



(51) International Patent Classification:

C09D 5/00 (2006.01) **C09D 163/00** (2006.01)
C09D 5/08 (2006.01)

(21) International Application Number:

PCT/US2018/038487

(22) International Filing Date:

20 June 2018 (20.06.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/522,979 21 June 2017 (21.06.2017) US

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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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

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

(54) Title: ALUMINUM COATING

(57) Abstract: A coating is provided containing a film former, a thermosetting resin mixture comprising at least two of a triazine, a benzoxazine, or a maleimide, and a crosslinker. When applied to aluminum substrates the coating improves the adhesion of subsequently applied adhesives, provides under-bond corrosion resistance, and serves as a primer for topcoat applications. In particular, the coating allows for robust bonding of aluminum alloy substrates.



ALUMINUM COATING

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority under 35 U.S.C. § 119(e) from U.S. Provisional Patent Application Serial No. 62/522,979 filed June 21, 2017, entitled “Aluminum Coating”, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The invention relates to coating compositions provided to enhance corrosion resistance of metallic substrates and act as a primer for subsequent adhesive bonding. In particular, the coating compositions of the invention are particularly well suited for aluminum substrates as a replacement for conventional wash primers.

BACKGROUND OF THE INVENTION

[0003] Bonding of aluminum substrates can be achieved with a number of structural adhesives, typically epoxy based. The aluminum substrates are typically treated with chemistries that improve the adhesion of the structural adhesives and provide resistance to under-bond corrosion that otherwise compromises bond integrity.

[0004] Current technology relies upon the use of inorganic salts and phosphate solutions applied as wash primers. These wash primers often fail to provide acceptable under-bond corrosion resistance, particularly on high strength aluminum alloys such as 7075-T6, as well as other 7- and 8- thousand series aluminums. Additionally, operation of the baths used to deposit wash primers on aluminum substrates requires careful control of bath chemistries.

[0005] Thus there is a need for a coating for aluminum that provides corrosion resistance to all grades of aluminum and aluminum alloys, and can function as a primer for adhesives to enable bonding of coated aluminum substrates.

SUMMARY OF THE INVENTION

[0006] In one embodiment of the present invention, a coating is provided comprising a film former, a thermosetting resin mixture comprising at least two of a triazine, a benzoxazine, or a maleimide, and a crosslinker. In a preferred embodiment of the present invention, the maleimide comprises a bismaleimide, and in another preferred embodiment of the present invention, the film former comprises a phenoxy resin based on bisphenol A, and/or a methacrylic acid grafted phenoxy resin.

[0007] In a further embodiment of the present invention, the coating further comprises at least one of a corrosion inhibitor or an adhesion promoter, and the corrosion inhibitor preferably comprises a triazole or phosphate, and the adhesion promoter preferably comprises a ureidosilane.

[0008] In another embodiment of the present invention, the crosslinker comprises trifluoromethane sulfonic acid, acid catalyst, diphenyl phosphate / 1-methylimidazole, or tetrol. And in another embodiment of the present invention, the acid catalyst comprises at least one of a covalently blocked dinonylnaphthalenesulfonic acid (DNNSA) catalyst or an amine neutralized dinonylnaphthalenesulfonic acid (DNNDSA) catalyst.

[0009] In a preferred embodiment of the present invention, the thermosetting resin mixture comprises a triazine, a benzoxazine, and a maleimide and the ratio of benzoxazine to maleimide is about 1:1. And in another embodiment of the present invention, the ratio of triazine to benzoxazine is 2:1.

[0010] State of the art chemistry applied in embodiments of the present invention utilizes organic film formers and thermosetting resins in combinations that offer performance advantages over the use of existing wash primer systems, including adhesion to a broader array of aluminum alloys, enhanced corrosion resistance, and metal-priming function outside of the bond line.

[0011] As will be realized by those of skill in the art, many different embodiments of an aluminum coating according to the present invention are possible. Additional uses, objects, advantages, and novel features of the invention are set forth in the detailed description that follows and will become more apparent to those skilled in the art upon examination of the following or by practice of the invention.

[0012] Thus, there has been outlined, rather broadly, the more important features of the invention in order that the detailed description that follows may be better understood and in order that the present contribution to the art may be better appreciated. There are, obviously, additional features of the invention that will be described hereinafter and which will form the subject matter of the claims appended hereto. In this respect, before explaining several embodiments of the invention in detail, it is to be understood that the invention is not limited in its application to the details and construction and to the arrangement of the components set forth in the following description or illustrated in the drawings. The invention is capable of other embodiments and of being practiced and carried out in various ways.

[0013] It is also to be understood that the phraseology and terminology herein are for the purposes of description and should not be regarded as limiting in any respect. Those skilled in

the art will appreciate the concepts upon which this disclosure is based and that it may readily be utilized as the basis for designating other structures, methods and systems for carrying out the several purposes of this development. It is important that the claims be regarded as including such equivalent constructions insofar as they do not depart from the spirit and scope of the present invention.

DETAILED DESCRIPTION

[0014] The thermosetting coating compositions of embodiments of the present invention offer exceptional compatibility with a broad array of structural adhesives, particularly including epoxy formulations. In their cured form, they are very thermally stable and provide excellent adhesion to both the aluminum substrates and the structural adhesives. One embodiment of the present invention discloses a system that utilizes a multiple-catalyst approach to facilitate the proper cure of the coating in combination with corrosion inhibitors that further improve under-bond corrosion resistance.

[0015] Use of these aluminum coatings improves the adhesion of the structural adhesives, provides under-bond corrosion resistance, and serves as a primer for topcoat applications. The coating may find application opportunities in automotive light-weighting and product assembly. The aluminum coating may be applied prior to parts forming operations as a coil coating or after parts forming is completed. Use as a primer prior to the application of hem flange adhesives and sealants, such as may be used in truck bed assemblies, enables the use of higher grade aluminum alloys than may be used with existing wash primer technologies due to limitations in under-bond corrosion resistance.

[0016] In a first embodiment of the present invention, the aluminum coating composition comprises a film former, a thermosetting resin mixture, a crosslinker, and a carrier fluid.

[0017] In one embodiment of the present invention, the film former comprises a monomer or pre-polymer. The film former is provided to produce a contiguous film on a substrate that offers a physical barrier to ingress and impedance to electrolytic solutions that otherwise facilitate corrosion. In a preferred embodiment of the present invention, the film former comprises a phenoxy resin, preferably a bis-A based phenoxy resin, and most preferably a methacrylic acid-grafted phenoxy resin. Preferably, the film former is chosen to provide synergy with benzoxazine resin (i.e. through formation of a monolithic layer wherein the benzoxazine enhances the adhesion of the composite), compatibility with epoxy-based structural adhesives (i.e. attributable to appropriate functionalization), and an affinity for aluminum bonding (i.e. through ligand formation). In a preferred embodiment of the present

invention comprising a methacrylic acid grafted phenoxy resin, it is believed that the carboxylic acid functionality provides for additional crosslinking sites and improves adhesion to aluminum substrates.

[0018] Solvent-soluble phenoxy resins are known in the art from a number of producers, however particularly suitable examples of phenoxy resins for solvent-based adhesives include the solid PKHH grade sold by Phenoxy Associates or PKHS-40, which is a PKHH grade pre-dissolved in methylethyl ketone (MEK). Likewise, aqueous phenoxy resins are also available from this same supplier under the PKHW grade.

[0019] The thermosetting resin mixture employed in the present invention combines at least two thermosetting resins. Preferred thermosetting resins comprise rigid, heavily crosslinked polymeric materials with higher mechanical strength and higher heat resistance than common thermoplastics. In a preferred embodiment of the present invention, the thermosetting resin mixture comprises at least two of a triazine resin, a benzoxazine resin, and a maleimide resin.

[0020] Triazine resins promote thermal stability, corrosion resistance, ligand bonding to metals including copper, and have established use in automotive primers and coil coatings. Preferred triazine resins comprise melamine formaldehyde resins. Benzoxazine resins are known to have excellent adhesion to aluminum, are compatible with phenoxy resin (same backbone), and have high thermal and mechanical properties. Maleimides and particularly bismaleimides are known to be synergistic with benzoxazine, improve the cure rate, and may reduce the need for catalysts.

[0021] In another embodiment of the present invention, the adhesive further comprises a maleimide compound. Maleimide containing adhesives of this embodiment are particularly useful for bonding peroxide cured adhesives. The maleimide compound comprises any compound containing at least two maleimide groups. The maleimide groups may be attached to one another or may be joined to and separated by an intervening divalent radical such as alkylene, cyclo-alkylene, epoxydimethylene, phenylene (all 3 isomers), 2,6-dimethylene-4-alkylphenol, or sulfonyl. An example of a maleimide compound wherein the maleimide groups are attached to a phenylene radical is m-phenylene bismaleimide and is available as HVA-2 from E.I. Du Pont de Nemours & Co. (Delaware, U.S.A.).

[0022] The maleimide compound crosslinker may also be an aromatic polymaleimide compound. Aromatic polymaleimides having from about 2 to 100 aromatic nuclei wherein no more than one maleimide group is directly attached to each adjacent aromatic ring are preferred. Such aromatic polymaleimides are common materials of commerce and are sold

under different trade names by different companies, such as BMI-M-20 and BMI-S aromatic polymaleimides supplied by Mitsui Chemicals, Incorporated.

[0023] In an additional embodiment of the present invention, the coating comprises a compound that cures the resins and promotes the crosslinking of the constituent materials. These materials are known as crosslinkers, curatives, catalysts, and/or reaction accelerators. These are selected so as to match the crosslinking of the constituent materials with the required cure profiles to best coincide with subsequent bonding and coating processes. In a preferred embodiment of the present invention, the crosslinker comprises at least one of trifluoromethane sulfonic acid, which is an effective catalyst with all resins listed in formulary, acid catalysts such as a covalently blocked dinonylnaphthalenesulfonic acid (DNNSA) catalyst (NaCure 1419) or an amine neutralized dinonylnaphthalenesulfonic acid (DNNDSA) catalyst (NaCure X49-110), which are a potential alternative for triflic acid when maleimide resin is included in the formulation, diphenyl phosphate / 1-methylimidazole, which is synthesized in-house, and tetrol, which crosslinks with resins used and improves adhesion. Additional known crosslinkers such as peroxides and the like may also be employed in embodiments of the present invention.

[0024] In another embodiment of the present invention, the coating composition optionally comprises one or more additives or modifiers, such as phenol which improves mobility of triazine after vitrification, and reduces crosslink density after first thermal cycle. Another useful modifier is a UV indicator such as Tinopal NFW to aid in film detection upon application to the substrate. In a further embodiment of the present invention, an adhesion promoter is selected to facilitate bonding of the coating to aluminum substrates. In a preferred embodiment of the present invention the adhesion promoter comprises a ureidosilane.

[0025] In an additional embodiment of the present invention, the coating composition comprises a corrosion inhibitor. Preferred corrosion inhibitors comprise materials that passivate the metal surface and ion exchange anticorrosive pigments. In a most preferred embodiment of the present invention, the corrosion inhibitor comprises a triazole or phosphate corrosion inhibitor, with triazole inhibitors being particularly effective with copper, since copper is a common additive in aluminum alloys.

[0026] In another embodiment of the present invention, the coating composition is provided in a carrier fluid to promote application and handling characteristics. Preferred carrier fluids include: cyclohexanone, methyl ethyl ketone, which is rapid drying; di methyl carbonate, which is a good solvent for benzoxazine and bismaleimide resins and is VOC friendly; glycol ethers such as Dowanol PM which is a tail solvent and solubilizes the Tinopal NFW if used,

and combinations of these and other carrier fluids. In another embodiment of the present invention, the carrier fluid comprises water.

[0027] The coating described in embodiments of the present invention are particularly well suited for use with aluminum and aluminum alloy substrates, however other materials such as steel and copper may be coated.

[0028] The coating may be used as a metal protectant to protect the metal substrate from corrosion and oxidation, or may be used in conjunction with an adhesive to bond the metal substrate to another substrate.

[0029] The coating may be brushed, rolled, sprayed, or otherwise applied to the substrate to a desired thickness preferably not to exceed 0.70 mils, and preferably about 0.50 mils. The coating is then dried at about 150°F for 30 minutes, and preferably cured by heating it to about 400°F for 30 minutes. If used as a primer, it is advantageous to dry the primer as above, then apply the adhesive, then complete the bonding/baking operation.

[0030] Although the present invention has been described with reference to particular embodiments, it should be recognized that these embodiments are merely illustrative of the principles of the present invention. Those of ordinary skill in the art will appreciate that the compositions, apparatus and methods of the present invention may be constructed and implemented in other ways and embodiments. Accordingly, the description herein should not be read as limiting the present invention, as other embodiments also fall within the scope of the present invention as defined by the appended claims.

EXAMPLES

[0031] Throughout the examples, the coatings were prepared, applied, bonded, and tested as described below, unless otherwise described in the individual example.

[0032] Coating Manufacture: As will be appreciated by one of skill in the art, some of the components need to be ground to a smaller particle size via ball mill, sandmill, or Kady mill, while other components can be rolled in since they are in solution or already dispersed in water as received. The coatings were prepared according to the formulations below, and applied, bonded, cured as described below.

[0033] Coating Application: Typical application of the prepared adhesive is to spray apply the coating to the aluminum substrate and allow to dry.

[0034] Testing Parameters: Typically, adhesive bond quality is tested in several manners. One such test measures the lap shear strength. In this test, two substrates are joined together in an overlap fashion, using the coating as a primer and a structural adhesive, with a typical adhesive area of 6.5 cm². The lap shear specimen is then pulled apart on an Instron®-type machine at 180 degrees and a rate of 50 mm/min and force and failure mode are measured. Another such test is outlined in ASTM D429 Method B.

Example 1:

[0035] Formula #1: Composition is shown below

Description	Function	% Total Solids	Dry Weight	Wet Weight
PKHH Phenoxy	Film former	25	22.5	90
Resimene 747 (Triazine)	Thermosetting Resin	100	2.7	2.7
Benzoxazine ¹	Thermosetting Resin	100	2.7	2.7
K-Pure CXC-1615 (amine salt of trifluoromethanesulfonic acid)	Crosslinker	61.25	0.6	0.98
K-Pure 4308 (Triazole)	Corrosion inhibitor	100	0.3	0.3
K-Pure 4321 (tetrol)	Reaction accelerator	43.89	0.9	2.05
NaCure X49-110	Crosslinker	37.39	0.3	0.8

¹ Made in house at LORD Corporation

[0036] The formulation in Example 1 demonstrates a coating according to the present invention which comprises two thermosetting resins, a triazine and a benzoxazine. This coating was applied to aluminum substrates and bonded with a structural adhesive demonstrating satisfactory primary adhesion.

Example II:

[0037] Formula # 2: Composition is shown below

Description	Function	% Total Solids	Dry Weight	Wet Weight
PKHH Phenoxy	Film former	100	22.5	24.38
Resimene 747 (Triazine)	Thermosetting Resin	100	2.7	2.93
Benzoxazine ¹	Thermosetting Resin	100	2.7	2.93
Homide 122G (Bismaleimide)	Thermosetting resin	100	2.7	2.93
K-Pure CXC-1615 (amine salt of trifluoromethanesulfonic acid)	Crosslinker	61.25	0.06	0.11
K-Pure 4308 (triazole)	Corrosion inhibitor	100	0.3	0.33
K-Pure 4321 (tetrol)	Reaction accelerator	43.89	0.9	2.22
NaCure X49-110	Crosslinker	37.39	0.3	0.87
Phenol	Additive	100	0.04	0.04
Tinopal NFW	Additive	100	0.1	0.11
Dowanol PM	Additive	0		2.0
Dimethyl carbonate	Carrier fluid	0		61.17

¹ Made in house at LORD Corporation

[0038] The reduced acid catalyst loading and synergistic use of Homide 122G bismaleimide and benzoxazine demonstrated superior performance. Additionally, phenol was added to provide triazine mobility after vitrification of coating.

Performance of coating according to Formula 2:

[0039] Lap shear strength of prototype formulation versus uncoated control. Five aluminum samples were prepared employing coating 2, including a control with no coating, two samples at 0.15mil coating thickness and two samples at 0.50mil coating thickness, with each set of film thickness tested with a 150°F dry cycle of 15 seconds and a 400°F bake cycle of 30 minutes completed after adhesive application. The samples were then bonded with LORD® 320/322 adhesive, a general purpose, two-component epoxy adhesive system available from LORD Corporation, Cary, NC. The adhesive was applied at a thickness of about 2.5 microns and dried. Lap shear was recorded for the bonded assemblies. The environmental resistance was then measured by subjecting the bonded assemblies to 1080 hours of salt fog exposure, then pulling the assemblies apart to observe the decrease in bond strength. Results are presented in the table below:

Table 1: Bond Strength and Environmental Resistance

Sample #	Thickness/Heat	Lap Shear (pli)	% Bond Strength
1	0.15 mil / 150 °F Dry	1293.3	10
2	0.50 mil / 150 °F Dry	815.33	31
3	0.15 mil / 400 °F Prebake	1388.2	98
4	0.50 mil / 400 °F Prebake	1351.8	50
Control	(none)	804.33	0

[0040] Differential scanning calorimetry of the samples showed vitrification of the coating after the first heat cycle. Vitrification ensures the coating remains in place when the coated part is handled, and the first of multiple crosslinkings has occurred without fully crosslinking the system.

Example III:**[0041]** Aqueous coating formulation 3

Description	Function	% Total Solids	Dry Weight	Wet Weight
PKHW-35 Phenoxy	Film former	35	5.25	40
Royoxy RAR 941 Benzoxazine	Thermosetting Resin	100	4.5	7
Bismaleimide M20	Thermosetting resin	100	15.25	5.18
Dicumyl peroxide	Crosslinker	100		0.42
Polyvinyl Alcohol	Additive	100		0.7
Triton XN-455	Surfactant	100		0.28
Diphenyl Phosphate	Additive	100		0.42
Dimethyl Carbonate	Co-solvent	100		5.91
Water	Carrier Fluid			40.09
Total				100.00

[0042] The aqueous adhesive according to the formulation above was applied to 6061T6 aluminum at a coating thickness of 0.50 mils and dried. BetaMate 4601 adhesive (available from Dow Automotive) was applied and a second coated aluminum coupon was bonded thereto. The bonded assemblies were cured at 178°C for 30 minutes and tested for primary adhesion by the lap shear test and environmental resistance by exposure to salt spray for 1080 hours, then pulled. A total of 12 assemblies were tested by each method with the results as follows:

Primary adhesion = 3067 pli (21 MPa)

Post Corrosion = 3040 pli (21 MPa)

[0043] As such, the coating exhibited excellent properties when used as a primer along with a structural adhesive, and exhibited no degradation in bond strength when exposed to salt spray.

CLAIMS

What is claimed is:

1. A coating comprising a film former, a thermosetting resin mixture comprising at least two of a triazine, a benzoxazine, or a maleimide, and a crosslinker.
2. The coating of claim 1, wherein the maleimide comprises a bismaleimide.
3. The coating of claim 2, wherein the film former comprises a phenoxy resin based on bisphenol A.
4. The coating of claim 3, wherein the film former comprises a methacrylic acid grafted phenoxy resin.
5. The coating of claim 1, further comprising at least one of a corrosion inhibitor or an adhesion promoter.
6. The coating of claim 5, wherein the corrosion inhibitor comprises a triazole or phosphate.
7. The coating of claim 1, wherein the crosslinker comprises trifluoromethane sulfonic acid, acid catalyst, diphenyl phosphate / 1-methylimidazole, or tetrol.
8. The coating of claim 7, wherein the acid catalyst comprises at least one of a covalently blocked dinonylnaphthalenesulfonic acid (DNNSA) catalyst or an amine neutralized dinonylnaphthalenesulfonic acid (DNNDSA) catalyst.
9. The coating of claim 5, wherein the adhesion promoter comprises a ureidosilane.
10. The composition of claim 1, further comprising a carrier fluid.

11. The coating of claim 10, wherein the carrier fluid comprises at least one of cyclohexanone, methyl ethyl ketone, glycol ether, dimethyl carbonate, or water.
12. The coating of claim 1, wherein the thermosetting resin mixture comprises a triazine, a benzoxazine, and a maleimide and the ratio of benzoxazine to maleimide is about 1:1.
13. The coating of claim 12, wherein the ratio of triazine to benzoxazine is 2:1.
14. The coating of claim 1 applied to an aluminum substrate.
15. The coating of claim 14, wherein the coating is spray applied to the substrate.
16. The coating of claim 14, wherein the coating is cured at a temperature above 150°C for about 30 minutes.
17. The coating of claim 14, wherein an adhesive is applied on top of the coated aluminum substrate.
18. The coating of claim 17, wherein the adhesive comprises at least one of an acrylic, epoxy, or urethane based adhesive.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/038487

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/00 C09D5/08 C09D163/00
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 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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	paragraphs [0014], [0020] - [0038]; claims 1,6-8,15,16; examples 1-3; tables 1,6,11,16	8,9
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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

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"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

8 August 2018

Date of mailing of the international search report

18/09/2018

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2018/038487

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Information on patent family members

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