(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 511 400 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
17.10.2012 Bulletin 2012/42

(21) Application number: **10835855.7**

(22) Date of filing: **30.11.2010**

(51) Int Cl.:
C25D 3/62 *(2006.01)*

(86) International application number:
PCT/JP2010/071304

(87) International publication number:
WO 2011/070933 (16.06.2011 Gazette 2011/24)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **09.12.2009 JP 2009279409**

(71) Applicant: **Metalor Technologies (Japan) Corporation**
Minato-ku, Tokyo 108-0075 (JP)

(72) Inventors:
- **FURUKAWA, Masato**
  Numazu-shi
  Shizuoka 410-0314 (JP)
- **SON, Injoon**
  Numazu-shi
  Shizuoka 410-0314 (JP)

(74) Representative: **Gulde Hengelhaupt Ziebig & Schneider**
Patentanwälte - Rechtsanwälte
Wallstrasse 58/59
10179 Berlin (DE)

(54) ELECTROLYTIC HARD GOLD PLATING SOLUTION AND PLATING METHOD USING SAME

(57) Disclosed is a plating solution which does not generate pinholes in a gold film even if the gold film has a thickness of less than 0.1μm. Partial plating is performed using an electrolytic hard gold plating solution containing gold cyanide and/or gold cyanide salt, water-soluble cobalt salt or water-soluble nickel salt, an electric conductive salt of organic acid, an aromatic sulfonic acid compound, a combination of one or more items selected from group consisting of carboxylic acids, oxycarboxylic acids, and the salts thereof, and a nitrogen-containing five-membered heterocyclic compound. Consequently, pinholes are not generated in a gold film even if the gold film has a thickness of less than 0.1μm.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to an electrolytic hard gold plating solution capable of forming a plating film which hardly generates pinholes even when formed in a thin film and which is dense, as well as to a plating method using the plating solution. The present invention relates particularly to an electrolytic hard gold plating solution preferably used for selective plating of electronic parts such as connector and the like, as well as to a plating method using the plating solution.

Background Art

[0002] Owing to the recent progress of IT, electronic apparatuses such as mobile phone, note type personal computer and the like have rapidly come to possess a lighter weight, a smaller size and a higher performance. In connection therewith, needs for smaller size and higher reliability have become stronger for electronic parts constituting the above-mentioned electronic apparatuses. Gold plating is in wide use in the electronic parts constituting the above-mentioned electronic apparatuses.

[0003] For example, hard gold plating superior in abrasion resistance is applied to a contact member which becomes an electric contact of a connector electrically connecting electronic apparatuses or electronic parts.

[0004] Contact member for electronic parts is produced generally by the following method. First, nickel plating is applied on a base material (e.g. copper material), whereby a nickel film is formed. Next, hard gold plating is applied on the nickel film, whereby a gold film is formed. In this way, there is obtained a contact member in which a nickel film and a gold film have been formed on a copper material in this order.

[0005] Since gold is expensive, gold film is made thin for gold saving. However, when a gold film is formed using a conventional gold plating solution, a large number of pinholes appears therein when the gold film has a thickness of 0.1 μm or smaller. When pinholes are present in a gold film, the nickel film (which is a lower film) undergoes air oxidation via the pinholes, generating nickel oxide. This nickel oxide gives rise to, for example, an increase in electric resistance at contact point, causing a change in electric properties of electronic apparatus. As a result, the electronic apparatus comes to have inconveniences.

[0006] Thus, a gold film having a large number of pinholes therein has no sufficient protectability for nickel film. Accordingly, it is desired that the gold film has no pinhole.

[0007] In Patent Literature 1, it is described that selective plating is applied to a contact member using a hard gold plating solution containing a lustering agent. This plating solution enables uniform electrodeposition. With this plating solution, however, the lustering agent component is taken into the gold film formed. When the additive component such as lustering agent component or the like is taken into the gold film, the gold purity of the gold film is reduced. As a result, the contact member comes to have an increased contact resistance or have a reduced corrosion resistance.

Citation List

Patent Literature

[0008] PTL 1: Patent No. 3933930

Summary of Invention

Technical Problem

[0009] A task to be achieved by the present invention is to provide an electrolytic hard gold plating solution which is preferably used in selective plating, etc. and which gives no pinhole in the gold film formed even when the film has a thickness of 0.1 μm or smaller.

[0010] Other task to be achieved by the present invention is to provide a plating method using such an electrolytic hard gold plating solution.

Solution to Problem

[0011] In order to achieve the above task, the present inventors made an investigation first on selective plating. As a result, it was found that, when an organic oxidizing agent is compounded in a plating solution, deposition of gold can be suppressed uniquely in a low current density range, and a patent application was made on this finding (Japanese Patent Application 2009-165730). This organic oxidizing agent raises the oxidation and reduction potential of gold uniquely in a low current density range (a current density of 20 A/dm^2 or lower) and suppresses gold deposition. Meanwhile, the organic oxidizing agent does not suppress gold deposition in a medium to high current density range (a current density of 20 to 200 A/dm^2). Thus, the area in which a plating film is formed, can be controlled by controlling the current density employed. For the above reason, an electrolytic hard gold plating solution containing an organic oxidizing agent can be preferably used in selective plating.

[0012] Next, the present inventors made an investigation on thin-film formation of gold film. As a result, it was found that, when the above-mentioned plating solution contains an organic crystal-controlling agent of the present invention, the gold film formed therewith generates no pinhole even when the gold film formed has a thickness of about 0.05 μm. The present inventors further found that the above-mentioned plating solution can form a gold film of high gold purity. The present inventors completed the present invention based on the above findings.

[0013] The present invention which has achieved the above task, is as described below.

[0014] [1] An electrolytic hard gold plating solution comprising
at least one member of a gold cyanide and a gold cyanide salt,
a water-soluble cobalt salt or a water-soluble nickel salt,
an electric conductive salt of organic acid,
an aromatic sulfonic acid compound,
at least one member selected from the group consisting of a carboxylic acid, an oxycarboxylic acid, and salts thereof, and
a nitrogen-containing five-membered heterocyclic compound.

[0015] [2] The electrolytic hard gold plating solution according to [1], wherein the concentration of the nitrogen-containing five-membered heterocyclic compound is 1 ~ 50 g/L.

[0016] [3] The electrolytic hard gold plating solution according to [1], wherein the pH of the plating solution is in a range of 3 to 7.

[0017] [4] A plating method which comprises spraying the electrolytic hard gold plating solution of [1] onto a to-be-plated area of a to-be-plated material to form a gold film on the to-be-plated area.

Advantageous Effects of Invention

[0018] The gold film formed with the electrolytic hard gold plating solution of the present invention generates no pinhole even when the film has a thickness of about 0.05 μm. The nickel film beneath the gold film is completely covered and protected by the gold film and, therefore, the material plated with the present plating solution has high corrosion resistance. Further, with the present electrolytic hard gold plating solution, the use amount of gold can be made small, resulting in superior economy.

Description of Embodiments

(Electrolytic hard gold plating solution)

[0019] In-depth description is made below on the electrolytic hard gold plating solution of the present invention.

[0020] In the electrolytic hard gold plating solution of the present invention, at least either of a gold cyanide and a gold cyanide salt is compounded as a source of gold. Both of them may be compounded. As the gold cyanide salt, there are mentioned, for example, gold potassium cyanide, gold sodium cyanide and gold ammonium cyanide. They may be compounded singly or in two or more kinds.

[0021] In the present electrolytic hard gold plating solution, the concentration of the gold cyanide and the gold cyanide salt is 0.1 to 20 g/L, preferably 2 to 15 g/L, particularly preferably 3 to 10 g/L in terms of total gold concentration. With a gold concentration of lower than 0.1 g/L, the cathode current efficiency is low, making it impossible to obtain a gold film of intended thickness. With a gold concentration higher than 20 g/L, the cathode current efficiency does not increase in proportion to the gold concentration and there is no advantage of using a high gold concentration; further, the drag out of plating solution in plating operation is large, resulting in large waste of plating solution.

[0022] In the present electrolytic hard gold plating solution, an aromatic sulfonic acid compound is compounded. The aromatic sulfonic acid compound acts as an organic oxidizing agent. As the aromatic sulfonic acid compound, there are mentioned, for example, 2-nitrobenzenesulfonic acid, 3-nitrobenzenesulfonic acid, 4-nitrobenzenesulfonic acid, 2,4-dinitrobenzenesulfonic acid, 2-aminobenzenesulfonic acid, 3-aminobenzenesufonic acid, 4-aminobenzenesulfonic acid, and salts thereof. Of these, an aromatic sulfonic acid compound having nitro group as a substituent is preferred. They may be compounded singly or in two or more kinds.

[0023] The electrolytic hard gold plating solution containing such an aromatic sulfonic acid compound raises the oxidation reduction potential of gold uniquely in a low current density range (a current density of lower than 20 A/dm^2). As a result, gold deposition is suppressed in a low current density range. Meanwhile, the electrolytic hard gold plating solution containing such an aromatic sulfonic acid compound does not suppress gold deposition in a medium to high current density range (a current density of 20 to 200 A/dm^2). As a result, a normal gold film is formed in a medium to high current density range.

[0024] With the electrolytic hard gold plating solution of the present invention, formation of plating film can be suppressed at an area of to-be-plated material other than the to-be-plated area thereof, by controlling the current density employed.

[0025] The concentration of the organic oxidizing agent compounded in the present electrolytic hard gold plating solution is 0.1 to 20 g/L, preferably 0.5 to 5 g/L, particularly preferably 1 to 3 g/L. With a concentration of organic oxidizing agent of lower than 0.1 g/L, the effect of suppression of gold deposition in a low current density range is small. With a concentration of organic oxidizing agent of higher than 20 g/L, the effect of suppression of gold deposition in a low current density range is unchanged and high.

[0026] In the present electrolytic hard gold plating solution, a carboxylic acid or an oxycarboxylic acid or a salt thereof is compounded. They act as a complexing agent. As the carboxylic acid, the oxycarboxylic acid or the salt thereof, there are mentioned, for example, formic acid, glycolic acid, lactic acid, oxybenzoic acid, succinic acid, malonic acid, malic acid, tartaric acid, phthalic acid, diglycolic acid, citric acid, and salts thereof. As the salt, there are preferred alkali metal salts such as sodium salt, potassium salt and the like; alkaline earth metal salts such as calcium salt and the like; and salts of ammonia, amine, etc. They may be compounded singly or in two or more kinds.

[0027] In the present electrolytic hard gold plating solution, the concentration of complexing agent is 1 to 100 g/L, preferably 5 to 600 g/L. With a concentration of complexing agent of lower than 1 g/L, the inorganic impurities dissolving out from the plated material tend to be taken into the gold film formed. The inorganic impurities taken into the gold film reduce the gold purity of the gold film. As a result, the gold film has inferior appearance, and the contact member has an increased contact resistance and has lower corrosion resistance. With a concentration of complexing agent of higher than 100 g/L, no effect corresponding to such a high concentration is obtained, and such a concentration is not economical.

[0028] In the present electrolytic hard gold plating solution, a water-soluble cobalt salt or a water-soluble nickel salt is compounded. As the cobalt salt, there are mentioned, for example, cobalt sulfate, cobalt nitrate, cobalt chloride, and basic cobalt carbonate. As the nickel salt, there are mentioned, for example, nickel sulfate, nickel sulfamate, nickel sulfite, and nickel chloride. They may be compounded singly or in two or more kinds.

[0029] In the present electrolytic hard gold plating solution, the concentration of cobalt salt or nickel salt is 0.01 to 10 g/L, preferably 0.1 to 1.0 g/L. With a concentration of cobalt salt or nickel salt of lower than 0.01 g/L, the gold film formed has a low hardness. With a concentration of cobalt salt or nickel salt of higher than 10 g/L, no effect corresponding to such a high concentration is obtained, and such a concentration is not economical. By compounding the cobalt salt or the nickel salt in the above concentration, the gold film formed has a hardness of 150 to 200 HV. Incidentally, "water-soluble" of the cobalt salt or the nickel salt, compounded in the present electrolytic hard gold plating solution refers to such a water solubility that the salt can be dissolved in water in the above-mentioned concentration.

[0030] In the present electrolytic hard gold plating solution, an electric conductive salt of organic acid is compounded. As the electric conductive salt of organic acid, there are mentioned, for example, potassium formate, potassium citrate, potassium phosphate, potassium nitrate, and potassium succinate. They may be compounded singly or in two or more kinds.

[0031] In the present electrolytic hard gold plating solution, the concentration of electric conductive salt of organic acid is 10 to 200 g/L, preferably 50 to 100 g/L. With a concentration of electric conductive salt of organic acid of lower than 10 g/L, the gold film formed has inferior appearance and no normal gold film is obtained. With a concentration of electric conductive salt of organic acid of higher than 200 g/L, no effect corresponding to such a high concentration is obtained, and such a concentration is not economical.

[0032] In the present electrolytic hard gold plating solution, a nitrogen-containing five-membered heterocyclic compound is compounded. The nitrogen-containing five-membered heterocyclic compound acts as an organic crystal-controlling agent. The present inventor considers as follows. The nitrogen-containing five-membered heterocyclic compound is adsorbed on the gold cyanide ion present in the plating bath, or is adsorbed or forms a complex with the gold ion after ligand disengagement (cyanide ion), in an electric double layer, whereby the growth of gold crystal is controlled and a dense gold film is formed. The nitrogen-containing five-membered heterocyclic compound used in the present invention is not taken into the gold film formed; therefore, the gold film has a high gold purity.

[0033] As the nitrogen-containing five-membered heterocyclic compound, there are mentioned, for example, imidazole, 2-methylimidazole, pyrazole, 3,5-dimethylpyrazole, 2-imidazoline, 2-pyrrolidone, hydantoin, 5,5-dimethylhydantoin, allantoin, succinic acid imide, DL-pyroglutamic acid, and salt thereof.

[0034] In the present electrolytic hard gold plating solution, the concentration of nitrogen-containing five-membered heterocyclic compound is 1 to 50 g/L, preferably 5 to 20 g/L, particularly preferably 8 to 12 g/L. With a concentration of nitrogen-containing five-membered heterocyclic compound of lower than 1 g/L, the effect of crystal controlling is small and no dense gold film is obtained. With a concentration of nitrogen-containing five-membered heterocyclic compound of higher than 50 g/L, no effect corresponding to such a high concentration is obtained, and such a concentration is not economical.

[0035] The present electrolytic hard gold plating solution is usable in a pH range of 3.0 to 7.0, and is used preferably in a pH range of 4.0 to 5.0. When the pH is lower than 4.0, the cathode current efficiency is low, making it difficult to obtain a gold film having an intended thickness. Meanwhile, when the pH is higher than 5.0, the gold film formed has a reddish appearance, making it difficult to obtain a normal gold film. Incidentally, as the pH-adjusting agent, there are mentioned, for example, sodium hydroxide, potassium hydroxide, ammonium hydroxide and dilute sulfuric acid.

[0036] The present electrolytic hard gold plating solution may contain other substances as long as the effect of the present invention is not impaired thereby.

[0037] The plating with the present electrolytic hard gold plating solution can be conducted by a known plating method. The plating can also be conducted by a selective plating method of using a platinum-made nozzle as an anode and a to-be-plated material as a cathode and spraying the present electrolytic hard gold plating solution from the platinum-made nozzle onto the to-be-plated material.

Examples

[0038] The constitution of the test equipment used and the evaluation method used are as follows.

[0039] A copper plate of 32 mm x 150 mm x 0.2 mm was prepared. On this copper plate was formed a nickel film in a thickness of 2 μm, using a nickel sulfamate plating solution, and the resulting plate was used as a sample. On this sample was superimposed a silicon rubber-made masking plate having a square opening of 10 mm x 10 mm, and they were fixed.

[0040] A plating solution was sent to the injection orifice of plating solution using a pump. The plating solution was injected from the injection orifice onto the opening of the masking plate. Thereby, selective plating was conducted on the sample. A platinum nozzle of 5 mm in diameter was fitted to the injection orifice of plating solution, and this nozzle was used as an anode.

[0041] The measurement of the thickness of the gold film formed was conducted using a fluorescent X-ray film thickness tester SEA 5120 manufactured by SII.

[0042] The pinholes generated in the gold film were evaluated by the test method by exposure to nitric acid vapor (JIS H 8620 10.5) which is a porosity test described in Japanese Industrial Standards (JIS). In the porosity test, the sizes and numbers of pinholes in plating layer are measured. In the test by exposure to nitric acid vapor, the above sample after selective plating is placed on a ceramic plate put in a desiccator containing nitric acid at the bottom and is allowed to stand for 1 hour at about 23°C. The nitric acid vapor generated in the desiccator passes through the pinholes of sample and corrodes the nickel film of sample. When the nickel film (under layer) is corroded, spots appear on the gold film. The condition of spots was examined referring to the rating number standard chart specified in Method of corrosion resistance test (JIS H 8502 11.5).

(Example 1)

[0043]

Potassium cyanide: 5 g/L (as Au)
Potassium citrate: 70 g/L
Citric acid: 50 g/L
Potassium formate: 20 g/L
Cobalt sulfate: 0.96 g/L
2-Nitrobenzenesulfonic acid: 2 g/L
Imidazole: 10 g/L

[0044] A plating solution was prepared using the above composition. The plating solution was adjusted to a pH of 4.2, and selective plating was conducted on a sample at a solution temperature of 55°C and at a current density of 40 A/dm^2 so as to give a gold film thickness of 0.05 μm. The gold film formed on the sample had a lemon yellow color and uniform and good appearance. With respect to the corrosion test, the rating number was 9.5-5 and the total corroded area ratio was above 0.02% but 0.05% or below.

(Examples 2 to 5) (Comparative Examples 1 to 2)

[0045] Each plating solution was prepared according to the formulation shown in Table 1 and, using the solution, selective plating was conducted on each sample in the same manner as in Example 1. The gold film formed on each sample had a lemon yellow color and uniform and good appearance. The results of corrosion test are shown in Table 2.

[0046]

Table 1

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Comp. Ex. 1	Comp. Ex. 2
Concentrations of plating solution components (g/L)	Gold cyanide (as gold)	5	5	5	5	5	5	5
	Potassium citrate	70	70	70	70	70	70	70
	Citric acid	50	50	50	50	50	50	50
	Potassium formate	20	20	20	20	20	20	20
	Cobalt sulfate	0.96	0.96	0.96	-	-	0.96	0.96
	Nickel sulfate	-	-	-	0.90	0.90	-	-
	2-Nitrobenzenesulfonic acid	2	2	2	2	2	-	-
	Sodium m-nitrobenzenesulfonate	-	-	-	-	-	2	-
	Imidazole	10	-	-	10	-	-	-
	2-Pyrrolidone	-	10	-	-	-	-	-
	5,5-dimethylhydantoin	-	-	10	-	10	-	-
Conditions of plating	pH	4.2	4.2	4.2	4.2	4.2	4.2	4.2
	Solution temperature (°C)	55	55	55	55	55	55	55
	Current density (A/dm^2)	40	40	40	40	40	40	40

[0047]

Table 2

	Rating number	Total corroded area ratio %
Ex. 1	9.5-5	Above 0.02% but 0.05% or below
Ex. 2	9.3-3	Above 0.05% but 0.07% or below
Ex. 3	9.5-6	Above 0.02% but 0.05% or below
Ex. 4	9.5-3	Above 0.02% but 0.05% or below
Ex. 5	9.3-6	Above 0.05% but 0.07% or below
Comp. Ex. 1	4-1	Above 2.50% but 5.00% or below
Comp. Ex. 2	4-4	Above 2.50% but 5.00% or below

[0048] In Examples 1 to 5, corrosion was significantly suppressed as compared with Comparative Examples 1 to 2.

[0049] As is clear from above, the electrolytic hard gold plating solution of the present invention can form a gold film which is extremely few in pinholes even when the film has a thickness of 0.1 μm or smaller and which is dense. As a result, the material plated with the present plating solution is superior in corrosion resistance.

Claims

1. An electrolytic hard gold plating solution comprising
at least one member of a gold cyanide and a gold cyanide salt,
a water-soluble cobalt salt or a water-soluble nickel salt,
an electric conductive salt of organic acid,

an aromatic sulfonic acid compound,
at least one member selected from the group consisting of a carboxylic acid, an oxycarboxylic acid, and salts thereof, and
a nitrogen-containing five-membered heterocyclic compound.

2. The electrolytic hard gold plating solution according to Claim 1, wherein the concentration of the nitrogen-containing five-membered heterocyclic compound is 1 ~ 50 g/L.

3. The electrolytic hard gold plating solution according to Claim 1, wherein the pH of the plating solution is in a range of 3 to 7.

4. A plating method which comprises spraying the electrolytic hard gold plating solution of Claim 1 onto a to-be-plated area of a to-be-plated material to form a gold film on the to-be-plated area.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/071304

A. CLASSIFICATION OF SUBJECT MATTER
C25D3/62(2006.01)i

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)
C25D3/62

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2003-502513 A (Degussa Galvanotechnik GmbH), 21 January 2003 (21.01.2003), paragraphs [0017], [0020] to [0021] & DE 10007325 A & DE 10007325 A1 & WO 2000/079031 A1 & EP 1192297 A & CN 1357060 A & US 6814850 B1 & TW 234591 B & HK 1047773 A & DE 50013952 D	1-4
A	JP 2009-7656 A (Japan Pure Chemical Co., Ltd.), 15 January 2009 (15.01.2009), (Family: none)	1-4
A	JP 63-7390 A (Nippon Engelhard Ltd.), 13 January 1988 (13.01.1988), (Family: none)	1-4

☒ Further documents are listed in the continuation of Box C. ☐ See patent family 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 application or patent 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
"&" document member of the same patent family

Date of the actual completion of the international search 28 February, 2011 (28.02.11)	Date of mailing of the international search report 08 March, 2011 (08.03.11)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/071304

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 50-75531 A (Deutsche Gold-und Silber-Scheideanstalt Vormals Roessler), 20 June 1975 (20.06.1975), & BE 821923 A & BE 821923 A1 & SE 7413961 A & NL 7413010 A & DE 2355581 A & FR 2249979 A & US 3929595 A & GB 1426849 A & BR 7409243 A & ES 430054 A & IT 1020940 A & CH 603825 A	1-4

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 3933930 A **[0008]**
- JP 2009165730 A **[0011]**