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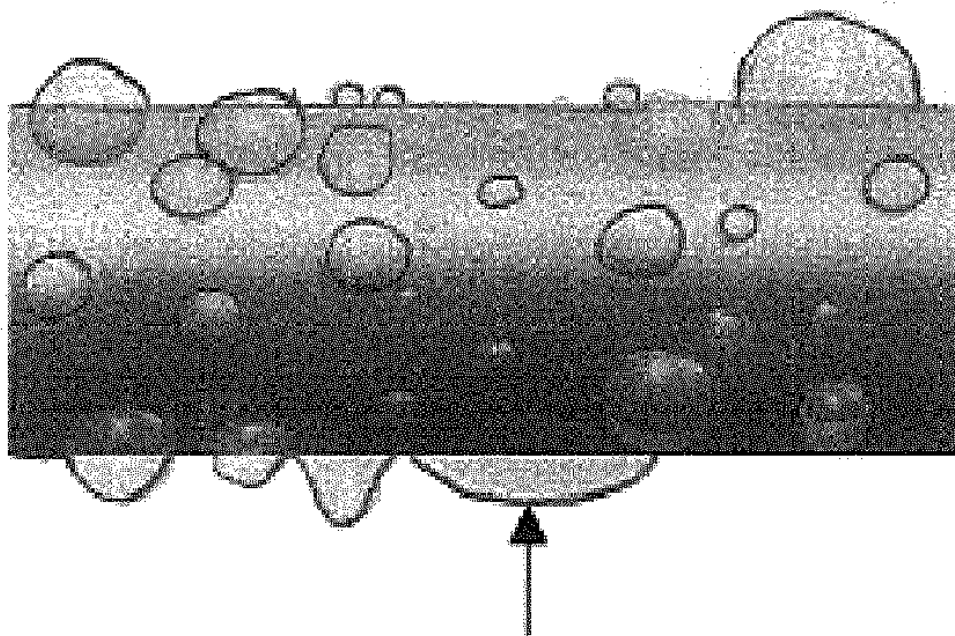
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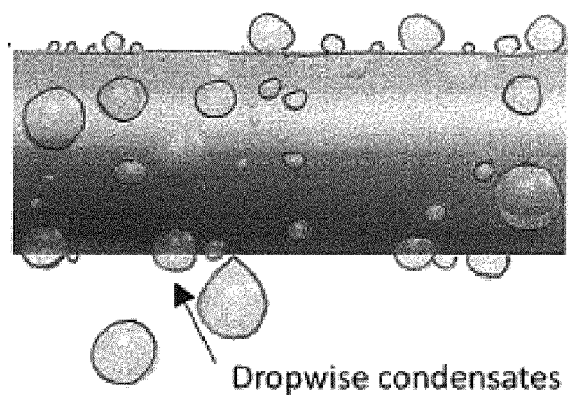
(54) **FUNCTIONAL COATINGS ENHANCING CONDENSER PERFORMANCE**

(57) Coatings for enhancing performance of materials surfaces, methods of producing the coating and coated substrates, and coated condensers are disclosed herein. More particularly, exemplary embodiments provide chemical coating materials useful for coating condenser components.



**Filmwise condensates**

**FIG. 1A**



**FIG. 1B**

**Description**

## CROSS REFERENCE TO RELATED APPLICATIONS

**[0001]** This application is a continuation-in-part of co-pending U.S. Patent Application Serial No. 14/268,757, filed May 2, 2014, which claims the benefit of U.S. Provisional Patent Application Serial No. 61/818,631, filed May 2, 2013, the contents of which is incorporated herein by reference in its entirety.

## FIELD

**[0002]** The present disclosure relates to the field of coatings for enhancing performance of materials surfaces. More particularly, exemplary embodiments provide chemical coating materials useful for coating condenser components.

## BACKGROUND

**[0003]** The effect of surfaces on changes of state in materials, including condensation, boiling, freezing and thawing have long been appreciated and investigated in the art. With the advent of microtechnology and nanotechnology, even smaller scale implications of surface structure, composition, porosity and texture have been evaluated and determined.

**[0004]** Nanoscale surface modification is also of importance in macro-application. For example, condenser tubes play an important role in electrical power generation. In general, an electrical power plant, such as a coal fired power plant, operates by burning fuel (i.e. coal) to heat water in a boiler. The steam produced by the boiler is transferred to a power generator which, in some systems, includes a water box. As steam enters the water box, it comes in contact with condenser tubes supplied with an external coolant, such as water from an external source (e.g. river water). When the hot steam come in contact with condenser tubes in the water box, the steam changes phase from gas to liquid by forming a condensate on the condenser tubes. The phase change from gas to liquid causes a pressure drop within the water box that compels a turbine that is connected to the water box to rotate, thus creating electricity.

**[0005]** With environmental concerns mounting related to the production of greenhouse gases, such as CO<sub>2</sub>, the power industry is increasingly faced with pressure to reduce greenhouse gas emissions and reduce its carbon footprint. In general, a 1% enhancement of the overall heat transfer coefficient could be translated into \$100,000/yr/power plant savings through reduced use of fuel. One skilled in the art will appreciate that a more efficient mode of condensation, will create a greater pressure drop, which will in turn produce an increased and more efficient power generation per weight of fuel introduced into the plant. Further one skilled in the art will appreciate that a more efficient heat transfer will provide the desired increase in power output per weight of fuel. By increasing the efficiency, a power plant can produce the same amount of electricity with less fossil fuel, and reduce CO<sub>2</sub> emissions. Accordingly, there is a great need for improved materials and methods for providing improved heat transfer condensation.

## SUMMARY

**[0006]** Improved heat-transfer surfaces are provided with metal or polymer-based porous coatings to alter the mode of liquid condensation and heat transfer properties on, from and to those surfaces. These polymers-based particles may have number average diameters of between 50 nm and 5 microns and may further contain additives to further modify the physical properties of the polymer-based compounds or to alter chemical properties to resist deterioration of the particles during use. The surfaces of the metal particles may be in the form of thin oxides or may be coated in a manner to minimize reduction in thermal transfer properties, as thicker coatings tend to act as insulators on a condenser. Better tailoring of hydroscopic or hygroscopic surface properties of the particles is enabled.

**[0007]** In exemplary embodiments, a condenser system is provided comprising at least one vapor condensing surface having metal or polymer-based compounds distributed across the surface of the vapor-condensing surface to form a porous coating on the vapor-condensing surface. The particles preferably have an average size distribution within a range of  $\pm 100$ ,  $\pm 50\%$  or  $\pm 20\%$  within an average size range of 50 nm to 5  $\mu\text{m}$ , or within 100 nm to 3  $\mu\text{m}$ . The particles may provide a static water contact angle (SWCA) on the vapor-condensing surface of between 90 to 160 degrees or 100 and 160 degrees with deionized water at a temperature of 70-90°C.

**[0008]** In further embodiments, the disclosure provides a condenser system comprising a vapor condensing surface having metal coating and optionally a top coating comprising a perfluorinated compound or a polymer-based compound. In some embodiments, the disclosure provides a method of producing a condenser system or coated condenser tube comprising a. contacting a condenser tube with a metal coating solution to provide a metal nanoparticle coated surface (also described herein as a treated metal), and b. optionally contacting the metal nanoparticle coated surface with a top coating comprising a perfluorinated compound or a polymer-based compound. In some embodiments, the metal coating is silver. In some embodiments, the metal coating solution is an aqueous silver nitrate solution. In some embodiments,

the metal coating solution is an aqueous silver nitrate solution having a concentration of less than or equal to about 0.5 mM. In some embodiments, the metal coating solution is an aqueous silver nitrate solution having a concentration of about 0.5 mM. In some embodiments, the perfluorinated compound is applied in a solution of an alcohol solvent. In some embodiments, the alcohol solvent is methanol or ethanol. In some embodiments, the perfluorinated compound is applied as a perfluorinated compound solution comprising about a 0.3 to about 1.5 wt% of the perfluorinated compound in an alcohol solvent. In some embodiments, the perfluorinated compound is a perfluoroalkyl trialkoxysilane. In some embodiments, the perfluorinated compound is a perfluorooctyl triethoxysilane. In some embodiments, the perfluorinated compound solution is about 0.5 wt% perfluorooctyl triethoxysilane in ethanol. In some embodiments, the perfluorinated compound solution is about 1 wt% perfluorooctyl triethoxysilane in ethanol.

**[0009]** Various embodiments of the disclosure can be described in the following set of enumerated clauses. It will be appreciated that any of the enumerated clauses provided below can be combined with any of the other embodiments described herein to the extent that such combination is not in conflict with one another. One of skill in the art will appreciate such combinations.

Clause 1. A condenser system comprising a substrate having a vapor condensing surface, wherein the vapor condensing surface comprises a metal coating and a top coating; wherein the top coating comprises a perfluorinated compound or a polymer-based compound; and wherein the metal coating is produced by applying an aqueous solution of metal particles to the vapor condensing surface, wherein the aqueous solution of metal particles is in a concentration of less than or equal to about 0.5 mM.

Clause 2. The condenser system of clause 1, wherein the substrate is a copper substrate or a copper alloy substrate.

Clause 3. The condenser system of clause 1 or 2, wherein the metal coating is silver.

Clause 4. The condenser system of any one of the preceding clauses, wherein the aqueous solution of metal particles is an aqueous solution of silver nitrate.

Clause 5. The condenser system of any one of the preceding clauses, wherein the top coating is a perfluorinated compound.

Clause 6. The condenser system of any one of the preceding clauses, wherein the perfluorinated compound is perfluorooctyl triethoxysilane.

Clause 7. A coated condenser tube comprising a condenser tube having a vapor condensing surface, wherein the vapor condensing surface comprises a metal coating and a top coating; wherein the top coating comprises a perfluorinated compound or a polymer-based compound; and wherein the metal coating is produced by applying an aqueous solution of metal particles to the vapor condensing surface, wherein the aqueous solution of metal particles is in a concentration of less than or equal to about 0.5 mM.

Clause 8. The coated condenser tube of clause 7, wherein the condenser tube is copper tube or a copper alloy tube.

Clause 9. The coated condenser tube of clause 7 or 8, wherein the metal coating is silver.

Clause 10. The coated condenser tube of any one of clauses 7-9, wherein the aqueous solution of metal particles is an aqueous solution of silver nitrate.

Clause 11. The coated condenser tube of any one of clauses 7-10, wherein the top coating is a perfluorinated compound.

Clause 12. The coated condenser tube of any one of clauses 7-11, wherein the perfluorinated compound is perfluorooctyl triethoxysilane.

Clause 13. A method of manufacturing a coated condenser tube comprising (a) contacting a condenser tube with an aqueous solution of metal particles having a concentration of less than or equal to about 0.5 mM, to provide a metal nanoparticle coated surface; and (b) contacting the metal nanoparticle coated surface with a top coating mixture comprising a perfluorinated compound or a polymer-based compound.

Clause 14. The method of clause 13, wherein the condenser tube is copper tube or a copper alloy tube.

Clause 15. The method of clause 13 or 14, wherein the aqueous solution of metal particles is an aqueous solution of silver nitrate.

Clause 16. The method of any one of clauses 13-15, wherein the top coating mixture comprises a perfluorinated compound.

Clause 17. The method of any one of clauses 13-16, wherein the top coating mixture further comprises an alcohol solvent.

Clause 18. The method of any one of clauses 13-17, wherein the alcohol solvent is methanol or ethanol.

Clause 19. The method of any one of clauses 13-18, wherein perfluorinated compound is perfluorooctyl triethoxysilane.

Clause 20. The method of any one of clauses 13-19, wherein the top coating mixture is about 0.3 to about 1.5 wt% of perfluorooctyl triethoxysilane in ethanol.

# BRIEF DESCRIPTION OF THE DRAWINGS

## [0010]

FIG. 1A is a schematic view of images of a film-wise condensation (FWC) mode.

FIG. 1B shows a schematic view of snap shot images of a drop-wise condensation (DWC) mode.

FIG. 2A is a schematic illustration of a condensation heat transfer experimental setup.

FIG. 2B is a schematic view of a detail of FIG. 2A.

FIG. 3A is a SEM image of silver self-assembled on the primary surface-treated copper in 1mM concentration silver nitrate solution.

FIG. 3B is a SEM image of silver self-assembled on the primary surface-treated copper in 10 mM concentration silver nitrate solution.

FIG. 3C is a SEM image of silver self-assembled on the primary surface-treated copper in 100 mM concentration silver nitrate solution.

FIG. 3D is a SEM image of silver self-assembled on the primary surface-treated copper in 1mM concentration silver nitrate solution for 20 sec.

FIG. 3E is a SEM image of silver self-assembled on the primary surface-treated copper in 1mM concentration silver nitrate solution at higher magnification (Example 1).

FIG. 3F is a SEM image of silver self-assembled on the primary surface-treated copper in 100 mM concentration silver nitrate solution at higher magnification.

FIG. 4 graphically shows EDX element mapping.  $K\alpha$  and  $L\alpha$  peaks of fluorine, sulfur, copper, and silver are shown at 0.525 and 2.984 keV, respectively. Approximate atomic ratio is Ag:O=1:1.

FIG. 5A is a photograph of SWCA measurement of SANP on copper tubes (prior to dodecanethiol coating) in 1 mM Ag solution (93°). Parenthesis represents SWCA.

FIG. 5B is a photograph of SWCA measurement of SANP on copper tubes (prior to dodecanethiol coating) in 10 mM Ag solution (63°). Parenthesis represents SWCA.

FIG. 5C is a photograph of SWCA measurement of SANP on copper tubes (prior to dodecanethiol coating) in 100 mM Ag solution (53°). Parenthesis represents SWCA.

FIG. 5D is a photograph of SWCA measurement of SANP on copper tubes (prior to dodecanethiol coating) in 100 mM Ag solution (31°). Parenthesis represents SWCA.

FIG. 6A is a photograph of SWCA measurements of dodecanethiol (1 w/w) SAM-coated SANP on copper tubes in (a) 1 mM Ag solution (101°). Parenthesis represents WCA.

FIG. 6B is a photograph of SWCA measurements of dodecanethiol (1 w/w) SAM-coated SANP on copper tubes in 10 mM Ag solution (101°). Parenthesis represents WCA.

FIG. 6C is a photograph of SWCA measurements of dodecanethiol (1 w/w) SAM-coated SANP on copper tubes in 100 mM Ag solution (101°). Parenthesis represents WCA.

FIG. 6D is a photograph of SWCA measurements of dodecanethiol (1 w/w) SAM-coated SANP on copper tubes in 100 mM Ag solution (101°). Parenthesis represents WCA.

FIG. 7A is a photograph showing AWCA measurements with plain surface - water.

FIG. 7B is a photograph showing AWCA measurements with plain surface-CH2I2.

FIG. 7C is a photograph showing AWCA measurements with SAM-coated surface - water.

FIG. 7D is a photograph showing AWCA measurements with SAM-coated-CH<sub>2</sub>I<sub>2</sub>.

FIG. 7E is a photograph showing AWCA measurements with SANP-coated surface- water.

FIG. 7F is a photograph showing AWCA measurements with SANP-coated surface-CH<sub>2</sub>I<sub>2</sub>.

FIG. 8A is a graph showing results for External condensation test results of Comparator Example 2: (a)  $q''$  vs.  $T_{sub}$ .

FIG. 8B is a graph showing results for External condensation test results of Comparator Example 2:  $h$  vs.  $T_{sub}$ .

FIG. 9A is a photograph from video-recording of a tube: plain surface - FWC. Scale bar represents 1 cm.

FIG. 9B is a photograph from video-recording of a tube: SAM-coated surface - mixed DWC and FWC. Scale bar represents 1 cm.

FIG. 9C is a photograph from video-recording of a tube: SANP-deposited surface - DWC. Scale bar represents 1 cm.

FIG. 10A is a photograph of DWC of the SAM copper oxide at  $T_{sub} \sim 5.2$ , with a condensate diameter of 3.3 mm and height mm:  $t^* = 2.06$  ( $t = 33$  ms).

FIG. 10B is a photograph of DWC of the SAM copper oxide at  $T_{sub} \sim 5.2$ , with a condensate diameter of 3.3 mm and height mm:  $t^* = 4.13$  ( $t = 66$  ms).

FIG. 10C is a photograph of DWC of the SAM copper oxide at  $T_{sub} \sim 5.2$ , with a condensate diameter of 3.3 mm and height mm:  $t^* = 29.13$  ( $t = 466$  ms).

FIG. 10D is a photograph of DWC of the SAM copper oxide at  $T_{sub} \sim 5.2$ , with a condensate diameter of 3.3 mm and height mm:  $t^* = 35.38$  ( $t = 566$  ms).

FIG. 11A is a photograph of DWC of the SAM copper oxide at  $T_{sub} \sim 5.2$ , with a condensate diameter of 3.3 mm and height mm:  $t^* = 2.06$  ( $t = 33$  ms).

FIG. 11B is a photograph of DWC of the SAM copper oxide at  $T_{sub} \sim 5.2$ , with a condensate diameter of 3.3 mm and height mm:  $t^* = 47.9$  ( $t = 766$  ms).

FIG. 11C is a photograph of DWC of the SAM copper oxide at  $T_{sub} \sim 5.2$ , with a condensate diameter of 3.3 mm and height mm:  $t^* = 54.1$  ( $t = 866$  ms).

FIG. 11D is a photograph of DWC of the SAM copper oxide at  $T_{sub} \sim 5.2$ , with a condensate diameter of 3.3 mm and height mm:  $t^* = 56.2$  ( $t = 900$  ms).

FIG. 12A is a graph of long term performance of the SANP tubes during 500 hour test runs:  $q''$  vs  $T_{sub}$ .

FIG. 12B is a graph of long term performance of the SANP tubes during 500 hour test runs:  $h$  vs  $T_{sub}$ .

FIG. 13A is a photograph of spatial condensate (contour) distribution and the corresponding condensate population at a still time frame 4.2 sec. of a silver-coated surface. In order to estimate the diameter, each condensate contour was obtained from video recorded images. The condensate perimeter was then estimated by ImageJ analysis.

FIG. 13B is an illustration of spatial condensate (contour) distribution and corresponding condensate population of FIG. 12A.

FIG. 13C is a photograph of spatial condensate (contour) distribution and the corresponding condensate population at a still frame time of 4.9 sec. of a silver-coated surface. In order to estimate the diameter, each condensate contour was obtained from video recorded images. The condensate perimeter was then estimated by ImageJ analysis.

FIG. 13D is an illustration of spatial condensate (contour) distribution and corresponding condensate population of FIG. 12C.

FIG. 13E is a photograph of spatial condensate (contour) distribution and the corresponding condensate population at a still frame time of 5.3 sec. of a silver-coated surface. In order to estimate the diameter, each condensate contour was obtained from video recorded images. The condensate perimeter was then estimated by ImageJ analysis.

FIG. 13F is an illustration of spatial condensate (contour) distribution and corresponding condensate population of FIG. 13E.

FIG. 13G is a photograph of spatial condensate (contour) distribution and the corresponding condensate population at a still frame time of 5.8 sec. of a silver-coated surface. In order to estimate the diameter, each condensate contour was obtained from video recorded images. The condensate perimeter was then estimated by ImageJ analysis.

FIG. 13H is an illustration of spatial condensate (contour) distribution and corresponding condensate population of FIG. 13G.

FIG. 13I is a population histogram estimated from the still frame of FIG. 13A.

FIG. 13J is a population histogram estimated from the still frame of FIG. 13B.

FIG. 13K is a population histogram estimated from the still frame of FIG. 13C.

FIG. 13L is a population histogram estimated from the still frame of FIG. 13D.

FIG. 14 shows graphic results for External condensation test results of Inventive Example 2 tubes compared to uncoated control copper alloy 122 tubes:  $h$  (KW/m<sup>2</sup>/K) vs.  $T_{sub}$ . (■) Inventive Example 2 tube; (♦) Control tube.

FIG. 15 shows a plot of the ratio of the overall heat transfer coefficient (UA) of the coated tube over the overall heat transfer coefficient (UA') of the uncoated (control) tube. The results show that over a >30 day period, the coated tube at tube set T4A4 in the TVA power plant water box provided a 15-22% heat transfer enhancement.

## DETAILED DESCRIPTION

**[0011]** Described herein are embodiments of coating materials, methods of forming the coating materials, methods of coating a substrate, surfaces (e.g., a condenser surface) coated with the coating materials, and a coated article formed by methods disclosed herein. Instead of forming a film on a surface, water forms as droplets on coated surfaces as described herein.

**[0012]** In an illustrative embodiment, a coating of a metal substrate (i.e., a transition metal) includes bound or embedded metal particles and at least one layer of polymer. In an embodiment, a metal substrate includes copper, zinc, nickel, iron, aluminum, and alloys thereof. In an embodiment, the metal particles can be nano particles. In an embodiment, the metal particles can be of an average size of 200 nm to 3  $\mu\text{m}$ . The metal substrate can be treated and then immersed in an aqueous solution comprising the metal particles (e.g., a silver solution, e.g.,  $\text{AgNO}_3$ ). In an embodiment, metal particles (e.g., silver or gold) coat and/or embed into the surface of the metal substrate. In an embodiment, a polymer or combination of polymers coat a surface of the treated metal. Thereby, a polymer or a combination of polymers coats a surface that is embedded or bound with metal particles. In an embodiment, a perfluorinated compound or combination of perfluorinated compounds coat a surface of the treated metal. Thereby, a perfluorinated compound or combination of perfluorinated compounds coats a surface that is embedded or bound with metal particles. In an embodiment, the surface is an inside surface, an outside surface, or both inside and outside surfaces. In an embodiment, a copper or copper alloy substrate includes silver self-assembled nanoparticles bound to the surface and further coated with a polymer. In an embodiment, a copper or copper alloy substrate includes silver self-assembled nanoparticles bound to the surface and further coated with a perfluorinated compound.

**[0013]** A polymer should be stable to a moist environment so that a robust condensing surface is provided. Polymers may vary across the spectrum of hydrophilicity and hydrophobicity and may include fluorinated polymers (e.g., perfluorinated polymers of halogenated polymers comprising at least 25% by number of the halogen atoms as fluorine), olefinic polymers, sulfonated hydrocarbon polymers, phosphonated hydrocarbon polymers, silicone polymers and the like. Among specific polymers identified are poly(phenylene-sulfide), polytetrafluorethylene, and the like. Other classes of polymers useful in the practice of the present technology may include, by way of non-limiting examples, silicone polymers, polysiloxanes, and the like. A perfluorinated compound should be stable to a moist environment so that a robust condensing surface is provided. Perfluorinated compounds may vary across the spectrum of hydrophilicity and hydrophobicity and may include fluorinated trialkoxysilanes, such as perfluorooctyl triethoxysilane.

**[0014]** In an illustrative embodiment, the thickness of the coating on a surface is less than about 2  $\mu\text{m}$ , about 1.9  $\mu\text{m}$ , about 1.8  $\mu\text{m}$ , about 1.7  $\mu\text{m}$ , about 1.6  $\mu\text{m}$ , about 1.5  $\mu\text{m}$ , about 1.4  $\mu\text{m}$ , about 1.3  $\mu\text{m}$ , about 1.2  $\mu\text{m}$ , about 1.1  $\mu\text{m}$ , about 1  $\mu\text{m}$ , about 975 nm, about 950 nm, about 925 nm, about 900 nm, about 875 nm, about 850 nm, about 825 nm, about 800 nm, about 775 nm, about 750 nm, about 725 nm, or about 700 nm.

**[0015]** Properly promoted "drop-wise" condensation (DWC) has been known to improve substantially Condensation Heat Transfer Coefficient (CHTC) compared to that of the traditional "film-wise" condensation (FWC) (A. K. Das, H. P. Kilty, Marto, ASME J. Heat Transfer 7, 109 (2000)). As schematically illustrated in FIG. 1A, representing an FWC mode, a large portion of liquid condensate with poor thermal conductivity hampers efficient heat transfer passage. Residing liquid film prevents refreshing the surface and nucleating liquid condensates.

**[0016]** On the contrary, DWC mode shows discrete rupture of drops/droplets on the heat transfer surface in FIG. 1b. Drop-shaped condensates roll-off and merge with adjacent premature condensates during sweeping the surface. DWC mode leads to a continuous cycle of condensate nucleation. Eventually, DWC mode increases condensate detachment frequency, which reduces the effect of thermal resistance due to condensate on the heat transfer surface.

**[0017]** A hydrophobic coating with enhanced interfacial tension induces neighboring tiny condensates to coalesce and leads to droplet-shaped condensates. Research has focused on fabrication of a hydrophobic surface/coating with high Water Contact Angle (WCA), which is measured by a sessile drop. For instance, organic coating materials with low surface energy have received considerable attention since it is assumed that hydrophobic capabilities of the coated-surface promote DWC. Due to superhydrophobic WCA ( $> 150^\circ$ ), numerous droplets were shown throughout the axis of the test tubes. However, condensates on the polymer-based coatings rarely rolled-off and resided on the surface until they reached critical radius.

**[0018]** A porous surface with hydrophobic coating escalate its WCA into superhydrophobic regime and shows rolling-off motion (B. J. Zhang, K. J. Kim, H. K. Yoon, Bioinsp. Biomim. 7, 036011 (2012). C. Y. Lee, B. J. Zhang, J. Y. Park, K. J. Kim, Int. J. Heat Mass Transfer 55, 2151 (2012)). During condensation phase change, vapor cluster impinges onto the condensing surface. Numerous condensates fill into the condensing surface. Eventually, condensate drops experience additional drag and lead to longer retention on the surface. Once a condensate surface becomes wet, additional driving forces are needed to be separate out of the condensing surface (F. C. Wang, F. Yang, Y. P. Zhao, Appl. Phys. Lett. 98, 053112 (2011)).

**[0019]** Thus, coatings and coated surfaces as described herein achieve DWC augmentation. A silver nano particle deposited coating (i) has low surface energy, (ii) reduces liquid drag, and (iii) can optimize silver nano-particles for

condensation. These features promote effective DWC and lead to a substantial DWC enhancement by increasing nucleating sites and liquid condensate detachment frequency.

**[0020]** The metal particles may be any metal or metalloid that can form and maintain solid particles within the operating temperature range (about 20°C to about 280°C depending on the type of material) of vapors and liquids to which they will be subjected during use. The ability to form thin, oxide coatings on the surface that will resist deep oxidation of the metal is desirable, but not essential. Given that background, metals/metalloids and alloys thereof such as aluminum, chromium, copper, chrome-steel, stainless steel, iron, tin, titanium, or a combination thereof can coat the inside, outside, or both the inside and outside of tubes/tubing and fins used in various condensation applications.

**[0021]** The size range of the particles may vary over an average size range of 50 nm to 5 μm, as stated above. Both smaller and larger average diameter particles and averages may be used with varying efficiencies.

**[0022]** The particles may be bound to the surface of the condenser plate by fusion of the polymeric surface of the particles to the condenser surface, a coating provided on the particles bonding the particles to the condenser plate surface (the coating must provide the surface properties to the particles that offer the benefits of the technology) or a thin adhesive layer may be present on the condenser plate to cause the particles to adhere to that surface.

**[0023]** There are various general characteristics that can be discussed within the concept of non-limiting estimations of general, but not exclusive attributes, dimensions, parameters and specifications within which the present technology may be discussed. The thickness of the coatings may be in similar ranges, although with smaller particles, multi-particle layer thickness is more desirable, while with the larger diameter size particles (e.g., 750 nm to 5 μm), mono-particle layer thicknesses can be more useful. As shown in FIG. 3, the SEM images show a thickness of the particle coatings of 1-2 μm.

**[0024]** The coating may be a monolayer or multiple-particle layer of the metal, metalloid, or alloy substrate as described herein. A coating can include a polymer or material comprising a silane or thiol end group. One coating that can be used is 1-dodecanethiol, which consists of saturated carbon backbone with a thiol (-SH) group. In ethanolic solution, 1-dodecanethiol does not polymerize with other particles. Once the solution is sprayed out on a metal substrate, a thiol group can interact with hydrogen binding sites on a metal substrate, and in particular metal particles (e.g., silver or gold) coated on or embedded in the substrate. Individual monomers (e.g. 1-dodecanethiol) chemically interact (via covalent interaction) and parallel align with each other, thereby forming single-layered molecular level coating. Thickness of single-layered molecular coating for that particular material, composition and particle size is less or equal to about 1 μm. In an embodiment, the coating thickness is about 750 nm to about 1 μm, about 800 nm to about 1 μm, about 825 nm to about 1 μm, about 850 nm to about 1 μm, about 875 nm to about 1 μm, about 900 nm to about 1 μm, about 925 nm to about 1 μm, about 950 nm to about 1 μm, or about 975 nm to about 1 μm. Coatings as described herein that less or equal to about 1 μm remain durable.

**[0025]** Hydrophobic coatings (1-dodecanethiol) are not exclusively polymer-based. To control surface wetting, hydroxyl group-functionalized coating (mercapto-based) can be used. For dropwise condensation application, hydrophilicity does not need to be considered since it will not help condensation. In some embodiments, hydrophobic coatings include perfluoroalkyl trialkoxysilane coatings. In some embodiments, the hydrophobic coating can be a perfluorooctyl triethoxysilane coating.

**[0026]** An aspect of the disclosure includes a method of forming the coated material. In an embodiment, a metal substrate is contacted with a metal particle solution. In an embodiment, the contacting is substrate immersion in a liquid metal solution. In embodiment, the metal substrate is copper or a copper alloy. In an embodiment, the metal particle solution is a silver solution. In an embodiment, the silver solution is silver nitrate. In an embodiment, the silver nitrate solution is about 1 to about 100 mM, about 10 to about 100 mM, about 20 to about 100 mM, about 25 to about 100 mM, about 30 to about 100 mM, about 40 to about 100 mM, about 50 to about 100 mM, about 60 to about 100 mM, about 70 to about 100 mM, about 75 to about 100 mM, about 1 to about 50 mM, about 1 to about 75 mM, or about 10 to about 50 mM. In some preferred embodiments, the silver nitrate solution is less than 1 mM. In some particularly preferred embodiments, the silver nitrate solution is less than 0.5 mM. In one particularly preferred embodiment, the silver nitrate solution is about a 0.5 mM aqueous silver nitrate solution.

**[0027]** The nanoparticles in a silver solution can be about 200 nm to about 3 μm. In an embodiment, silver nanoparticles deposited on, coated on, or embedded within a substrate service can be about 200 nm to about 3 μm, 300 nm to about 3 μm, 400 nm to about 3 μm, 500 nm to about 3 μm, 600 nm to about 3 μm, 700 nm to about 3 μm, 800 nm to about 3 μm, 900 nm to about 3 μm, 1 μm to about 3 μm, 2 μm to about 3 μm, about 200 nm to about 2 μm, 300 nm to about 2 μm, 400 nm to about 2 μm, 500 nm to about 2 μm, 600 nm to about 2 μm, 700 nm to about 2 μm, 800 nm to about 2 μm, 900 nm to about 2 μm, 1 μm to about 2 μm, about 200 nm to about 1 μm, 300 nm to about 1 μm, 400 nm to about 1 μm, 500 nm to about 1 μm, 600 nm to about 1 μm, 700 nm to about 1 μm, 800 nm to about 1 μm, or 900 nm to about 1 μm.

**[0028]** In an illustrative embodiment, silver particles are embedded in the surface of the substrate. In an embodiment, the silver particles both cluster on the surface of the substrate and are embedded in the surface of the substrate. The silver particles provide a binding platform for a coating (e.g., coating comprising a silane or thiol end group). In an embodiment, areas of silver on and/or embedded in the surface of the substrate are heavily hydroxylized and can



covalently bond to a self-assembled monolayer. In an embodiment, the self-assembled monolayer is a hydrocarbon or fluorocarbon. In an embodiment, the hydrocarbon or fluorocarbon is silane-based or contains a thiol end group. For condenser applications, it was discovered that the SANP should not have a hierarchical structures. As shown in coated surfaces of the prior art, for example Gu, C. et al., Micro/Nanobinary Structure of Silver Films on Copper Alloys with Stable Water-Repellent Property under Dynamic Conditions, Langmuir, 2009, 25(20, 1299-12307, coated surfaces that are prepared at concentrations of 1 mM or higher and using longer dip times for the surface coating (25 min to 45 min), show superhydrophobicity at atmospheric pressure, but the surface also contains hierarchical structures. Without being bound by theory, it is believed that the hierarchical structures of surfaces produced under such conditions create air cavities in the surface that, when exposed to condenser system conditions, will cause water to impregnate the substructures within the hierarchical structures to fill the air cavities. It is believed that this process will prevent heat transfer by creating a thermal resistance, and thus retard the condensation process.

**[0029]** It was surprisingly discovered that surfaces prepared by immersion of a copper tube in a lower concentration silver nitrate solution, such as about 0.5 mM or lower, for less than about 1 minute, provided a surface suitable for enhanced heat transfer, and suitable for condenser applications. Accordingly, in some embodiments, the dip time of the manufacturing process is less than about one minute per dip cycle. In some embodiments, the dip time of the manufacturing process is less than about 30 seconds per dip cycle. In some embodiments, the dip time of the manufacturing process is less than about 20 seconds per dip cycle. In some embodiments, the dip time of the manufacturing process is less than about 15 seconds per dip cycle. In some embodiments, the dip time of the manufacturing process is less than about 10 seconds per dip cycle. In some embodiments, the dip time of the manufacturing process is less than about 5 seconds per dip cycle. It will be appreciated that such short dip times per dip cycle can be repeated from 1 to 100 times depending on the application. In some embodiments, the coating process is conducted in about 3 to about 50 dip cycles. In some embodiments, the coating process is conducted in about 3 to about 25 dip cycles. In some embodiments, the coating process is conducted in about 3 to about 10 dip cycles. In some embodiments, the coating process is conducted in about 10 to about 40 dip cycles. It will be appreciated that depending on the application, the number of dip cycles can be any chosen value between 1 and about 100 dip cycles.

**[0030]** In an embodiment, the self-assembled monolayer is 1-dodecanethiol. In an embodiment, a copper or copper alloy substrate comprises silver particles clustered on or embedded in at least one surface, and further comprising a self-assembled monolayer of 1-dodecanethiol. In an embodiment, the coated surface provides a water contact angle of about 90° to about 115°, about 95° to about 115°, about 100° to about 115°, about 105° to about 115°, about 90° to about 110°, about 95° to about 110°, about 100° to about 110°, about 101° to about 110°, about 102° to about 110°, about 103° to about 110°, about 104° to about 110°, about 105° to about 110°, about 106° to about 110°, about 107° to about 110°, about 108° to about 110°, or about 109° to about 110°.

**[0031]** In an embodiment, a surface coated as described herein comprises a condensate detachment frequency of about 0.5 Hz to about 2.0 Hz, 0.5 Hz to about 1.9 Hz, 0.5 Hz to about 1.8 Hz, 0.5 Hz to about 1.7 Hz, 0.5 Hz to about 1.6 Hz, 0.5 Hz to about 1.5 Hz, about 0.5 Hz to about 1.4 Hz, about 0.5 Hz to about 1.3 Hz, about 0.5 Hz to about 1.2 Hz, about 0.5 Hz to about 1.1 Hz, 0.6 Hz to about 1.5 Hz, about 0.6 Hz to about 1.4 Hz, about 0.6 Hz to about 1.3 Hz, about 0.6 Hz to about 1.2 Hz, about 0.6 Hz to about 1.1 Hz, 0.7 Hz to about 1.5 Hz, about 0.7 Hz to about 1.4 Hz, about 0.7 Hz to about 1.3 Hz, about 0.7 Hz to about 1.2 Hz, about 0.7 Hz to about 1.1 Hz, 0.8 Hz to about 1.5 Hz, about 0.8 Hz to about 1.4 Hz, about 0.8 Hz to about 1.3 Hz, about 0.8 Hz to about 1.2 Hz, about 0.8 Hz to about 1.1 Hz, 0.9 Hz to about 1.5 Hz, about 0.9 Hz to about 1.4 Hz, about 0.9 Hz to about 1.3 Hz, about 0.9 Hz to about 1.2 Hz, about 0.9 Hz to about 1.1 Hz, about 1 Hz to about 2 Hz, about 1 Hz to about 1.9 Hz, about 1 Hz to about 1.8 Hz, about 1 Hz to about 1.7 Hz, about 1 Hz to about 1.6 Hz, about 1 Hz to about 1.5 Hz, about 1 Hz to about 1.4 Hz, about 1 Hz to about 1.3 Hz, about 1 Hz to about 1.2 Hz, or about 1 Hz to about 1.1 Hz.

**[0032]** Condensation is the change of the physical state of matter from a gaseous phase into a liquid phase, and is the reverse of vaporization. Condensers are used in a variety of technical fields. They may be used for capturing specific vapors, and especially water vapor, from the air, condensing steam in power generation systems, such as nuclear reactors and coal burning generators. The condensation systems may be powered or passive. Among the various types of condensers includes air well or aerial well generators, which are structures or devices that collect water by promoting the condensation of moisture from air. Designs for air wells are many and varied, but the simplest designs are completely passive, require no external energy source and have few, if any, moving parts.

**[0033]** Three principal designs are used for air wells: high mass, radiative and active. High-mass air wells were used in the early 20th century, but the approach failed. From the late 20th century onwards, low-mass, radiative collectors proved to be much more successful. Active collectors collect water in the same way as a dehumidifier; although the designs work well, they require an energy source, making them uneconomical except in special circumstances. New, innovative designs seek to minimize the energy requirements of active condensers or make use of renewable energy resources.

**[0034]** The vanes, blades, coils, tubes, fins, or other condenser surfaces may be metals, alloys, composites, ceramic, metal oxides and the like as known in the art. Such vanes, blades, tubes, fins, coils, or other condenser surfaces may

be coated with a coating as described herein.

**[0035]** Coated surfaces as disclosed herein increase energy efficiency of heat transfer materials (e.g., condenser based systems). For example, embodiments of coated surfaces can increase the heat coefficient by changing how water interacts with materials (e.g., a condenser surface). Instead of forming a film on a surface, water forms as droplets on coated surfaces as described herein (e.g., condenser coils). The droplets roll off coated surfaces as described herein faster, thereby allowing new water droplets to form on the surface. Thereby the cycle of droplet formation and collection occurs more quickly. Thus, heat can be removed more efficiently. In embodiments as described herein, the heat coefficient of coated surfaces is 100 to 150% greater than uncoated surfaces. In some embodiments, the overall heat transfer coefficient (UA) of coated surfaces as described herein, such as coated copper alloy condenser tubes, is from about 5% to about 40% greater than uncoated tubes. In some embodiments, the overall heat transfer coefficient (UA) of coated surfaces as described herein, such as coated copper alloy condenser tubes, is from about 10% to about 30% greater than uncoated tubes. In some embodiments, the overall heat transfer coefficient (UA) of coated surfaces as described herein, such as coated copper alloy condenser tubes, is from about 15% to about 25% greater than uncoated tubes. In some embodiments, the overall heat transfer coefficient (UA) of coated surfaces as described herein, such as coated copper alloy condenser tubes, is from about 15% to about 22% greater than uncoated tubes.

**[0036]** The disclosed coating can also coat condenser fins, such as those used in air conditioning units. For examples, condenser fins can be located on an outdoor portion of an air conditioner near a compressor. Air conditioner fins can be a part of the condenser that assists heat in moving away from the air conditioner so that the heat disperses more quickly. Condensers with at least one vapor condensing surface coated as disclosed herein, can be included in air conditioning units for multiple applications, such as industrial air conditioners, consumer (e.g., home) air conditioners, automotive air conditioners, aircraft air conditioners, etc. In an embodiment, the water comes off of a coated fin and collected at the bottom and not blown out of the air conditioner.

**[0037]** In an embodiment, condenser systems include at least one coated vapor condensing surface as discussed herein, wherein the surface has a total surface energy of less than about 20 mJ/m<sup>2</sup> to about 40 mJ/m<sup>2</sup>, 25 mJ/m<sup>2</sup> to about 40 mJ/m<sup>2</sup>, 26 mJ/m<sup>2</sup> to about 40 mJ/m<sup>2</sup>, 27 mJ/m<sup>2</sup> to about 40 mJ/m<sup>2</sup>, 28 mJ/m<sup>2</sup> to about 40 mJ/m<sup>2</sup>, 29 mJ/m<sup>2</sup> to about 40 mJ/m<sup>2</sup>, 30 mJ/m<sup>2</sup> to about 40 mJ/m<sup>2</sup>, about 20 mJ/m<sup>2</sup> to about 35 mJ/m<sup>2</sup>, about 25 mJ/m<sup>2</sup> to about 35 mJ/m<sup>2</sup>, about 26 mJ/m<sup>2</sup> to about 35 mJ/m<sup>2</sup>, about 27 mJ/m<sup>2</sup> to about 35 mJ/m<sup>2</sup>, about 28 mJ/m<sup>2</sup> to about 35 mJ/m<sup>2</sup>, about 29 mJ/m<sup>2</sup> to about 35 mJ/m<sup>2</sup>, about 30 mJ/m<sup>2</sup> to about 35 mJ/m<sup>2</sup>, about 20 mJ/m<sup>2</sup> to about 30 mJ/m<sup>2</sup>, about 25 mJ/m<sup>2</sup> to about 30 mJ/m<sup>2</sup>, about 26 mJ/m<sup>2</sup> to about 30 mJ/m<sup>2</sup>, about 27 mJ/m<sup>2</sup> to about 30 mJ/m<sup>2</sup>, about 28 mJ/m<sup>2</sup> to about 30 mJ/m<sup>2</sup>, about 29 mJ/m<sup>2</sup> to about 30 mJ/m<sup>2</sup>, about 20 mJ/m<sup>2</sup> to about 29 mJ/m<sup>2</sup>, 25 mJ/m<sup>2</sup> to about 29 mJ/m<sup>2</sup>, 26 mJ/m<sup>2</sup> to about 29 mJ/m<sup>2</sup>, 27 mJ/m<sup>2</sup> to about 29 mJ/m<sup>2</sup>, 28 mJ/m<sup>2</sup> to about 29 mJ/m<sup>2</sup>, about 20 mJ/m<sup>2</sup> to about 28 mJ/m<sup>2</sup>, 25 mJ/m<sup>2</sup> to about 28 mJ/m<sup>2</sup>, 26 mJ/m<sup>2</sup> to about 28 mJ/m<sup>2</sup>, or 27 mJ/m<sup>2</sup> to about 28 mJ/m<sup>2</sup>. In an embodiment, condenser systems include at least one coated vapor condensing surface as discussed herein, wherein the surface has a total surface energy of less than about 40 mJ/m<sup>2</sup>, about 39 mJ/m<sup>2</sup>, about 38 mJ/m<sup>2</sup>, about 37 mJ/m<sup>2</sup>, about 36 mJ/m<sup>2</sup>, about 35 mJ/m<sup>2</sup>, about 34 mJ/m<sup>2</sup>, about 33 mJ/m<sup>2</sup>, about 32 mJ/m<sup>2</sup>, about 31 mJ/m<sup>2</sup>, about 30 mJ/m<sup>2</sup>, about 29 mJ/m<sup>2</sup>, or about 28 mJ/m<sup>2</sup>. In an embodiment, the total surface energy can be calculated according to the formula  $\gamma = \gamma^h + \gamma^d$ , where  $\gamma^h$  is a surface energy component due to a hydrogen bonding and dipole-dipole interactions and  $\gamma^d$  is a dispersion component of surface energy. In an embodiment,

$$\gamma^h = \left( \frac{137.5 + 256.1 \cos \theta_{H_2O} - 118.6 \cos \theta_{CH_2I_2}}{44.92} \right)^2$$

and

$$\gamma^d = \left( \frac{139.9 + 181.4 \cos \theta_{CH_2I_2} - 41.5 \cos \theta_{H_2O}}{44.92} \right)^2.$$

**[0038]** In an embodiment, the nanoparticle coating on a surface with a total energy as described above is self-assembled. In yet another embodiment, a condenser component (e.g., a fin, a coil, etc.) is coated with silver nanoparticles and/or has silver nanoparticles embedded into a surface and is further coated with a polymer. In an embodiment, the polymer coating is a hydrocarbon or fluorocarbon polymer. In an embodiment, the coating is 1-dodecanethiol.

**[0039]** Condenser systems having at least one coated vapor condensing surface as discussed herein have various applications. Such condenser systems can be utilized in dehumidification, desalination, electric power plants, refrigeration, water generation, and chemical separation processes. For example, water desalination systems typically comprise

a) an evaporator for evaporating saline to produce water vapor and b) a condenser for condensing the water vapor. In an embodiment, a water desalination system comprises tubes (e.g., stainless steel) arranged either horizontally or vertically in a condenser-evaporator chamber. The energy to evaporate the water can be obtained from film or drop-wise condensation of desorbed water vapor. A water desalination system can include a condenser system comprising at least one vapor condensing surface coated according to the disclosure herein. In another embodiment, water desalination includes vapor compression where feed water can be preheated (e.g., in a heat exchanger) outside tubes of a condenser-evaporator. After heating (e.g., boiling), the vapor release is compressed and directed to condense inside the tubes of the condenser-evaporator. Such tubes can be according to the disclosure herein.

**[0040]** Condenser systems as disclosed herein can also be utilized in steam power generation (e.g., air-steam, pure steam, etc.). For example, a condenser system as disclosed herein in a steam powered turbine can include an exhaust gas inlet part that introduces turbine exhaust gases containing steam and non-condensable gases. In another embodiment, a geothermal steam turbine comprises a condenser system as disclosed herein. For example, a condensing system as disclosed herein can be connected to a steam jet ejector for condensing geothermal steam into geothermal water including substantially no non-condensed gas by directly contacting the steam to the condensate from the main condenser. In another embodiment, a low pressure condensing steam turbine includes a condenser system as disclosed herein. The condenser converts exhaust back to water and thereby condensation of the steam and the change of the steam from a vapor to water creates a partial vacuum that pulls the exhaust through the last stages of the low pressure turbine. These examples are non-limiting as a condenser system as disclosed herein can be used in a multitude of steam power generators. In some embodiments, the condenser system as described herein can be a water box as conventionally known in the art of power generation systems. In some embodiments, the condenser system as described herein can be a water box comprising a plurality of condenser tubes having one or more vapor condensing surfaces comprising a metal coating, as described herein, and optionally a top coating comprising a perfluorinated compound or a polymer-based compound, as described herein. Depending on the size of the water box, the number of condenser tubes varies from 10,000 to 100,000 in the water box. In some embodiments, the condenser tubes in a water box can be arranged in a plurality of tube sets. In some embodiments, the plurality of tube sets can be arranged at a variety of depths within the water box, such that the condenser tubes are exposed to a varying range of heat, from steam to cooled water, and a varying range of volume, from heated vapor to full emersion, depending on the location of the tube sets within the water box. It has been surprisingly discovered that the vapor condensing surfaces as described herein can provide enhanced heat transfer and more efficient condensation on condenser tubes located in a preferred environment within a water box, as described herein.

**[0041]** In an embodiment, a condenser component is formed by contacting a liquid metal solution to at least one surface of the condenser component. In an embodiment, the condenser component is a tube, coil, fin, or vane. In an embodiment, the liquid metal solution is a silver solution. In an embodiment, the silver solution is silver nitrate, as described herein. In an embodiment, the contacting is immersion in the metal solution. In an embodiment, the contacting is spraying at least one surface of the condenser component with a metal solution. The method further comprises depositing a self-assembled monolayer of a polymer on the treated condenser component (also referred to herein as a metal nanoparticle coated surface or a treated metal). The polymer can be a hydrocarbon polymer or a fluorocarbon polymer. In an embodiment, the self-assembled monolayer can be 1-dodecanethiol. The method further comprises depositing a coating of a perfluoroalkyl trialkoxysilane on the treated condenser component (also referred to herein as a metal nanoparticle coated surface or a treated metal). The perfluoroalkyl trialkoxysilane can be perfluorooctyl triethoxysilane.

**[0042]** A further embodiment includes a method of forming a condenser system as disclosed herein. In an illustrative embodiment, at least one vapor condensing surface is etched. The surface is initially cleaned with deionized water and then dried with compressed air. Once dry, the surface is submerged into an acid solution for 5 minutes. In an embodiment, the acid solution comprises a 1:1 mixture (by weight) of 70 wt% nitric acid and 1 M sulfuric acid.

## EXAMPLES

**[0043]** Coated copper alloy tubes were produced according to methods disclosed herein and tested for surface properties.

**[0044]** Silver nano-particle deposition: Copper alloy 122 tubes with an outside diameter of 15.9 mm and a thickness of 0.813 mm were primary surface-treated by using emery sand paper (#320) and subsequently by wire wool. The tubes were thoroughly rinsed with deionized water and ethanol. To prepare aqueous silver nitrate stock solution, silver nitrate (99.9% metal basis, Alfa Aesar) was dissolved in DI water at different concentrations (0.1-100 mM). Silver self-assembled nano particles were introduced via a wet chemistry process. Scalability of silver nano particle was governed by a self-assembly process, which was proportional to concentration of silver nitrate and immersion time. Silver self-assembled nano particles (SANPs) were examined by Field Emission-Scanning Electron Microscopy (FE-SEM) and Energy Dispersion X-ray (EDX).

a. Inventive Example 1: Copper alloy 122 tubes were coated with 1.0 mM silver nitrate solution according to the procedure described above (*Silver nano-particle deposition*), and in conformance with the product described in Zhang, B.J., et al. "Dropwise steam condensation on various hydrophobic surfaces: Polyphenylene sulfide (PPS), polytetrafluoroethylene (PTFE) and self-assembled micro/nano silver (SAMS)" Int. J. Heat and Mass Trans. 89 (2015) 353-358.

b. Inventive Example 2: Copper alloy 122 tubes were coated with 0.5 mM silver nitrate solution according to the procedure described above (*Silver nano-particle deposition*).

**[0045] *Water Contact Angle (WCA) measurements:*** The contact angles of liquids (i.e. water, methyl iodide) on the surfaces were measured by a CAM-100 type contact angle apparatus (KSV Instruments, Finland) with an accuracy of  $\pm 0.5^\circ$  at room temperature to assess wetting characteristics. A standard syringe was used to introduce approximately a volume of 5  $\mu$ l drop onto the surfaces.

**[0046] *Surface energy measurements:*** Surface energies of different surface-treated coatings were estimated from the WCA measurements using two different fluids: water ( $H_2O$ ) and methylene iodide ( $CH_2I_2$ ).

**[0047] *Condensation heat transfer experiments:*** Several surface-treated tubes were used in external condensation tests using the experimental setup shown in FIGS. 2A and 2B. The test setup consisted of three main parts: a test section, a cooling loop, and a boiler. The test section is composed of a condensing chamber housing three condensing tubes, view ports, valves with plumbing, and measuring instruments. The cooling loop consisted of a chiller/circulator (Affinity, RWE-012K) and the outlet temperature of which can be maintained within  $\pm 1^\circ C$  of the present value. The boiler generated steam by a submerged heating coil. Hot compressed water controlled by the heater (Advantage Engineering, Sentra SK-1035 HE) was flowing inside of the heating coil of the boiler to generate steam. The inlet and outlet of the coolant temperatures were measured by resistance temperature detectors (RTDs, OMEGA, class A,  $\pm 0.35^\circ C$ ), and the chamber and steam temperature were measured by T-type thermocouples ( $\pm 0.5^\circ C$ ). The pressure of the chamber and boiler were measured by pressure transducers (AST, AST4300, 0 - 345 kPa,  $\pm 0.5\%$ ). The coolant flow rate was measured by a rotameter (Blue & White, F-440, 0- 5 GPM,  $\pm 4\%$  of full scale).

**[0048]** Before the test run, the condensing chamber was fully evacuated until the water could boil at vacuum pressure. Non-condensable gases can be expelled to atmosphere. Once the system reached a steady state condition, relevant heat transfer data were acquired. Pressure and coolant inlet temperature were controlled at 97.8 - 67.5 kPa and 50 - 90 $^\circ C$  during data acquisition.

**[0049] *Power Station Pilot:*** Using the methods described herein, 20 sets of coated Cu-Ni tubes (Admiralty Brass Tubes purchased from Admiralty Industries) were coated with 0.5 mM  $AgNO_3$  and top coated with 0.5 wt% perfluorooctyl triethoxysilane in ethanol. The tubes were installed at the Tennessee Valley Authority Power Plant at Paducah Kentucky, Shawnee Plant in 10 tube sets at varying depths of the water box with the remaining tubes left as untreated tubes. Heat transfer coefficient (UA) was measured over time for both the inventive tubes and the control tubes. Representative results for coated tube at tube set position T4A4 are provided in FIG. 15. The results provided as a ratio of the heat transfer coefficient of the coated tube (UA) over the heat transfer coefficient of the control uncoated tube (UA') demonstrated that the coated tube produced a 15-22% heat transfer enhancement from the condenser tube at condenser tube position T4A4.

## Results and discussion

**[0050] *Surface characterization:*** Produced SANPs at different concentrations were examined by FE-SEM and EDX. As shown in FIGS. 3A-D, the size of individual SANPs was scalable by varying concentration of stock solutions and immersion time. Each nano particle had a characteristic faceted crystal and the average size of SANP was 200 nm - 3  $\mu$ m.

**[0051]** For elemental analysis, EDX mapping was executed in FIG. 4. The majority of elements consists of fluorine, sulfur, copper, and silver. In aqueous silver nitration solution, silver and nitrate were ionized. Individual ions interacted with copper and eventually crystallize into silver:  $Cu_{(s)} + 2Ag^+_{(aq)} + 2NO_3^-_{(aq)} \rightarrow 2Ag_{(s)} + Cu(NO_3)_2_{(aq)}$ .

**[0052] *WCA measurements:*** Surface wetting is closely related to surface roughness and surface energy. Scalability of SANPs influences surface wetting, which was visualized by Static Water Contact Angle (SWCA) in FIG. 5. The reference surface (plain copper surface) has a SWCA of approximately 77 $^\circ$ . As SANP concentration increased (1-100 mM), the SWCA decreased. It is assumed that enhanced wetting phenomena was caused by hydrophilic SANP surface profiles and led to the Wenzel effect.

**[0053]** As shown in FIG. 3, scalable nano- and micro-bumps on the substrate can lead to surface wetting transition from a Wenzel (wetting) surface to a Cassie-Baxter (less wetting) surface due to hydrophobic coating. In general, a hydrophobic coating prevents liquid impingement into surface profiles and entraps noncondensable gas into surface roughness. Dodecanethiol consists of a hydrophobic carbon backbone, which lowers surface energy and leads to hydrophobicity. Dodecanethiol (1 w/w) was dissolved in ethanol and was spray-coated several times.

**[0054]** As shown in FIG. 6, a hydrophobic coating dramatically increased SWCA ( $\geq 100^\circ$ ). This result implies that a hydrophobic coating prevents liquid from impinging into surface roughness. A hydrophobic coating leads to a surface wetting transition from a Wenzel surface to a Cassie-Baxter surface by entrapping gas. Most surfaces showed SWCA of  $100^\circ$ . This phenomenon was assumed to be related to surface profiles as shown in FIG 3. Density of micro bumps at given surface area increased with silver concentration. However, aspect ratio of micro bumps is not significantly enhanced until exposure time increases. To improve SWCA of structured-surfaces, aspect ratio of the substructure was assumed to be the key (B. J. Zhang, K. J. Kim, H. K. Yoon, *Bioinsp. Biomim.* 7, 036011 (2012); C. Y. Lee, B. J. Zhang, J. Y. Park, K. J. Kim, *Int. J. Heat Mass Transfer* 55, 2151 (2012)).

**[0055]** *Surface energy measurements:* In order to obtain a hydrophobic surface, surface roughness and low surface energy were essential factors. The surface energy of SANP was estimated using the formula suggested by Owen and Wendt (D. K. Owen, R. C. Wendt, *Appl. Polymer Sci.* 13, 1741 (1967)):

$$\gamma = \gamma^h + \gamma^d \quad (1)$$

where  $\gamma$  is the total surface energy.  $\gamma^h$  is the surface energy component due to a hydrogen bonding and dipole-dipole interactions and  $\gamma^d$  is a dispersion component of surface energy.

**[0056]** As shown in FIG. 7, the SWCA of various surfaces (a plain copper surface and self-assembled monolayer of copper) are shown for comparison. For water, a wide range of SWCA ( $77^\circ$ - $157^\circ$ ) occurred (FIGS. 7A-C. For methylene iodide, SWCAs were almost halved ( $33^\circ$ - $75^\circ$ ) compared to water (FIGS. 7D-F. Obtained results of SWCA measurements are summarized in Table 2.

**[0057]** To obtain the surface energy using Eq. (1), individually measured SWCAs of different polar liquids were plugged into empirical formulations suggested by Baojin et al. (Q. Baojin, Z. Li, X. Hong, S. Yan, *Exp. Therm. Fluid Sci.* 35, 211 (2011)):

$$\gamma^h = \left( \frac{137.5 + 256.1 \cos \theta_{H_2O} - 118.6 \cos \theta_{CH_2I_2}}{44.92} \right)^2 \quad (2)$$

$$\gamma^d = \left( \frac{139.9 + 181.4 \cos \theta_{CH_2I_2} - 41.5 \cos \theta_{H_2O}}{44.92} \right)^2 \quad (3)$$

Estimated surface energies of various surfaces are summarized in Table 2. For a SANP, the surface energy was significantly lower (45%) than that of a plain surface.

Table 2. Estimated surface energy for various surfaces

|                             | Plain surface | SAM-coated surface | SANP-deposited surface |
|-----------------------------|---------------|--------------------|------------------------|
| $\theta_{H_2O} (^\circ)$    | 77            | 157                | 101                    |
| $\theta_{CH_2I_2} (^\circ)$ | 33            | 75                 | 58                     |
| $\gamma_{sv} (mJ/m^2)$      | 44            | 33                 | 28                     |

**[0058]** *Condensation results:* Test tubes (inner and outer diameters were 14.3 and 15.9 mm, respectively) were cleaned with acid solution ( $HCl:HNO_3$ ) to remove any organic residues. After acid cleaning, the tubes were thoroughly rinsed several times with distilled-water. A test tube was chemically treated with 10 mM Ag solution and 2 wt % ethanolic dodecanethiol was sprayed three times (Comparator Example 2). As shown in FIG. 8, the temperature of subcool ( $T_{sub}$ ) of the external condensation heat transfer tests results were plotted with respect to heat flux and the Condensation Heat Transfer Coefficient (CHTC). For comparison, the test results of the SANP-deposited condenser were compared to that of a plain copper tube and Self-assembled Monolayer (SAM) of copper. The CHTC of the SANP-deposited condenser was approximately 2 to 2.5 times (100-150%) higher than non-surface treated (FIG. 8B). For SAM-coated condenser, CHTC was approximately 25% less than non-surface treated.

**[0059]** FIG. 14 shows the condensation test results for Inventive Example 2 tubes compared to control (uncoated) tubes. Tubes coated with 0.5 mM  $AgNO_3$  generated about 20-25 percent heat transfer enhancement at 1.1 kPa. By comparison, in a similar experiment conducted with tube prepared in conformance with Zhang, B.J., et al. (Inventive

Example 1), the coated tubes prepared with 1.0 mM AgNO<sub>3</sub> showed about 35 percent at 10.0-14.0 kPa. Accordingly, the surface prepared according to the invention (Inventive Example 2) advantageously provided similar heat transfer performance as Inventive Example 1 surface, but at 1/10 of the pressure. Such enhanced performance at lower pressure provides a surface suitable for condenser systems in such an application as a water box in a power plant.

[0060] All test-runs of all the test tubes were recorded for condensation dynamics visualization. FIG. 9A shows a snapshot from the video-recording for a plain surface. Once initial condensate nucleates in the top part of tube, the condensate immediately begins to coalesce with adjacent ones and forms liquid patches. On the bottom of the tube, dangling condensates with a diameter up to 10 mm and height up to 9 mm were observed. After drop/droplet detachment, very thin residues remained on the surface. A dangling drop and thin liquid layer can play a role in thermal resistances. As heat flux increases, complete FWC appeared along the axial length of the tube.

[0061] In FIG. 9B, A SAM-coated surface had a different condensation pattern compared to that of a plain surface (FIG. 9A). In general, a hydrophobic coating provided nucleation site improvement. In the top part of the tube, numerous condensates nucleated and coalesced with neighboring condensates. Due to enhanced surface tension on the droplet rim, a sweeping mode was prevented and droplets grew horizontally. The residing droplet retarded the nucleation of condensates and deteriorated heat transfer performance. Similar phenomena were observed on the bottom of the tube. To note, a larger droplet dangling on the surface turned into a liquid patch, which induced FWC.

[0062] Still-frame of the SANP-deposited surface in FIG. 9C shows DWC mode throughout the horizontal tube. Significant rolling-off motion refreshed the entire surface and triggered immediate nucleation of tiny condensates. The average diameter of detaching condensates was estimated to be approximately 3 mm. The SWCA was not a critical factor in determining DWC mode. As shown in FIG. 7B-C, the SAM copper oxide was 50% enhanced WCA compared to the SANP. Once the cavity of the superhydrophobic surface becomes wet, additional driving force and/or energy are required. During condensation test, most of superhydrophobic surface showed strong WCA hysteresis, which restricted rolling-off motion and condensate detachment.

[0063] To analyze dynamic condensate movement, the growth period of the condensates was video-recorded and was normalized using the characteristic length ( $l_0$ ), velocity ( $u_0$ ), and time ( $t_0$ ) defined as [Y. Nam, E. Aktinol, V. K. Dhir, Y. S. Ju, Int. J. Heat Mass Transfer 54, 1572 (2011)]:

$$l_0 = \sqrt{\frac{\sigma}{g(\rho_l - \rho_v)}} \quad (4)$$

$$u_0 = \sqrt{g \cdot l_0} \quad (5)$$

$$t_0 = \frac{l_0}{u_0} \quad (6)$$

$$t^* = \frac{t}{t_0} \quad (7)$$

where  $\sigma$ ,  $g$ ,  $\rho_l$ , and  $\rho_v$  are surface tension, gas constant, and density of liquid and solid, respectively.

[0064] We calculated  $t_0 = 1.6 \times 10^{-2}$  s and  $l_0 = 2.5 \times 10^{-3}$  m for water at 1 atm. In FIG. 10A, the flow-visualization of the SAM-copper oxide surface showed condensate (arrowed) detachment at  $t^* = 2.06$ . During detachment, the film partially detached (see the next frame FIG. 10B). Then, the droplet grew horizontally and vertically. At  $t^* = 35.38$ , the droplet was removed from the surface again (FIG. 10D). The detachment frequency was approximately 1.7 Hz. The drop-visualization of the SANP surface is shown in FIG. 11. At  $t^* = 2.06$ , a droplet-shaped condensate (arrowed) was removed from the test tube. At the same spot, several condensates are shown in FIG. 11B. These condensates instantaneously merged and detached from the surface. Consecutive frame (FIG. 11D) shows that there is nearly no residue left after detachment. The detachment frequency was approximately 1.1 Hz (faster than the SAM copper oxide). The SANP surface significantly increased droplet-detachment frequency and also minimized the droplet-residuals, which led to an increase in conden-

sation heat transfer.

[0065] To check long term performance of the SANP tubes, longevity test was performed for a 500 hours test run. As shown in FIG. 12A, heat flux over subcool temperature was rarely influenced after 500 hours test run. Heat flux information was converted into a condensation heat transfer coefficient (CHTC) and compared to the initial condition in FIG. 12B.

There was no significant change of the SANP-deposited surface after 100 hours of operation.

[0066] FIG. 13A depicts the contour of liquid condensate distributions of the silver-coated surface, which were taken at specified time periods. FIG. 13A shows that discrete liquid condensates coalesced rolling off along the horizontal tube. Once the liquid droplet began to roll off, the mean base radius was approximately 2 mm. As the liquid droplet moved along the tube surface, its mean base radius increased to about 3 mm. Growing liquid condensate swiveled around and removed premature liquid condensates (< 1 mm) before reaching the critical radius to have enough momentum to roll off. The time frames of FIG. 13A-D show the renewal area. Instantaneously, micro-sized liquid condensates nucleated over the condensing surface, as shown in FIG. 13B.

[0067] Considering that the contour of the liquid condensates was outlined based upon a visually identifiable size, there might have been millions of unidentified liquid condensates. In FIG. 13C, numerous liquid condensates densely populated the given surface area. Before the liquid droplets were fully grown, the largest droplet began to roll off and swivel around the adjacent premature liquid droplets, as shown in FIG. 13D.

[0068] The histogram shown below the contour map in FIG. 13 represents the amount of condensate droplet population. In FIG. 13E, droplets were distributed widely since large condensates were swept already. Once nucleation began (FIG. 13B), liquid droplets grew homogeneously, and the population histogram localized within a few microns regime (FIG. 13F). As droplets grew, the localized histogram peak diminished (FIG. 13G). The histograms shifted and were broadly distributed on a wide range of droplet radii. As shown in FIG. 13H, by immediately merging adjacent liquids, population peaks decreased significantly and histograms populated widely (200 - 2,000  $\mu\text{m}$ ).

## Claims

1. A condenser system comprising a substrate having a vapor condensing surface, wherein the vapor condensing surface comprises a metal coating and a top coating; wherein the top coating comprises a perfluorinated compound or a polymer-based compound; and wherein the metal coating is produced by applying an aqueous solution of metal particles to the vapor condensing surface, wherein the aqueous solution of metal particles is in a concentration of less than or equal to about 0.5 mM.
2. The condenser system of claim 1, wherein the substrate is a copper substrate or a copper alloy substrate.
3. The condenser system of claim 2, wherein the metal coating is silver.
4. The condenser system of claim 3, wherein the aqueous solution of metal particles is an aqueous solution of silver nitrate.
5. The condenser system of claim 4, wherein the top coating is a perfluorinated compound.
6. The condenser system of claim 5, wherein the perfluorinated compound is perfluorooctyl triethoxysilane.
7. A coated condenser tube comprising a condenser tube having a vapor condensing surface, wherein the vapor condensing surface comprises a metal coating and a top coating; wherein the top coating comprises a perfluorinated compound or a polymer-based compound; and wherein the metal coating is produced by applying an aqueous solution of metal particles to the vapor condensing surface, wherein the aqueous solution of metal particles is in a concentration of less than or equal to about 0.5 mM.
8. The coated condenser tube of claim 7, wherein the condenser tube is copper tube or a copper alloy tube.
9. The coated condenser tube of claim 8, wherein the metal coating is silver.
10. The coated condenser tube of claim 9, wherein the aqueous solution of metal particles is an aqueous solution of silver nitrate.
11. The coated condenser tube of claim 10, wherein the top coating is a perfluorinated compound.

12. The coated condenser tube of claim 11, wherein the perfluorinated compound is perfluorooctyl triethoxysilane.

13. A method of manufacturing a coated condenser tube comprising

- 5           a. contacting a condenser tube with an aqueous solution of metal particles having a concentration of less than or equal to about 0.5 mM, to provide a metal nanoparticle coated surface; and  
          b. contacting the metal nanoparticle coated surface with a top coating mixture comprising a perfluorinated compound or a polymer-based compound.

10       14. The method of claim 13, wherein the condenser tube is copper tube or a copper alloy tube.

15. The method of claim 14, wherein the aqueous solution of metal particles is an aqueous solution of silver nitrate.

15       16. The method of claim 15, wherein the top coating mixture comprises a perfluorinated compound.

17. The method of claim 16, wherein the top coating mixture further comprises an alcohol solvent.

18. The method of claim 17, wherein the alcohol solvent is methanol or ethanol.

20       19. The method of claim 18, wherein perfluorinated compound is perfluorooctyl triethoxysilane.

20. The method of claim 19, wherein the top coating mixture is about 0.3 to about 1.5 wt% of perfluorooctyl triethoxysilane in ethanol.

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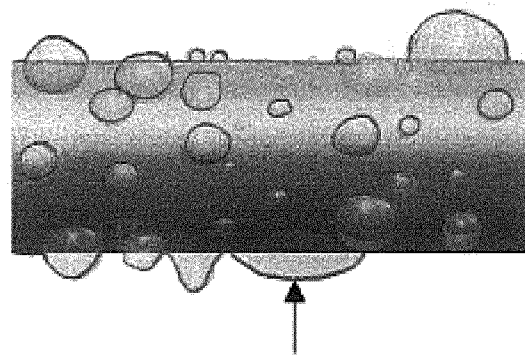
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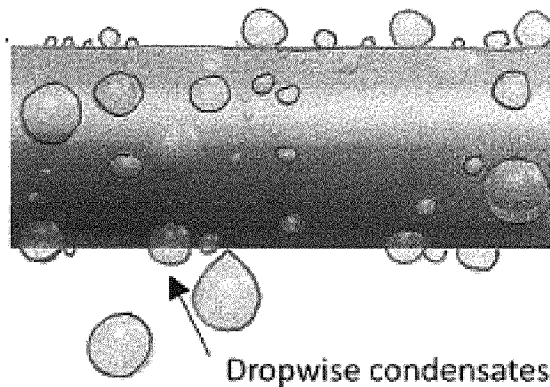
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Filmwise condensates

FIG. 1A



Dropwise condensates

FIG. 1B

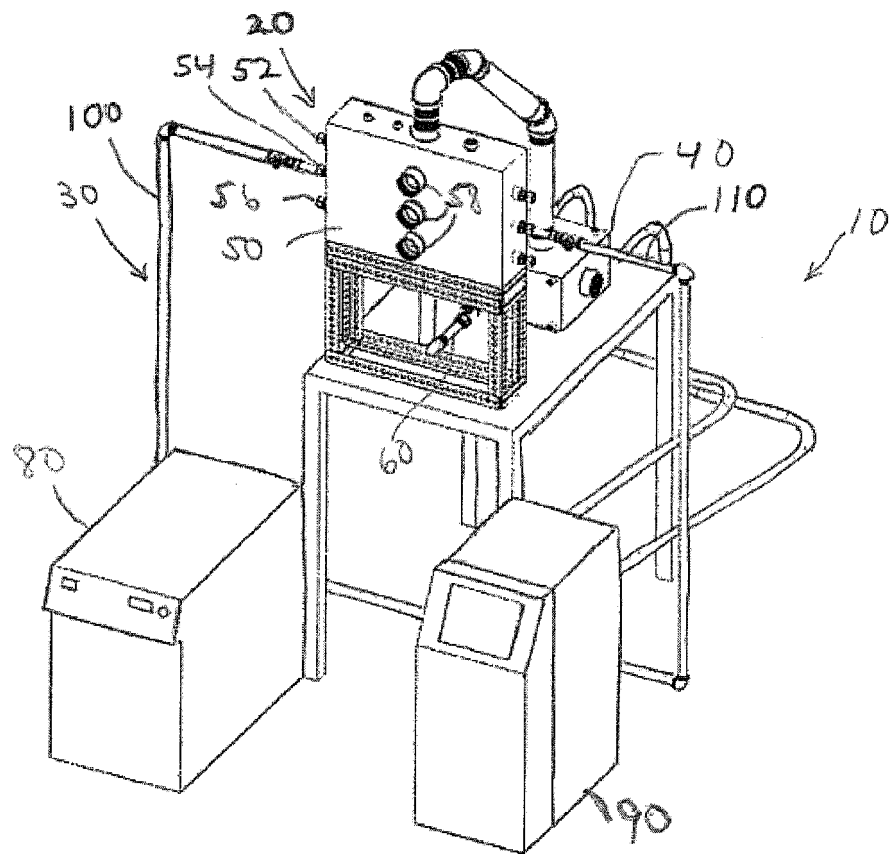


Figure 2A

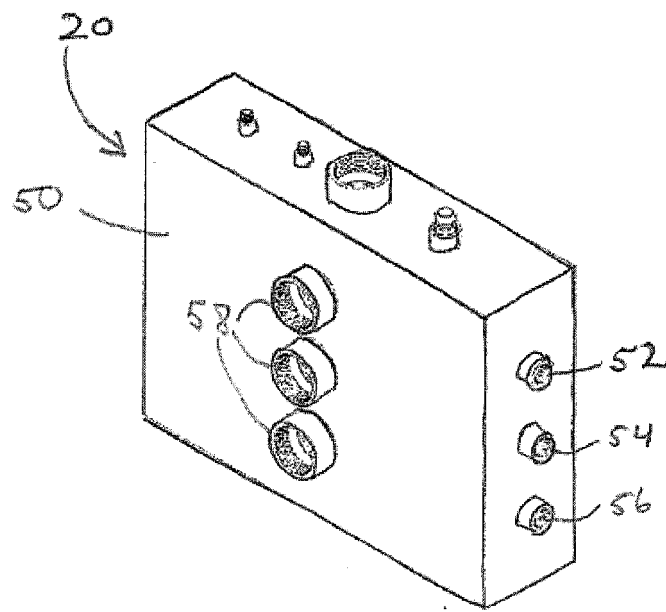
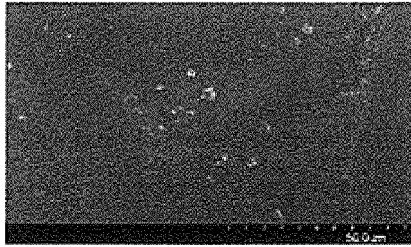
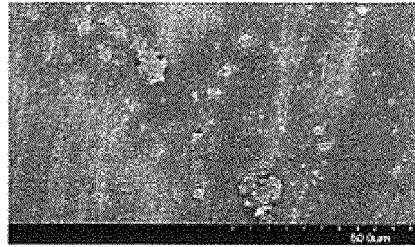


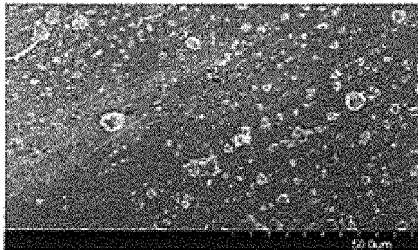
Figure 2B



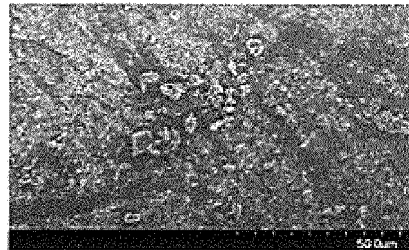
**FIG. 3A**



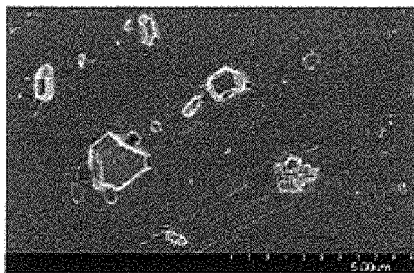
**FIG. 3B**



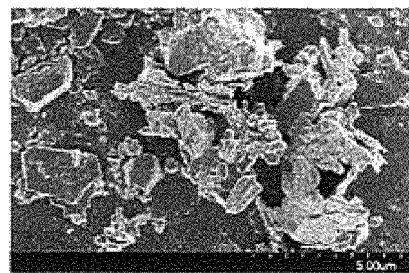
**FIG. 3C**



**FIG. 3D**

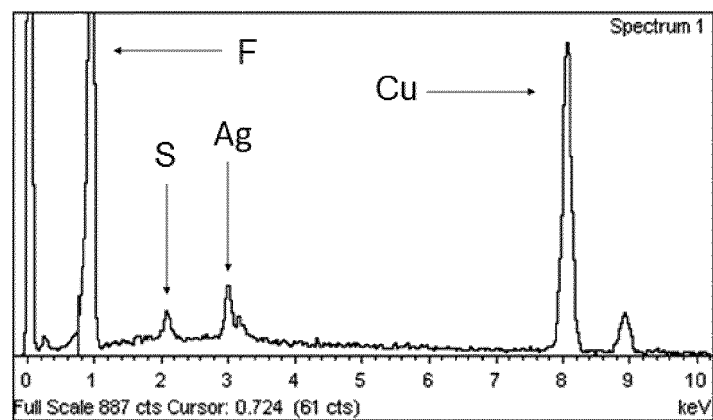


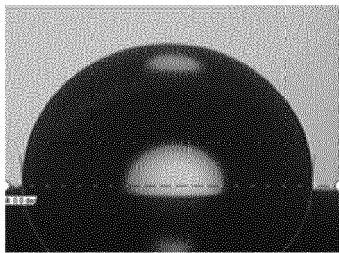
**FIG. 3E**



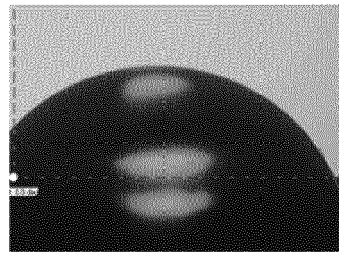
**FIG. 3F**

**FIG. 4**

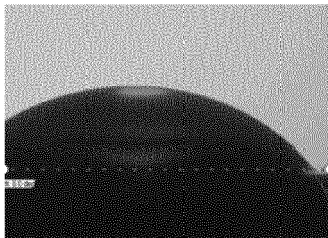




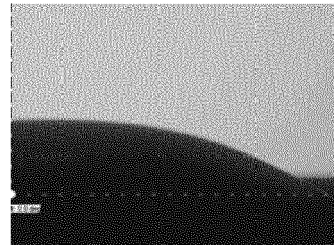
**FIG. 5A**



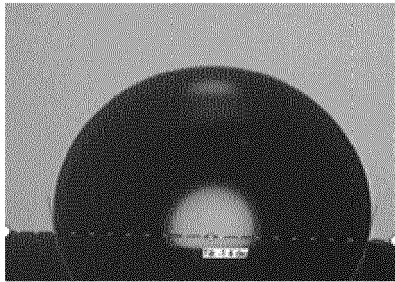
**FIG. 5B**



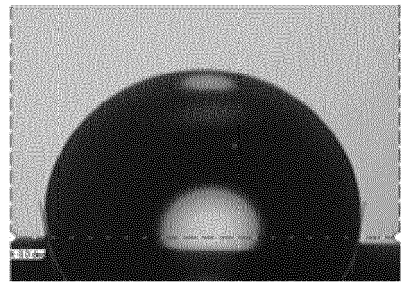
**FIG. 5C**



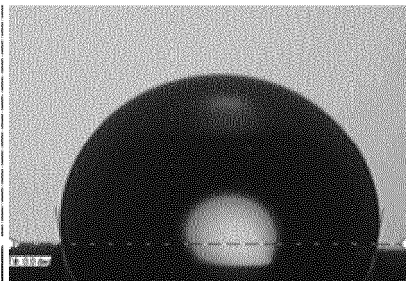
**FIG. 5D**



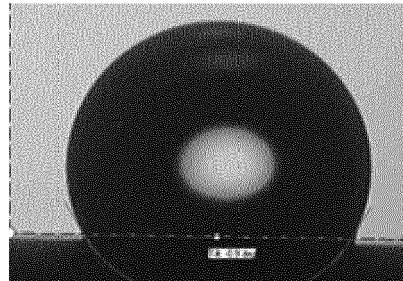
**FIG. 6A**



**FIG. 6B**



**FIG. 6C**



**FIG. 6D**

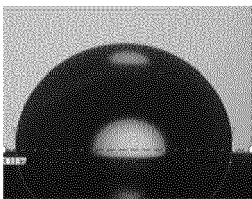


FIG. 7A

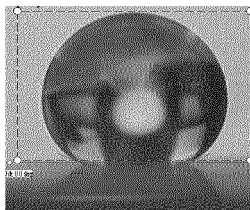


FIG. 7B

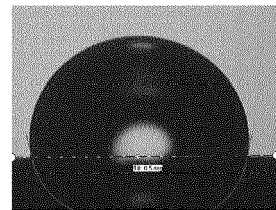


FIG. 7C

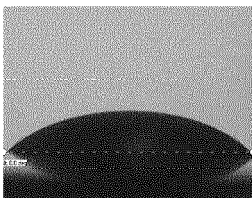


FIG. 7D

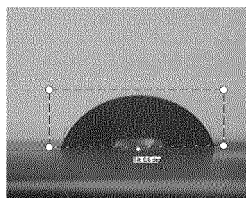


FIG. 7E

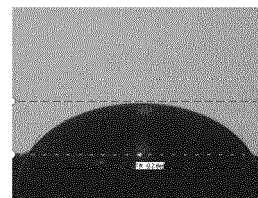


FIG. 7F



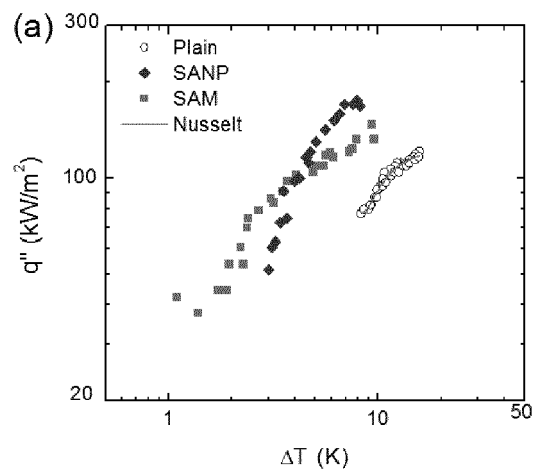


FIG. 8A

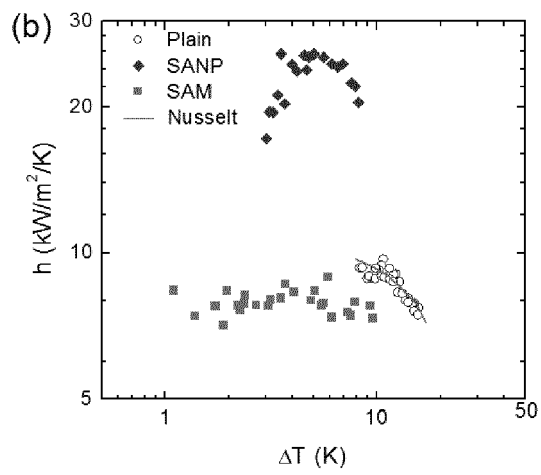
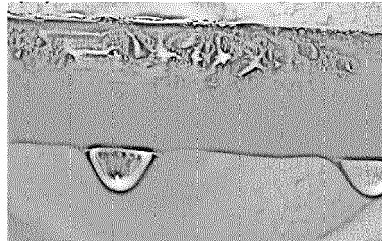
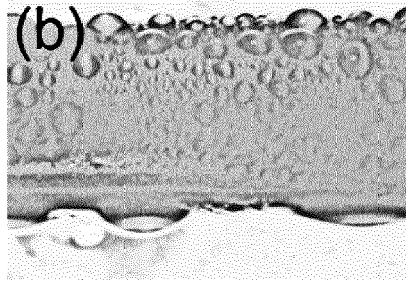


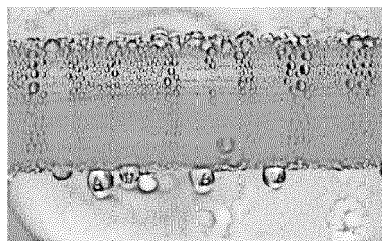
FIG. 8B



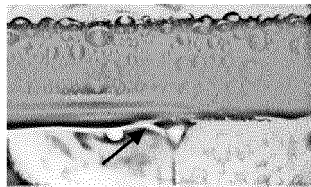
**FIG. 9A**



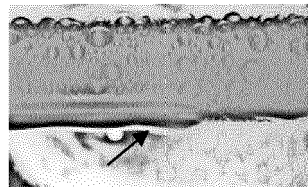
**FIG. 9B**



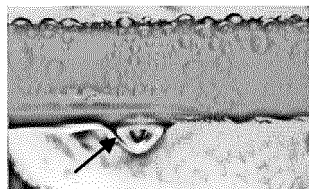
**FIG. 9C**



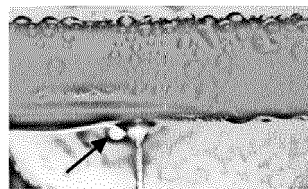
**FIG. 10A**



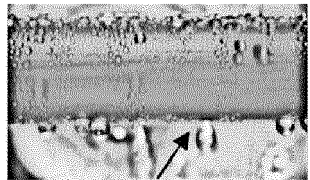
**FIG. 10B**



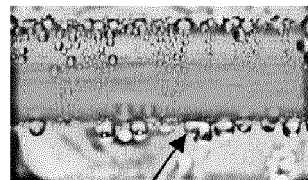
**FIG. 10C**



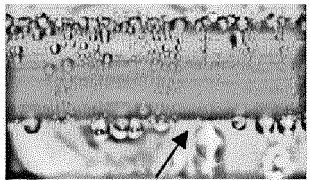
**FIG. 10D**



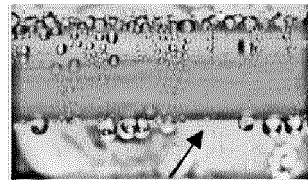
**FIG. 11A**



**FIG. 11B**



**FIG. 11C**



**FIG. 11D**

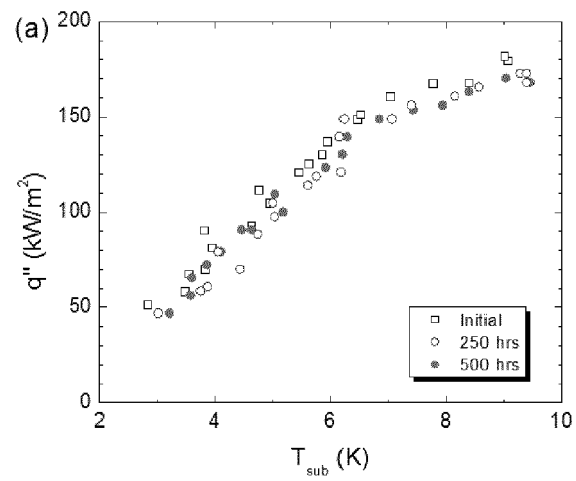


FIG. 12A

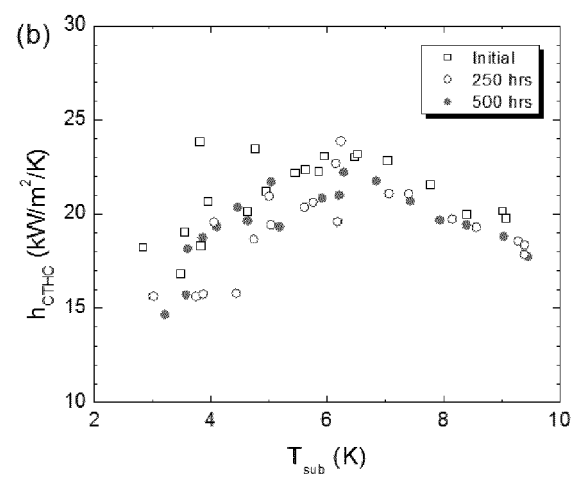


FIG. 12B

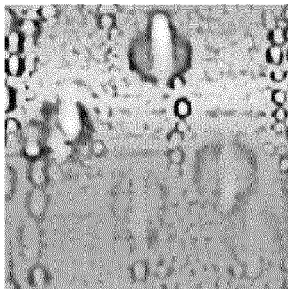


FIG. 13A

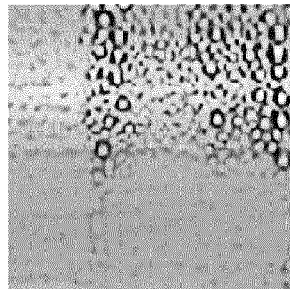


FIG. 13C

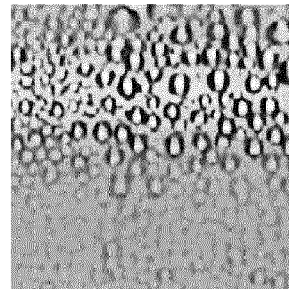


FIG. 13E

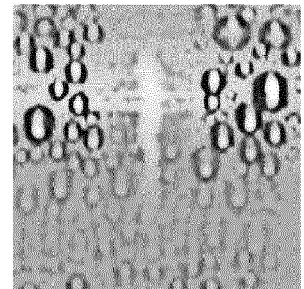


FIG. 13G

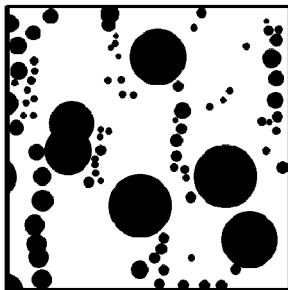


FIG. 13B

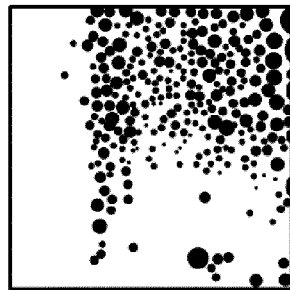


FIG. 13D

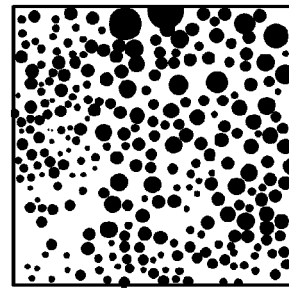


FIG. 13F

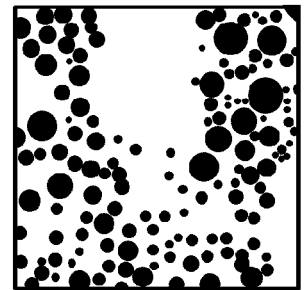
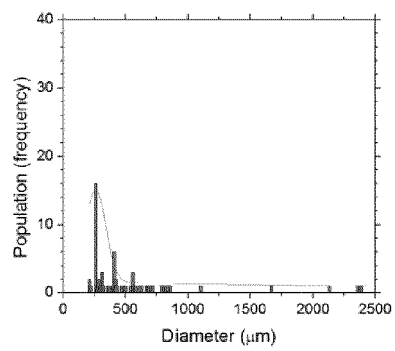


FIG. 13H

(e)

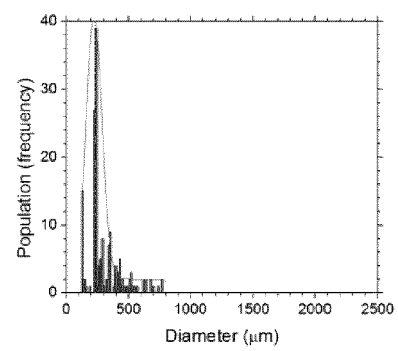


**FIG. 13I**

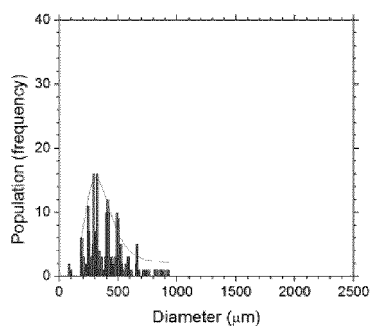
(f)

(g)

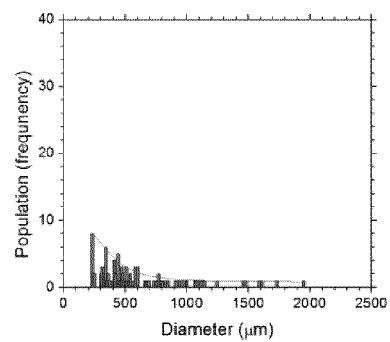
(h)



**FIG. 13J**



**FIG. 13K**



**FIG. 13L**

FIG. 14

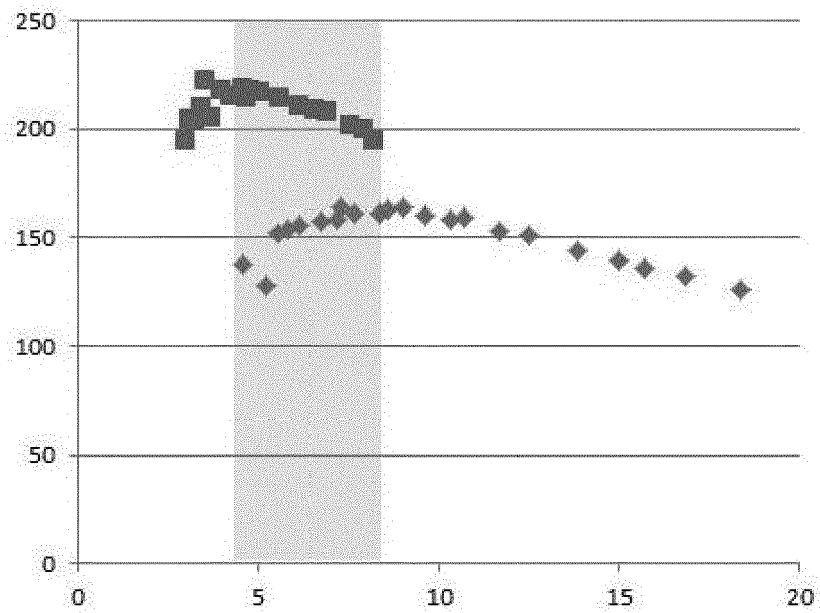
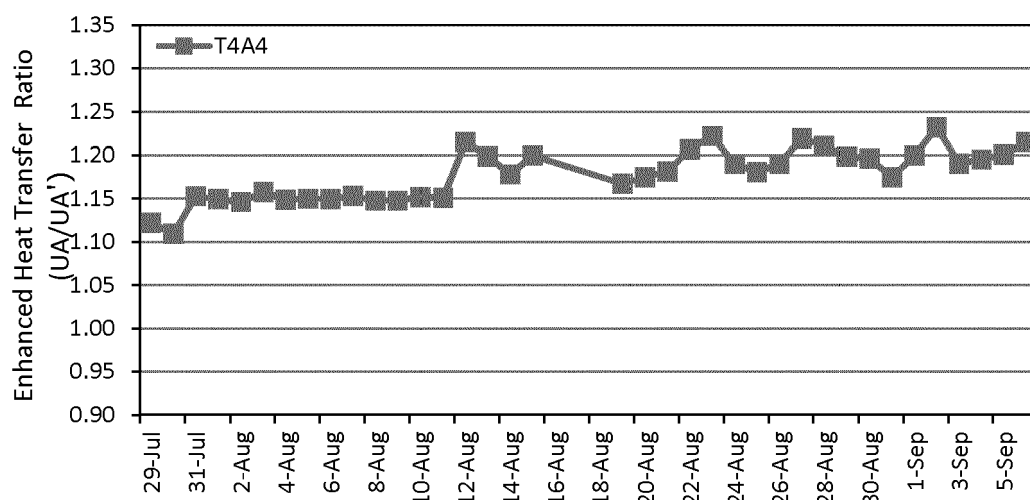




FIG. 15





## EUROPEAN SEARCH REPORT

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| DOCUMENTS CONSIDERED TO BE RELEVANT  |   |   |   |
|--|---|---|---|
| Category   | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim                                 | CLASSIFICATION OF THE APPLICATION (IPC)         |
| X  | US 2010/143741 A1 (BELL STEVEN ERNEST JOHN [GB] ET AL) 10 June 2010 (2010-06-10)  | 1-5, 7-11, 13-18                                  | INV.<br>F28F13/18<br>B05D7/14<br>B05D1/18       |
| A  | * paragraphs [0018] - [0020], [0026] - [0033], [0042], [0047] - [0049], [0056] - [0068], [0082] - [0094] *<br>* paragraphs [0112], [0114], [0116], [0120], [0156]; examples 1-4; table 2 *  | 6,12,19, 20                                       |   |
| X,D  | BONG JUNE ZHANG ET AL: "Dropwise steam condensation on various hydrophobic surfaces: Polyphenylene sulfide (PPS), polytetrafluoroethylene (PTFE), and self-assembled micro/nano silver (SAMS)", INTERNATIONAL JOURNAL OF HEAT AND MASS TRANSFER., vol. 89, 3 June 2015 (2015-06-03), pages 353-358, XP055467638, GB<br>ISSN: 0017-9310, DOI: 10.1016/j.ijheatmasstransfer.2015.05.060 | 1-4, 7-10, 13-15                                  |   |
| A  | * abstract *<br>* Sections 2, 3.1; figures 1,2 *  | 5,6,11, 12,16-20                                  | TECHNICAL FIELDS SEARCHED (IPC)<br>B05D<br>F28F |
| X,D  | CHANGDONG GU ET AL: "Micro/Nanobinary Structure of Silver Films on Copper Alloys with Stable Water-Repellent Property under Dynamic Conditions", LANGMUIR, vol. 25, no. 20, 20 October 2009 (2009-10-20), pages 12299-12307, XP055467647, US<br>ISSN: 0743-7463, DOI: 10.1021/la902936u   | 1-4, 7-10, 13-15                                  |   |
| A  | * Sections 1, 2, 3.1, 4 *   | 5,6,11, 12,16-20                                  |   |
| -----<br>-/--  |   |   |   |
| The present search report has been drawn up for all claims   |   |   |   |
| Place of search<br>Munich  |   | Date of completion of the search<br>23 April 2018 | Examiner<br>Tsipouridis, P                      |
| CATEGORY OF CITED DOCUMENTS<br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document<br>T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |   |   |   |

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## EUROPEAN SEARCH REPORT

Application Number  
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| DOCUMENTS CONSIDERED TO BE RELEVANT  |  |   |   |
|--|--|---|---|
| Category   | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim                                 | CLASSIFICATION OF THE APPLICATION (IPC) |
| A  | WO 2014/064450 A1 (OXFORD NANOSYSTEMS [GB]) 1 May 2014 (2014-05-01)<br>* page 5, line 24 - page 6, line 9 *<br>* page 9, line 16 - page 11, line 28 *<br>----- | 1-20  |   |
|  |  |   | TECHNICAL FIELDS SEARCHED (IPC)         |
|  |  |   |   |
| The present search report has been drawn up for all claims   |  |   |   |
| Place of search<br>Munich  |  | Date of completion of the search<br>23 April 2018 | Examiner<br>Tsipouridis, P              |
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