AUSTRALIA

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Notice of Entitlement

We, ERCROS, S.A., of Avenida de la Diagonal, 593-595, 08014 Barcelona, Spain, being the Applicant and Nominated Person in respect of Application No. 86663/91, state the following:

The actual inventors of the invention of Application No. 86663/91 are Jose Ramon OCHOA GOMEZ and Juan Luis MARTIN RAMON.

The basic application listed on the PCT Request form, namely, Spanish Application No. 9002523 was filed in our name as assignee of the actual inventors.

The said basic application listed in the declaration under Article 8 of the PCT is the first application made in a Convention country in respect of the invention.

We have entitlement from the actual inventors by assignment.

Our address for service is care of E. F. WELLINGTON & CO., Patent and Trade Mark Attorneys, 312 St. Kilda Road, Melbourne, Victoria, 3004.

DATED this 29th day of May, 1992

For and on behalf of
ERCROS, S.A.,
By:

. . . . . .
BRUCE S. WELLINGTON
Patent Attorney for
Applicant/Nominated Person

To: The Commissioner of Patents,
Commonwealth of Australia

C/KA/6650/2

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(12) PATENT ABRIDGMENT (11) Document No. AU-B-86663/91
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(54) Title
METHOD FOR OBTAINING ACETIC ACID DERIVATIVES

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(57) Claim

1. A process for rejuvenating a Raney copper catalyst, suitable for use in the conversion of amino alcohols to amino acids, which comprises treating a spent Raney copper catalyst under reflux conditions with formic acid.

6. A process for producing amino acids which comprises contacting an amino alcohol selected from the group consisting of monoethanol amine, diethanol amine and triethanol amine, with an alkali metal hydroxide in the presence of a Raney copper catalyst wherein at least some of the Raney copper catalyst has been rejuvenated by treating the catalyst under reflux conditions with formic acid.

PCT ORGANIZACION MUNDIAL DE LA PROPIEDAD INTELECTUAL
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(71) Solicitante *(para todos los Estados designados salvo US)*: EFCROS S.A. [ES/ES]; Avda. de la Diagonal, 593-595, E-08014 Barcelona (ES).

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(81) Estados designados: AT, AT (Patente europea), AU, BB, BE (Patente europea), BF (Patente OAPI), BG, BJ (Patente OAPI), BR, CA, CF (Patente OAPI), CG (Patente OAPI), CH, CH (Patente europea), CI (Patente OAPI), CM (Patente OAPI), DE, DE (Patente europea), DK, DK (Patente europea), ES (Patente europea), FI, FR (Patente europea), GA (Patente OAPI), GB, GB (Patente europea), GN (Patente OAPI), GR (Patente europea), HU, IT (Patente europea), JP, KP, KR, LK, LU, LU (Patente europea), MC, MG, ML (Patente OAPI), MR (Patente OAPI), MW, NL, NL (Patente europea), NO, PL, RO, SD, SE, SE (Patente europea), SN (Patente OAPI), SU*,TD (Patente OAPI), TG (Patente OAPI), US.

Publicada
Con informe de búsqueda internacional.
Antes de la expiración del plazo previsto para la modificación de las reivindicaciones, será publicada nuevamente si se reciben tales modificaciones.

(54) Title: METHOD FOR OBTAINING ACETIC ACID DERIVATIVES

(54) Título: PROCEDIMIENTO PARA LA OBTENCION DE DERIVADOS DE ACIDO ACETICO

(57) Abstract

Method for obtaining acetic acid derivatives, such as glycin, IDA and NTA by dehydrogenation of mono-, di- and triethanolamine, respectively, in the presence of a Copper-Raney catalyst. Such method includes a step consisting in regenerating the catalyst spent in order to reuse it in successive reaction cycles. The regeneration method is comprised of the treatment of the spent catalyst with backflowing formic acid, filtering and repulping it with demineralized water and NaOH till the washing waters reach a sligthly alkaline value. The regenerated catalyst may be reused in successvie reaction cycles maintaining an average efficency of 87 %, that is to say of the same order of magnitude as when using a new catalyst.

(57) Resumen

Procedimiento de obtención de derivados de ácido acético, tales como glicina, IDA y NTA por deshidrogenación de mono-, di- y trietanolamina, respectivamente, en presencia de un catalizador de Cobre-Raney. Este prodecimiento incluye una etapa consistente en regenerar el catalizador utilizado para poder reutilizarlo en sucesivos ciclos de reacción. El proceso de regeneración consiste en tratar el catalizador usado con ácido fórmico a reflujo, filtrarlo y repulparlo con agua dismineralizada y NaOH hasta que las aguas de lavado alcancen un valor ligeramente alcalino. El catalizador regenerado puede ser reutilizado en sucesivos ciclos de reacción manteniendo un rendimiento medio del 87 %, esto es, del mismo orden de magnitud que cuando se utiliza catalizador nuevo.

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* Véase al dorso

PROCEDURE FOR OBTAINING DERIVATIVES OF ACETIC ACID

Scope of the invention

The present invention relates to a procedure for obtaining derivatives of acetic acid, specifically glycine, iminodiacetic acid and nitrilotriacetic acid by oxidizing monoethanolamine, diethanolamine and triethanolamine respectively, using a Raney copper catalyst. In specific terms, the procedure of the invention refers to a regeneration treatment of the catalyst used in a previous reaction cycle which allows it to be used again in successive reactions, whilst maintaining a conversion and net yield in all trials carried out with the regenerated catalyst of the same order of magnitude as that obtained when using a new catalyst (85-92%).

Background to the invention

Glycine, iminodiacetic acid (IDA) and nitrilotriacetic acid (NTA), described in numerous patents, have many applications in various fields. Glycine, for example, has applications as a nutrient and both IDA and NTA are intermediates in the synthesis of herbicides, among other applications. Since the appearance of these materials on the market, various procedures for obtaining them have been described and patented.

The Japanese patent 53/7709, in the name of Mitsui Toatsu Chemical Co. Ltd., provides a procedure for obtaining IDA and NTA by oxidizing diethanolamine and triethanolamine respectively, with gaseous oxygen in an alkaline aqueous solution employing a noble metal (Pt and Pd) as the catalyst of the reaction. Although this procedure enables the said acids to be obtained, the yield obtained for IDA (69%) as well as for NTA (60%) is rather low and it also has the disadvantage that possible losses of the noble metal employed as the catalyst make this process hardly economical. Moreover, it is known by experts in the catalytic field that the losses of noble metals that occur during catalytic processes, whether acidic or alkaline, through solution of the said metal in the reaction water, necessitate complex processes in order to recover the metal, in addition to those normal losses that occur during the handling of the said catalysts. Consequently, these types of processes are hardly profitable

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in the case of end products with limited added value.

It would therefore be advantageous to have a procedure that enabled adequately pure glycine, IDA and NTA to be obtained in good yields by oxidizing mono-, di- and triethanolamine respectively in the presence of a non-noble metal catalyst (for example, Raney copper), which would minimize the economic disadvantages indicated above.

In this regard, Japanese patents Nos. 60/78.948, 60/78.949, 60/97.945, 60/100.545 and 61/65.840, in the name of Nippon Catalytic Chem. Ind., provide a procedure for obtaining glycine, IDA and NTA by dehydrogenating mono-, di- and triethanolamine, respectively, in an alkaline aqueous solution employing Raney copper as the catalyst, but with oxygen obtained by the decomposition of water, according to the following equations:

$C_2H_7ON + H_2O \rightarrow C_2H_5O_2N + 2H_2$ (glycine)

$C_4H_{11}O_2N + 2H_2O \rightarrow C_4H_7O_4N + 4H_2$ (IDA)

$C_6H_{15}O_3N + 3H_2O \rightarrow C_6H_9O_6N + 6H_2$ (NTA)

Although this procedure enables high yields of glycine, IDA and NTA to be obtained, the operation start-up causes loss of activity of the catalyst, which, together with the cost of the flameproof equipment required to carry out this procedure, directly affects the end production cost of the required product to the point where the process can become economically unviable.

A way of making this procedure economically viable would be to minimize the losses of the Raney copper catalyst. It would be particularly advantageous if the catalyst employed in the reaction cycle were simple and regenerated economically with the object of recovering its catalytic activity so that it could be reused in successive reaction cycles. None of the above-mentioned Japanese patents mentions the possibility of reusing or of regenerating the used Raney copper catalyst.

The present invention has therefore for its object to provide improvements to the procedure of dehydrogenating mono-, di- and triethanolamine in the presence of a Raney copper catalyst. The aim of these improvements is to regenerate the

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activity of the Raney copper catalyst through a simple regeneration procedure of the said catalyst which enables its reuse in successive reaction cycles, thereby rendering the said procedure of dehydrogenating mono-, di- and triethanolamine economically viable. Through the process of regenerating the catalyst, it recovers its catalytic activity and consequently may be introduced into other successive reaction cycles in order to obtain glycine, IDA or NTA with adequate yields and purity (of the same order of magnitude as that obtained when a new catalyst is used, between 85% and 92%), which results in the production of these acids being economically profitable and industrially viable, which would not be so in the case of glycine, IDA or NTA being produced using the catalyst immediately after its first use without prior regeneration or of its inability to be reused because its catalytic activity had become exhausted. Since the catalyst regenerated by the procedure of this invention can be reused on successive occasions, whilst maintaining the reaction conversions and yields, the cost effect of the catalyst in the end product is minimized.

Brief description of the invention

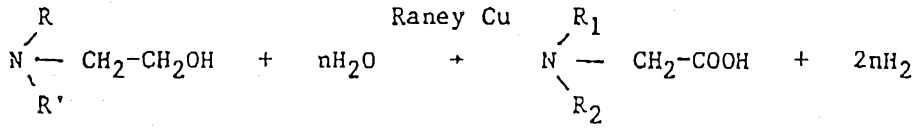
The improvements provided by the invention may be summarized as minimizing the cost effect of the catalyst in the end products obtained, thereby rendering economically viable on an industrial scale a procedure which would otherwise not be viable. In order to minimize the effect of the catalyst on the end products, the invention proposes a procedure for regenerating the catalyst used in the reaction with formic acid under reflux, thereby allowing all the oxidized copper (Cu^{2+}) which would be produced during the reaction process to be withdrawn from the used catalyst. Oxidized copper and other possible contaminating materials are precipitated onto the catalyst, poisoning it and producing considerably reduced yields of the reactions performed by reusing the catalyst without subjecting it to the regeneration process mentioned. These reduced yields are demonstrated in Examples 2 to 4 given in this description, in which it may be seen that the reaction yield after reusing the unregenerated catalyst drops to 36% in the fourth reaction cycle. If, on the contrary, the catalyst is regenerated, as will be described in detail below, when the catalyst regenerated

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according to the procedure of the invention is reused, the reaction yields are maintained at around 85-92% (Examples 5 to 9).

Detailed description of the invention

The invention provides a series of considerable improvements compared to the patents referred to above in Background to the invention, as it minimizes the cost effect of the catalyst on the end products obtained. In these patents, a procedure is described for obtaining glycine, IDA and NTA using a Raney copper catalyst which may be represented by the following equations:



(II) (I)

where R and R' may independently be H or groups $-CH_2-CH_2OH$;
R_1 and R_2 may independently be H or groups $-CH_2-COOH$;
n may be 1, 2 or 3.

As may be seen, when R = R' = H, the amino alcohol (II) is monoethanolamine and the compound (I) obtained is glycine ($R_1 = R_2 = H$). Similarly, when one of R or R' is H and the other is $-CH_2-CH_2OH$, the compound (II) is diethanolamine and the compound (I) obtained is iminodiacetic acid (one of R_1 or R_2 is H and the other is $-CH_2-COOH$), and when $R = R' = -CH_2-CH_2OH$ the compound (II) is triethanolamine and the compound (I) obtained is nitrilotriacetic acid.

The reaction can be performed at temperatures between 25°C and 215°C, and preferably between 150°C and 205°C, and at a pressure between 6 and 15 kg/cm^2. Water is used as a solvent, to which an alkaline hydroxide is added in a molar ratio compared to the initial amino alcohol hydroxide groups (II) of between 5% and 20% in stoichiometric excess, and preferably between 5% and 10%. This means that from 1.05 to 1.10 moles of alkaline hydroxide per mole of monoethanolamine, between 2.10 and 2.20 moles of the said hydroxide per mole of diethanolamine and between 3.15 and 3.30 moles of alkaline hydroxide per mole of triethanolamine

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are used. Any alkaline hydroxide may be employed provided that the salts formed with the acids produced are soluble in the reaction medium. Examples of suitable alkaline hydroxides are sodium hydroxide and potassium hydroxide.

The initial concentration of amino alcohols (II) may be between 20% and 35% by weight compared to the initial total weight of the components of the reaction mass, and preferably between 30% and 35% by weight. Higher concentrations may result in reduced yields due to problems of diffusion of oxidizing gas, and lower concentrations reduce productivity without improving the results.

The catalyst employed in the procedure of the invention is Raney copper, although it is also possible to use a Raney nickel catalyst if a few modifications are made to the process. The Raney copper catalyst is easily manufactured by leaching an Al_2Cu alloy with sodium hydroxide in a reducing atmosphere, according to procedures already described. The catalyst is added in a quantity between 5% and 15% by weight compared to the initial amino alcohol content (II), although with an average percentage of 7.5%, excellent results can be obtained.

The reaction time under these conditions is between 3.5 and 5.0 hours depending on the number of times the catalyst is used.

The reaction is continued by measuring the conversion of the initial amino alcohol (II) and the appearance of the acetic acid derivative (I). Once the reaction is finished, the reaction medium undergoes a hot filtration process, at a temperature of between 80°C and 95°C, and preferably between 85°C and 90°C, with the aim of recovering the used catalyst. The regeneration procedure is then carried out on the used Raney copper catalyst according to the new process that is being claimed in the present patent application and which constitutes the essential claim of the patent. This regeneration procedure of the catalyst provides the improvements claimed and renders the above-mentioned procedure viable economically and on an industrial scale since, otherwise, the said procedure would not be viable for the reasons set out in the Background to the invention.

The Raney copper catalyst regeneration procedure of the present invention

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basically consists of treating the Raney copper catalyst that has already been used in a previous reaction cycle with formic acid under reflux so that subsequently, and after further filtration, it can be digested with demineralized water and sodium hydroxide diluted repeatedly until a slightly alkaline pH (9-11) in the wash water is achieved. The treated catalyst may be stored under a dilute aqueous solution of sodium hydroxide (0.5-1.0%) until it is employed in the next reaction cycle.

The concentration of formic acid to be employed may be between 20% and 85% by weight, and this concentration is preferably 40%.

The alkaline solution of the reaction medium, which contains the soluble alkaline salts of the acetic acid derivatives formed, is isolated and treated to obtain the corresponding purified formula (I) acids. This treatment may be performed either chemically, by crystallization at temperatures between 75°C and 85°C, and preferably between 80°C and 85°C, of the reaction solution that has been previously treated with hydrochloric acid to obtain a pH between 0.5 and 2.5, depending on the acid obtained, or electrochemically, by an electrodialysis procedure as claimed in the Spanish patent application no. 9000130 in the name of the holder of the present patent application.

As may be seen from the examples given in this description, when the unregenerated Raney copper catalyst is reused, the reaction yield falls to 36% in the fourth reaction cycle, whilst reusing the catalyst regenerated by the procedure of the invention maintains the reaction yield in the fourth reaction cycle at around 87%, that is, of the same order of magnitude as that obtained when a new catalyst is employed (85-92%).

The present invention may be clearly illustrated by the following examples which should not be considered limitative of, but illustrative of the invention, and which enable the nature of its procedure to be more clearly understood.

Example 1

In a flameproof, 2-litre capacity, stainless steel autoclave reactor (AISI 316), are loaded in the following order and with stirring: 263.7 g of 97% sodium

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hydroxide; 640 g of demineralized water; 326.4 g of 98% pure diethanolamine; 45.7 g of Raney copper with an approximate moisture content of 30%, which effectively means using 32 g net of catalyst in the trial; and, finally, an additional 40 g of demineralized water to wash away any trace of the previous reagents. The inside of the reactor is then flushed twice with nitrogen (10 kg/cm^2) and twice more with hydrogen (10 kg/cm^2). The last sweep of hydrogen is depressurized to 2 kg/cm^2 and, with the reactor closed, heating of the reactants is commenced. Once 14-16 kg/cm^2 has been reached inside the reactor, it is depressurized to 10 kg/cm^2 and, with the vent open but maintaining the said internal pressure, heating is continued to 170-175°C, when the timing of the reaction begins. After four hours from the start of the reaction, it is considered finished and cooled to 90°C, filtered through a Buchner and Kitasato, and the Raney copper catalyst recovered. After washing well, it is stored under formic acid so that once it has been regenerated it may be reused in successive reactions. After analysis, the reaction solution provides a yield of 90.2% IDA in the form of its disodium salt which, when submitted to conventional electrodialysis, results in an almost quantitative recovery of free IDA with a purity above 98%.

Examples 2 to 4

These experiments were carried out to establish the behaviour of the catalyst employed in Example 1, in three consecutive trials, without submitting the catalyst to any regeneration process. The three trials were performed using the same methodology as that used in Example 1. However, in these trials the catalysts employed always originated from the unregenerated one used in the previous trial, though allowing for estimated handling losses. The reaction yields obtained after 4 hours in Example 2 and after 4.5 hours in Examples 3 and 4 were 82.6%, 60.6% and 36% respectively.

Examples 5 to 9

These experiments were carried out using the same methodology as that of Example 1. However, in these experiments the catalyst employed was new in the first trial and submitted to regeneration treatment in the four remaining trials. The catalyst regeneration in Examples 6 to 9, inclusive, was carried out as follows:

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32 g net of catalyst already used in Example 5 were suspended in 13.6 g of 85% formic acid and 15.2 g of demineralized water. The suspension was placed in a 100 cc capacity glass flask and maintained under reflux for 1 hour, after which the catalyst was vacuum-filtered through a Buchner and Kitasato and digested initially with 32 g of demineralized water and after filtering again was digested with 24 g of 2% sodium hydroxide, thereby achieving a pH of approximately 10.32 in the final wash water. The treated catalyst was employed in the next trial. The yields obtained in the various experiments were 92.6%, 85.6%, 85.1%, 87.1% and 85.2%. The final average yield was 87.12%. In all cases, the free acids obtained were isolated and purified by electrodialysis.

The following table shows the yields obtained in Examples 2-4 and 6-9 (without regenerating and with regenerating the catalyst, respectively) in various reaction cycles. A significant reduction in the reaction yield from the third cycle can be seen when an unregenerated catalyst is employed.

	Yield %	
Reaction cycle	U.C.	R.C.
2	82.6	85.6
3	60.6	85.1
4	36	87.1
5	-	85.2

U.C. Unregenerated catalyst.

R.C. Regenerated catalyst according to the procedure of the invention.

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The claims defining the invention are as follows:

1. A process for rejuvenating a Raney copper catalyst, suitable for use in the conversion of amino alcohols to amino acids, which comprises treating a spent Raney copper catalyst under reflux conditions with formic acid.

2. A process of Claim 1 wherein the Raney copper catalyst is further washed with water and an alkali metal hydroxide, and washed with water until the wash water has a pH between about 9-11.

3. A process of Claim 1 or 2 wherein the concentration of formic acid is between about 20% and about 80% by weight.

4. A process of Claim 1, substantially as hereinbefore described with reference to the practical Examples.

5. A Raney copper catalyst when rejuvenated by the process of any one of Claims 1-4.

6. A process for producing amino acids which comprises contacting an amino alcohol selected from the group consisting of monoethanol amine, diethanol amine and triethanol amine, with an alkali metal hydroxide in the presence of a Raney copper catalyst wherein at least some of the Raney copper catalyst has been rejuvenated by treating the catalyst under reflux conditions with formic acid.

7. A process of Claim 6 wherein the amount of alkali metal hydroxide is between about 5% and about 20% in stoichiometric excess over that required to produce the amino acid salt.

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8. A process of Claim 6 or 7 wherein the reaction is carried out at a temperature between 25°C and about 215°C.

9. A process of Claim 8 wherein the temperature is between about 150°C and about 205°C.

10. A process of any one of claims 6 to 9 wherein the Raney copper catalyst is rejuvenated by treating the catalyst under reflux conditions with formic acid having a concentration between about 20% and about 80% by weight.

11. A process of Claim 10 wherein the Raney copper is further washed with water and an alkali metal hydroxide, and thereafter washed with water until the wash water has a pH between about 9 and about 11.

12. A process of Claim 6, substantially as hereinbefore described with reference to the practical Examples.

13. An amino acid when prepared by the process of any one of Claims 6 to 12.

DATED this 3rd day of December, 1992

ERCROS, S.A.,
By its Patent Attorneys,
E. F. WELLINGTON & CO.,
By:

(B. S. Wellington)

A/RR/1612/5

AUSTRALIAN PATENT OFFICE

INTERNATIONAL SEARCH REPORT

International Application No PCT/ES 91/00061

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.[5] C 07 C 227/02

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
Int.Cl.[5]	C 07 C 227/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	GB,A,2148287 (NIPPON SHOKUBAI KAGAKU KOGYO CO.LTD) 30 May 1985, see claims, & JP,A,60078948 (4 May 1985) cited in the application	1-4

* Special categories of cited documents: [10]

"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

"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.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
04 March 1992 (04.03.92)	26 March 1992 (26.03.92)
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. ES 9100061 SA 54132

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 19/03/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2148287	30-05-85	JP-B- 1053863	15-11-89
		JP-C- 1567316	10-07-90
		JP-A- 60078948	04-05-85
		JP-B- 1053864	15-11-89
		JP-C- 1567317	10-07-90
		JP-A- 60078949	04-05-85
		JP-B- 1053865	15-11-89
		JP-C- 1567318	10-07-90
		JP-A- 60097945	31-05-85
		JP-B- 1053866	15-11-89
		JP-C- 1567319	10-07-90
		JP-A- 60100545	04-06-85
		US-A- 4782183	01-11-88

INFORME DE BUSQUEDA INTERNACIONAL

Solicitud Internacional Nº PCT/ES 91/00061

I. CLASIFICACION DE LA INVENCION (caso de ser aplicables varios simbolos de clasificación, indicarlos todos) [6]

Según la clasificación internacional de patentes (CIP) o según la clasifación nacional y la CIP

CIP.5 C 07 C 227/02

II. SECTORES COMPRENDIDOS POR LA BUSQUEDA

Documentación minima consultada [7]

Sistema de clasificación	Simbolos de clasificación
CIP.5	C 07 C 227/00

Otra documentación consultada además de la documentación minima en la medida en que tales documentos forman parte de los sectores comprendidos por la búsqueda [8]

III. DOCUMENTOS CONSIDERADOS PERTINENTES [9]

Categoria *	Identificación de los documentos citados, [11] con indicación, en caso necesario, de los pasajes pertinentes [12]	Nº de las reivindicaciones a las que se refieran [13]
A	GB,A,2148287 (NIPPON SHOKUBAI KAGAKU KOGYO CO. LTD) 30 Mayo 1985, ver reivindicaciones, & JP, A, 60078948 (4 Mayo 1985) citado en la solicitud	1-4

* Categorias especiales de documentos citados: [10]

"A" documento que define el estado general de la técnica, no considerado como particularmente pertinente

"E" documento anterior, publicado ya sea en la fecha de presentación internacional o con posterioridad a la misma

"L" documento que pueda plantear dudas sobre una reivindicación de prioridad o que se cita para determinar la fecha de publicación de otra cita o por una razón especial (como la indicada

"O" documento que se refiere a una divulgación oral, a un empleo, a una exposición o a cualquier otro tipo de medio

"P" documento publicado antes de la fecha de presentación internacional, pero con posterioridad a la fecha de prioridad reivindicada

"T" documento ulterior publicado con posterioridad a la fecha de prioridad y que no pertenece al estado de la técnica pertinente pero que se cita para comprender el principio o la teoria que constituye la base de la invención

"X" documento particularmente pertinente: la invención reivindicada no puede considerarse como nueva ni que implique una actividad inventiva

"Y" documento particularmente pertinente: la invención reivindicada no puede considerarse que implique una actividad inventiva cuando el documento se asocia a otro u otros documentos de la misma naturaleua, cuya combinación resulta evidente para un experto en la materia

"&" documento que forma parte de la misma familia de partentes

IV. CERTIFICACION

Fecha en al que se ha concluido efectivamente la búsqueda internacional	Fecha de expedición del presente informe de búsqueda internacional
04-03-1992	26. 03. 92
Administración encargada de la búsqueda internacional	**Firma del funcionario autorizado**
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ANEXO AL INFORME DE BUSQUEDA INTERNACIONAL RELATIVO A LA SOLICITUD INTERNACIONAL DE PATENTE Nº

ES 9100061
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Este anexo enumera los miembros de familias de patentes relativos a los documentos de patentes citados en el informe de búsqueda internacional mencionado.
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Documento de patente citado en el informe de búsqueda	Fecha de publicación	Miembro(s) de familia de patentes	Fecha de publicación
GB-A- 2148287	30-05-85	JP-B- 1053863	15-11-89
		JP-C- 1567316	10-07-90
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		JP-B- 1053864	15-11-89
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		US-A- 4782183	01-11-88

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