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(54) Title: METHODS AND COMPOSITIONS FOR PASSIVATING HEAT EXCHANGER SYSTEMS

(57) Abstract: A method for treating parts in a heat exchanger system is provided. In the method, heat exchanger parts with metal surfaces which chemically and detrimentally interact with additives in coolant fluids in the heat exchanger system are treated by contacting the metal surfaces with a phosphate-containing solution for the phosphate-containing solution to passivate the metal surface for subsequent contact with the coolant fluids.

## Methods and Compositions for Passivating Heat Exchanger Systems

### FIELD OF THE INVENTION

[001] The invention relates generally to compositions and methods for  
5 passivating surfaces of components and parts in heat exchanger systems that employ  
coolants for heat transfer.

### BACKGROUND

[002] Methods for producing heat exchange systems have changed over the years  
10 with increased used for lighter materials such as aluminium and alloys thereof.  
Construction methods have also changed with the use of brazing, e.g., controlled  
atmosphere brazing or CAB with the brazing in a controlled N<sub>2</sub> gas environment using a  
potassium fluoroaluminate flux. Flux is applied to the surfaces of the heat exchange parts  
to be joined, the assembled unit is heated in a N<sub>2</sub> environment, and joining occurs.

[003] Coolants (heat transfer fluids) are used to take away heat from heat exchange  
15 systems such as engines. It is known to add corrosion inhibitors to coolants to reduce  
corrosion of metallic systems. For example, US Patent No. 4664833 discloses a coolant  
system with a corrosion inhibiting amount of a nitrate salt. US Patent No 4,587,028  
discloses non-silicate antifreeze formulations containing alkali metal salts of benzoic acid,  
20 dicarboxylic acids and nitrate. US patent No 4,647,392 discloses a corrosion inhibitor  
comprising the combination of an aliphatic monoacid or salt, a hydrocarbyl dibasic acid or  
salt and a hydrocarbonyl triazole.

[004] Brazed materials have been in use in cooling systems for decades.  
Previously (see ASTM STP 705 (1979 April)) "Corrosion Testing of Furnace and Vacuum  
25 Brazed - Aluminum Radiators"), it was thought that materials used to braze aluminium  
were chemically inert towards cooling system fluids. Recent investigations show that the  
presence of flux in heat exchanger systems such as radiators generally leads to an increase  
in the corrosion rate of coolant fluids used in the systems. See "Investigation of  
Interaction Between Coolant Formulations and Flux Loading / Compositions in Controlled  
30 Atmosphere Brazed (CAB) Aluminium Surfaces in Heat Exchanger Applications" by  
Jeffcoate et al., Journal of ASTM International, Vol. 4, No. 1, paper ID JAI100421. Other  
tests have shown a fast depletion of some coolant inhibitors in heat exchangers,

specifically nitrogen and silicate-based inhibitors, along with an increase in the pH of the coolant fluids used in the systems which severely impact the performance of the coolant.

[005] It is known in the art to treat metal surfaces by dipping in acidic aqueous phosphate solutions containing controlled amounts of zinc ions and phosphate ions for a sufficient period of time to form a uniformly dense phosphating coating with adhesion and anticorrosion properties, and specifically useful as an under coat for electrodeposition coating. However, phosphate salts although known to inhibit aluminum corrosion, are unacceptable to a number of original equipment manufactures. See for example, Ford Engineering Material Specifications "Coolant, Organic Additive Technology, Concentrate," Specification No. WSS-M97BB44-C.

[006] There is a need to extend the life of coolant fluids in heat exchanger systems employing aluminium and alloy parts, particularly systems having brazed parts. In one embodiment, the invention relates to a novel method to extend the life of coolant fluids in heat exchanger systems, utilizing a solution containing phosphate ions to wash / passivate the aluminium parts and components of the heat exchanger systems prior to contact with the coolant fluids.

#### SUMMARY OF THE INVENTION

[007] In one aspect, there is provided a method for treating parts in a heat exchanger system, which parts have metal surfaces which chemically and detrimentally interact with additives in coolant fluids in the heat exchanger system, by contacting the metal surfaces with a phosphate-containing solution for the phosphate-containing solution to passivate the metal surface for subsequent contact with the coolant fluids.

[008] In another aspect, the invention relates to the use of a phosphate-containing solution having a pH of 4.0 – 12.0 and containing 0.005 to 30 g/l of phosphate ions to treat parts in a heat exchanger system, which parts have metal surface that chemically and detrimentally interact with additives in coolant fluids in the heat exchanger system. In the treatment process, the phosphate ions in the phosphate-containing solution reduce the chemical activity of the metal surface for subsequent contact with the coolant fluid.

#### DETAILED DESCRIPTION

[009] Definitions for the following terms are provided herein to promote a further understanding of the invention.

[010] As used herein, the term “heat exchange system” refers to applications wherein cooling systems are used, including but not limited to fuel cell assemblies, appliances and engine applications. Non-limiting examples include heater cores and radiators for engines as commonly used in automobiles, trucks, motorcycles, aircrafts, trains, tractors, generators, compressors, for various stationary engine and equipment applications, marine engine applications and the like.

[011] As used herein, the term “heat exchange component” refers to parts, bodies, or components of heat exchange systems, including but not limited to radiators, water pump, thermostats, engine head, cylinder liners, separator plates in fuel cells, heater cores, and the like.

[012] As used herein, the term “treat,” “treating” or “treated” may be used interchangeably with “passivate,” “passivating,” or “passivated,” referring to one embodiment of the invention, wherein the heat exchanger part is washed (brought into contact) with the phosphate-containing solution to reduce the chemical reactivity of the washed surface, which is to be subsequently in contact with coolant fluids in the heat exchanger system.

[013] The term “heat transfer fluid” refers to a fluid which flows through a heat exchange system in order to prevent its overheating, transferring the heat produced within the system to other systems or devices that can utilize or dissipate the heat.

[014] As used herein, the term “antifreeze” composition (or fluid or concentrate) may be used interchangeably with “coolant,” “heat transfer fluid” or “de-icing fluid” (composition or concentrate).

[015] As used herein, “glycol-based” includes glycols, glycerins, as well as glycol ethers.

[016] In one embodiment of the invention, a method to treat heat exchanger parts, e.g., surfaces such as heater cores, radiators and brazed parts, etc., is provided. The parts are treated with a passivating solution to reduce the chemical reactivity of their surfaces.

[017] Passivating Solution: The composition for passivating surfaces in heat exchange systems contains as its essential ingredient phosphate ions, in a pH range of 4.0

– 12.0. In a second embodiment, the composition is a neutral to slight alkaline solution containing phosphate ions having a pH of 6.5 – 11.

[018] The phosphate ions are present in the solution in a sufficient amount to reduce the chemical activity of the surfaces in contact with the coolant fluid. In one  
5 embodiment, the sufficient amount of phosphate ions is from 0.005 to 30 g/l of solution. In a second embodiment, the phosphate ions are present in an amount from 0.01 to 25 g/l of solution. In a third embodiment, from 1 to 15 g/l. In a fourth embodiment, from 0.5 to 12 g/l. In a fifth embodiment, from 0.3 to 10 g/l.

[019] The phosphate ions can be introduced to the solution in the form of any  
10 soluble phosphate compound including alkali metal phosphates, ammonium phosphates, polyphosphates, pyrophosphates, phosphoric acid, and the like. In one embodiment, the passivating solution comprises di potassium hydrogen phosphate ( $K_2HPO_4$ ) in solution. In a second embodiment, the solution comprises mono potassium phosphate ( $KH_2PO_4$ ) in aqueous solution. In a third embodiment, the passivating solution is a solution of  
15 diammonium phosphate.

[020] In one embodiment, the passivating solution is aqueous based, with the aqueous medium being selected from the group consisting of water, neutral aqueous solutions, acidic aqueous solutions and basic aqueous solutions. In a second embodiment, the passivating solution comprises di potassium hydrogen phosphate in a water base with  
20 a sufficient amount of at least an alkali metal hydroxide, e.g., NaOH or KOH, added for its pH to be between 7 and 10. In a third embodiment, the passivating solution has as its base a glycol based or non-glycol based coolant, as the heat transfer fluid to be used in the system is subsequently a glycol or non-glycol based antifreeze.

[021] In one embodiment, the phosphate-containing passivating solution has as its  
25 base a glycol-based solution containing glycol or glycol ether in an amount of 2 to 97 wt. % of total weight of a final passivating solution. In a second embodiment, the amount of glycol or glycol ether ranges from 2 to 50 wt. %. Non-limiting examples include alkylene glycols, such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol; triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol,  
30 dipropylene glycol, tripropylene glycol, tetrapropylene glycol, pentapropylene glycol, hexapropylene glycol and mixtures thereof and glycol monoethers such as the methyl, ethyl, propyl, and butyl ethers of ethylene glycol, and mixtures thereof.

[022] In yet another embodiment, the phosphate-containing passivating solution has as its base a non-glycol aqueous medium containing at least an alkali metal salt of anions selected from acetates, formates, proprionates, adiates, and succinates, in an amount of 2 to 97 wt. % of total weight of a final passivating solution. Suitable examples of non-glycol based aqueous medium include but are not limited to glycerine, ethanol, potassium formate, potassium propionate, potassium acetate, dipotassium adipate, and mixtures thereof.

[023] In one embodiment, one or more components known in the art as “phosphating accelerators” can be optionally added to the passivating solution, allowing the surfaces to be treated more uniformly with the phosphate ions. Examples include m-nitrobenzene sulfonate ions at 0.05 to 2 g/L, hydroxylamine in free or bound form at 0.1 to 10 g/l, m-nitrobenzoate ions at 0.05 to 2 g/l, p-nitrophenol at 0.05 to 2 g/l, hydrogen peroxide in free or bound form at 1 to 70 mg/l, organic N-oxides at 0.05 to 10 g/l, nitroguanidine at 0.1 to 3 g/l, nitrite ions at 1 to 500 mg/l, and chlorate ions 0.5 to 5 g/l.

[024] In yet another embodiment, traditional corrosion inhibitors known in the art can be optionally added to the phosphate containing solution in an amount ranging from 0.005 to 10 wt. %. Non-limiting examples include triazoles, nitrates, nitrites, silicates, borates, molybdates, organic aromatic and aliphatic acid salts and mixtures thereof. In one embodiment, the phosphate containing passivating solution further comprises at least a corrosion inhibitor selected from the group of alkali metal borates, alkali metal silicates, alkali metal benzoates, alkali metal nitrates, alkali metal nitrites, alkali metal molybdates, hydrocarbyl thiazoles, and mixtures thereof.

[025] The combination of soluble phosphate compounds and optional additives can be blended into the aqueous medium matrix individually or in various sub-combinations to formulate the passivating solution. The passivating solution may be in the form of a single package or in the form of two packages, with one containing the passivating solution (with the phosphate ions), and one containing a coolant which can be a diluted form of the coolant fluid to be subsequently used in the heat exchanger system.

[026] Method for Treating / Passivating Surfaces in Heat Exchanger Systems: In one embodiment, the treatment / passivating process is carried out at a temperature ranging from 10 to 140°C, with the passivating solution maintained at a temperature ranging from 20 to 90°C. In one embodiment, the treating process is carried out at room temperature.

[027] The passivating solution can be applied to the surface to be treated using methods known in the art, including spraying, immersions, circulation of fluid in cooling system or by a no-rinse method such as using rollers. Whether the passivating solution is applied by spray, no-rinse method, or immersion, in one embodiment, the treating time is between 5 seconds and 12 hours. In a second embodiment, the time is from 30 seconds and 6 hours. In a third embodiment, the treatment time is between 5 minutes and 2 hours. In a fourth embodiment, the treatment time ranges from 15 - 60 minutes.

[028] In one embodiment, after treatment with the passivating solution, the heat exchanger system may be drained and the treated parts are optionally rinsed with a rinse solvent, e.g. deionized water. In another embodiment, the system may be rinsed with a diluted concentration of the coolant fluid to be added to the heat exchanger system, thus minimizing the amount of and / or any residual effect of any passivating solution that may be retained in the system. Lastly, after the treatment (and optional rinsing step), coolant fluids for the normal operation of the heat exchanger system can be finally added to the system.

[029] In one embodiment, the treatment with the passivating solution may clean the surfaces of the parts / components in the heat exchange systems. The solution may also remove oil, sludge, corrosion products and other undesirable contaminants and / or deposits on the surface of the parts. The composition may disperse and / or dissolve these species into the solution, which solution is subsequently removed / drained away along with the undesirable species in the optional rinsing step.

[030] Applications: The passivating solution is useful for treating heat exchanger systems having metal parts comprising components that chemically and detrimentally interact with additives in coolant fluids. As used herein, "chemically and detrimentally interact with additives" means that at least an additive in the coolant fluid is reduced in efficacy and / or useable lifetime, as measured by the amount of active ingredients in the additive, with a reduction of at least 25% reduction in at least an additive such as a corrosion inhibitor after 2 weeks in use. The detrimental chemical interaction can also be shown in a change in the pH of the coolant over time, e.g., a change in the pH of at least  $\pm 1$  after 2 wks.

[031] In one embodiment, the method is for treating heat exchanger parts formed by processes including casting, rolling, forming, brazing, and combinations of the above.

In another embodiment, the method is for treating heat exchanger parts comprising zinc, magnesium, aluminium, alloys of these materials. In yet another embodiment, the method is for treating heat exchanger parts comprising aluminium and / or alloys thereof.

[032] In one embodiment, the method is for treating heat exchanger parts brazed with flux materials that chemically and detrimentally interact with additives in coolant fluids. In another embodiment, the method is for treating parts brazed with a fluorine-containing flux. Non-limiting examples of fluorine-containing fluxing material include potassium fluoroborate, potassium fluoroaluminate, cesium fluoroaluminate, potassium fluorozincate, cesium fluorozincate, and mixtures thereof.

[033] In one embodiment, the treatment using the passivating solution substantially inactivates the chemical reactivity of the metal surfaces in heat exchanger systems towards coolant fluids. In one embodiment of an Organic Acid Technology (OAT) coolant employing a traditional inhibitor such as nitrite, the treatment stabilizes the nitrite depletion when the coolant fluid is added to a heat exchanger system employing treated part, with a reduction in the nitrite level of less than 25% after 2 weeks in use. In a second embodiment, the nitrite reduction level is less than 10%. In a third embodiment, the stability effect of the passivating treatment is shown in the pH level of the coolant, with the coolant pH remains essentially stable, i.e., showing a variation of less than 10% after 2 wks. in use.

[034] EXAMPLES. The following Examples are given as non-limitative illustration of aspects of the present invention.

[035] In the examples, two different coolant formulations are employed, an OAT coolant and a traditional mineral based coolant, both are from Chevron Corporation. The coolants have compositions with components as listed in Table 1.

Table 1

INHIBITOR	OAT Coolant	Traditional mineral based coolant
Monoacid	X	X
Dibasic acid	X	-
Aromatic acid	-	X
SiO <sub>3</sub> <sup>2-</sup>	-	X
NO <sub>3</sub> <sup>-</sup>	-	X
B <sub>4</sub> O <sub>7</sub> <sup>2-</sup>	-	X
PO <sub>4</sub> <sup>3-</sup>	-	-
Triazole	X	X
MoO <sub>4</sub> <sup>2-</sup>	X	-
NO <sub>2</sub> <sup>-</sup>	X	X

[036] In the examples, coupons (cubes) of ½” to 1” in size of brazed aluminium radiator parts were treated by immersion in washing fluids from 15 minutes to overnight (10 hrs.). The parts were brazed with potassium fluoro aluminates as flux materials – which were previously considered an inert material under normal conditions. After washing, the coupons were immersed in the OAT coolant for a period of 2 weeks, with the coolant bath temperature being maintained at about 195°F. For all examples, the OAT coolant has a starting pH of 8.5 and a nitrite level of 580 ppm. pH level, nitrite and fluoride contents in the OAT coolant are measured after the 2 wk. test.

[037] Washing fluid formula E is an aqueous solution employing 1 – 2 wt. % di potassium hydrogen phosphate (K<sub>2</sub>HP0<sub>4</sub>). The corrosion inhibitor components making up the washing fluid formulae C – G are shown in Table 2 below, with the phosphate ions in washing fluid formulae E-G provided by di potassium hydrogen phosphate (K<sub>2</sub>HP0<sub>4</sub>) in the aqueous washing solutions:

Table 2

Washing fluid inhibitors	C	D	E	F (OAT Coolant)	G (Traditional coolant)
Monoacid	X	X		X	
Dibasic acid	X	X		X	
Aromatic acid					X
SiO <sub>3</sub> <sup>2-</sup>		X			X
NO <sub>3</sub> <sup>-</sup>					X
B <sub>4</sub> O <sub>7</sub> <sup>2-</sup>					
PO <sub>4</sub> <sup>3-</sup>			X	X	X
Triazole	X	X		X	X
MoO <sub>4</sub> <sup>2-</sup>					X
NO <sub>2</sub> <sup>-</sup>					X

[038] In Example 1, the coupon was not treated / washed at all. In Example 2, the coupon was washed with water. In Examples 3 – 7, the coupons were treated with the washing fluids having compositions shown in Table 2, with the washing fluid compositions E – G having 0.4-2 wt. % of K<sub>2</sub>HP0<sub>4</sub> in water, the OAT coolant, or a traditional mineral coolant.

[039] It was found that the passivating treatment was as effective with a short treatment time (e.g., 15 minutes) as with a longer treatment period (overnight). The results of the examples in Table 3 show that once the surface treated with E and F are brought in contact with standard coolant fluids, neither abnormal depletion nor pH shift are observed.

Additionally, there is no drastic release of fluoride that is indicative of the reactivity of the potassium fluoro aluminates with the coolant fluid typically used in the heat exchanger system.

Table 3

Example	Washing Procedure	Initial pH	pH after immersing	Initial nitrite	Nitrite after immersing	Fluoride content (ppm)
1	A* (none)	8.5	10.3	580	0	174
2	B* (water)	8.5	10.1	580	0	138
3	C* (OAT coolant)	8.5	9.6	580	103	80
4	D* (traditional coolant)	8.5	10.7	580	0	180
5	E (phosphate)	8.5	8.0	580	535	75
6	F (phosphate with OAT)	8.5	8.3	580	572	55
7	G (phosphate w/ traditional)	-	-	-	-	-

5

[040] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. It is noted that as used herein, the singular forms "a," "an," and "the," include plural referents unless expressly and unequivocally limited to one referent. As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

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[041] This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. The patentable scope is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims. All citations referred herein are expressly incorporated herein by reference.

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## CLAIMS:

1. A process for treating parts in a heat exchanger system which have, at least in part, a metal surface which chemically and detrimentally interact with additives in coolant fluids in the heat exchanger system, the process comprises the step of  
5 contacting the metal surface with a phosphate-containing solution,  
wherein the phosphate-containing solution passivates the metal surface for subsequent contact with the coolant fluids.
- 10 2. The process of claim 1, wherein the heat exchange system comprises components containing aluminium and / or alloys thereof, and wherein the metal surface to be passivated by the phosphate-containing solution is brazed.
- 15 3. The process of claim 2, where the metal surface is brazed with a fluorine-containing flux.
- 20 4. The process of claim 3, wherein the fluorine-containing fluxing material is selected from the group of potassium fluoroborate, potassium fluoroaluminate, potassium fluoroaluminate, cesium fluoroaluminate, potassium fluorozincate, cesium fluorozincate, and mixtures thereof.
- 25 5. The process of claim 1, for treating heat exchanger systems selected from the group of radiators, water pump, thermostats, engine head, cylinder liners, separator plates in fuel cells, and heater cores.
6. The process of claim 1, for treating heat exchanger systems having parts formed by at least one of casting, brazing, forming, rolling, and combinations thereof.
- 30 7. The process of claim 1, wherein the phosphate-containing solution contains 0.005 to 30 g/l of phosphate ions and has a pH of 4.0 – 12.0.
8. The process of claim 7, wherein the composition has a pH of 6.5 – 11.

9. The process of claim 7, wherein the phosphate ions in the phosphate-containing solution are derived from at least one of alkali metal phosphates, ammonium phosphates, polyphosphates, pyrophosphates, phosphoric acid, and mixtures thereof.

5 10. The process of claim 7, wherein the phosphate-containing solution comprises 1-2 wt. %  $K_2HP0_4$  in solution.

10 11. Use of a phosphate-containing solution having a pH of 4.0 – 12.0 and containing 0.005 to 30 g/l of phosphate ions for treating parts in a heat exchanger system which have, at least in part, a metal surface which chemically and detrimentally interact with additives in coolant fluids in the heat exchanger system, wherein phosphate ions in the phosphate-containing solution reduce chemical activity of the metal surface for subsequent contact with the coolant fluid.

15 12. The use of claim 11, wherein the phosphate ions in the phosphate-containing solution are derived from at least one of alkali metal phosphates, ammonium phosphates, polyphosphates, pyrophosphates, phosphoric acid, and mixtures thereof.

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INTERNATIONAL SEARCH REPORT

International application No  
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A. CLASSIFICATION OF SUBJECT MATTER  
INV. C23C22/66 C23C22/68 C23F11/18 C09K5/20 F28F19/02

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)  
C23C C23F C09K F28F

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, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99/07918 A (PRESTONE PRODUCTS CORP [US]) 18 February 1999 (1999-02-18)	1-8
Y	page 6, line 29 - page 9, line 5	9-12
X	WO 2007/002558 A (HONEYWELL INT INC [US]; YANG BO [US]; WOYCIESJES PETER M [US]; GERSHUN) 4 January 2007 (2007-01-04)	1-6
Y	claims 1,16-18,34-38	7-12
X	US 4 664 833 A (CASSIN THOMAS R [US] ET AL) 12 May 1987 (1987-05-12)	1,5-12
Y	cited in the application column 1, lines 15-32; examples 1,2	7-12
X	US 2007/163761 A1 (MINAMI KAZUHIKO [JP] ET AL) 19 July 2007 (2007-07-19)	1,2,5,6
	claims; examples 1,10-12	
	-/--	

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 document but published on or after the international filing date
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Date of the actual completion of the international search

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Name and mailing address of the ISA/

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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	<p>JEFFCOATE C ET AL: "Investigation of interaction between coolant formulations and flux loading/compositions in Controlled Atmosphere Brazed (CAB) aluminum surfaces in heat exchanger applications" JOURNAL OF ASTM INTERNATIONAL JANUARY 2007 AMERICAN SOCIETY FOR TESTING AND MATERIALS US, vol. 4, no. 1, January 2007 (2007-01), XP009107562 cited in the application the whole document</p>	1-12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No  
PCT/US2008/071123

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