HEAT EXCHANGER PLATES WITH ANTI-FOULING PROPERTIES

The present invention relates to a plate, a plate pack, a plate heat exchanger and a method of producing plate for a plate heat exchanger. The present invention improves anti-fouling properties and facilitates cleaning of plate heat exchangers.

[Continued on next page]
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HEAT EXCHANGER PLATES WITH ANTI-FOULING PROPERTIES

Field of the Invention
The present invention relates to a plate for a plate heat exchanger, a plate pack, a plate heat exchanger and a method of producing a plate for a plate heat exchanger for improving anti-fouling properties and facilitating cleaning of plate heat exchangers.

Background
In many industrial processes fouling of heat transfer equipment is of concern. In order to keep a satisfying performance of the equipment regular service and cleaning it is necessary to remove build up of deposits on the heat transfer plates. The deposits arise e.g. from the fluids in the equipment, microbial growth and/or dirt.

Plate heat exchangers (PHE) in use may over time get fouled which leads to a decreased heat transfer and increased pressure drop, and thus leads to an overall reduced performance of the heat exchanger. Thus heat exchangers which are not permanently joined will eventually need to be opened and cleaned. Depending e.g. on the fluids used in the heat exchanger plates may be seriously fouled and difficult to clean, thus requiring strong detergents and/or powerful mechanical cleaning over a substantial time period in order to restore the performance of the heat exchanger. The cleaning of PHE may both be time consuming and costly. Also, the process to which the PHE normally is connected to may have to be shut down during said cleaning of the PHE.

The plates of heat exchangers are made of metal sheets. The base material, i.e. metals used, have a high surface free energy that results in most liquids easily wetting the surface of the sheets.

Also, when heat exchanger plates are produced the forming operation of sheet metal increases the surface roughness which often is associated with faster build up of fouling deposits.

WO2009034359 discloses provision of a coating to reduce biofouling of surfaces in aquatic environments wherein the coating is applied by use of Plasma Assisted Chemical Vapour Deposition (PACVD).
US200901 23730 discloses a surface of a heat exchanger which is to be soldered by means of a flux, and said surface is in addition to the flux also provided with at least one more layer containing an additive. The additive is reacted in order to modify the surface during soldering.

WO20081 19751 discloses production of a hydrophobic coating for condensers wherein the coating comprises sol-gel materials based on e.g. silicon oxide sol.

JP2000345355 relates to improving corrosion resistance and discloses a film consisting of 55-99 wt% SiO2 and 45-1 wt% ZrO2 which film is formed using sol-gel processing.

US2006/01 96644 discloses a heat exchanger provided with a hydrophilic surface coating comprising a gel produced by sol-gel processing.

It would be desirable to find new ways to ensure less fouling of heat exchangers and their plates in order to keep the heat exchangers running for longer time periods as well as more easily cleaned heat exchangers and plates. Also, a reduced shut down time for processes where PHEs are involved would be desirable.

A problem encountered with presently known antifouling coatings is the poor wear resistance of the coatings in applications with abrasive heat exchanging media, e.g. sand or other particulate material which enters the PHE with the heat exchanging fluids. Furthermore, cracks in the coating may occur due to torque and tension forces acting on the plate packages in applications under high pressures.

Summary of the invention

It is an object of the present invention to provide improved plates for a PHE, which show a reduced fouling of the plates when in use in a PHE. Another object is to achieve plates for a PHE having an antifouling surface which are wear resistant in abrasive environments and have high resistance against formation of cracks.

This object is achieved by plates being coated with a sol-gel composition which results in plates with reduced fouling of the plate when in use in a heat exchanger. By applying a coating composition comprising sol-
gel material with organosilicon compounds to the heat exchanger plate both
the surface free energy and roughness is lowered, leading to reduction of
fouling and easy cleaning of heat exchanger plates. Moreover, the sol-gel
coated PHE plates of the invention exhibit an excellent wear resistance and
have a flexibility that reduces the risk of cracks appearing in the coating.

The present invention also relates to a heat exchanger and a plate
pack for plate heat exchangers comprising a number of heat transfer plates of
the kinds as defined herein.

The present invention further relates to a method of producing a heat
transfer plate comprising the steps of:
   a) forming a plate for a plate heat exchanger from a base material,
   b) preparing a composition by means of sol-gel processing on at least
      a part of the plate, which composition comprises organosilicon compounds,
   c) drying and/or curing said composition to form a coating comprising
silicon oxide (SiOx).

Brief Description of the Drawings

Fig. 1 is a schematic drawing of the M20 PHE plate pack with the
relative position of the plates used in tests, both plates coated according to
the present invention and conventional uncoated plates.

Fig. 2 shows pictures of plates according to the present invention and a
conventional plate after disassembly after operation for 7 months.

Fig. 3 is a schematic cross section of a plate for a plate heat exchanger
having an anti fouling coating according to the invention.

Detailed description of the invention

The coating used according to the present invention may be referred to
as a non-stick coating and makes it easy to clean the plates of a fouled heat
exchanger. The coated plates according to the present invention show a
better heat transfer over time compared to conventional heat exchanger
plates since the latter ones gets fouled much quicker and thus decrease the
heat transfer performance to a larger extent. The coating of the plates also
results in a much more even surface thus resulting in better flow
characteristics. Also the pressure drop is reduced over time for a plate heat exchanger according to the present invention in comparison with conventional plate heat exchangers, since the buildup of impurities, microorganisms and other substances is not as pronounced.

The coated plates according to the present invention may easily be cleaned just using high pressure washing with water. With a plate according to the present invention there is no need for extensive time consuming mechanical cleaning or cleaning using strong acids, bases or detergents, such as e.g. NaOH and HNO3.

According to the present invention a plate for use in a plate heat exchanger is coated with a composition comprising organosilicon compounds using a sol-gel process. The organosilicon compounds are starting materials used in the sol-gel process and are preferably silicon alkoxy compounds. In the sol-gel process a sol is converted into a gel to produce nano-materials.

Through hydrolysis and condensation reactions a three-dimensional network of interlayered molecules is produced in a liquid. Thermal processing stages serve to process the gel further into nano-materials or nanostructures resulting in a final coating. The coating comprising said nano-materials or nanostructures mainly comprise silicon oxide, SiO₃, having an atomic ratio of O/Si > 1, preferably an atomic ratio of O/Si ≥ 1.5-3, and most preferably O/Si ≥ 2-2.5. A preferred silicon oxide is silica, SiO₂. The siliconoxide forms a three dimensional network having excellent adhesion to the plates.

The coating of the present invention further has a content of carbon such as found in hydrocarbon chains. The hydrocarbons may or may not have functional groups such as found in hydrocarbon chains or aromatic groups, e.g. C=O, C-O, C-O-C, C-N, N-C-O, N-C=O, etc. Preferably the carbon content is ≥ 10 atomic%, preferably ≥ 20-60 atomic%, and most preferably ≥ 30-40 atomic%. The hydrocarbons impart flexibility and resilience to the coating which is especially important in gasketed plate heat exchangers since the plates move during operation due to high pressures exerted on the plates in the plate package. The hydrocarbon chains are hydrophobic and oleophobic which results in the non-stick properties of the coating.
In Fig 3 is shown a schematic drawing of a plate for a plate heat exchanger provided with a siliconoxide sol gel coating. Between the plate itself and the siliconoxide layer is an interface between the coating siloxane and and a metal oxide film of the plate. The coating bulk that follows said interface is the siloxane network with organic linker chains and voids that impart flexibility to the coating. The outermost layer is a functional surface, i.e., a hydrophobic/oleophobic surface for fouling reduction.

By the combination of a durable and yet flexible coating, a plate for a plate heat exchanger is achieved which has excellent non-stick properties and also is wear and crack resistant. The flexibility of the coating is especially important in plate heat exchangers provided with gaskets between the plates since it is a well known problem that the plate package is not rigid resulting in that coatings on the plates tend to crack when the flexible plates move and bend in relation to each other, a phenomenon called "snakeing".

In one embodiment of the present invention at least one sol comprising organosilicon compounds is applied to the surface to be coated. The surface may be wetted/coated with the sol in any suitable way. It is preferable for the surface coating to be applied by spraying, dipping or flooding. At least a part of one side of the heat exchanger plate is to be coated. Alternatively, all surfaces of at least one side of a plate which during use in a PHE would be in contact with a fluid are coated. Also, at least one side of a heat exchanger plate may be entirely coated. Alternatively, both sides of the plate may be coated. If both sides are coated, they may be partly or fully coated, in any combination. Naturally, more surfaces than the surfaces intended to be in contact with fluid may be coated. Preferably, all surfaces in contact with a fluid giving rise to fouling are coated. Also the gaskets may be coated with the composition according to the present invention. The coating composition is preferably only applied on the surface of gaskets designated to be in contact with at least one fluid when in use in a PHE. In view of the above the coating composition according to the present invention may be applied to bare PHE plates or PHE plates with gaskets attached to them. When discussed in the present application surfaces of plates and gaskets in contact with at least one
fluid is intended to relate to surfaces in contact with fluid(s) within the heat exchanger.

In another embodiment the method comprises a pretreatment of at least the surfaces on the heat exchanger plates to be coated with at least one sol. This pretreatment is also preferably carried out by means of dipping, flooding or spraying. The pretreatment is used to clean the surfaces to be coated in order to obtain increased adhesion of the latter coating to the heat exchanger plate. Examples of such pretreatments are treatment with acetone and/or alkaline solutions, e.g. caustic solution.

In another embodiment the method comprises thermal processing stages, e.g. a drying operation may be carried out after a pretreatment and a drying and/or curing operation is often necessary after the actual coating of the plate with said sol. The coating is preferably subjected to heat using conventional heating apparatus, such as e.g. ovens.

The composition comprising SiOx is applied to a plate to be used in a plate heat exchanger. The application of the composition is done by means of sol-gel processing. The resulting film of said composition on the plate is preferably between 1 and 30 μm thick. The thickness of the coated film is important for the use of the plate in a not permanently joined heat exchanger. A film thickness below 1 μm is considered being not enough wear resistant since the plates in a plate heat exchanger in use are able to move slightly in relation to each other. This slight movement causes wear on the film and with time the coating will become worn down. Also the thickness of the film has an upper limit since the application of substances on the heat transfer plates influences the heat transfer and thus the performance of the plate heat exchanger. The upper limit for the applied film is preferably 30 μm. Thus, the film thickness of the silicon oxide sol containing composition is 1-30 μm, preferably 1.5-25 μm, preferably 2-20 μm, preferably 2-15 μm, preferably 2-10 μm and preferably 3-10 μm.

The base material for the plates may be chosen from several metals and metal alloys. Preferably, the base material is chosen from titanium, nickel, copper, any alloys of the before mentioned, stainless steel and/or
carbon steel. However, titanium, any alloys of the before mentioned or stainless steel is preferred.

Examples
In the search for prolonged operational time of off-shore equipment, tests were conducted on low surface energy glass ceramic coatings. Two low surface energy glass ceramic coatings Coat 1 and Coat 2 were tested and the results are presented below. Coat 1 is a silan terminated polymer in butyl acetate and Coat 2 is a polysiloxan-urethan resin in solvent naphtha/butylacetate.

Phase A
The analysis documents the properties of coatings concerning substrate wetting and adhesion, contact angel, coating thickness and stability towards 1.2 % HNO$_3$ in H$_2$O, 1 % NaOH in H$_2$O and crude oil. The results are summarized below in Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Coat 1</th>
<th>Coat 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate wetting</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Substrate adhesion</td>
<td>Al: 0/0</td>
<td>Al: 0/0</td>
</tr>
<tr>
<td></td>
<td>Stainless steel: 0/0</td>
<td>Stainless steel: 0/0</td>
</tr>
<tr>
<td></td>
<td>Ti: 0/0 (see below)</td>
<td>Ti: 0/0 (see below)</td>
</tr>
<tr>
<td>Contact angle measurements</td>
<td>H$_2$O: 102-103 °</td>
<td>H$_2$O: 102-103 °</td>
</tr>
<tr>
<td>Coating thickness</td>
<td>4-10 μm</td>
<td>2-4 μm</td>
</tr>
<tr>
<td>Stability</td>
<td>1.2 % HNO$_3$ in H$_2$O: 1½ h at 75 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1% NaOH in H$_2$O: 3 h at 85 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Crude oil: 6 months at RT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.2 % HNO$_3$ in H$_2$O: 1½ h at 75 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1% NaOH in H$_2$O: 2 h at 85 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Crude oil: 6 months at RT</td>
<td></td>
</tr>
</tbody>
</table>

Both coatings showed excellent wetting when spray coated onto either stainless steel or titanium substrates.

Adhesion was determined by cross-cut/tape test according to DIN EN ISO 2409. Rating is from 0 (excellent) to 5 (terrible). 0 or 1 is acceptable while
2 to 5 is not. First digit indicates rating after cross cut (1 mm grid) and the second digit gives rating after tape has been applied and taken off again. To obtain the best adhesion for Coat 1 and Coat 2 the substrates required pre-treatment.

To obtain the best adhesion of Coat 1 on stainless steel the substrate must be pre-treated. The substrate is submerged in an alkaline cleaning detergent for 30 minutes. Afterwards the substrate is washed with water and demineralized water and dried before Coat 1 is applied within half an hour to achieve the optimal adhesion. Tests have shown the adhesion is reduced if cleaning of the substrate is only carried out with acetone. Pre-treatment is also necessary for stainless steel substrates coated with Coat 2. This coating displayed unaffected adhesion whether an alkaline detergent or acetone was used as pre-treatment. If the pre-treatment step is neglected or not made correctly it will affect coating adhesion.

Both coatings showed good stability under acidic condition. The coatings were stable for 1½ hour at 75 °C and more than 24 hours at room temperature.

Under alkaline conditions Coat 1 showed a better result than Coat 2. Coat 1 could withstand the alkaline conditions for 3 hours at 85 °C and Coat 2 for 2 hours at 85 °C. Both coatings showed no decomposition or reduction in oleophobic properties after being submerged for 6 months in crude oil at room temperature.

Phase B

M3 heat exchanger plates with gaskets were partly coated and then tested. To examine whether the partly coated gaskets would compromise the operation of the PHE, these test included pressure tests. It was concluded that partly coating of gaskets with the coatings did not impact operation. The M3 plates were not operated with crude oil.
Phase C

Coating of PHE plates

Coat 1 and Coat 2 were applied to a total of 30 titanium M20 heat exchange plates (measuring 175 x 62 cm) used in a crude oil cooler. All plates underwent pre-treatment which consisted of:

1. Submerging in liquid nitrogen (-196 °C) to remove gaskets
2. Treatment with acidic and alkaline solutions to remove fouling
3. High pressure washing of the plates with water
4. Assembly of the PHE stack for pressure testing
5. Disassembly of the PHE stack. Plates left to dry before application

This pre-treatment was completed the day before Coat 1 and Coat 2 were applied to the plates. Consequently, this procedure did not follow the recommended approach as outlined in Phase A. As the plates have been left to dry at ambient temperature, some plates were still wet. 15 plates were treated with Coat 1 and the remaining 15 plates with Coat 2 by spray coating. The heat exchanger plates were coated on both sides and then placed in a rack. As the plates had glued gaskets on them, both the plates and the gaskets were coated. The final film thickness was measured to be 2-4 µm and the coating was applied on both sides of the plates. Curing/drying was performed at elevated temperatures of 200 °C or 160 °C respectively for 1½ hour in an on-site oven. Upon completion the coated heat exchangers were weighed and coating thickness was measured. It was observed that some plates had some coating imperfections and small defects.

All plates were stamped with a unique number for later identification.

The heat exchanger plates were then assembled with the remaining untreated 319 plates. The coated plates were placed respectively in the front, middle and end of the assembled unit and the position of the coated plates in the PHE stack are shown in Fig 1. The evaluation of the coated plates was performed after more than seven months of operation.

The plates that later, after termination of off-shore operation, were chosen for detailed analysis were positioned at the left (plate no. 3 and 6), middle (plate no. 12 and 17) and the right (plate no 22 and 29) positions in Figure 1.
Phase D

Determination of content in coating by XPS analysis

Three different silicon oxide-coated Ti substrates were analyzed before and after use by means of XPS (X-ray Photoelectron Spectroscopy), also known as ESCA (Electron Spectroscopy for Chemical Analysis). The XPS method provides quantitative chemical information - the chemical composition expressed in atomic% - for the outermost 2-10 nm of surfaces.

The measuring principle is that a sample, placed in high vacuum, is irradiated with well-defined x-ray energy resulting in the emission of photoelectrons. Only those from the outermost surface layers reach the detector. By analyzing the kinetic energy of these photoelectrons, their binding energy can be calculated, thus giving their origin in relation to the element and the electron shell.

XPS provides quantitative data on both the elemental composition and different chemical states of an element (different functional groups, chemical bonding, oxidation state, etc). All elements except hydrogen and helium are detected and the surface chemical composition obtained is expressed in atomic%.

XPS spectra were recorded using a Kratos AXIS Ultra\textsuperscript{DLD} x-ray photoelectron spectrometer. The samples were analyzed using a monochromatic Al x-ray source. The analysis area was below 1 mm\textsuperscript{2}.

In the analysis, wide spectra were run to detect elements present in the surface layer. The relative surface compositions were obtained from quantification of detail spectra run for each element.

The following three samples were XPS analyzed:

1. Silicon oxide (new) on Ti-plate - coating on both sides.
2. Silicon oxide (used) on Ti-plate - coating on one side
3. Silicon oxide on DIN 1.4401 stainless steel plate, coating on both sides.

The analysis was performed in one position per sample, except for sample 1, where two positions were analyzed. The results are summarized in Table 2 showing the relative surface composition in atomic% and atomic ratio O/Si.
Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>O/Si</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 new (pt 1)</td>
<td>2.25</td>
<td>64.1</td>
<td>23.5</td>
<td>10.5</td>
<td>4.2</td>
</tr>
<tr>
<td>2 new (pt 2)</td>
<td>2.30</td>
<td>62.0</td>
<td>23.9</td>
<td>10.4</td>
<td>4.1</td>
</tr>
<tr>
<td>2 used</td>
<td>2.29</td>
<td>68.0</td>
<td>19.5</td>
<td>8.6</td>
<td>3.1</td>
</tr>
<tr>
<td>3</td>
<td>1.46</td>
<td>41.9</td>
<td>34.3</td>
<td>23.4</td>
<td>(0.2)*</td>
</tr>
</tbody>
</table>

*weak peak in detail spectra, signal close to noise level

As seen in Table 2 mainly C, O and Si were detected on the outermost surfaces, i.e. 41.9-68.0 atomic% C, 19.5-34.3 atomic% O and 8.6-23.4 atomic% Si.

Note that in the atomic ratios O/Si, the total amount of oxygen is used. This means that also oxygen in functional groups with carbon is included.

Otherwise for silica, from theory is expected a ratio O/Si of 2.0 for the bulk pure silica SiO2.

Inspection during operation

After four months of operation an off-shore pre-inspection by thermo-imaging was performed. Thermo-image of the mid region of heat exchanger in operation. The identity of the two coating systems was presumed from the installation, but it was obvious that two sets of PHE plates show increased heat transfer compared to the rest of the PHE unit.

The inspection showed an elevation temperature at the coated plates. The non-coated plates showed a lower operating temperature. The difference in temperature is presumed due to reduced fouling, hence a higher crude oil flow in the coated region which produces an elevated temperature.

Inspection of plates after operation

The term fouling is used to describe the deposits formed on the PHE plates during operation. The fouling are residues and deposits formed by the crude oil and consists of a waxy, organic part and a mineral/inorganic part.

The visual inspection revealed that the plates with the coating designated Coat 1 was covered with the least amount of fouling on the crude oil facing plate side. Also, the other coating system designated Coat 2 had a
reduced amount of fouling on the crude oil facing plate side compared to the
bare titanium surface but to a lesser extent then Coat 1. The bare titanium
plates at the end of the plate pack were completely covered in a thick layer of
crude oil derived fouling.

Images taken off-shore during the disassembly (Fig 2) showed
significant reduction in fouling on both of the coated plates compared to the
uncoated plates.

By subtracting the average weight of a clean plate from the weight
recorded for the individual fouled plates the average amount of fouling per
surface type was calculated (table 3). Note, the weight of the coating was not
compensated for and so the real fouling reduction is slightly higher. For a
T20-M plate the heat transfer surface is 0.85 m² so for a plate with a 4 µm thick coating on front and back the total volume is around 6.8 cm³. If the
coating is estimated to be pure SIO₂ (density 2.6 g/cm³) then the amount of
coating per plate is about 20 g.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Average fouling* (g)</th>
<th>STDEV</th>
<th>Fouling reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>585</td>
<td>125</td>
<td>-</td>
</tr>
<tr>
<td>Coat 1</td>
<td>203</td>
<td>48</td>
<td>65</td>
</tr>
<tr>
<td>Coat 2</td>
<td>427</td>
<td>144</td>
<td>27</td>
</tr>
</tbody>
</table>

For both coating systems the fouling of the plates were more easily
removed compared to the fouling adhering to the bare titanium surface, see
Table 4. The difference in cleaning requirements was tested by manually
wiping of the plates with a tissue and by high pressure water cleaning. Just
wiping the plates with a tissue showed that the fouling was very easily
removed from the coated plates, contrary to the uncoated plates. By using
water jet all fouling except for one or two small patches could be removed
from the Coat 1 coated surface. On the Coat 2 coated surface some more
fouling was present after water jet cleaning. This fouling had the appearance
of slightly burnt oil.
Some loss of coating was observed in the contact points but overall the coated surface that had been in contact with the crude oil was in a good condition.

On the sea water facing side both coatings had deteriorated and could be peeled off quite easily.

Table 4

<table>
<thead>
<tr>
<th>View</th>
<th>Coat 1</th>
<th>Coat 2</th>
<th>Non-coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>View</td>
<td>very little fouling compared</td>
<td>reduced fouling</td>
<td>fouling significant and widespread</td>
</tr>
<tr>
<td>Wipe with tissue</td>
<td>very easy to remove fouling</td>
<td>very easy to remove fouling</td>
<td>fouling was not removed</td>
</tr>
<tr>
<td>High pressure water washing</td>
<td>the plates appeared as new</td>
<td>most of the fouling was removed</td>
<td>even after attempts of manual removal of fouling, still a considerable layer remains</td>
</tr>
</tbody>
</table>

The coating tolerance to immersion in liquid nitrogen for gasket removal was tested. One Coat 1 and one Coat 2 plate were treated in liquid nitrogen, at -196 °C, to remove the rubber gaskets. The coatings did not appear do suffer from the extreme temperature changes. Subsequently the plates were washed by high pressure water, which removed almost all fouling. No coating delimitation or failure was observed for either coating system.
Claims

1. A plate for a plate heat exchanger, characterized in that said plate has a coating comprising silicon oxide, SiOₓ, having an atomic ratio of O/Si > 1, a content of carbon ≥ 10 atomic% and a coating layer thickness of about 1-30 µm, which coating was prepared by sol-gel processing and applied to at least a part of the plate.

2. A plate according to claim 1, wherein the layer thickness of said coating on the plate is 1.5-25 µm, preferably 2-20 µm, more preferably 2-15 µm, even more preferably 2-10 µm, and most preferably 3-10 µm.

3. A plate according to claim 1 or 2, wherein the coating comprising silicon oxide, SiOₓ, has an atomic ratio of O/Si ≥ 1.5-3, preferably O/Si ≥ 2-2.5.

4. A plate according to any one of claims 1-3, wherein the composition has a content of carbon ≥ 20-60 atomic%, preferably ≥ 30-40 atomic%.

5. A plate according to any one of claims 1-4, wherein said coating is applied to the surface of a gasket designated to be in contact with at least one fluid when the plate is in a plate heat exchanger in use.

6. A plate according to any one of claims 1-5, wherein said plate is made of a base material chosen from titanium, nickel, copper, any alloys of the before mentioned, stainless steel and/or carbon steel.

7. A plate pack for a plate heat exchanger, characterized in that it comprises a number of plates of the kinds as defined in any one of claims 1-6.

8. A plate heat exchanger, characterized in that it comprises a number of heat plates of the kind as defined in any one of claims 1-6.
9. Method of producing a plate for a plate heat exchanger according to any one of claims 1-6, comprising the steps of:
   a) forming a plate from a base material,
   b) preparing a composition comprising organosilicon compounds by means of sol-gel processing and applying it to at least a part of the plate,
   c) drying and/or curing said coating, whereafter the coating on the plate comprises silicon dioxide.
Five plates coated with Coat 1
Labeled 6-10

Five plates without coating

Five plates coated with Coat 2
Labeled 1-5

Five plates coated with Coat 1
Labeled 16-20

Five plates without coating

Five plates coated with Coat 2
Labeled 11-15

Five plates coated with Coat 1
Labeled 26-30

Five plates without coating

Five plates coated with Coat 2
Labeled 21-25

**Fig. 1**
Heat exchanger plate with immediately after off-shore disassembly.
Left, Coat 1. Middle Coat 2. Right, uncoated plate.

Fig. 2

---

![Diagram]

Functional surface
Siloxane network
Coating/plate interphase
Metal plate

Fig. 3
### A. CLASSIFICATION OF SUBJECT MATTER

INV. F28D9/00 F28F3/00 F28F3/08 F28F19/02 C23C18/12

**ADD.**
According to International Patent Classification (IPC) or both national classification and IPC.

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

- F28D
- F28F
- C23C

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
- WPI Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>Y</td>
<td>DE 10 2006 012131 AI (AASLEPP HELMUT [DE]) 20 September 2007 (2007-09-20), the whole document</td>
<td>1-9</td>
</tr>
</tbody>
</table>

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
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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**Date of the actual completion of the international search**

9 November 2011

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**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
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Le Hervet, Morgan
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