Anticorrosion coating for an alloy

Citation for published version (APA):
van Benthem, R. A. T. M., de With, G., van der Ven, L. G. J., Foyet, A., & Wu, T. (2012). Anticorrosion coating for an alloy. (Patent No. *WO/2012/079748*). Dutch Polymer Institute.

Document status and date:
Published: 21/06/2012

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

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Download date: 05. Oct. 2023

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
21 June 2012 (21.06.2012)

(10) **International Publication Number**
WO 2012/079748 A1

(51) **International Patent Classification**:
C09D 5/24 (2006.01)

(21) **International Application Number**:
PCT/EP2011/006303

(22) **International Filing Date**:
14 December 2011 (14.12.2011)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
10015710.6 16 December 2010 (16.12.2010) EP

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: ANTICORROSION COATING FOR AL ALLOY

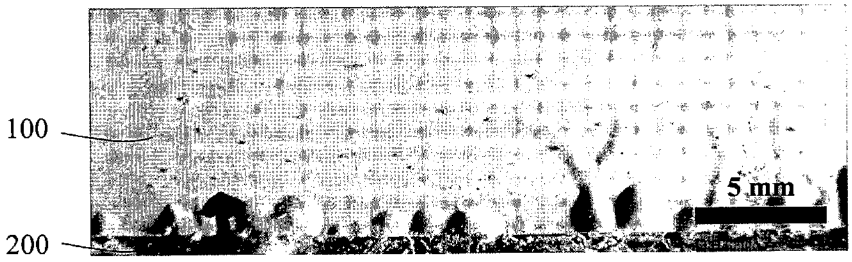

Figure 2

(57) **Abstract**: The invention relates to a coating comprising a resin and electron-conductive particles dispersed in the resin, wherein the coating is not ion-conductive and the coating has a specific electrical resistivity of from 10^2 to 10^{10} Ω·cm. The invention further relates to an Al or Al alloy substrate provided with the coating, wherein the resistivity between the substrate and the coating is at most a factor 200 higher than that of the coating.

WO 2012/079748 A1

Anticorrosion coating for Al alloy

The present invention relates to an anticorrosion coating for Al or Al alloy and a process for making thereof.

Aluminum and its alloys are widely used in a variety of applications, including aerospace and automotive construction, building construction and public utilities. Many of these applications involve the use of aluminum and its alloys in exposure to the environment or otherwise in corrosive atmospheres. Aluminum typically undergoes relatively rapid oxidation which, over time, can detract from its functional and/or structural viability, and its appearance. Accordingly, to preserve the functional and/or structural viability, as well as the appearance in some cases, of aluminum and its alloys, it is desirable to reduce or eliminate the corrosion of aluminum.

CA2312807 discloses a process for the corrosion preventive treatment of surfaces of galvanized or alloy galvanized steel or of aluminum or alloys thereof, wherein the surfaces are contacted with a chromium-free corrosion protective and then dried. The protective contains water and hexafluoroanions of Ti (IV) and/or Zr (IV), V, Co and phorphoric acid. The protective may further contain 1 to 30 g/l of a conductive pigment and an organic film-former.

JP2010-174273 discloses an anticorrosion coating for Al or Al alloy substrate comprising a base layer of conductive particles and a surface layer of a conductive polymer. The base layer is formed on the substrate by spin-coating a solution comprising the conductive particles and firing the coated layer to burn off the organic solvent.

US2008/0305341 discloses a process for coating metallic surfaces with an anti-corrosive composition that contains a conductive polymer and is a dispersion that contains the at least one conductive polymer mainly or entirely in particulate form, as well as a binder system. The conductive polymer is at least one polymer based on polyphenylene, polyfuran, polyimidazole, polyphenanthrene, polypyrrole, polythiophene and/or polythiophenylene charged with anti-corrosive mobile anions. Alternatively, the metallic surfaces can be first coated with a dispersion based on conductive polymers in particulate form, then coated with a composition which contains a binder system.

Metals in the anticorrosion coatings may not be desirable from environmental point of view. Anticorrosion coatings based on conductive polymers have a disadvantage that these conductive polymers are not stable over time, due to e.g. thermo-oxidation etc.

While these anticorrosion coatings have been described in the art, there is still a need for anticorrosion coatings having satisfactory anticorrosion properties.

An object of the present invention is to provide an anticorrosion coating where the above-mentioned and/or other needs in the art are met.

An aspect of the present invention relates to a coating comprising a resin and electron-conductive particles dispersed in the resin, wherein the coating is not ion-conductive and the coating has a specific electrical resistivity of from 10^2 to 10^{10} $\Omega\cdot$cm.

A further aspect of the present invention relates to an Al or Al alloy substrate provided with a coating comprising a resin and electron-conductive particles dispersed in the resin, wherein the coating is not ion-conductive and the coating has a specific electrical resistivity of from 10^2 to 10^{10} $\Omega\cdot$cm and wherein the electrical resistivity between the substrate and the coating is at most a factor 200, preferably a factor 100, more preferably a factor of 50, more preferably a factor of 20, more preferably a factor of 5, higher than that of the coating.

The coating according to the invention showed a surprisingly high anti-corrosion performance. The rate of delamination from the damaged area of the substrate was remarkably decreased.

It is herein understood that the term ‘not ion-conductive’ is defined according to the following method:

A bath with two compartments separated by the coating according to the present invention is provided. One of the compartments is filled with a salt solution, preferably a 3 wt% solution of NaCl in water, and the other compartment is filled with pure water with specific resistivity higher than $3 \cdot 10^6$ $\Omega\cdot$cm (25 °C). If the increase in resistivity of the water is less than a factor of ten after 1 day, the film is considered to be not ion-conductive.

For the coating to be not ion-conductive, the coating should contain substantially no ions. Particularly undesirable ions include SO_4^{2-}, NO_3^-, ions of halogen and alkali metals and alkaline earth metals which are known to be the cause of corrosion. Furthermore, the electron conductive particles in the coating should not be ion conductive. For example, particles of conductive polymers which are both electron conductive and ion conductive are excluded from the electron conductive particles in the present invention.

The specific electrical resistivity of the coating of the present invention can be easily measured as a freestanding film using the two-point method with electrodes applied to opposite sides of the film.

The resistance of contacts can be crudely estimated by comparing the results of a two-point measurement on a free film to the results of a two-point measurement made on a coating applied on an aluminium substrate with one electrode applied to the top of the coating and the other at the bottom of the substrate using an ohmmeter. The electrical resistivity between the substrate and the coating is at most a factor 100, preferably a factor of 50, more preferably a factor of 20, more preferably a factor of 5, higher than that of the coating.

The invention is based on the realization that the electron-conductive particles form a percolation path for electron, which changes the corrosion mechanism of Al or Al alloy. The percolation path from the surface of the substrate to inside or the opposite surface of the coating can change the corrosion mechanism from anodic undermining to cathodic delamination. The particles in the coating makes the electrical resistance between the substrate and the coating low enough that the electrons travel from the substrate to the coating. The percolation path formed by the particles allows further traveling of the electrons in the coating. The delamination sites of Al are hence shifted from the interface between the substrate and the film to inside or the opposite surface of the coating. By this shift of the delamination sites, the corrosion of Al is retarded. Also, the structure of the percolation path may be adjusted by the amount of the electron-conductive and non-ion-conductive particles and their dispersion state.

Since the coating according to the present invention is not ion-conductive, OH^- ion formed on the surface of the coating does not reach the substrate. Alternatively there is no in-flux of positively charged metal ions into the interface between the substrate and the coating driven by the presence of hydroxide ions.

Preferably, the electron-conductive and non-ion-conductive particles are selected from the group consisting of gallium-doped zinc oxide (GZO), aluminum-doped zinc oxide (AZO), indium tin oxide (ITO), indium zinc oxide (IZO), antimony tin oxide (ATO), carbon black (CB) and carbon nano tube (CNT). More preferably, the particles are carbon black particles.

Preferably, the coating comprises 0.75 -5 vol% of the electron-conductive particles with respect to the volume of the resin in which the particles are dispersed. The coating comprising 0.75 vol% of the electron-conductive particles has a resistivity level just above the percolation threshold where particles start to form conductive paths. More preferably, the coating comprises at least 1 vol%, 1.25% or 1.5 vol % of the electron-conductive particles with respect to the volume of the resin.

Preferably, the coating has a thickness of between 100 nm to 500 µm, more preferably 500 nm to 100 µm, even more preferably 1 µm to 50 µm, even more preferably 20 µm to 40 µm. The robustness of the coating increases with the increase of thickness, but when the coating thickness is too large, the adhesion of the coating to the substrate is decreased. The preferred ranges of the thickness show a good balance of robustness of the coating and the adhesion to the substrate.

The electron-conductive particles preferably have an average diameter of 1-50 nm, preferably 10-40 nm. In thicker coatings of a thickness of at least 1 µm, larger particles may also be used up to 100 nm. The average diameter of the particles may be determined by e.g. SEM. By preference the particles form a percolative pathway. Methods to determine the percolative structures are known to those skilled in the art.

The resin used in the present invention may be any known non-ion conductive polymer which has enough adhesion to Al or Al alloy substrate. The resin may be selected, for example, from epoxy, polyurethane, polyester, alkyd and polymers or copolymers of styrene, butadiene, acrylic acid, methacrylic and and/or maleic acid and esters of these acids.

A further aspect of the present invention relates to a process for the preparation of the substrate provided with the coating according to the present invention. The process comprises the steps of providing a dispersion of the electron-conductive particles in an organic component, applying the dispersion to the substrate and curing the organic component to obtain the resin.

The dispersion medium for the electron-conductive particles may essentially consist of the organic component to be cured, or may further contain water and/or organic solvent. The presence and the content of the water and/or the organic solvent may be chosen according to the method for applying the coating.

The coating may be applied by any known coating application method, such as dip coating, spray coating, spin coating, screen printing and tape casting. The coating may also be applied as powder coating. The coating composition may take suitable form depending on the coating method, e.g. solution, latex or powder.

In preferred embodiments, the resin is an epoxy resin, which may be formulated as a single component having an integrated hardener or as two components having a separate hardener. Amines or polyamines, such as Jeffamine D230, Jeffamine EDR148, and Dytek A, are particularly suitable as hardeners for epoxy resins. Especially preferred are epoxy wherein the epoxide-to-amine (N-H) molar ratio is 0.8-1.4.

It was found that the development of the percolation structure is strongly correlated with the polymer mobility. The conductivity of the coating increases as the organic component is cured to the resin, until the conductivity reaches a plateau. The curing is preferably done in a relatively moderate condition. Preferably, the curing is done at a temperature of at most 150 °C. More preferably, the curing is done between 10 °C and 100 °C. More preferably, the curing is done between 10 °C and 40 °C. This temperature has the advantage that higher electrical conductivity is obtained. Particularly preferred range is between 20 and 40 °C in view of the final electrical conductivity. The curing time may e.g. be between 10 minutes and 5 days, preferably at least 30 minutes, 1 hour, 2 hours, 4 hours. It will be appreciated that the higher curing temperature requires less curing time. Typically preferred are at 20 °C for at least 1 day, preferably 4 days; at 40-100 °C for at least 30 minutes, preferably 60 minutes. When the curing is done below 40 °C, preferably a subsequent post-curing step follows. For example, the post-curing may be done at 100 °C for 4 hours.

The coating may be further provided with a protective layer. The protective layer should be of an insulating material which may be the same or different from the resin of the coating. This has an advantage that pitting corrosion risks are limited. It will be appreciated that such a protective layer on top of the electrically conductive layer should be removed when measuring the electrical conductivity of the film.

In carrying out the process of this invention the substrate is preferably first cleaned, being degreased by using a cleaner such as Scotch-Brite ® together with an organic solvent such as acetone. The cleaned metal is preferably rinsed with the organic solvent or water and is blown dry by dry air or nitrogen before the coating composition is applied.

A further aspect of the present invention relates to the use of the coating of the present invention for anticorrosion of an Al or Al alloy substrate.

It is noted that the invention relates to all possible combinations of features described herein, particularly features recited in the claims.

Figure 1 shows a photo of the surface of a coating according to comparative example;

Figure 2 shows a photo of the surface of an example of a coating according to the present invention and

Figure 3 shows a photo of the surface of a further example of a coating according to the present invention.

The invention is hereinafter illustrated by the following non-limiting examples.

Following materials were used.
organic component: epoxy resin in which the molar ratio of epoxide to NH is 1.2
electron-conductive particles: carbon black particles having diameters of 30-50 nm
substrate: aluminum alloy 2024, thickness 0.8 mm

Ex.1
The electron-conductive particles were dispersed into the epoxy resin to provide a dispersion comprising 0.75 vol% of the electron-conductive particles.

Then the amine was added to the dispersion to provide a mixture, which was applied to the substrate at room temperature by the doctor blade technique. After 4 days in the room temperature the coated substrate was subjected to a temperature of 100 °C for 4 hours to complete the curing. The coating thickness was 40-55 µm.

The electric resistivity between the substrate and the coating was measured by applying one electrode to the top of the coating and the other at the bottom of the substrate using an ohmmeter.

The same mixture was cast into an aluminum cup and cured in the same manner as Ex. 1. The resulting film was peeled off from the cup. A freestanding film having a thickness of 2 mm was obtained.

The electric resistance of the film was measured by the two-point method with electrodes applied to opposite side of the film. Specific electrical resistivity of the freestanding film was 6 x10^6 Ω·cm.

The ratio between the resistivity between the substrate and the coating and the resistivity of the coating was 180.

Ex. 2
Ex. 1 was repeated except that the mixture comprised 1.25 vol% of the electron-conductive particles.

Specific electrical resistivity of the freestanding film was 3 x10^5 Ω·cm.

The ratio between the resistivity between the substrate and the coating and the resistivity of the coating was 14.3.

Comp. Ex. A
Ex. 1 was repeated except that the coatings were made without the use of the electron-conductive particles.

Specific electrical resistivity of the freestanding film was not measurable.

To study the influence of particle percolation structure on their corrosion resistance, these samples were scratched and put into a salt spray cabinet for 7 weeks. The whole testing process was based on ISO 7253.

The test results for Comp. Ex. A, Ex.1 and Ex.2 are shown in figures 1-3, respectively. The figures show the surface 100 of the coating with a scratch 200.

After 7 weeks being put in a corrosive environment, the anticorrosive behaviors of these samples are quite different. For the coating without any particles inside, the corrosion took place from along the scratch, propagating into the coating, and formed blisters and filiform corrosion defects. When the filiform corrosion continually developed, they merged and formed a larger area of coating delamination with irregular edges, as shown in figure 1. An arrow indicates the length of the corrosion defect. The average length of corrosion propagation was around 4 mm.

However, for the coating with particle concentration 0.75 vol%, the corrosion- induced coating delamination was clearly inhibited. Much less and smaller blisters were formed with a few filiform corrosion developed from them. The average length of corrosion propagation is around 2 mm, as shown in figure 2.

When the resistivity of coating is further decreasing due to the increasing of particle concentration to well above the percolation threshold, reaching 1.25 vol%, the corrosion propagation was significantly suppressed. No corrosion defect can be seen on the testing area, as shown in figure 3. Based on these experiments, it can be concluded that introducing conductive paths formed by percolated electron-conductive particles in the coating can effectively improve the corrosion inhibition.

CLAIMS

1. A coating comprising a resin and electron-conductive particles dispersed in the resin, wherein the coating is not ion-conductive and the coating has a specific electrical resistivity of from 10^2 to 10^{10} $\Omega\cdot$cm.
2. The coating according to claim 1, wherein the electron-conductive particles are selected from the group consisting of gallium-doped zinc oxide (GZO), aluminum-doped zinc oxide (AZO), indium tin oxide (ITO), indium zinc oxide (IZO), antimony tin oxide (ATO), carbon black (CB) and carbon nano tube (CNT).
3. The coating according to claim 1 or 2, wherein the coating comprises 0.75 - 5 vol% of the electron-conductive particles with respect to the volume of the resin in which the particles are dispersed.
4. The coating according to any one of claims 1-3, wherein the coating has a thickness of between 100 nm to 500 µm, more preferably 500 nm to 100 µm, even more preferably 1 µm to 50 µm, even more preferably 20 µm to 40 µm.
5. The coating according to any one of claims 1-4, wherein the electron-conductive particles have an average diameter of 1-50 nm, preferably 10-40 nm.
6. The coating according to any one of claims 1-5, wherein the resin is selected from epoxy, polyurethane, polyester, alkyd and polymers or copolymers of styrene, butadiene, acrylic acid, methacrylic and and/or maleic acid and esters of these acids.
7. The coating according to any one of claims 1-6, wherein a protective layer is provided on the coating.
8. An Al or Al alloy substrate provided with the coating according to any one of claims 1-7, wherein the resistivity between the substrate and the coating is at most a factor 200, preferably a factor 100, more preferably a factor of 50, more preferably a factor of 20, more preferably a factor of 5, higher than that of the coating.
9. A process for the preparation of the substrate according to claim 8, comprising the steps of: providing a mixture of the electron-conductive particles and an organic component, applying the dispersion to the substrate and curing the organic component to obtain the coating.

10. The process according to claim 9, wherein the organic component comprises epoxide and amine at the ratio of 0.8-1.4.

11. The process according to claim 9 or 10, wherein the curing is done at a temperature between 10 °C and 150 °C.

12. The process according to claim 9, 10 or 11 wherein the curing is done for a period of 10 minutes to 5 days, preferably at least 30 minutes, 1 hour, 2 hours, or 4 hours.

13. Use of the coating according to any one of claims 1-7 for anticorrosion of an Al or Al alloy substrate.

Figure 1

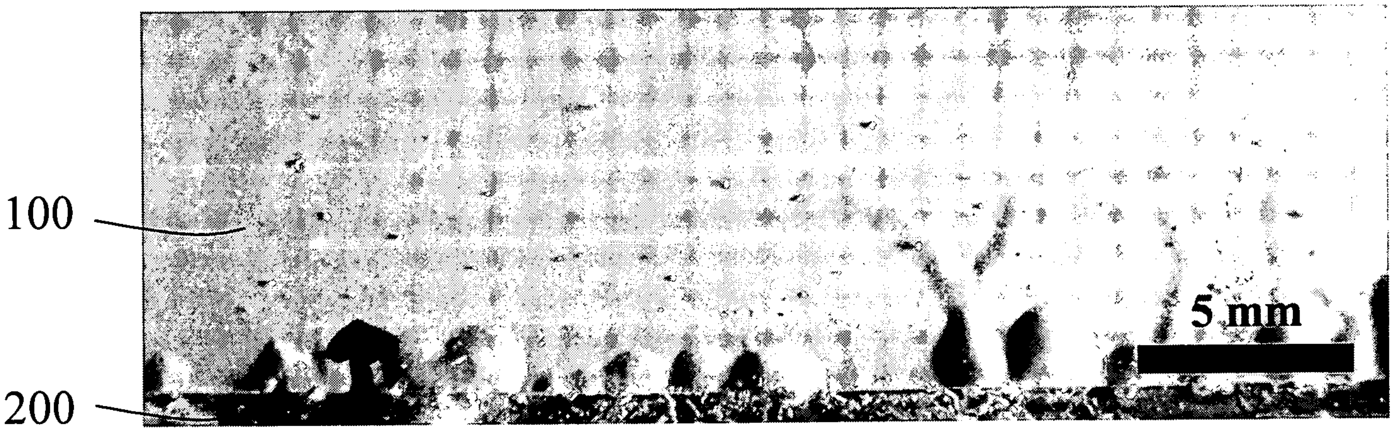

Figure 2

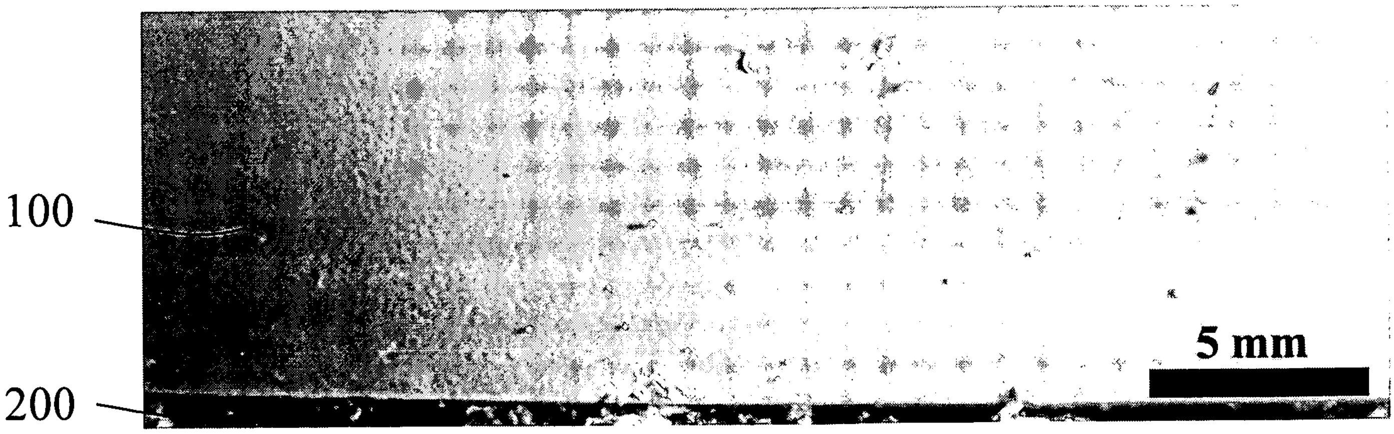

Figure 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/006303

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/24
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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2010 174273 A (UNIV HIROSHIMA) 12 August 2010 (2010-08-12) the whole document -----	1-13
X	DE 197 54 108 A1 (HENKEL KGAA [DE]) 10 June 1999 (1999-06-10) claims 1-11; examples 1-11 -----	1-13
X	WO 2006/015756 A1 (CHEMETALL GMBH [DE]; PLIETH WALDFRIED [DE]; RAMMELT URSULA [DE]; HEBES) 16 February 2006 (2006-02-16) claims 1-30; examples 1-94 -----	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search 1 March 2012	Date of mailing of the international search report 08/03/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Glomm, Bernhard

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2011/006303

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