

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
3 January 2003 (03.01.2003)

PCT

(10) International Publication Number  
**WO 03/000815 A1**

(51) International Patent Classification<sup>7</sup>: **C09J 4/00**

(21) International Application Number: PCT/US02/20518

(22) International Filing Date: 26 June 2002 (26.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/888,555 26 June 2001 (26.06.2001) US

(71) Applicant: **HENKEL LOCTILE CORPORATION**  
[US/US]; 1001 Trout Brook Crossing, Rocky Hill, CT  
06067 (US).

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

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

(72) Inventors: **GRISMALA, Roger, J.**; 39 Laural Park, Enfield, CT 06082 (US). **O'CONNOR, John, T.**; 93 Cheshire Road, Wallingford, CT 06492 (US).

(74) Agent: **CUNNINGHAM, Marina, E.**; CityPlace II, 185 Asylum Street, Hartford, CT 06103-3402 (US).

**Published:**

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: CYANOACRYLATE COMPOSITIONS

(57) Abstract: This invention relates to cyanoacrylate-containing compositions that include, in addition to the cyanoacrylate component, the combination of two accelerators to improve fixture speeds on certain substrates.



**WO 03/000815 A1**

CYANOACRYLATE COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

5           This invention relates to cyanoacrylate-containing compositions that include, in addition to the cyanoacrylate component, the combination of two accelerators to improve fixture speeds on certain substrates.

10   Brief Description of Related Technology

          Cyanoacrylate adhesive compositions are well known, and widely used as quick setting, instant adhesives with a wide variety of uses. See H.V. Coover, D.W. Dreifus and J.T. O'Connor, "Cyanoacrylate Adhesives" in Handbook of Adhesives,  
15 27, 463-77, I. Skeist, ed., Van Nostrand Reinhold, New York, 3rd ed. (1990). See also, G.H. Millet "Cyanoacrylate Adhesives" in Structural Adhesives: Chemistry and Technology, S.R. Hartshorn, ed., Plenum Press, New York, p. 249-307 (1986).

20           Nonetheless, various techniques have been used to improve further the fixture times of such adhesive

compositions for certain applications where it is important to be able to secure one substrate to another quickly, while allowing the bond strength to develop over time. In addition, substrates constructed of certain materials have proven in the past difficult to bond, irrespective of the application to which the adhesive and the substrate are to be placed.

To combat these issues, Loctite Corporation developed a technology based on calixarene and oxacalixarene compounds. Generally, the addition of such materials to a cyanoacrylate allow for accelerated fixturing of substrates to-be-bonded together. See U.S. Patent Nos. 4,556,700, 4,622,414, 4,636,539, 4,695,615, 4,718,966, and 4,855,461.

In addition to calixarene compounds, Loctite Corporation also developed technology based on the addition of silacrown compounds to cyanoacrylate adhesive compositions to accelerate fixturing. For instance, U.S. Patent No. 4,906,317 (Liu) is directed to cyanoacrylate adhesive compositions which include silacrown compounds as additives to give substantially reduced fixture and cure times on de-activating substrates such as wood. The silacrown compounds are preferably employed at levels of about 0.1-5% by weight of the composition.

More recently, Henkel KgAA developed technology based on the addition to cyanoacrylate compositions of cyclodextrins to accelerate fixturing. In U.S. Patent No. 5,312,864 (Wenz), the acceleration of the setting properties of a cyanoacrylate adhesive composition by adding thereto a hydroxyl group derivative of an  $\alpha$ -,  $\beta$ - or  $\gamma$ -cyclodextrin which is at least partly soluble in the cyanoacrylate is described.

Other approaches have also been investigated, such as in U.S. Patent Nos. 4,170,585 (Motegi), in which it is reported the use of crown ethers in cyanoacrylate adhesive

compositions, and in 4,837,260 (Sato), in which thixotropic silica has been included in such components.

Notwithstanding the state-of-the-technology it would be desirable to provide alternative technologies to improve  
5 the fixturing speed of cyanoacrylates.

#### **SUMMARY OF THE INVENTION**

The present invention is directed to a cyanoacrylate-based composition, which includes beyond the  
10 cyanoacrylate component, two accelerator components, the combination of which demonstrates improved fixture speeds, particularly on substrates constructed of certain materials, namely steel and epoxy glass, and demonstrated comparable fixture speeds on certain other substrates, namely leather and  
15 the woods, balsawood and maple.

The two accelerator components are (a) calixarenes and oxacalixarenes, and (b) crown ethers.

The inventive composition may be rendered thixotropic by the addition of thixotropy-conferring agent.  
20 The viscosity of the inventive composition may also be increased by the addition of a thickener.

This invention is also directed to a method of bonding together two substrates, at least one of which is constructed of certain materials, namely steel and epoxy  
25 glass, leather and the woods, balsawood and maple. The method includes applying to at least one of the substrates a composition as described above, and thereafter mating together the substrates.

In addition, the present invention is directed to  
30 reaction products of the inventive compositions.

Also, the invention is directed to a method of preparing the inventive compositions.

The invention will be more fully understood by a reading of the section entitled "Detailed Description of the  
5 Invention", which follows.

#### **DETAILED DESCRIPTION OF THE INVENTION**

As noted above, this invention is directed to a cyanoacrylate-based composition, which includes beyond the  
10 cyanoacrylate component, the two accelerator components, the combination of which demonstrates improved fixture speeds, particularly on substrates constructed of certain materials, namely steel and epoxy glass, and demonstrated comparable fixture speeds on certain other substrates, namely leather and  
15 the woods, balsawood and maple.

The cyanoacrylate component includes cyanoacrylate monomers which may be chosen with a raft of substituents, such as those represented by  $H_2C=C(CN)-COOR$ , where R is selected from  $C_{1-15}$  alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl,  
20 aryl, allyl and haloalkyl groups. Desirably, the cyanoacrylate monomer is selected from methyl cyanoacrylate, ethyl-2-cyanoacrylate, propyl cyanoacrylates, butyl cyanoacrylates (such as n-butyl-2-cyanoacrylate), octyl cyanoacrylates, allyl cyanoacrylate,  $\beta$ -methoxyethyl  
25 cyanoacrylate and combinations thereof. A particularly desirable one is ethyl-2-cyanoacrylate.

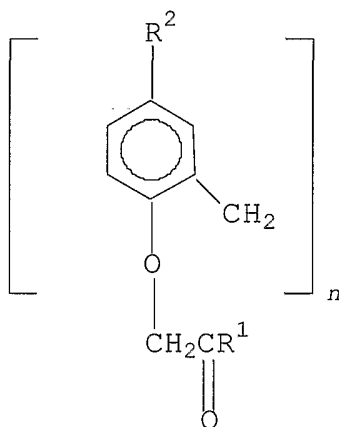
The cyanoacrylate component should be included in the compositions in an amount within the range of from about 50% to about 99.98% by weight, with the range of about 90% to  
30 about 99% by weight being desirable, and about 95% by weight of the total composition being particularly desirable.

The first accelerator may be selected from calixarenes, oxacalixarenes, and combinations thereof.

Of the calixarenes and oxacalixarenes, many are known, and are reported in the patent literature. See e.g.,  
5 U.S. Patent Nos. 4,556,700, 4,622,414, 4,636,539, 4,695,615, 4,718,966, and 4,855,461, the disclosures of each of which are hereby expressly incorporated herein by reference.

For instance, as regards calixarenes, those within structure I are useful herein:

10



I

where R<sup>1</sup> is alkyl, alkoxy, substituted alkyl or substituted alkoxy; R<sup>2</sup> is H or alkyl; and n is 4, 6 or 8.

15 One particularly desirable calixarene is tetrabutyl tetra[2-ethoxy-2-oxoethoxy]calix-4-arene.

The second accelerator is a crown ether.

A host of crown ethers are known. For instance, examples which may be used herein either individually or in  
20 combination, or in combination with other first accelerators include 15-crown-5, 18-crown-6, dibenzo-18-crown-6, benzo-15-crown-5, dibenzo-24-crown-8, dibenzo-30-crown-10, tribenzo-18-

crown-6, asym-dibenzo-22-crown-6, dibenzo-14-crown-4, dicyclohexyl-18-crown-6, dicyclohexyl-24-crown-8, cyclohexyl-12-crown-4, 1,2-decalyl-15-crown-5, 1,2-naphtho-15-crown-5, 3,4,5-naphthyl-16-crown-5, 1,2-methyl-benzo-18-crown-6, 1,2-methylbenzo-5, 6-methylbenzo-18-crown-6, 1,2-t-butyl-18-crown-6, 1,2-vinylbenzo-15-crown-5, 1,2-vinylbenzo-18-crown-6, 1,2-t-butyl-cyclohexyl-18-crown-6, asym-dibenzo-22-crown-6 and 1,2-benzo-1,4-benzo-5-oxygen-20-crown-7. See U.S. Patent No. 4,837,260 (Sato), the disclosure of which is hereby expressly  
10 incorporated here by reference.

The first accelerator component, calixarene and/or oxacalixarene, should be included in the compositions in an amount within the range of from about 0.1% to about 5% by weight, with the range of about 0.1 to about 0.5% by weight  
15 being desirable, and about 0.2% by weight of the total composition being particularly desirable.

The second accelerator component, crown ethers, should be included in the compositions in an amount within the range of from about 0.01% to about 10% by weight, such as  
20 about 0.1% to about 5% by weight, with the range of about 0.1 to about 0.5% by weight being desirable, and about 0.4% by weight of the total composition being particularly desirable.

The inventive compositions may also be rendered thixotropic by the addition of thixotropy-conferring agents, such as fumed silicas. See U.S. Patent Nos. 4,477,687  
25 (Litke), 4,533,422 (Litke) and Re. 32,889 (Litke) and 4,837,260 (Sato). Thixotropy-conferring agents should be included in the inventive compositions an amount less than about 12%, such as within the range of about 4 to about 8%, by  
30 weight of the total composition.

The inventive compositions may also be thickened by the addition of thickeners, such as polymethyl(meth)acrylate, in order to increase viscosity. Thickeners should be included in the inventive composition in an amount less than about 12%,  
5 such as within the range of about 4 to about 8%, such as about 6%, by weight of the total composition.

Additives may be included in the inventive compositions to confer additional physical properties, such as improved shelf-life stability, color, improved toughness, and  
10 enhanced resistance to thermal degradation. Such additives therefore may be selected from free radical stabilizers, anionic stabilizers, dyes, toughening agents, thermal degradation enhancers, and combinations thereof.

In another aspect of the invention, there is  
15 provided a method of bonding together two substrates, at least one of which is constructed certain materials, namely steel and epoxy glass, leather and the woods, balsawood and maple. The method includes applying to at least one of the substrates a composition as described above, and thereafter mating  
20 together the substrates for a time sufficient to permit the adhesive to fixture. For many applications, the substrate should become fixed in less than 30 seconds, and depending on substrate as little as 1-5 seconds.

In yet another aspect of the invention, there is  
25 provided reaction products of the so-described compositions.

In still another aspect of the invention, there is provided a method of preparing the so-described compositions. The method includes providing a cyanoacrylate component, and combining therewith with mixing a first and second accelerator  
30 component.

In an additional aspect of the invention, there is provided a method of bonding together two substrates, at least one of which is constructed of a material selected from the group consisting of certain materials, namely steel and epoxy glass, leather and the woods, balsawood and maple, using the compositions of this invention. The method includes applying a the compositions to at least one of the substrates and mating together the substrates for a time sufficient to permit the composition to fixture.

These aspects of the invention will be further illustrated by the examples which follow.

#### **EXAMPLES**

We prepared four samples to evaluate their fixture speeds on a variety of substrates. The samples were prepared by mixing together the constituents in any order for a sufficient period of time to ensure substantial homogeneity of the constituents. If desired, certain materials may be added to inhibit cyanoacrylate polymerization thereby conferring stability to the formulation (such as conventional acidic materials), or removal (through conventional filtration and/or separation technology) of materials which if present would cause cyanoacrylate polymerization. Removal of such materials should improve the shelf life of the formulation (e.g., catalysts used to prepare that constituent, or starting materials or by products from the preparation thereof). The constituents of these samples are listed below in Table 1.

**Table 1**

| Component                                            | Sample No./Weight % |        |        |        |        |
|------------------------------------------------------|---------------------|--------|--------|--------|--------|
|                                                      | 1                   | 2      | 3      | 4      | 5      |
| Ethyl-2-cyanoacrylate                                | 88                  | 87.2   | 83.8   | 87.6   | 93.8   |
| Tetrabutyl tetra(2-ethoxy-2-oxoethoxy) calix(4)arene | --                  | 0.8    | --     | 0.2    | 0.2    |
| 15-Crown-5                                           | --                  | --     | 0.2    | 0.2    | --     |
| Methane sulfonic acid                                | 10 ppm              | 15 ppm | 10 ppm | 10 ppm | 10 ppm |
| Sulfur dioxide                                       | 10 ppm              | 15 ppm | 10 ppm | 10 ppm | 10 ppm |
| Polymethylmethacrylate                               | 6.0                 | 6.0    | 6.0    | 6.0    | 6.0    |
| Silica                                               | 6.0                 | 6.0    | --     | 6.0    | --     |

We applied each of Sample Nos. 1-5 to the substrates listed below in Table 2, and measured their fixture speeds.

5 More specifically, we applied each sample to one substrate, and then placed the other substrate over the sample-applied substrate. The substrates were mated and held motionless with the application of finger pressure. The substrates were then pulled in a tensile shear mode to determine the time required  
10 for the substrates to support their own weight and resist firmly being pulled apart. That time was recorded as the fixture time, and the results are shown below in Table 2.

**Table 2**

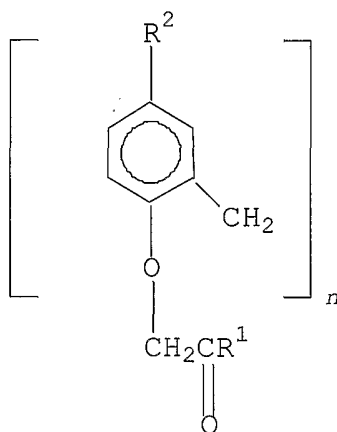
| Property             | Substrate   | Sample No. |      |    |     |     |
|----------------------|-------------|------------|------|----|-----|-----|
|                      |             | 1          | 2    | 3  | 4   | 5   |
| Fixture Times (secs) | Paper       | 55         | 8    | 2  | 3   | 3   |
|                      | Steel       | 240        | 225  | 30 | 10  | 25  |
|                      | Epoxy Glass | 160        | 35   | 25 | 20  | 95  |
|                      | Leather     | >300       | 20   | 10 | 5   | 5   |
|                      | Balsawood   | 45         | 110  | -- | 1   | 2   |
|                      | Maple       | 220        | 250  | 40 | 40  | 120 |
|                      | Birch       | >300       | 245  | 30 | 35  | 60  |
|                      | Oak         | >300       | >300 | 90 | 110 | 150 |
|                      | Pine        | 295        | >300 | 35 | 55  | 100 |
|                      | Walnut      | >300       | >300 | 90 | 90  | 110 |

As can be seen, Sample No. 4 (cyanoacrylate in combination with a calixarene and a crown ether) demonstrates improved fixture speeds on certain substrates, namely steel and epoxy glass, and demonstrated comparable fixture speeds on  
5 certain other substrates, namely leather and the woods, balsawood and maple.

**What is Claimed is:**

1. A cyanoacrylate adhesive composition comprising:  
a cyanoacrylate component;  
(b) a first accelerator component selected from the group consisting of calixarenes, oxacalixarenes, and combinations thereof; and  
(c) at least one crown ether.
2. The composition according to Claim 1, wherein the cyanoacrylate component is selected from materials within the structure  $\text{H}_2\text{C}=\text{C}(\text{CN})-\text{COOR}$ , wherein R is selected from  $\text{C}_{1-15}$  alkyl, alkoxyalkyl, cycloalkyl, alkenyl, aralkyl, aryl, allyl and haloalkyl groups.
3. The composition according to Claim 1, wherein the cyanoacrylate component comprises ethyl-2-cyanoacrylate.

4. The composition according to Claim 1, wherein the calixarene is within the following structure



where  $R^1$  is alkyl, alkoxy, substituted alkyl or substituted alkoxy;  $R^2$  is H or alkyl; and  $n$  is 4, 6 or 8.

5. The composition according to Claim 1, wherein the calixarene is tetrabutyl tetra[2-ethoxy-2-oxoethoxy]calix-4-arene.

6. The composition according to Claim 1, wherein the first accelerator component is an oxacalixarene.

7. The composition according to Claim 1, wherein the crown ether is selected from members within the group consisting of 15-crown-5, 18-crown-6, dibenzo-18-crown-6, benzo-15-crown-5, dibenzo-24-crown-8, dibenzo-30-crown-10, tribenzo-18-crown-6, asym-dibenzo-22-crown-6, dibenzo-14-crown-4, dicyclohexyl-18-crown-6, dicyclohexyl-24-crown-8, cyclohexyl-12-crown-4, 1,2-decalyl-15-crown-5, 1,2-naphtho-15-crown-5, 3,4,5-naphthyl-16-crown-5, 1,2-methyl-benzo-18-crown-6, 1,2-methylbenzo-5, 6-methylbenzo-18-crown-6, 1,2-t-butyl-18-crown-6, 1,2-vinylbenzo-15-crown-5, 1,2-vinylbenzo-18-crown-6, 1,2-t-butyl-cyclohexyl-18-crown-6, asym-dibenzo-22-crown-6, and 1,2-benzo-1,4-benzo-5-oxygen-20-crown-7 and combinations thereof.

8. The composition according to Claim 1, wherein the first accelerator component is used in an amount within the range of from about 0.01% by weight to about 5% by weight based on the total composition.

9. The composition according to Claim 1, wherein the crown ether is used in an amount within the range of from about 0.01% by weight to about 5% by weight based on the total composition.

10. The composition according to Claim 1, further comprising a thixotropy-conferring component.

11. The composition according to Claim 1, further comprising a thickener.

12. The composition according to Claim 1, further comprising an additive selected from the group consisting of free radical stabilizers, anionic stabilizers, dyes, toughening agents, thermal degradation enhancers, and combinations thereof.

13. A cyanoacrylate adhesive composition comprising:

- (a) a cyanoacrylate component;
- (b) a first accelerator component selected from the group consisting of calixarenes, oxacalixarenes, and combinations thereof;
- (c) at least one crown ether; and
- (d) a thixotropy-conferring component.

14. The composition according to Claim 1, further comprising:

- (d) a thixotropy-conferring component; and
- (e) a thickener component.

15. Cured products of the composition according to Claim 1.

16. A method of bonding together two substrates, at least one of which is constructed of a material selected from the group consisting of steel, epoxy glass and wood, comprising the steps of:  
applying a cyanoacrylate-containing composition according to Claim 1, to at least one of the substrates and  
mating together the substrates for a time sufficient to permit the adhesive to fixture.

17. A method of preparing a cyanoacrylate-containing composition according to Claim 1, comprising the steps of:  
providing a cyanoacrylate component, and combining therewith  
with mixing a first accelerator component and a crown ether.

18. A cyanoacrylate adhesive consisting essentially of:  
(a) a cyanoacrylate component;  
(b) a first accelerator component selected from the group consisting of calixarenes, oxacalixarenes, and combinations thereof; and  
(c) at least one crown ether.

19. The composition according to Claim 18, further comprising a thixotropy-conferring component.

20. The composition according to Claim 19, further comprising a thickener component.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/20518

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09J4/00

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 C09J

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          | FR 2 791 985 A (TOAGOSEI CO LTD)<br>13 October 2000 (2000-10-13)<br>page 3, line 29 - line 34<br>page 24, line 1 - line 11<br>page 28, line 10 - line 12<br>----                                | 1-20                  |
| P,X        | US 6 294 629 B1 (O'DWYER LIAM P ET AL)<br>25 September 2001 (2001-09-25)<br>claims<br>----                                                                                                      | 1-20                  |
| A          | EP 0 151 527 A (LOCTITE IRELAND LTD)<br>14 August 1985 (1985-08-14)<br>cited in the application<br>page 1, line 9 -page 2, line 24<br>& US 4 556 700 A<br>3 December 1985 (1985-12-03)<br>----- | 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.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

11 September 2002

Date of mailing of the international search report

19/09/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Andriollo, G

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 02/20518

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|----|---------------------|----------------------------|---------------------|
| FR 2791985                                | A  | 13-10-2000          | JP 2000290601 A            | 17-10-2000          |
|                                           |    |                     | DE 10017246 A1             | 09-11-2000          |
|                                           |    |                     | FR 2791985 A1              | 13-10-2000          |
| US 6294629                                | B1 | 25-09-2001          | NONE                       |                     |
| EP 0151527                                | A  | 14-08-1985          | US 4622414 A               | 11-11-1986          |
|                                           |    |                     | AT 28658 T                 | 15-08-1987          |
|                                           |    |                     | AU 585759 B2               | 22-06-1989          |
|                                           |    |                     | AU 3809085 A               | 01-08-1985          |
|                                           |    |                     | BR 8500364 A               | 10-09-1985          |
|                                           |    |                     | CA 1284653 A1              | 04-06-1991          |
|                                           |    |                     | DE 3560401 D1              | 03-09-1987          |
|                                           |    |                     | EP 0151527 A1              | 14-08-1985          |
|                                           |    |                     | ES 539876 D0               | 01-04-1986          |
|                                           |    |                     | ES 8606236 A1              | 01-10-1986          |
|                                           |    |                     | JP 1859387 C               | 27-07-1994          |
|                                           |    |                     | JP 5072946 B               | 13-10-1993          |
|                                           |    |                     | JP 60179482 A              | 13-09-1985          |
|                                           |    |                     | JP 2826559 B2              | 18-11-1998          |
|                                           |    |                     | JP 6092895 A               | 05-04-1994          |
|                                           |    |                     | US 4912183 A               | 27-03-1990          |
|                                           |    |                     | US 4556700 A               | 03-12-1985          |
|                                           |    |                     | US 4642362 A               | 10-02-1987          |
|                                           |    |                     | US 4636539 A               | 13-01-1987          |
|                                           |    |                     | US 4699966 A               | 13-10-1987          |
|                                           |    |                     | US 4718966 A               | 12-01-1988          |