date of mailing (day/month/year)

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Applicant's or agent's file reference

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Applicant

DSM N.V. et al

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

EP : AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR
National : AU, BG, CA, CN, DE, GB, IL, JP, KP, KR, MN, NO, PL, RO, RU, SK, US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

AP : GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW

EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

OA : BF, BJ, CF, CG, CI, CM, GA, GN, GO, GW, ML, MR, NE, SN, TD, TG

National : AE, AG, AL, AM, AT, AZ, BA, BB, BR, BY, BZ, CH, CO, CR, CU, CZ, DK, DM, DZ, EC, EE,
ES, FI, GD, GE, GH, GM, HR, HU, ID, IN, IS, KE, KG, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG,
MK, MW, MX, MZ, NZ, OM, PH, PT, SD, SE, SG, SI, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU,
ZA, ZM, ZW

3. The applicant is reminded that he must enter the "national phase" before the expiration of 30 months from the priority date before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 338.89.65

Authorized officer:

PETRESKA Gorica

Telephone No. (41-22) 338 9999

PATENT COOPERATION TREATY

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From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

To:

VERHAEGEN, Lise Maria Michel
DSM Patents & Trademarks
P.O. Box 9
NL - 6160 MA Geleen
PAYS-BAS

AMU 2138

Date of mailing (day/month/year)	17.10.2003
-------------------------------------	------------

Applicant's or agent's file reference 4394WO	IMPORTANT NOTIFICATION
International application No. PCT/NL02/00558	International filing date (day/month/year) 23.08.2002
Priority date (day/month/year) 27.08.2001	
Applicant DSM N.V.	

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.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the International preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523858 epmu d Fax: +49 89 2399 - 4485	Authorized Officer Ambroa, J.R. Tel. +49 89 2399-8012
---	---



PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference 4394WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/418)	
International application No. PCT/NL02/00558	International filing date (day/month/year) 23.08.2002	Priority date (day/month/year) 27.08.2001
International Patent Classification (IPC) or both national classification and IPC C07D223/10		
Applicant DSM N.V.		
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 6 sheets, including this cover sheet. ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT). These annexes consist of a total of sheets.		
3. This report contains indications relating to the following items: I ☒ Basis of the opinion II ☐ Priority III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV ☐ Lack of unity of invention V ☒ Reasoned statement under Rule 66.2(a)(II) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI ☐ Certain documents cited VII ☐ Certain defects in the international application VIII ☐ Certain observations on the international application		
Date of submission of the demand 19.03.2003	Date of completion of this report 17.10.2003	
Name and mailing address of the International preliminary examining authority:  European Patent Office D-80296 Munich Tel. +49 89 2399 - 0 Tx: 523656 apmu d Fax: +49 89 2399 - 4485	Authorized Officer Usuelli, A Telephone No. +49 89 2399-7366 	

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/NL02/00558**

I. Basis of the report

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

Description, Pages

1-8 as originally filed

Claims, Numbers

1-20 as originally filed

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

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

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

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

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

4. The amendments have resulted in the cancellation of:

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

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/NL02/00558**

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

1. Statement

Novelty (N)	Yes: Claims	1-20
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-20
Industrial applicability (IA)	Yes: Claims	1-20
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NL02/00558

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

1- In the present Communication, reference is made to the following documents cited in the Search Report:

d1: US-A-4457807

d2: US-A-4360461

d3: US-A-5496941

d4: DE-A-3825524

d5: DD-A-202870

d6: US-A-3944543

2- Novelty

The present application appears to meet the requirements of Art. 33.2 PCT .

D1 relates to a process for purifying ϵ -caprolactam obtained through Beckmann rearrangement. The process comprises a two-stage distillation under reduced pressure. According to example 1, 8,827 g of ϵ -caprolactam (purity 99.4%) are distilled in the presence of 0,2 mg of NaOH per gram of ϵ -caprolactam (cf. lines 16-22, column 3). It appears that this amount of NaOH is approximately equivalent to 5 meq per kg of ϵ -caprolactam. However, the argument that the alkalinity of the product to be distilled, not only depends on the amount and kind of base added but also on the alkalinity of the caprolactam itself before the addition of any base, has to be taken into account.

Although the experimental conditions of the example 1 of d1 are very similar to the conditions of present examples, it has to be considered that the amount of NaOH added in the example d1 would determine an alkalinity of 5 meq per kg of capriocatam in the case in which the caprolactam were neutral before the addition of the base. Thus, a minimal variation of alkalinity of the caprolactam could have the effect to increase the alkalinity of the product to be distilled to a level outside the range defined in present claim 1 (less than 5 meq). Under these circumstance it may not be concluded, beyond all reasonable doubts, that the disclosure of d1 anticipates present claims.

In the example 1 of d2, 5000 g of caprolactam containing 0.6 meq of volatile base per Kg are added to a sample of 500 g of lactam and then distilled (see column 4, lines 6-21). However, since there is no direct relation between amount of volatile base and alkalinity (see present Table 1), it is not possible to draw any conclusion about the

alkalinity of the product to be distilled.

In d3 the amount of base used in the distillation is chosen in the range from 0.05 to 0.9 mol%, based on caprolactam (cf. column 7, 32-35). This range appears to overlap with the range of alkalinity defined in the present process (less than 5 meq per kg of caprolactam). In the single example of d3, it is not clear which is the degree of alkalinity.

None of the processes disclosed in the documents d4-d6, comprises a distillation of caprolactam having an alkalinity of less than 5 meq per kg.

3- Inventive step

All the above cited documents disclose processes for the preparation of caprolactam which include a step of purification through a distillation process. Document d1 can be regarded as the closest state of the art. The technical problem underlying the present invention can be seen in the provision of an alternative process for the preparation of caprolactam.

It is a general teaching derivable from the documents of the prior art, that the distillation of caprolactam should be carried out in alkaline solution (see in particular d1 and d3). Although it is not possible to determine precisely the alkalinity of the products distilled in the prior art because the alkalinity of the products before the addition of the base is not known, it has to be noted that the experimental conditions of the processes of the prior art, in particular d1, are very close to the experimental conditions of the examples of the present application. In this respect it is noted that the alkalinity data disclosed in present Table 1, suggest that the caprolactam products before the addition of NaOH are virtually neutral, because the final alkalinity is nearly identical to the alkalinity that would be obtained adding the same amount of NaOH in neutral solutions. In present examples, the caprolactam is obtained by Beckmann rearrangement of cyclohexanone oxime in the presence of oleum. Since the same process it is used in the example 1 of d1, it appears reasonable to argue that also the caprolactam obtained in d1 is nearly identical. This means, that after addition of NaOH the product of d1 has an alkalinity very close to 5 meq per kg of caprolactam (see paragraph novelty). The distillation of the present process is therefore carried out under conditions which are very close to the conditions of the distillation of d1. Although this document does not provide the PAN of the product obtained after distillation, it is observed that d1 relates to the problem of providing a process for obtaining a pure ϵ -caprolactam (purity greater than 99.9 % according to claim 1). Accordingly, it appears that the skilled person with the aim of producing ϵ -caprolactam with a high degree of purity would consider the teaching of d1.

The mere fact that applying the process of the prior art lead to a product having a desired characteristic not disclosed in the prior art (i.e. the low PAN number), it is not an evidence of inventiveness insofar the skilled person would already have good reasons for applying said process.

In the process according to document d5, the distillation is carried out in the presence of an alkali salt of amino caproic acid. Thus, also this feature, does not involve any inventive activity.

In view of the above considerations it is considered that present claims do not comply with the requirements of Art. 33.3 PCT.

INTERNATIONAL SEARCH REPORT

PCT/NL 02/00558

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D223/10 C07D201/16

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 C07D

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 457 807 A (RULKENS PETER F M ET AL) 3 July 1984 (1984-07-03) example 1	1-20
X	US 4 360 461 A (FUCHS HUGO ET AL) 23 November 1982 (1982-11-23) column 4, line 7 - line 22; example 1	1-20
X	US 5 496 941 A (RITZ JOSEF ET AL) 5 March 1996 (1996-03-05) column 7, line 21 - line 39	1-20
A	DE 38 25 524 A (FRIULI CHIM SPA) 9 February 1989 (1989-02-09) claim 1	1-20
	— -/-	

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

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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

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

Date of the actual completion of the international search

7 October 2002

Date of mailing of the international search report

15/10/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Palatinen 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3018

Authorized officer

Usue111, A

INTERNATIONAL SEARCH REPORT

PCT/NL 02/00558

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DD 202 870 A (LEUNA WERKE VEB) 5 October 1983 (1983-10-05) claim 1	1-20
A	US 3 944 543 A (GOETTSCHE REIJER ET AL) 16 March 1976 (1976-03-16) column 1, line 39 - line 46	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/NL 02/00558

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4457807	A	03-07-1984	NL 8102280 A	01-12-1982
			BR 8202661 A	19-04-1983
			CA 1182775 A1	19-02-1985
			DE 3265204 D1	12-09-1985
			EP 0065168 A1	24-11-1982
			ES 511988 D0	01-02-1983
			ES 8303352 A1	01-05-1983
			IN 155613 A1	16-02-1985
			JP 57192358 A	26-11-1982
			KR 8600515 B1	02-05-1986
US 4360461	A	23-11-1982	DE 3030735 A1	25-03-1982
			CA 1157857 A1	29-11-1983
			DE 3161702 D1	26-01-1984
			EP 0046183 A1	24-02-1982
			JP 57054165 A	31-03-1982
US 5496941	A	05-03-1996	DE 19500041 A1	04-07-1996
			AU 4389396 A	24-07-1996
			BG 63387 B1	31-12-2001
			BG 101672 A	27-02-1998
			BR 9510187 A	23-12-1997
			CA 2209336 A1	11-07-1996
			CN 1171781 A , B	28-01-1998
			CZ 9701972 A3	18-03-1998
			DE 59509451 D1	30-08-2001
			WO 9620923 A1	11-07-1996
			EP 0801643 A1	22-10-1997
			ES 2160729 T3	16-11-2001
			JP 10511668 T	10-11-1998
			PL 321162 A1	24-11-1997
			RU 2159234 C2	20-11-2000
			SK 84097 A3	06-05-1998
DE 3825524	A	09-02-1989	IT 1222419 B	05-09-1990
			BR 8803787 A	21-02-1989
			CA 1309404 A1	27-10-1992
			DE 3825524 A1	09-02-1989
			ES 2007278 A6	01-06-1989
			IN 171456 A1	17-10-1992
			SU 1709905 A3	30-01-1992
DD 202870	A	05-10-1983	DD 202870 A1	05-10-1983
US 3944543	A	16-03-1976	NL 7308100 A	16-12-1974
			AR 203484 A1	15-09-1975
			BE 816209 A1	12-12-1974
			CS 183740 B2	31-07-1978
			DE 2428203 A1	09-01-1975
			ES 427168 A1	16-07-1976
			FR 2233321 A1	10-01-1975
			GB 1409522 A	08-10-1975
			IN 140825 A1	25-12-1976
			IT 1021557 B	20-02-1978
			JP 50052079 A	09-05-1975
			TR 18304 A	07-01-1977

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PATENT COOPERATION TREATY

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PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF RECEIPT OF
RECORD COPY

(PCT Rule 24.2(a))

To:

DAUTZENBERG, Josef, Marie, Andreas
DSM Patents & Trademarks
P.O. Box 9
NL-6160 MA Geleen
Netherlands

Amu 0160

Date of mailing (day/month/year) 19 September 2002 (19.09.02)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference 4394WO	International application No. PCT/NL02/00558

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

DSM N.V. (for all designated States except US)

GROOT ZEVERT, Louise, Annemarie et al (for US)

International filing date : 23 August 2002 (23.08.02)

Priority date(s) claimed : 27 August 2001 (27.08.01)

27 August 2001 (27.08.01)

27 August 2001 (27.08.01)

Date of receipt of the record copy
by the International Bureau : 09 September 2002 (09.09.02)

List of designated Offices :

AP : GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW

EA : AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

EP : AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR

OA : BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

National : AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ,
EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU,
LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer:

Abderrezak SMAHI (Fax 338.89.65)

Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

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PCT

From the INTERNATIONAL BUREAU

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

DAUTZENBERG, Josef, Marie, Andreas
DSM Patents & Trademarks
P.O. Box 9
NL-6160 MA Geleen
Netherlands

Date of mailing (day/month/year) 01 November 2002 (01.11.02)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference 4394WO	
International application No. PCT/NL02/00558	International filing date (day/month/year) 23 August 2002 (23.08.02)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 27 August 2001 (27.08.01)
Applicant DSM N.V. et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
27 Augu 2001 (27.08.01)	01203217.3	EP	30 Octo 2002 (30.10.02)
27 Augu 2001 (27.08.01)	01203215.7	EP	30 Octo 2002 (30.10.02)
27 Augu 2001 (27.08.01)	01203214.0	EP	02 Octo 2002 (02.10.02)

73 25 79

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Christine BACQUAERT (Fax 338.89.65)
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

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PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

DAUTZENBERG, Josef, Marie, Andreas
DSM Patents & Trademarks
P.O. Box 9
NL-6160 MA Geleen
Netherlands

Date of mailing (day/month/year)

03 September 2003 (03.09.03)

Applicant's or agent's file reference

4394WO

International application No.

PCT/NL02/00558

International filing date (day/month/year)

23 August 2002 (23.08.02)

IMPORTANT NOTIFICATION

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

Name and Address

DSM N.V.
Het Overloon 1
NL-6411 TE Heerlen
Netherlands

State of Nationality

NL

State of Residence

NL

Telephone No.

Facsimile No.

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☒ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

DSM IP ASSETS B.V.
Het Overloon 1
NL-6411 TE Heerlen
Netherlands

State of Nationality

NL

State of Residence

NL

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned
☐ the International Searching Authority ☒ the elected Offices concerned
☒ the International Preliminary Examining Authority ☐ other:The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 338.88.65

Authorized officer

Sita COPPOLINO

Telephone No. (41-22) 338 8451

SC.

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
PATENTE DE INVENCION	()	()
- Indicación de que se solicita la concesión de una patente.	()	()
- Datos de identificación del solicitante o de la persona que se presenta la solicitud.	()	()
- Descripción de la invención.	()	()
- Dibujos de ser estos pertinentes.	()	()
- Comprobante de Pago de las tasas establecidas.	()	()

COMPLETA () INCOMPLETA ()

DISEÑO INDUSTRIAL ()

- Indicación de que se solicita el registro de Diseño Industrial	()	()
- Datos de identificación del solicitante o de la persona que presenta la solicitud.	()	()
- Representación gráfica y fotográfica del Diseño Industrial o muestra del Material que incorpora el diseño.	()	()
- Comprobante de pago de las tasas establecidas	()	()

COMPLETA () INCOMPLETA ()

ESQUEMA DE TRAZADO ()

- Indicación de que solicita el registro de un Esquema de trazado.	()	()
- Datos de identificación del solicitante o de la persona que presenta la solicitud.	()	()
- Representación gráfica del esquema de trazado	()	()
- Comprobante de pago de las tasas establecidas.	()	()

COMPLETA () INCOMPLETA ()

Firma Responsable:

Fecha: Radicación : 04021423 00000000 Folios: 57
 Fecha (MM): 2004-03-09 16:00:02
 Trámite : 011 PCT-PATENT 379 FASE INCI 411 PRESENTAC
 Dependencia: 2020 DIVISION DE NUEVAS CREACIONES



2020
Bogotá, D.C.,

Doctor:
JIMENA ESCOBAR URIBE
Apoderado
DSM IP ASSETS B.V.

Oficio N° 04935

ASUNTO:	Radicación N°	04-21423
	Solicitud Internacional	PCT/NL02/00558
	Fecha Inicio fase nacional	27/03/2004
	Trámite	011
	Evento	379
	Actuación	430
	Folios	001

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

□ La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante. (Art. 26-k) Decisión 486).

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.


ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones.

El anterior requerimiento fue notificado por fijación en lista de
fecha, 14 MAYO 2004

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