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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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(54) Title: METHOD TO PREVENT DEACTIVATION OF METAL CATALYSTS IN CATALYTIC POLYMERISATION PROCESSES

(57) Abstract: The present invention relates to a method to prevent deactivation of the metal catalyst in a catalytic polymerisation process of polymeric binders whereby pyrithione biocides are present which method comprises the addition of a Zn, Cu or Na salt selected from Zn, Cu or Na salts of fatty acids such as e.g. Zn, Cu or Na octoate, Zn, Cu or Na acrylate, Zn, Cu or Na neodecanoate, or Zn, Cu or Na salts of beta diketones such as e.g. Zn, Cu or Na acetylacetonate.

METHOD TO PREVENT DEACTIVATION OF METAL CATALYSTS IN CATALYTIC POLYMERISATION PROCESSES

[0001] The present invention relates to a method to prevent deactivation of the metal catalyst in a catalytic polymerisation process of polymeric binders whereby pyrithione biocides are present which method comprises the addition of a Zn, Cu or Na salt selected from Zn, Cu or Na salts of fatty acids such as e.g. Zn, Cu or Na octoate; Zn, Cu or Na acrylate; Zn, Cu or Na neodecanoate; or Zn, Cu or Na salts of beta diketones such as e.g. Zn, Cu or Na acetylacetonate.

[0002] Pyrithione biocides such as e.g. zinc pyrithione, copper pyrithione, and sodium pyrithione are excellent broad-spectrum antimicrobial agents and are used as a biocide and preservative in fluids, paints, cosmetics etc.

[0003] Many plastic polymerization reactions are accelerated via metal catalysts (e.g., Pt, Co, Ag, Mg, …). Besides the basic polymerization reactants, often specific additives (anti-oxidants, anti-statics, flame retardants, pigments, fillers, antimicrobials, …) are incorporated in such plastic polymers, which should not significantly interfere with the catalyst. Additives with (trans)chelating properties, on the other hand, can dramatically disturb or even completely block the polymerization reaction by binding the metal catalyst thereby deactivating its catalytic properties. An example of such additives with (trans)chelating properties are the pyrithione biocides zinc pyrithione, copper pyrithione, and sodium pyrithione. In order to prevent the deactivation of the metal catalyst during the polymerization reaction, a suitable stabilizing agent should be added to the polymerization reaction in sufficient amounts, in order to shift the chelation of the catalyst towards chelation of the added metal of the metal salt.

[0004] It has now been found that the addition of suitable Zn, Cu or Na salts selected from Zn, Cu or Na salts of fatty acids such as e.g. Zn, Cu or Na octoate; Zn, Cu or Na acrylate; Zn, Cu or Na neodecanoate; or Zn, Cu or Na salts of beta diketones such as e.g. Zn, Cu or Na acetylacetonate, is helpful to prevent deactivation of the metal catalyst during the catalytic polymerisation process of polymeric binders.

[0005] Composite materials are engineered materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the

finished structure. In order to bind all constituent materials together a matrix material is used which is often a polymeric material obtained by a catalytic polymerisation process of polymeric binders. It can be beneficial to add a pyrithione biocide to such composite materials and in order to prevent deactivation of the metal catalyst during the catalytic polymerisation process one or more Zn, Cu or Na salts selected from Zn, Cu or Na salts of fatty acids such as e.g. Zn, Cu or Na octoate; Zn, Cu or Na acrylate; Zn, Cu or Na neodecanoate; or Zn, Cu or Na salts of beta diketones such as e.g. Zn, Cu or Na acetylacetonate can be added in accordance with the present invention.

[0006] An example of composite materials are e.g. fiber reinforced polyester ship hulls whereby a pyrithione biocide is added to prevent fouling.

[0007] The polymeric binder used in the catalytic polymerisation process of the present invention may be formed of a polymer, a mixture of polymers (for example, polyester and urethane), monomers, and mixtures of monomers and polymers. Examples of suitable polymers include polyester, unsaturated polyester, vinyl ester, epoxy, phenolic resin, urethane and mixtures thereof. Examples of monomers for the polymeric binder include alpha, beta-ethylenically unsaturated monomers, e.g., styrene and styrene derivatives; lower alkyl substituted styrenes; alpha-methyl styrene; vinyl toluene; divinyl benzene; acrylics; C_{1-18}alkyl esters of acrylic and methacrylic acids, e.g., methyl acrylate, ethyl acrylate, isopropyl acrylate, butyl acrylate, 2-ethyl-hexyl acrylate, methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, and butyl methacrylate; and phenols, furans and the like. These monomers may be used alone or in combination.

[0008] An often used polymeric binder is unsaturated polyester or unsaturated polyester resins (UP). Unsaturated polyester resins are solutions of unsaturated polyesters in copolymerizable monomers, preferably in styrene. Suitable unsaturated polyesters are the usual condensation products of polybasic, in particular dibasic carboxylic acids and their esterifiable derivatives, in particular their anhydrides, which are bonded in the way of an ester with polyhydric, in particular dihydric alcohols, and which may additionally contain residues of monobasic carboxylic acids or monohydric alcohols, with at least part of the starting materials being provided with ethylenically unsaturated, copolymerizable groups. Other unsaturated polyesters are those on the basis of maleic anhydride and orthophthalic acid or isophthalic acid, on the one hand, and propylene glycol, ethylene glycol, diethylene glycol and/or dipropylene glycol on the other hand.

[0009] Deactivation of the metal catalyst typically results in extended curing time or incomplete curing of the polymer formed in the catalytic polymerisation process. The addition of a Zn, Cu or Na salt in accordance with the present invention prevents deactivation of the metal catalyst resulting in reduced curing times.

[0010] The amount of a Zn, Cu or Na salt added in the catalytic polymerisation process is such that deactivation of the metal catalyst is prevented when pyrithione biocides are present so that curing time is not negatively impacted. In practice it has been found that the Zn, Cu or Na salt has to be added in an amount of at least a 0.1 : 1 weight ratio of Zn, Cu or Na salt vs. pyrithione biocide. A higher ratio of Zn, Cu or Na salt vs. pyrithione biocide has been found to yield shorter curing times. Typical weight/weight ratios in practice of Zn, Cu or Na salt vs. pyrithione biocide are 0.5:1, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 10:1 up to 20:1 which gives the following ranges : 0.1:1 to 20:1; 0.5:1 to 20:1; 1:1 to 20:1; 2:1 to 20:1; 3:1 to 20:1; 4:1 to 20:1; 5:1 to 20:1; 10:1 to 20:1; and also 3:1 to 10:1; 4:1 to 10:1; 5:1 to 10:1.

[0011] When the pyrithione biocide is zinc pyrithione than preferably the zinc salts of the fatty acids or beta diketones are used selected from zinc octoate, zinc acrylate, zinc neodecanoate, and zinc acetylacetonate.

[0012] When the pyrithione biocide is copper pyrithione than preferably the copper salts of the fatty acids or beta diketones are used selected from copper octoate, copper acrylate, copper neodecanoate, and copper acetylacetonate.

[0013] When the pyrithione biocide is sodium pyrithione than preferably the sodium salts of the fatty acids or beta diketones are used selected from sodium octoate, sodium acrylate, sodium neodecanoate, and sodium acetylacetonate.

[0014] The pyrithione biocide and the Zn, Cu or Na salts of the present invention can be added seperately to the catalytic polymerisation process whereby the sequence of addition can be first the pyrithione biocide followed by the Zn, Cu or Na salt, or it can be first the Zn, Cu or Na salt followed by the pyrithione biocide.

[0015] Alternatively the pyrithione biocide and the Zn, Cu or Na salts of the present invention can be added simultaneously to the catalytic polymerisation process either as seperate products or as a combination product. Said combination product can be any formulation comprising both the pyrithione biocide and the Zn, Cu or Na salt together with any optional excipients.

Experimental part

Experiment 1 : polyester polymer

Sample preparation :

- weigh the amount of unsaturated polyester resin (= polymeric binder) into a glass beaker
- add zinc pyrithione to the unsaturated polyester resin and homogenize by high-performance dispersing
- add zinc salt to the unsaturated polyester resin and homogenize by high-performance dispersing
- add cobalt catalyst to previous mixture and homogenize by gentle dispersing
- add peroxide radical initiator to previous mixture and homogenize by gentle dispersing
- pour the mixture into a glass casting and place sample at 80°C in the oven to allow curing of the polymer

The reaction exotherms as a function of time were measured.

Table 1 :

	Sample 1	Sample 2	Sample 3
Composition	Concentration (% w/w)	Concentration (% w/w)	Concentration (% w/w)
Zinc pyrithione	0,6	0,6	0,6
Zinc salt	1	2	4
Co catalyst (6%)	0,4	0,4	0,4
Peroxide	2	2	2
Unsaturated polyester resin	96	95	93

Table 2 :

	Sample 4	Sample 5	Sample 6
Composition	Concentration (% w/w)	Concentration (% w/w)	Concentration (% w/w)
Zinc pyrithione	0,8	0,8	0,8
Zinc salt	-	4	8
Co catalyst (6%)	0,4	0,4	0,4
Peroxide	2	2	2
Unsaturated polyester resin	96.8	92.8	88.8

Co catalyst : Nusa cobalt™ 6% (CAS : 83711-44-8) commercially available from Nusa Ibérica S.A., Rio Tajuña 5, 28850 Torrejón de Ardoz, Madrid, Spain
Unsaturated polyester resin : Synolite 9286-N-0™ commercially available from DSM, Netherlands, which is a a low viscous monomer free unsaturated polyester resin
Zinc compound used : zinc octoate
zinc acrylate
zinc neodecanoate
zinc acetylacetonate

The reaction exotherms as function of time for the samples 4, 5 and 6 has been depicted in Figure 1. As can be seen from the reaction exotherms, the addition of the zinc octoate as a zinc salt resulted in a reduction of the curing time of the polyester polymer. Sample 4 (no zinc salt present) had a curing time of about 29 minutes, sample 5 (4 % w/w zinc octoate) has a curing time of about 16 minutes and sample 6 (8% w/w zinc octoate) had a curing time of about 12 minutes.

Fig. 2 demonstrates two aspects :

a) the curing time of a sample with 0 ppm zinc pyrithione is much shorter (about 7 minutes) compared to the curing time of a sample with 6000 ppm zinc pyrithione (about 21 minutes)
b) a higher amount of zinc salt results in a more pronounced prevention of deactivation of the metal catalyst resulting in e.g. a faster curing time : the addition of 4% zinc octoate or 8% zinc octoate to a sample comprising 6% zinc pyrithione results in improved curing time to a sample comprising 6% zinc pyrithione without said zinc salts present

Description of the drawings

Figure 1 : reaction exotherm as function of time for samples 4, 5 and 6
Figure 2 : reaction exotherm as function of time for samples comprising no zinc pyrithione; 0.6% zinc pyrithione; 0.6% zinc pyrithione +4% zinc octoate; and 0.6% zinc pyrithione +8% zinc octoate

Claims

1. A method to prevent deactivation of a metal catalyst in a catalytic polymerisation process of polymeric binders whereby pyrithione biocides selected from zinc pyrithione, copper pyrithione, and sodium pyrithione, are present characterized by the addition of a suitable Zn, Cu or Na salt selected from Zn, Cu or Na salts of fatty acids or Zn, Cu or Na salts of beta diketones; whereby the Zn, Cu or Na salt is added in an amount of at least a 0.1 : 1 weight ratio of Zn, Cu or Na salt to pyrithione biocide.

2. The method according to claim 1 whereby the Zn, Cu or Na salt is added in an amount of at least a 3 : 1 weight ratio of Zn, Cu or Na salt to pyrithione biocide.

3. The method according to claim 2 wherein the Zn, Cu or Na salts of fatty acids are selected from Zn, Cu or Na octoate; Zn, Cu or Na acrylate; Zn, Cu or Na neodecanoate; and the Zn, Cu or Na salts of beta diketones are selected from Zn, Cu or Na acetylacetonate.

4. The method according to claim 3 wherein the weight/weight ratio of Zn, Cu or Na salt to pyrithione biocide ranges from 3:1 to 20:1.

5. The method according to claim 3 wherein the weight/weight ratio of Zn, Cu or Na salt to pyrithione biocide ranges from 3:1 to 10:1.

6. The method according to claim 3 wherein the weight/weight ratio of Zn, Cu or Na salt to pyrithione biocide is 5 : 1.

7. The method according to claim 3 wherein the weight/weight ratio of Zn, Cu or Na salt to pyrithione biocide is 10 : 1.

8. The method according to any one of the preceding claims wherein the pyrithione biocide is zinc pyrithione.

9. The method according to claim 8 wherein the Zn, Cu or Na salt is a Zn salt selected from zinc octoate, zinc acrylate, zinc neodecanoate, and zinc acetylacetonate.

10. The method according to claim 9 wherein the Zn, Cu or Na salt is a Zn salt selected from zinc octoate and zinc neodecanoate.

11. The method according to any one of claims 1 to 10 wherein the pyrithione biocide and the Zn, Cu or Na salt are added seperately to the catalytic polymerisation process.

12. The method according to any one of claims 1 to 10 wherein the pyrithione biocide and the Zn, Cu or Na salt are added simultaneously to the catalytic polymerisation process.

13. The method according to claim 11 wherein the pyrithione biocide and the Zn, Cu or Na salt are added as a combination product to the catalytic polymerisation process.

14. The method according to any one of the preceding claims wherein the metal catalyst comprises cobalt.

15. The method according to any one of the preceding claims wherein the polymeric binder is an unsaturated polyester resin.

Figure 1 : reaction exotherm as function of time for samples 4, 5 and 6

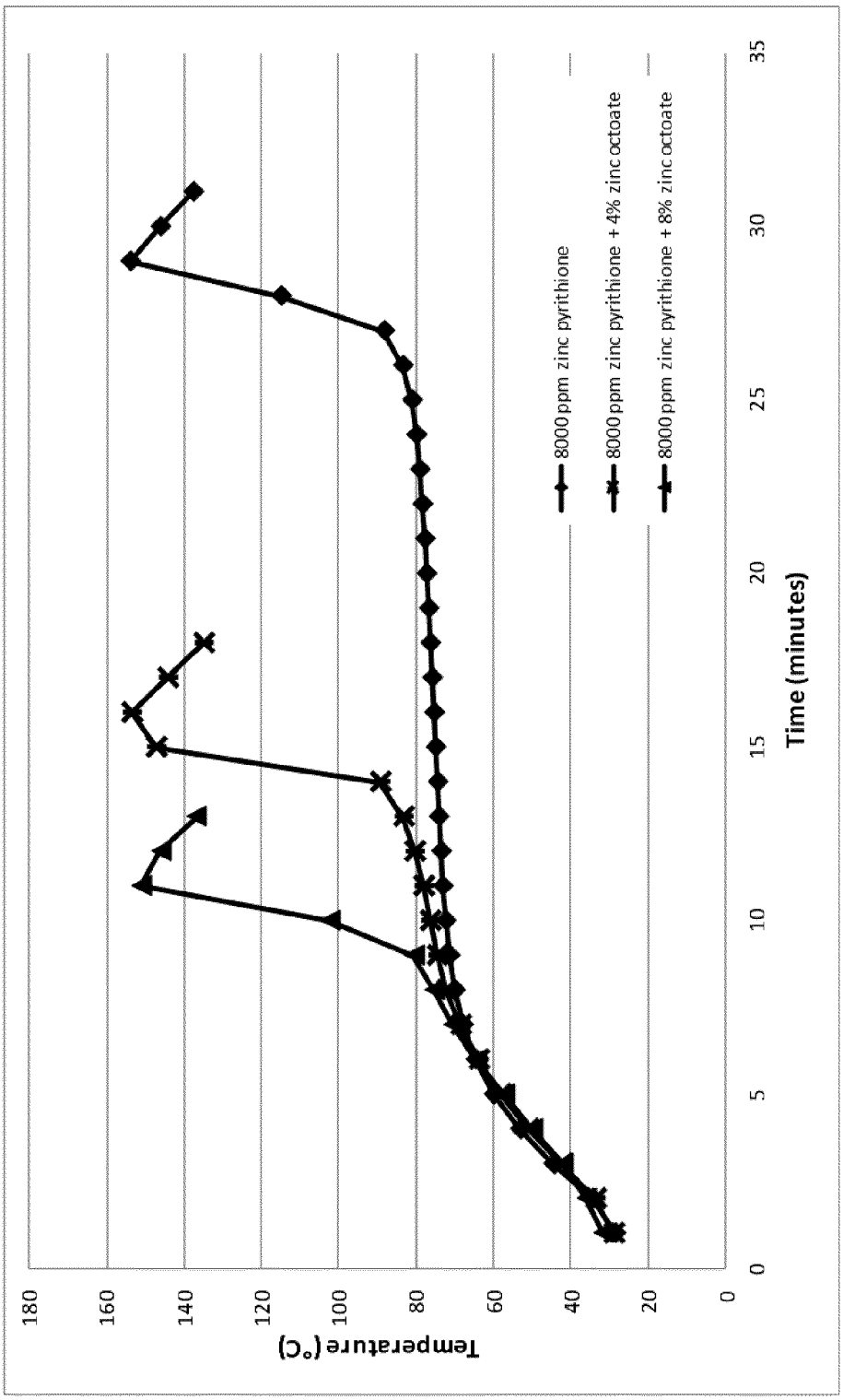
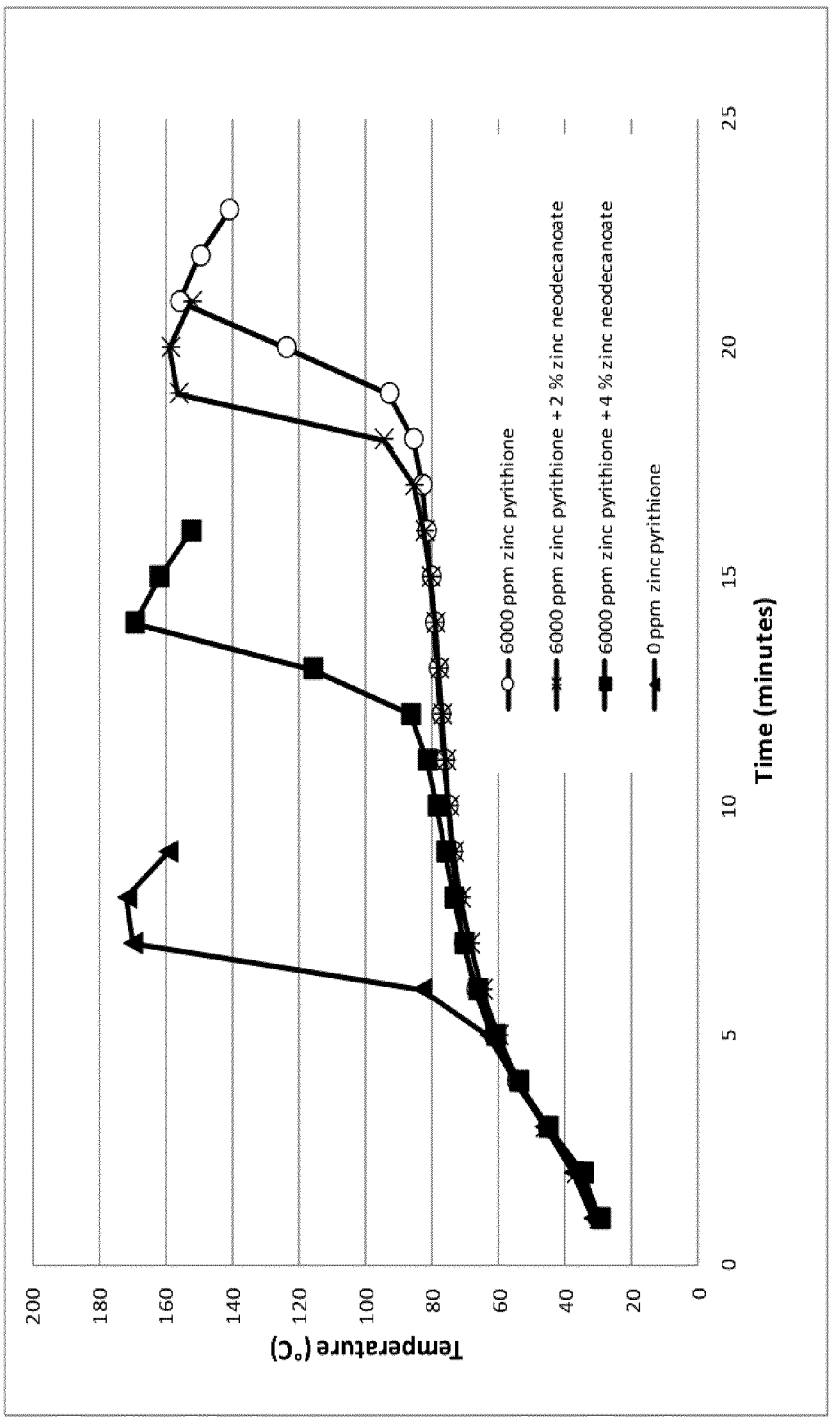


Figure 2 : reaction exotherm as function of time for samples comprising no zinc pyrithione, 0.6% zinc pyrithione, 0.6% zinc pyrithione +4% zinc octoate, and 0.6% zinc pyrithione +8% zinc octoate



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/052395

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F4/42 C09D5/16 C08F2/44 A01N43/40
ADD.

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)
C09D C08F B01J A01N

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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DOUGLAS K SIMPSON ET AL: "Long term protection with fungicide and algicide development", PPCJ. POLYMERS PAINT COLOUR JOURNAL, FMJ INTERNATIONAL, REDHILL, GB, vol. 186, 1 January 1996 (1996-01-01), pages 7-8, XP009159926, ISSN: 1357-731X page 7, middle column, last paragraph - page 7, right-hand column, paragraph 1; table 1 page 8, left-hand column, lines 12-17	1-15
A	US 5 883 154 A (KAPPOCK PAUL S [US] ET AL) 16 March 1999 (1999-03-16) column 4, lines 6-41; claims 1-5; examples 2,3 column 3, lines 47-53	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/053950 A1 (GAJANAN SHUKLA P [IN] ET AL) 8 March 2007 (2007-03-08) example all	1-15
A	US 5 137 569 A (WALDRON CRAIG [US] ET AL) 11 August 1992 (1992-08-11) the whole document	1-15
A	US 2007/117895 A1 (LEI DEQING [US] ET AL) 24 May 2007 (2007-05-24) the whole document	1-15
A	DATABASE WPI Week 201135 Thomson Scientific, London, GB; AN 2010-Q56357 XP002677059, -& BR PI0 900 643 A2 (ISOLUCKS DO BRASIL LTDA EPP) 9 November 2010 (2010-11-09) abstract	1-15
A	DATABASE WPI Week 200014 Thomson Scientific, London, GB; AN 2000-156859 XP002677060, -& JP 2000 017201 A (DAINIPPON TORYO KK) 18 January 2000 (2000-01-18) abstract	1-15
A	US 5 518 774 A (KAPPOCK PAUL S [US] ET AL) 21 May 1996 (1996-05-21) column 1, line 35 - column 3, line 31; claim 1	1-15

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/052395

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5883154 A	16-03-1999	AU 3208195 A	21-08-1996
		CA 2211374 A1	08-08-1996
		CN 1175274 A	04-03-1998
		DE 69523948 D1	20-12-2001
		DE 69523948 T2	20-06-2002
		DK 0807152 T3	04-03-2002
		EP 0807152 A1	19-11-1997
		JP 3839847 B2	01-11-2006
		JP H10513211 A	15-12-1998
		KR 19987001899 A	25-06-1998
		US 5562995 A	08-10-1996
		US 5883154 A	16-03-1999
		US 6096122 A	01-08-2000
		WO 9623850 A1	08-08-1996
US 2007053950 A1	08-03-2007	NONE	
US 5137569 A	11-08-1992	AU 656031 B2	19-01-1995
		DE 69216635 D1	20-02-1997
		DE 69216635 T2	04-09-1997
		DK 0610251 T3	07-07-1997
		EP 0610251 A1	17-08-1994
		ES 2095493 T3	16-02-1997
		GR 3022677 T3	31-05-1997
		HK 1008039 A1	30-04-1999
		JP 3242107 B2	25-12-2001
		JP H07501837 A	23-02-1995
		NO 941281 A	08-04-1994
		US 5137569 A	11-08-1992
		WO 9307223 A1	15-04-1993
US 2007117895 A1	24-05-2007	CN 101558112 A	14-10-2009
		EP 1954753 A2	13-08-2008
		JP 5031761 B2	26-09-2012
		JP 2009517496 A	30-04-2009
		KR 20080070686 A	30-07-2008
		MY 143747 A	15-07-2011
		US 2007117895 A1	24-05-2007
		WO 2007061546 A2	31-05-2007
BR PI0900643 A2	09-11-2010	NONE	
JP 2000017201 A	18-01-2000	JP 3046000 B2	29-05-2000
		JP 2000017201 A	18-01-2000
US 5518774 A	21-05-1996	AR 001868 A1	10-12-1997
		AU 5668196 A	30-01-1997
		BR 9609389 A	18-05-1999
		CN 1189110 A	29-07-1998
		DE 69623979 D1	31-10-2002
		DE 69623979 T2	28-05-2003
		DK 0857087 T3	03-02-2003
		EP 0857087 A1	12-08-1998
		HK 1027313 A1	14-03-2003
		JP 4001626 B2	31-10-2007
		JP 4512531 B2	28-07-2010
		JP H11508311 A	21-07-1999
		JP 2006001940 A	05-01-2006

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/052395

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		MY 115458 A	30-06-2003
		NO 976083 A	23-02-1998
		RU 2162870 C2	10-02-2001
		US 5518774 A	21-05-1996
		WO 9701397 A1	16-01-1997