

US 20140000857A1

(19) United States

(12) Patent Application Publication KING

(10) Pub. No.: US 2014/0000857 A1

(43) Pub. Date: Jan. 2, 2014

(54) REFRIGERANT REPELLING SURFACES

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- (21) Appl. No.: 13/922,181
- (22) Filed: Jun. 19, 2013

Related U.S. Application Data

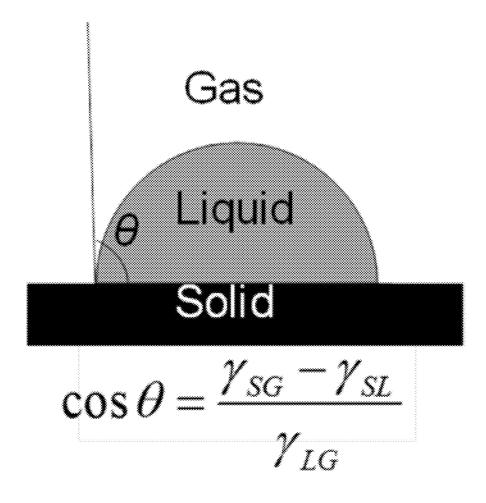
(60) Provisional application No. 61/661,701, filed on Jun. 19, 2012.

Publication Classification

(51) **Int. Cl.** F25B 39/04 (2006.01)

(57) ABSTRACT

Methods and devices for dropwise condensation of a refrigerant vapor on a surface are provided. The surface and various aspects of the system are configured to ensure the surface is refrigerant repelling, enhances droplet mobility, increases condensation rate and/or increases heat transfer rate. The refrigerant repelling surface may be configured so that a refrigerant that may normally wet a flat non-textured surface is instead repelled



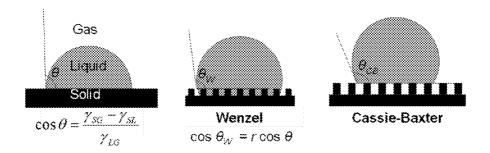


Fig. 1a

Fig. 1b

Fig. 1c

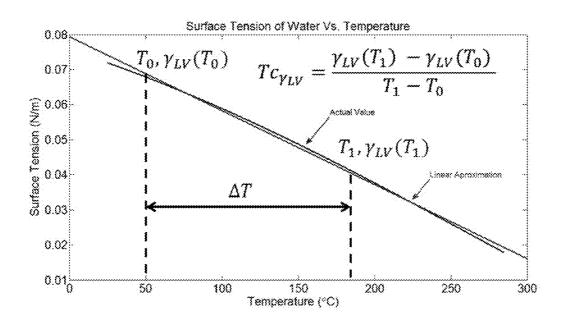


Figure 2

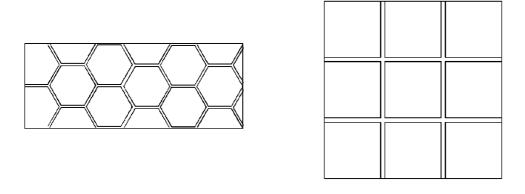


Figure 3A

Figure 3B

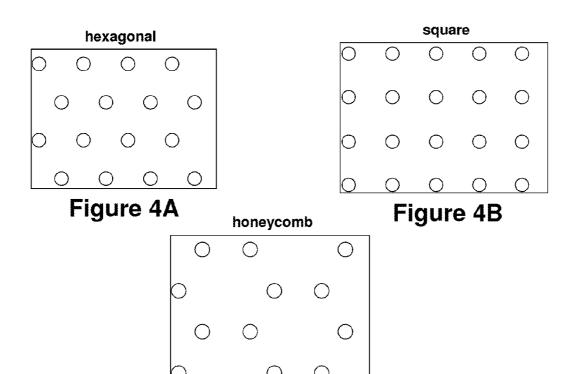


Figure 4C

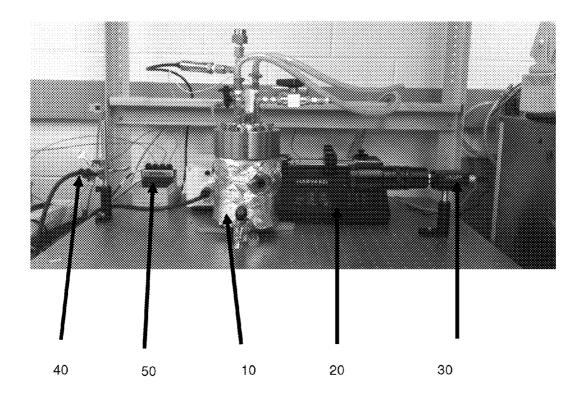
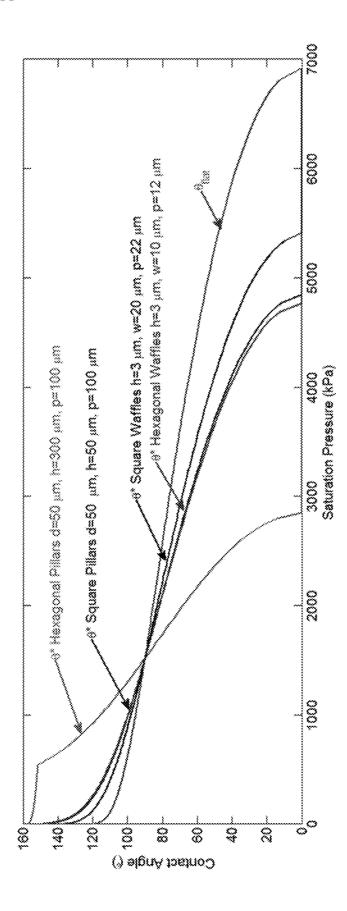


Fig. 5





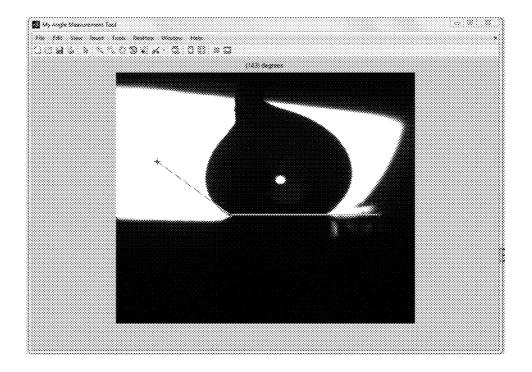


Figure 7

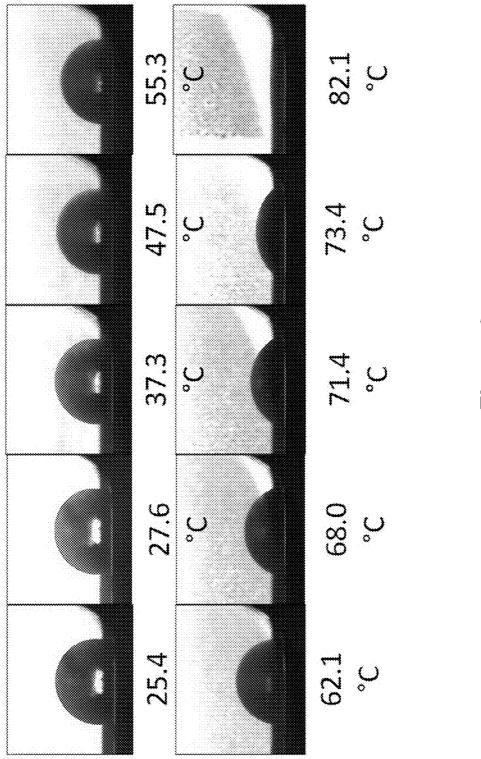


Figure 8

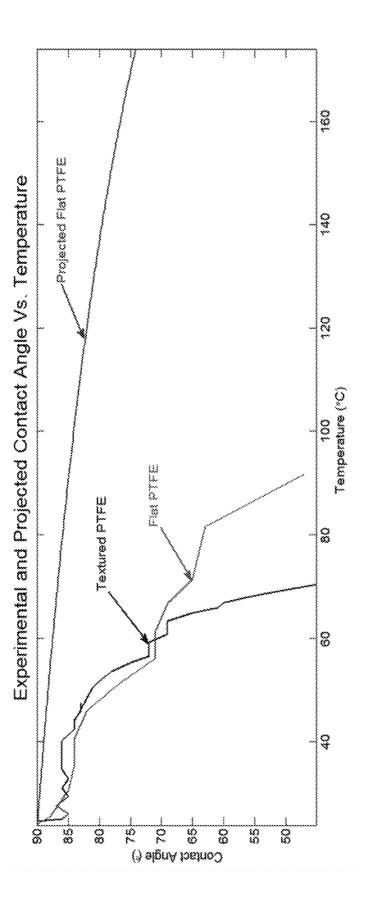
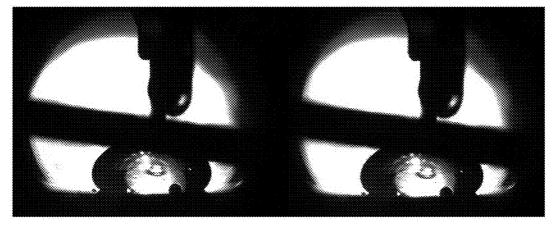
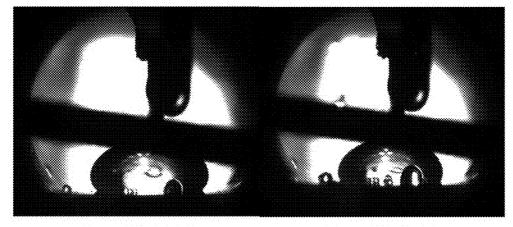


Figure 9



 $T = 31.7 \, ^{\circ}\text{C P} = 9.2 \, \text{kPa}$

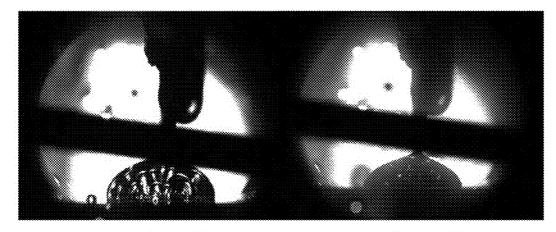
 $T = 33.9 \, ^{\circ}C$



T = 39.0 °C

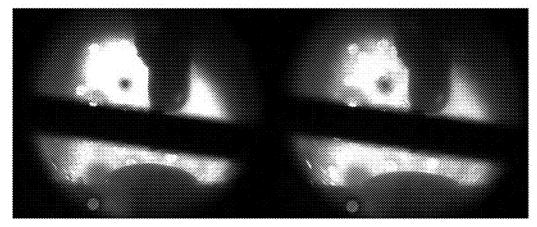
T = 43.2 °C

Figure 10A



T = 46.4 °C

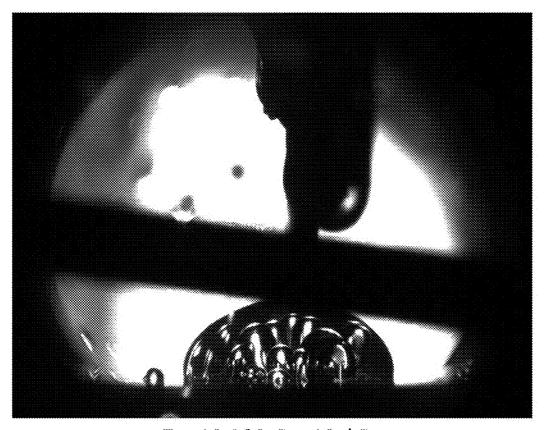
T = 46.9 °C



T = 52.6 °C

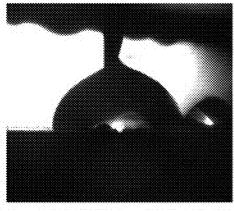
 $T = 54.1 \, ^{\circ}\text{C P} = 15.0 \, \text{kPa}$

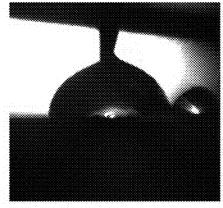
Figure 10B



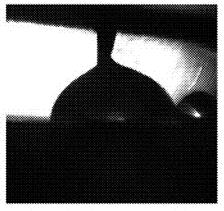
T = 46.4 °C, P = 12. kPa

Figure 10C





T = 29.2 °C P = 34.5 kPa T = 32.5 °C P = 45.5 kPa





T = 34.4 °C P = 51.0 kPa T = 34.4 °C P = 51.0 kPa

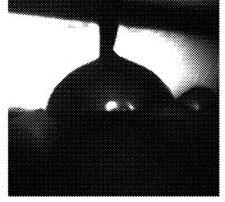




Figure 11

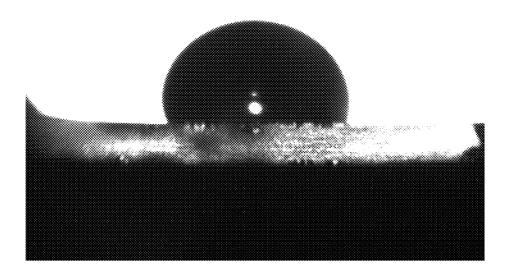


Figure 12

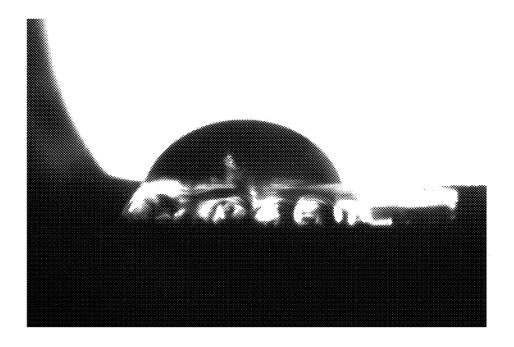
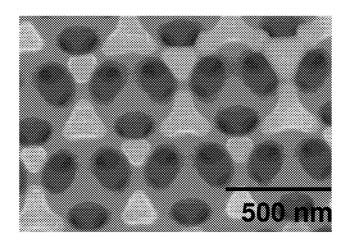


Figure 13



SEM Image of Textured Surface Figure 14

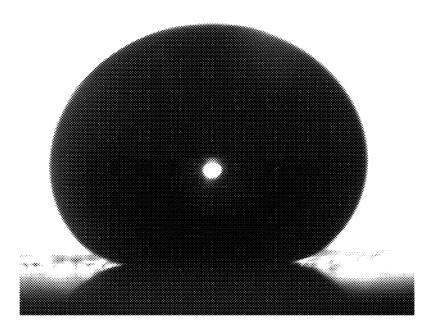
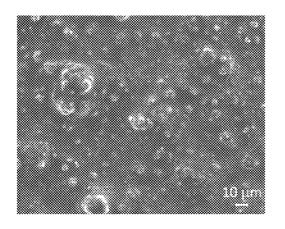


Figure 15



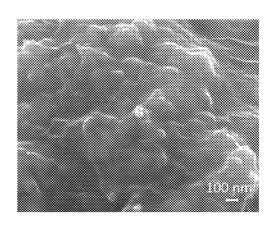


Fig. 16a

Fig. 16b

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Figure 17

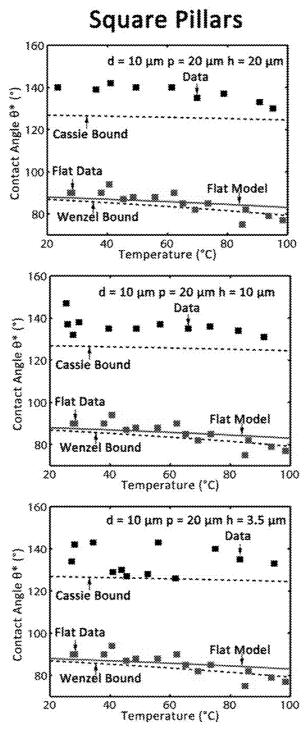


Fig. 18a

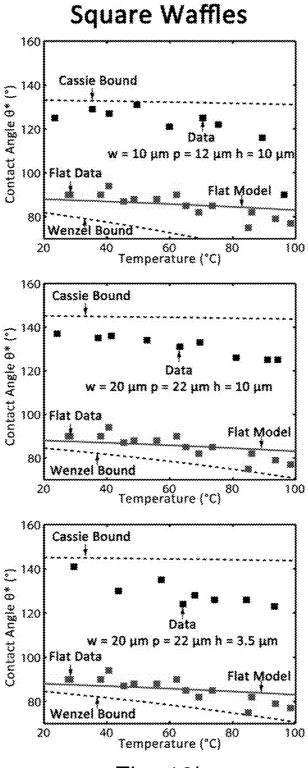


Fig. 18b

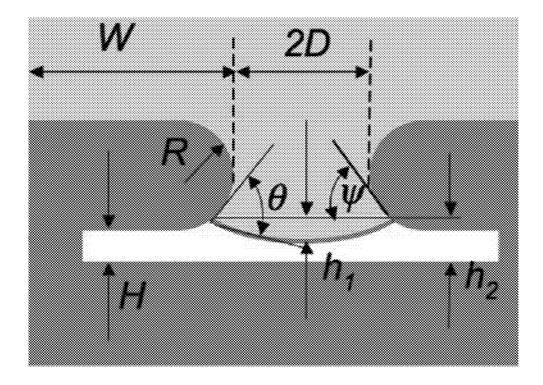


Fig. 19

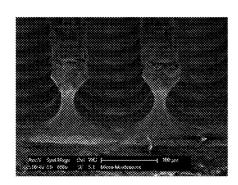


Fig. 20a

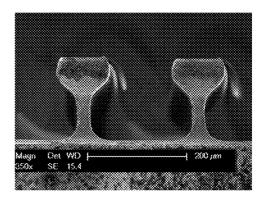


Fig. 20b

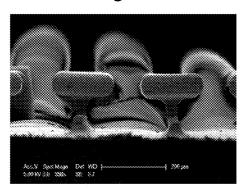


Fig. 20c

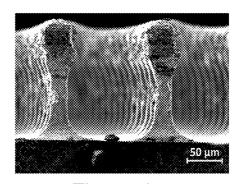


Fig. 20d

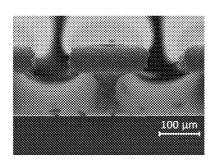


Fig. 20e

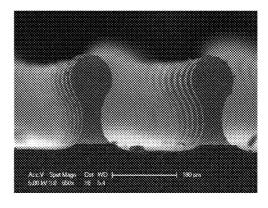


Fig. 20f

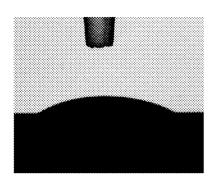


Fig. 21a

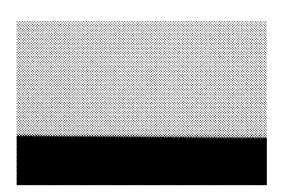


Fig. 21b

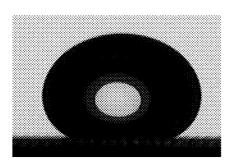


Fig. 21c

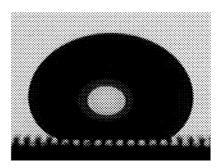
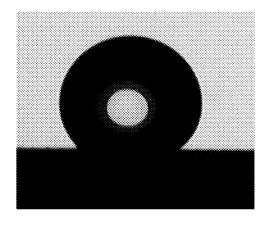


Fig. 21d



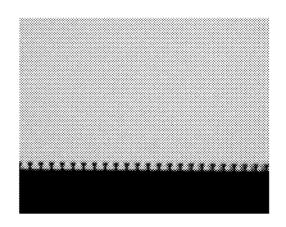
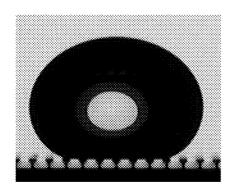


Fig. 22a

Fig. 22b





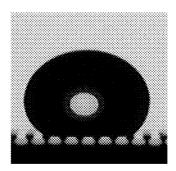


Fig. 22d

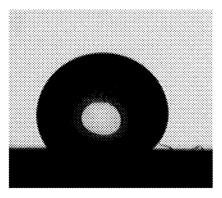


Fig. 23a

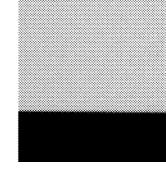


Fig. 23b

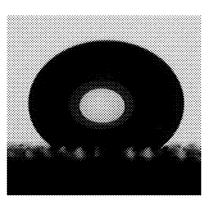


Fig. 23c

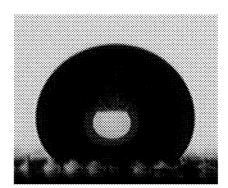
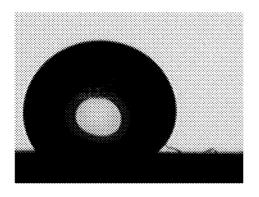


Fig. 23d



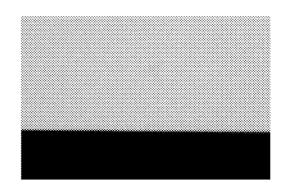
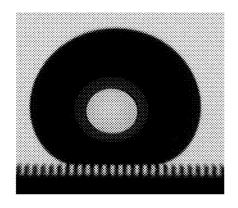


Fig. 24a

Fig. 24b



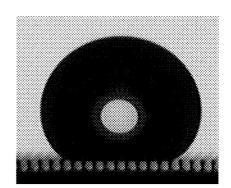
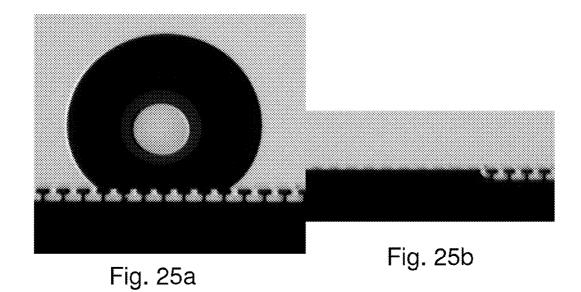


Fig. 24c

Fig. 24d



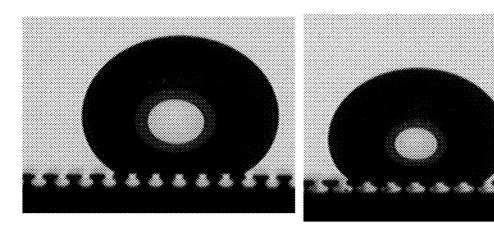


Fig. 25d Fig. 25c

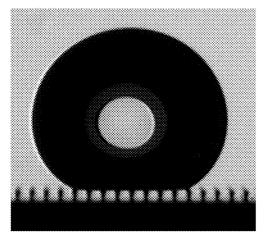
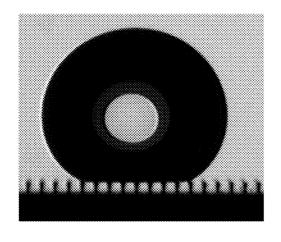




Fig. 26a

Fig. 26b





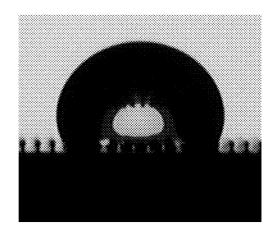


Fig. 26d

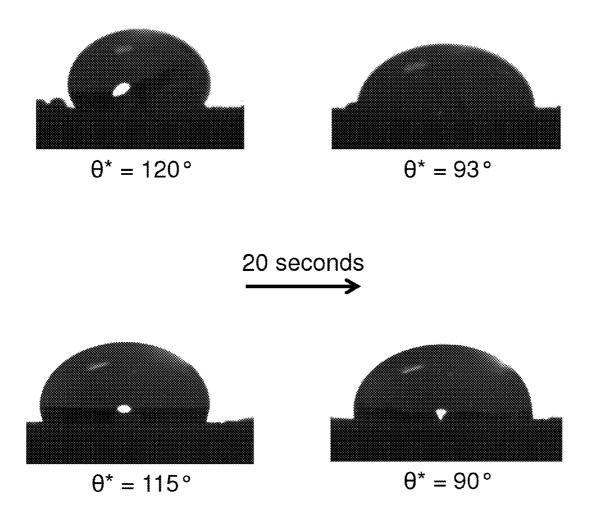


Figure 27

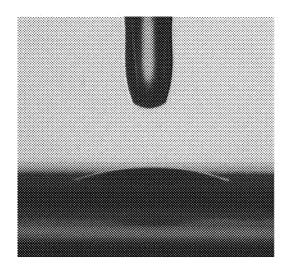


Fig. 28a

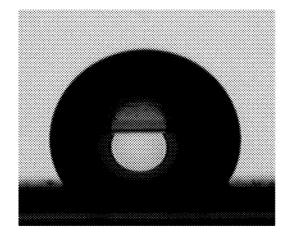


Fig. 28b

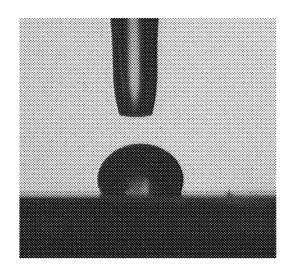
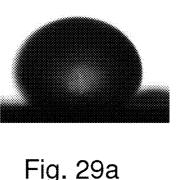


Fig. 28c



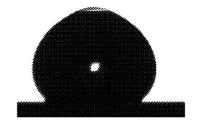


Fig. 29a

Fig. 29b





Fig. 29c

Fig. 29d





Fig. 29e

Fig. 29f



Fig. 30a



Fig. 30b



Fig. 30c



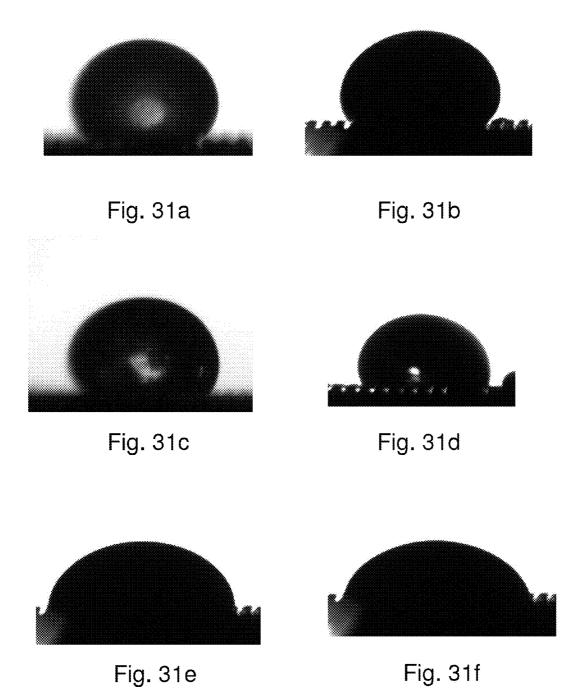
Fig. 30d

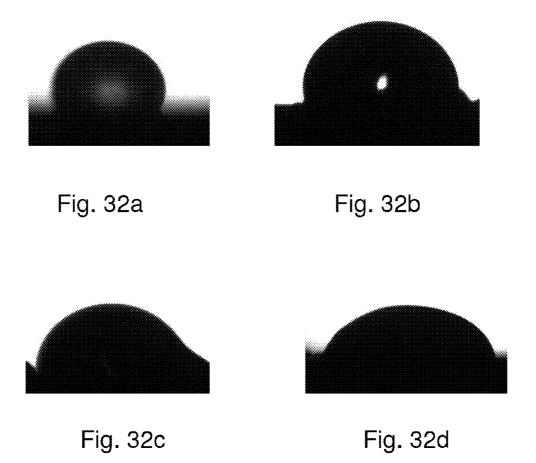


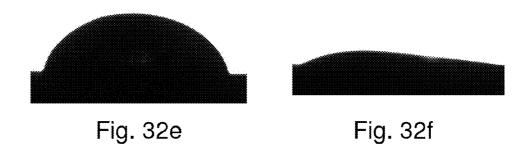
Fig. 30e

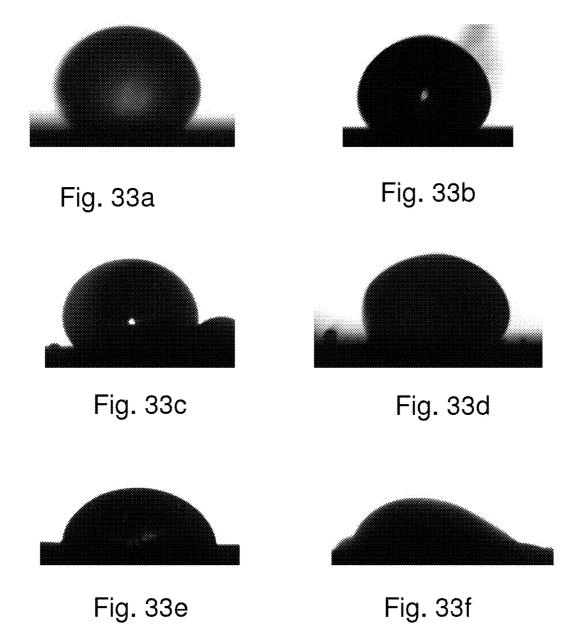


Fig. 30f









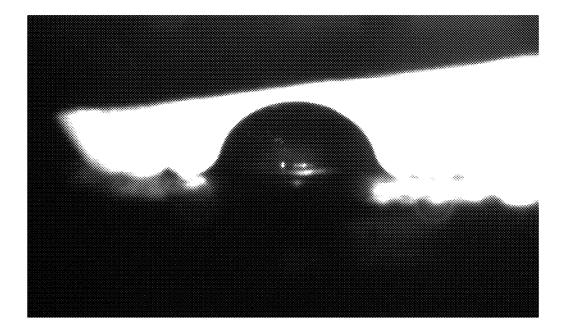
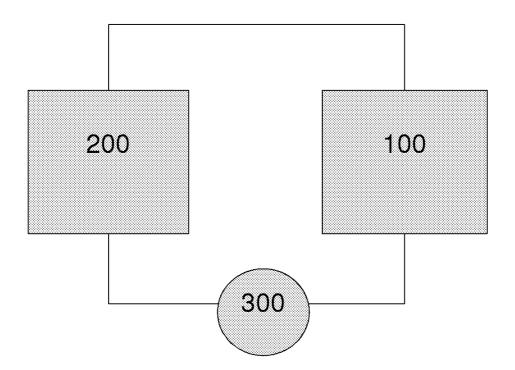


Fig. 34

Fig. 35



REFRIGERANT REPELLING SURFACES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application 61/661,701 filed Jun. 19, 2012, which is hereby incorporated by reference to the extent not inconsistent with the disclosure herein.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under contract number N00014-12-1-0014 awarded by the Office of Naval Research. The government has certain rights in the invention.

BACKGROUND

[0003] For a liquid droplet on a solid substrate, the contact angle may be defined as the interior angle formed by the substrate and the tangent to the interface between the liquid and gas or vapor at the apparent intersection of the substrate, liquid and gas or vapor phases (see FIG. 1a). The dimension of the droplet is often comparable to or smaller than the capillary length of the liquid. The contact angle may be measured or calculated from images of the droplet on the substrate. The substrate is characterized as being wetted if the contact angle between the droplet and the substrate is less than 90°; or non-wetted if the contact angle between the droplet and the substrate is greater than 90°. When the liquid is water, the surface is considered hydrophobic when the contact angle between the water droplet and the substrate is greater than 90°. Similarly, when the liquid is an oil, the surface is considered oleophobic when the contact angle between the refrigerant droplet and the substrate is greater than 90°.

[0004] On a relatively smooth surface, the relationship between the contact angle and the relevant surface and interfacial energies may be given by Young's equation (Equation 1). However, on a rough surface, the apparent contact angle of the droplet may differ from that measured on a smooth surface. In some cases, the droplet may sit on top of surface features so that a composite (solid-liquid-vapor) interface is formed, as shown in FIG. 1c (right, labeled Cassie-Baxter). Tuteja et al. (Science, 318, 1618, 2007) describe formation of composite interfaces on re-entrant curved surfaces with the drop sitting partially on air; contact angle measurements are given for octane on a silane coated smooth surface (advancing contact angle approx. 55°, receding approx.) 50° and a rough "microhoodo" surface (advancing contact angle approx. 163°, receding approx. 145°). Re-entrant curvature may be characterized by a surface topography which cannot be described by a simple univalued function z=h(x,y) and for which a vector projected normal to the x-y plane intersects the texture more than once (Tuteja et al, 2008, Proc. Nat. Acad. Sci, 105(47), 18200-18205).

[0005] Condensation of a liquid phase from a vapor phase occurs in condenser heat transfer devices used in power generation and refrigeration systems. When the latent heat of vaporization is released during condensation on a surface, heat is transferred to the surface. During the condensation process, the condensing liquid may form a film over the entire surface in a process termed filmwise condensation. Alternately the condensed liquid may form as drops on the surface

in a process termed dropwise condensation. Higher heat transfer coefficients have been reported for dropwise condensation of steam than filmwise condensation at atmospheric pressure (Rose 2002, Dropwise condensation theory and experiment: a review, Proc Instn Mech Engrs, 216(Part 4): 115-128).

BRIEF SUMMARY

[0006] Provided herein are methods and devices related to heat transfer, such as by dropwise condensation of a refrigerant vapor on a surface. In an aspect, the surface and various aspects of the system are configured to ensure the surface is refrigerant repelling. In an embodiment, the refrigerant repelling surface is configured so that a refrigerant that may normally wet a surface is instead repelled The surface and various aspects of the system may also be configured to enhance droplet mobility, condensation rate and/or the heat transfer coefficient.

[0007] In an embodiment, the systems and devices of the invention are configured so as to increase the contact angle between a condensed droplet and a surface. For example, the contact angle may be increased as compared to the contact angle on a droplet of the same liquid on a flat smooth surface of the same material. Relevant aspects that facilitate an increase in contact angle include surface characteristics, fluid characteristics, and physical process characteristics. Surface characteristics include surface composition and/or surface geometry, such as position and geometry of relief or recessed features. Relevant fluid characteristics include molecular weight, surface tension, liquid-vapor interfacial energy, liquid-solid interfacial energy, solid-vapor interfacial energy, vapor pressure, saturation temperature, saturation pressure, critical temperature, and critical pressure. Accordingly, any of the methods and devices provided herein can relate to selection of any one or more of these aspects so as to ensure a maximal or acceptable increase in contact angle. Whether or not a surface is considered a repelling surface may be influenced by contact angle between a condensed droplet and the contact surface. In an embodiment, a refrigerant-repelling surface may be textured to provide a nonwetting surface even for surface-refrigerant systems that may normally be considered as wetting systems.

[0008] Examples of relevant physical process characteristics affecting the refrigerant-repellency of a surface include pressure, temperature and composition of the atmosphere. Another process characteristic that may affect the refrigerantrepellency of the surface is the condensation rate within the heat transfer device. Provided herein are methods and devices for accurately operating at atmospheric pressure or at nonatmospheric pressures, including below atmospheric pressure, above atmospheric pressure and substantially above atmospheric pressure. In addition, many conventional systems suffer from the limitation of having air present in the atmosphere of the heat transfer system. Provided herein are methods and devices wherein the atmosphere composition is substantially vapor of the refrigerant, including an atmosphere which contains either no air or negligible amounts of air. It has been observed that the vapor pressure of refrigerant in the atmosphere can affect the contact angle of a droplet on a surface; in some cases the characteristic or apparent contact angle may be lower in a vapor saturated atmosphere as compared to an air atmosphere (see Example 2 and FIG. 17). In these cases, increasing the contact angle of a liquid droplet on a surface when the atmosphere is substantially vapor of the

refrigerant may be more difficult than for a droplet exposed to an atmosphere which is essentially air. In this manner, precise control over operating parameters are achieved, providing the ability tailor the process and device to particular refrigerant/ substrate systems to achieve maximum possible increase in contact angle, thereby increasing the repellency of the surface to condensed droplets of refrigerant vapor.

[0009] In one aspect, the invention provides methods for condensation heat transfer which lead to dropwise condensation of refrigerant or working fluid. In an embodiment, the dropwise condensation heat transfer methods of the invention can lead to heat transfer exceeding 1 kW/cm². In different embodiments, the condensation heat transfer processes of the invention take place under saturation conditions, under near saturation conditions, under conditions where the vapor is superheated, under conditions where the surface is undercooled or combinations thereof. In an embodiment, the condensation heat transfer processes of the invention take place under saturation conditions.

[0010] In an embodiment, the invention provides a method for condensation heat transfer comprising condensing a refrigerant vapor on a textured portion of an interior surface of a chamber to form a plurality of refrigerant droplets at a user selected pressure, thereby transferring heat from the refrigerant vapor to the interior surface wherein the user selected pressure is not atmospheric pressure, the textured portion of the interior surface comprises surface features, the surface features comprising a surface material and the apparent contact angle of the refrigerant droplets on the surface features is non-zero and greater than the characteristic contact angle of the refrigerant droplets on the surface material of the surface features.

[0011] In the methods of the invention, the apparent contact angle may be greater than the characteristic contact angle by at least 20 degrees or by at least 45 degrees. The methods of the invention may comprise condensing a refrigerant vapor on a textured surface to form a plurality of refrigerant droplets having an apparent contact angle greater than 90°. In different embodiments, the apparent contact angle of the droplets may be greater than 90° to less than or equal to 180°, 160°, 150°, 140°, 130°, 120°, or 110°. The refrigerant may comprise a halocarbon or hydrocarbon refrigerant and a lubricant such as a polyol ester or polyalkylene glycol lubricant. The composition of the refrigerant vapor may vary with position in the heat exchanger. In different embodiments, the refrigerant vapor may contain up to 5%, 10%, 15%, 20%, 25%, 30%, 40%, 45% or 50% by mass lubricant. The textured surface may comprise elevated or relief surface features. The surface features may form a "waffle" pattern as schematically illustrated in FIGS. 3A and 3B, Other surface features may have a reentrant geometry and may take the general form of "micromushrooms" schematically illustrated in cross-section in FIG. 19. In addition, the textured surface comprises a surface material. The surface material may be a material with relatively low surface energy such as a fluorosilane or a polymer formed as a coating on the interior of the chamber. Other suitable type of surface coating materials is a mixture comprising a polymer such as polydimethylsiloxane (PDMS) and a filler material, such as zinc oxide or silica. In an embodiment, nonwetting refrigerant droplets can be achieved on the textured surface even though droplets of the refrigerant wet nontextured surface material. In different embodiments of the present invention, the characteristic contact angle of the refrigerant on the surface materials is less than 75°, less than

 60° , less than 50° , less than 40° , less than 30° , less than 20° , less than 10° or less than 5° . In other embodiments, a plurality of refrigerant droplets on the textured surface have an apparent contact angle of 90° or less than 90° , but the apparent contact angle is greater than the characteristic contact angle of the refrigerant on the surface material. The temperature of the interior surface of the chamber where condensation occurs may be in a preselected temperature range and the surface tension of the refrigerant in the preselected temperature range may be from 5 mN/m to 25 mN/m, 5 mN/m to 20 mN/m, 5 mN/m to 15 mN/m or 5 mN/m to 10 mN/m.

[0012] The textured surface may be located inside a chamber such as a pressure vessel or vacuum chamber. The condensation process can take place under saturation conditions or near saturation conditions. The vapor may also be superheated and/or the surface may be supercooled in at least a portion of the chamber. In an embodiment, the pressure in the vessel may be from 5 kPa to 5 MPa, including specific subranges thereof such as above atmospheric pressure, below atmospheric pressure, or a pressure that is not atmospheric, including substantially not atmospheric. In an embodiment, standard atmospheric pressure may be taken as approximately 101.3 kPa. In an embodiment, the pressure in the vessel may be greater than atmospheric pressure and less than 5 MPa. "Substantially not atmospheric" refers to a pressure range that is at least 20% different from atmospheric. The temperature of the interior surface of the chamber where condensation occurs may be in a preselected range; the preselected range may be the saturation temperature of the refrigerant vapor+/-20%, 15%, 10% or 5%.

[0013] The methods of the invention may also comprise condensing a refrigerant vapor on a textured surface comprising a surface material to form a plurality of refrigerant droplets, wherein the mobility of the droplets is higher on the textured surface than the mobility of droplets formed on an "untextured" or "smooth" surface of the surface material, the condensation rate is higher on the textured surface than the condensation rate of an "untextured" or "smooth" surface of the surface material, and/or the heat transfer coefficient is higher for the textured surface than the heat transfer coefficient on an "untextured" or "smooth" surface of the surface material.

[0014] In another aspect, the invention provides a heat exchanger system which is a closed system containing both liquid and vapor phases. In an embodiment, at least a portion of the heat exchanger system comprises a textured portion, the textured portion of the system facilitating dropwise condensation of refrigerant vapor. The surface features of the texture may vary within the heat exchanger system in accordance with variations in vapor composition, pressure and temperature within the system. The portion of the heat exchanger system comprising the textured portion may be located in a condenser, and the system heat exchanger system may further comprises an evaporator configured to produce a vapor from a source liquid, the evaporator being in fluid communication with the condenser. FIG. 35 schematically illustrates a heat exchanger system comprising a condenser (100), evaporator (200) and compressor (300).

[0015] In an aspect, the invention provides a heat exchanger system for condensation heat transfer through condensation of a refrigerant vapor into droplets of the refrigerant, the heat exchanger system comprising: a chamber comprising an interior hollow portion and an interior surface, the interior surface comprising a textured portion, the textured portion of the

surface comprising surface features, the surface features comprising a surface material wherein the apparent contact angle of the refrigerant droplets on the surface features is greater than the characteristic contact angle of the refrigerant droplets on the surface material of the surface features.

[0016] In another aspect, the invention provides a heat exchanger system for condensation heat transfer, the heat exchanger system comprising:

[0017] a) a chamber comprising an interior hollow portion and an interior surface, the interior surface comprising a textured portion, the textured portion of the surface comprising surface features, the surface features comprising a surface material; and

[0018] b) a refrigerant positioned in the hollow portion of the chamber, the refrigerant being selected from the group consisting of halocarbon, hydrofluorocarbon (HFC), hydrofluoroolefin (HFO) and hydrocarbon (HC) wherein the characteristic contact angle of a refrigerant droplet on the surface material in an atmosphere substantially

comprising refrigerant vapor is less than 50° under saturation conditions. [0019] In another aspect, the invention provides a heat

exchanger system for condensation heat transfer, the heat exchanger system comprising:

[0020] a) a chamber comprising an interior hollow portion and an interior surface, the interior surface comprising a textured portion, the textured portion of the surface comprising surface features, the surface features a surface material; and

[0021] b) a refrigerant positioned in the hollow portion of the chamber, the refrigerant being selected from the group consisting of halocarbon, hydrofluorocarbon (HFC), hydrofluoroolefin (HFO) and hydrocarbon (HC) wherein as measured under saturation conditions or near saturation conditions the mobility of the droplets is higher on the textured surface than the mobility of droplets formed on an smooth surface of the surface material, the condensation rate is higher on the textured surface than the condensation rate of a smooth surface of the surface material, and/or the heat

transfer coefficient is higher for the textured surface than the heat transfer coefficient on a smooth surface of the surface

[0022] In the methods and devices of the invention, the refrigerant may be any suitable refrigerant known to the art. In an embodiment, the refrigerant may comprise a component selected from the group consisting of halocarbon, hydrofluorocarbon (HFC), hydrofluoroolefin (HFO), hydrocarbon (HC) and water or may be selected from the group consisting of halocarbon, hydrofluorocarbon (HFC), hydrofluoroolefin (HFO) and hydrocarbon (HC).

[0023] In an aspect of the invention, the surface characteristics are selected to contribute to refrigerant repellency, increased droplet mobility, increased condensation rate and/ or higher heat transfer coefficient. In an embodiment, the surface features on the interior surface of the pressure vessel comprise nanoparticles. In an embodiment, the average diameter of the nanoparticles is 2-300 nm and the average spacing between nanoparticles is 10-1000 nm. In an embodiment, the elevated features form a network of "walls" surrounding features of lower elevation (relative depressions) to form a "waffle" pattern. The elevated "wall" features may have an average width between 5 nm and 10 microns and an average spacing or pitch between 50 nm and 250 micron or from 5 micron to 100 micron, 10 to 50 microns or from 15 microns to

30 microns. The depth of the depressions may be from 50 nm to 250 microns, from 5 micron to 100 micron, 5 to 50 microns or from 15 microns to 30 microns. The pitch may be greater than the depth of the depressions.

[0024] In another embodiment the surface features comprise elevated features shaped like "micromushrooms" with a "cap" typically wider than the "stem". FIG. 19 illustrates several parameters which can be used to characterize such "micromushroom" structures. Suitable ranges of these parameters for the refrigerants described herein include, but are not limited to: D=40-70, W=20-100, R=25-40 and H=65-110, D=40-60, W=80-100, R=25-40 and H=90-110 and D=45-55, W=90-100, R=30-40 and H=100-110 and intermediate ranges.

[0025] A refrigerant repelling surface may have any surface texture capable of contributing to refrigerant repellency and may be such that the surface features of the textured surface provide a re-entrant geometry or such that surface features form a "waffle" or grid pattern. The surface material composing the refrigerant repelling material may have a relatively low surface energy and may comprise a polymer or a surface treatment material such as a silane coating. In some embodiments, the surface material comprises a fluoropolymer or a fluorosilane. Other materials proposed for use as relatively low surface energy coatings include diamond-like carbon and fluorinated diamond-like coatings.

[0026] In an embodiment, the atmosphere in the pressure vessel substantially comprises refrigerant vapor. For example, the amount of air present in the atmosphere of the pressure vessel may be less than 50%, less than 25%, less than 10%, less than 5%, or about zero.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] FIGS. 1a-1c: Standard conceptual models for a liquid droplet on a flat surface (1a), on a wetted rough surface (1b), and on a partially wetted surface (1c). The wetting state in the middle (1b) is the Wenzel mode, and the wetting state on the right (1c) is the Cassie-Baxter mode.

[0028] FIG. 2: Graphical Representation of $T_{C_{\gamma L^{\prime}}}$ [0029] FIGS. 3A-B: Schematic top view of a hexagonal waffle structure (FIG. 3A) and a grid-like waffle structure

[0030] FIGS. 4A-4C: Schematic top view of different configurations of pillar elements: hexagonal arrangement (FIG. 4A), square arrangement (FIG. 4B), and honeycomb arrangement (FIG. 4C).

[0031] FIG. 5: Experimental apparatus

[0032] FIG. 6: Contact angles plotted at the saturation pressure of water for a given temperature between 25 and 250° C.

[0033] FIG. 7: Image of a droplet of distilled water on a waffle patterned Si wafer coated in PTFE inside of pressure vessel. Image taken at 35.8° C. and 62.0 kPa. Vapor is water.

[0034] FIG. 8: Image sequence of a droplet of water evaporating on a flat Si wafer coated in PTFE inside of the pressure vessel. Images taken at labeled temperatures and corresponding saturation pressures.

[0035] FIG. 9: Plot of temperature dependent contact angle for a textured surface (pillars, d=50 μm h=50 μm p=100 μm) compared to a flat surface and the mathematical model. Vapor is water.

[0036] FIGS. 10a-10b: Image sequence of water droplet on waffle patterned Si wafer coated in PTFE. Droplet heated from 31.7° C. to 54.1° C. Droplet triple line expands outward due to expansion of trapped pockets of water vapor between droplet and surface until reaching a maximum at 46.4° C. Vapor is water. FIG. 10a shows 31.7° C. to 43.2° C. FIG. 10b shows 46.4° C. to 54.1° C.

[0037] FIG. 10c: magnified image of vapor expansion inside of water droplet. (from FIG. 10b) Vapor is water.

[0038] FIG. 11: Image sequence of water droplet on waffle textured (25 μ m squares 50 μ m pitch) Si wafer coated with PTFE inside pressure vessel. As triple line expands, Er decreases from ~90° to ~32° after the trapped water vapor completes expansion inside droplet. Vapor is water.

[0039] FIG. 12: Droplet of water on a glass slide with micro textured surfaces coated in silane inside of pressure vessel. Image taken at 22° C. and 100. 3 kPa. Vapor is water. Apparent contact angle 113°.

[0040] FIG. 13: droplet of water on a glass slide with micro textured surfaces without silane coating inside of pressure vessel. Image taken at 22° C. and 100. 3 kPa. Vapor is water. Apparent contact angle 60° .

[0041] FIG. 14: Scanning Electron Microscope (SEM) image of microtextures on glass slide.

[0042] FIG. 15: Water droplet on zinc-oxide nano particle coated glass slide. Image taken at 22° C. and 100. 3 kPa. Apparent contact angle 170 degrees. Vapor is water.

[0043] FIGS. 16a and b: SEM images of a PDMS:ZnO coating at two different magnifications

[0044] FIG. 17: Water droplets on a flat PTFE coated surface and various micro textured surfaces as indicated. All images taken at 22° C.

[0045] FIG. 18a: Apparent contact angle of water droplets on flat and square pillar textured surfaces in saturated water vapor. Model predictions also shown.

[0046] FIG. 18b Apparent contact angle of water droplets on flat and square waffle textured surfaces in saturated water vapor. Model predictions also shown.

[0047] FIG. 19: Schematic cross-sectional view of "micromushroom" features. Partial micromushroom shown at right and left edges.

[0048] FIGS. 20a-f: SEM images of micro mushrooms of various configurations.

[0049] FIGS. 21 a-d show sessile drops on a micromush-room texture with D=53 μ m W=66 μ m R=35 μ m and H=85 μ m. FIG. 21a: water on uncoated surface. FIG. 21b: oleic acid on uncoated surface. FIG. 21c: water on surface coated with Teflon® AF. FIG. 21d: oleic acid on surface coated with Teflon® AF.

[0050] FIGS. 22*a-d* show sessile drops on a micromush-room texture with D=68 μ m W=58 μ m R=30 μ m H=90 μ m. FIG. 22*a*: water on uncoated surface.

[0051] FIG. 22b: oleic acid on uncoated surface. FIG. 22c: water on surface coated with Teflon® AF. FIG. 22d: oleic acid on surface coated with Teflon® AF.

[0052] FIGS. 23*a-d* show sessile drops on a micromush-room texture with D=44 μ m W=92 μ m R=28 μ m H=107 μ m. FIG. 23*a*: water on uncoated surface.

[0053] FIG. 23b: oleic acid on uncoated surface. FIG. 23c: water on surface coated with Teflon® AF. FIG. 23d: oleic acid on surface coated with Teflon® AF.

[0054] FIGS. 24a-d show sessile drops on a micromush-room texture D=55 μm W=19 μm R=NA μm H=94 μm. FIG. 24a: water on uncoated surface.

[0055] FIG. 24b: oleic acid on uncoated surface. FIG. 24c: water on surface coated with Teflon® AF. FIG. 24d: oleic acid on surface coated with Teflon® AF.

[0056] FIGS. 25*a-d* show sessile drops on a micromush-room texture D=48 μ m W=96 μ m R=35.7 μ m H=107 μ m. FIG. 25*a*: water on uncoated surface.

[0057] FIG. 25b: oleic acid on uncoated surface. FIG. 25c: water on surface coated with Teflon® AF. FIG. 25d: oleic acid on surface coated with Teflon® AF.

[0058] FIGS. 26a-d show sessile drops on a micromush-room texture D=60 μ m W=31.5 μ m R=30 μ m H=67 μ m. FIG. 26a: water on uncoated surface.

[0059] FIG. 26b: oleic acid on uncoated surface. FIG. 26c: water on surface coated with Teflon® AF. FIG. 26d: oleic acid on surface coated with Teflon® AF.

[0060] $\,$ FIG. 27: Images of halocarbon 200 oil on ZnO particle coated slide. Image taken at 22° C. and 100. 3 kPa.

[0061] FIG. 28a: Image of RL 68H oil droplet on ZnO particle coated surface (5% ZnO, 2:1fPDMS). The apparent contact angle was measured as 25.4°.

[0062] FIG. 28b: Image of contact angle obtained for a PDMS:ZnO 2:1 coating at standard temperature and pressure (STP). The apparent contact angle obtained was 138.6°.

[0063] FIG. 28c: Image of RL 68H oil droplet on micropillar textured surface (d=10, p=22, h=20) coated with PTFE. The apparent contact angle was measured as 122.0°.

[0064] FIGS. 29*a-f*: Image of various R-134:RL 68H compositions at saturation on a micromushroom textured surface (D=68 μm W=58 μm R=30 μm H=90 μm) coated with Teflon® AF. FIG. 29*a*: 0% R-134a; FIG. 29*b*: 25% R-134a. FIG. 29*c*: 33% R-134a. FIG. 29*d*: 50% R-134a. FIG. 29*e*: 60% R-134a. FIG. 29*f*: 80% R-134a.

[0065] FIGS. 30a-f. Image of various R-134:RL 68H compositions at saturation on a micromushroom textured surface (D=55 μm W=19 μm R=NA μm H=94 μm) coated with Teflon® AF. FIG. 30a: 0% R-134a; FIG. 30b: 25% R-134a. FIG. 30c: 33% R-134a. FIG. 30d: 50% R-134a. FIG. 30e: 60% R-134a. FIG. 30f: 80% R-134a.

[0066] FIGS. 31a-f: Image of various R-134:RL 68H compositions at saturation on a micromushroom textured surface (D=48 μm W=96 μm R=35.7 μm H=107 μm) coated with Teflo® n AF. FIG. 31a: 0% R-134a; FIG. 31b: 25% R-134a. FIG. 31c: 33% R-134a. FIG. 31d: 50% R-134a. FIG. 31e: 60% R-134a. FIG. 31f: 80% R-134a.

[0067] FIGS. 32a-f: Image of various R-134:RL 68H compositions at saturation on a square waffle textured surface (p=12 μm) coated with Teflon® AF. FIG. 32a: 0% R-134a; FIG. 32b: 25% R-134a. FIG. 32c: 33% R-134a. FIG. 32d: 50% R-134a. FIG. 32e: 60% R-134a. FIG. 32f: 80% R-134a. [0068] FIGS. 33a-f: Image of various R-134:RL 68H compositions at saturation on a square waffle textured surface (p=22 μm) coated with Teflon® AF. FIG. 33a: 0% R-134a; FIG. 33b: 25% R-134a. FIG. 33c: 33% R-134a. FIG. 33d: 50% R-134a. FIG. 33e: 60% R-134a. FIG. 33f: 80% R-134a. [0069] FIG. 34: Image of R-134a droplet with a relatively high apparent contact angle on PTFE coated waffle pattern Si wafer in pressure vessel. Image taken at 24° C. and 645.8 kPa. Vapor is R134a.

[0070] FIG. 35: Schematic of heat exchanger system including a condenser, evaporator and compressor.

DETAILED DESCRIPTION

[0071] As used herein, a refrigerant is a substance used in a heat cycle that undergoes a phase change between gas and liquid. Accordingly, a refrigerant vapor is the gas phase of a refrigerant. If the refrigerant is a mixture of components, the composition of the vapor phase may differ from that of the

liquid. For example if the refrigerant is a mixture of a halocarbon refrigerant and a lubricant, the vapor of the mixture may be mostly halocarbon refrigerant vapor.

[0072] Refrigerants include inorganic refrigerants, halocarbon refrigerants, and hydrocarbon refrigerants. Refrigerants also include mixtures of inorganic refrigerants, halocarbon refrigerants and hydrocarbon refrigerants with additional components in the system such as lubricants. The methods and devices provided herein are compatible with a wide range of refrigerants, so long as the vapor is capable of condensing into liquid droplets on a surface, including onto a surface that is refrigerant repelling. Examples of certain refrigerants of interest in the context of the methods and devices provided herein include: R-11 Trichlorofluoromethane, R-12 Dichlorodifluoromethane, R-13 B1 Bromotrifluoromethane, R-22 Chlorodifluoromethane, R-32 Difluoromethane R-113, Trichlorotrifluoroethane, R-114 Dichlorotetrafluoroethane, R-123 Dichlorotrifluoroethane, R-124 Chlorotetrafluoroethane, R-125 Pentafluoroethane, R-134a Tetrafluoroethane, R-143a Trifluoroethane, R-152a Difluoroethane and R-245a Pentafluoropropane, 2,3,3,3-tetrafluoroprop-1-ene (HFO and rans-1,3,3-tetrafluoroprop-1-ene 1234zeE), R290 propane, R600 n-butane, R600a isobutene (2-methyl propane), R1150 ethylene and R1270 propylene, R-401A (53% R-22, 34% R-124, 13% R-152a), R-401B (61% R-22, 28% R-124, 11% R-152a), R-402A (38% R-22, 60% R-125, 2% R-290), R-404A (44% R-125, 52% R-143a, R-134a), R-407A (20% R-32, 40% R-125, 40% R-134a), R-407C (23% R-32, 25% R-125, 52% R-134a), R-502 (48. 8% R-22, 51.2% R-115) 0.283 4.1 and R-507 (45% R-125,

[0073] Inorganic refrigerants known to the art include air, ammonia, carbon dioxide sulfur dioxide and water. In an embodiment, water may be used as a refrigerant in the methods of the invention under selected process conditions (e.g. under saturation or near saturation conditions and the pressure is less than atmospheric pressure). The surface tension of water is 72.8 mN/m @ 20° C.

[0074] As used herein, the term halocarbon refers to a chemical compound including carbon and one or more of the halogens (bromine, chlorine, fluorine, iodine). In an embodiment, the halocarbon may also include hydrogen. Exemplary halocarbon refrigerants include R-11 Trichlorofluoromethane, R-12 Dichlorodifluoromethane, R-13 B1 Bromotrifluoromethane, R-22 Chlorodifluoromethane, R-32 Difluoromethane R-113, Trichlorotrifluoroethane, R-114 Dichlorotetrafluoroethane, R-123 Dichlorotrifluoroethane, R-124 Chlorotetrafluoroethane, R-125 Pentafluoroethane, R-134a Tetrafluoroethane, R-143a Trifluoroethane, R-152a Difluoroethane and R-245a Pentafluoropropane.

[0075] In an embodiment, the halocarbon refrigerant is a hydrofluorocarbon (HFC) or hydrofluoroolefin (HFO). Exemplary HFC refrigerants include, but are not limited to, R-125 Pentafluoroethane, R-134a Tetrafluoroethane, R-143a Trifluoroethane, R-152a Difluoroethane and R-245a Pentafluoropropane. Exemplary hydrofluorolefin refrigerants include but are not limited to 2,3,3,3-tetrafluoroprop-1-ene (HFO 1234yf) and rans-1,3,3-tetrafluoroprop-1-ene (HFO 1234zeE). Surface tension of R-134a is 14.6 mN/m @-20° C.; surface tension of HFO-1234yf is 2.0 @ 55° C., 9.5 @ 0° C.

[0076] As used herein, the term hydrocarbon refers to a chemical compound consisting of carbon and hydrogen. Hydrocarbon refrigerants include, but are not limited to R290

propane, R600 n-butane, R600a isobutene (2-methyl propane), R1150 ethylene and R1270 propylene.

[0077] Refrigerant mixtures are also possible. The mixture may be an azeotropic: mixture whose vapor and liquid phases retain identical compositions over a wide range of temperatures. The mixture may also be a zeotropic mixture whose composition in liquid phase differs from that in vapor phase. Zeotropic refrigerants therefore do not boil at constant temperatures unlike azeotropic refrigerants. Exemplary refrigerant mixtures are R-401A (53% R-22, 34% R-124, 13% R-152a), R-401B (61% R-22, 28% R-124, 11°/o R-152a), R-402A (38% R-22, 60% R-125, 2% R-290), R-404A (44% R-125, 52% R-143a, R-134a), R-407A (20% R-32, 40% R-125, 40% R-134a), R-407C (23% R-32, 25% R-125, 52% R-134a), R-502 (48.8% R-22, 51.2% R-115) 0.283 4.1R-507 (45% R-125, 55% R-143).

[0078] A variety of lubricants suitable for use in heat exchanger systems are known to the art. In different embodiments, the lubricant may be a polyol ester (POE) or a polyalkylene glycol (PAG). Polyol esters include, but are not limited to neopentyl glycols, trimethylolpropanes, pentaerythritols and dipentaerytrhitols. Specific polyol esters include, but are not limited to RL68H. In an embodiment, the viscosity of the lubricant may be described by an ISO viscosity grade number such as ISO 68, ISO 46 or ISO 100.

[0079] In the methods of the invention, the temperature and pressure of the vapor is generally less than the critical temperature and pressure of the refrigerant. The temperature and pressure of the vapor may vary within the heat exchanger apparatus. For example, the vapor may be superheated after exiting a compressor and be at a lower temperature, such as at or near its saturation temperature, adjacent to a surface of surface of the condenser. Under saturation conditions, the refrigerant can exist in both liquid and vapor form. The saturation temperature is the temperature where a substance changes between its liquid and its vapor phase (at a given pressure). Similarly, the saturation vapor pressure is the vapor pressure where a substance changes between its liquid and its vapor phase (at a given temperature). The relationship between the pressure and the temperature is fixed under saturation conditions. Near saturation conditions, where the pressure and temperature are close to but not at the steady state values, can also support evaporation and condensation. In different embodiments, near saturation conditions capable of supporting evaporation and condensation may involve pressures and temperatures which are within 20%, 15%, 10% or 5% of their saturation values. In an embodiment, the condensation heat transfer processes of the invention take place in an enclosure such as a pressure vessel under saturation or near saturation conditions.

[0080] As used herein, "characteristic contact angle" refers to the static contact angle of a droplet of refrigerant on an essentially flat or smooth solid surface of a given material, including under standard conditions. The characteristic contact angle may be taken as the mean or median of several measurements of contact angle. The characteristic contact angle is also referred to as θ . In different embodiments of the present invention, the characteristic contact angle of the refrigerant on a surface material is less than 50°, less than 40°, less than 30°, less than 20°, less than 10° or less than 5°. The characteristic contact angle may be a static contact angle, an advancing contact angle or a receding contact angle.

[0081] As used herein, "apparent contact angle" refers to the contact angle of a droplet of refrigerant on a textured surface and may also be referred to as θ^* . In an embodiment, the size of the droplet is greater than or equal to the size of the features creating the surface texture. For example, if the surface texture is created by particles on the surface, the droplet size may be greater than the particle size. In an embodiment, the apparent contact angle of a droplet of refrigerant on a textured surface of a given material is greater than the characteristic contact angle of the refrigerant on the same material (without texture) when the droplet size is greater than the size of the features creating the surface texture, the surrounding atmosphere, temperature and pressure being the same in both cases. In different embodiment, the apparent contact angle may be greater than the characteristic contact angle by greater than 45°. In an embodiment, the apparent contact angle of at least some of the droplets is greater than 90°. In an embodiment, the apparent contact angle on a given surface texture is assessed in the temperature or pressure range of interest under saturation conditions. The contact angle of a droplet may also depend on whether the measurement is a static measurement or a dynamic measurement.

[0082] In an aspect, the contact angle of a droplet with a surface may change during droplet formation. Accordingly, any of the methods and devices provided herein may measure contact angle at a user-defined times or stages, thereby providing the ability to better characterize and compare different systems. For example, the time point may be at specified time after droplet condensation begins, or may be at a specific stage of the process, such as immediately prior to exit of the moving droplet from the system or any stage between formation to exit, such as at a half-way point. Other relevant parameters may include rates or speed at which maximum contact angle is achieved as certain fluids may initially condense with a rather flat contact angle and then increased in contact angle as the droplet further forms. With this in mind, any of the devices and methods provided herein may be characterized in terms of a surface repellency ratio defined as θ^*/θ for a given system, such as a surface repellency ratio that is greater than or equal 2, including selected from a range that is greater than or equal to 2 and less than or equal 150, greater than or equal to 5 and less than or equal 100 ratio, or greater than or equal to 5 and less than or equal 15, or about 10 or more, with $\theta *>90^{\circ}$ and $\theta < 90^{\circ}$.

[0083] Surface composition (e.g. use of low energy surfaces or low energy surface coatings) can influence the wettability of the surface by the liquid. In some embodiments, the surface may comprise a fluoropolymer or fluorosilane. Suitable fluoropolymers include, but are not limited to, Polytetrafluoroethylene (PTFE) and amorphous PTFE (e.g. Teflon® AF). Commercially available fluorosilanes such as Dow Corning 2604, 2624, and 2634; DK Optool DSXTM; Shintesu OPTRONTM; heptadecafluoro silane (manufactured, for example, by Gelest); FLUOROSYLTM (manufactured, for example, by Cytonix).

[0084] In one aspect, textured surfaces useful for the invention have surface textures which facilitate droplet mobility along the surface. In this manner, as droplets form on a surface, the droplets move along the surface thereby avoiding film formation. In an embodiment, the refrigerant repelling surfaces of the invention facilitate droplet movement along the surface. One way to measure the ease of roll-off is to determine the angle of tilt from the horizontal needed before a drop will roll off a surface. The lower the tilt angle, the more easily the drop rolls off the surface.

[0085] As used herein, "surface texture" can refer to threedimensional features on a surface that intrudes into an interior volume that contains the refrigerant. In an aspect, surface texture may comprise relief and recess features. In this manner, an elevated surface feature is considered a relief feature, and the corresponding non-elevated portion may be considered, relative to the relief feature, a recess feature. For example, the "micromushroom" features shown in FIG. 19 may be considered to be relief features. Refrigerant behavior on textured surfaces may be compared to that on smooth surfaces. In an embodiment, a "smooth" surface has a surface roughness significantly less than (e.g. less than ½ of, less than 1/4 of or less than 1/10 of) the characteristic depth or height of features on the textured surface. In an embodiment, the surface texture of the interior of the pressure vessel includes topographically complex, three-dimensional microstructures or nanostructures with reentrant geometries. Surfaces having a reentrant geometry typically include a protruding portion configured to protrude toward a liquid and a reentrant portion opposite the protruding portion. Such reentrant structures can be formed by particles or fibers, whose curvature provides the reentrant feature. The reentrant structures can also be made with etching techniques. Nonwoven or woven fabrics, including fabrics woven of metal fibers, can also provide reentrant geometry.

[0086] In another embodiment, the surface features on the interior surface of the pressure vessel comprise nanoparticles. In an embodiment, the average diameter of the nanoparticles is 2-300 nm and the average spacing between nanoparticles 10-1000 nm. In an embodiment, the nanoparticles may be selected from the group consisting of ZnO and other metal oxides as well as silica and silicon dioxide. The surface of the nanoparticle may also be treated to adjust the wettability of the nanoparticle. For example, the nanoparticles can be halogenated, perfluorinated, or fluorinated nanoparticles, for example, perfluorinated or fluorinated silsesquipoxanes. Particle coatings are also described in Steele et al., 2009, Nano Letters, 9, 501-505, hereby incorporated by reference

[0087] In another embodiment the features of the textured surface form a periodically repeating array. FIG. 3A schematically illustrates a top view of features forming a "waffle" pattern of interconnected elevated "wall" or "ridge" features (indicated by double lines in the figure) surrounding hexagonal depressions. FIG. 3B schematically illustrates a top view of features forming a "waffle" pattern interconnected elevated grid-like "wall" or "ridge" features (indicated by double lines in the figure) surrounding square depressions. Such features may be characterized by the dimension of the depression (e.g. w or w), the pitch or microstructure period (dimension of depression+dimension of wall, e.g. p or p) and the depth of the depression (e.g. d or d) or height of the wall (e.g. h or h). In an embodiment, the elevated wall features in the "waffle" have an average width between 5 nm and 10 microns and an average spacing between 50 nm and 250 microns. The depth of the depressions/height of the elevated features may be on the order of the width of the depressions (spacing between the elevated features. In different embodiments, the depth of the depressions may be from 5 nm to 250 microns or 50 nm to 250 microns. The dimensions of the surface features are selected in accordance with operating conditions and refrigerant composition so as to ensure increase in the contact angle of a condensed droplet on the textured surface. In an embodiment, the surface texture is selected so that the surface is considered

refrigerant repelling, even though refrigerant may wet a flat surface of the surface material.

[0088] In another embodiment, the features of the textured surface resemble mushrooms, with a top cap portion that is wider than its stem. As illustrated by FIG. 19, this type of structure can be characterized by its cap width (2W), the height between the bottom of the cap and the surface (H), the cap radius (R) and the spacing between neighboring caps (2D). Suitable ranges of these parameters for the refrigerants described herein include: D=40-70, W=20-100, R=25-40 and H=65-110.

[0089] All references cited herein are hereby incorporated by reference to the extent not inconsistent with the disclosure herewith. All references throughout this application, patent application publications; and non-patent literature documents or other source material; are hereby incorporated by reference herein in their entireties, as though individually incorporated by reference, to the extent each reference is at least partially not inconsistent with the disclosure in this application (for example, a reference that is partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

[0090] All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art, in some cases as of their filing date, and it is intended that this information can be employed herein, if needed, to exclude (for example, to disclaim) specific embodiments that are in the prior art. For example, when a compound is claimed, it should be understood that compounds known in the prior art, including certain compounds disclosed in the references disclosed herein (particularly in referenced patent documents), are not intended to be included in the claim.

[0091] Every formulation or combination of components described or exemplified can be used to practice the invention, unless otherwise stated. Specific names of compounds are intended to be exemplary, as it is known that one of ordinary skill in the art can name the same compounds differently. When a compound is described herein such that a particular isomer or enantiomer of the compound is not specified, for example, in a formula or in a chemical name, that description is intended to include each isomers and enantiomer of the compound described individual or in any combination. One of ordinary skill in the art will appreciate that methods, device elements, starting materials, and synthetic methods other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such methods, device elements, starting materials and synthetic methods, and are intended to be included in this invention. Whenever a range is given in the specification, for example, a temperature range, a time range, or a composition range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure.

[0092] As used herein, "comprising" is synonymous with "including," "containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially

affect the basic and novel characteristics of the claim. Any recitation herein of the term "comprising", particularly in a description of components of a composition or in a description of elements of a device, is understood to encompass those compositions and methods consisting essentially of and consisting of the recited components or elements. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

[0093] The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

[0094] In general the terms and phrases used herein have their art-recognized meaning, which can be found by reference to standard texts, journal references and contexts known to those skilled in the art. The following definitions are provided to clarify their specific use in the context of the invention.

[0095] Although the description herein contains many specificities, these should not be construed as limiting the scope of the invention but as merely providing illustrations of some of the presently preferred embodiments of the invention. For example, thus the scope of the invention should be determined by the appended claims and their equivalents, rather than by the examples given.

[0096] The invention may be further understood by the following non-limiting examples.

Example 1

Surface Tension and Contact Angle Calculations

[0097] Equations 1 and 2 give relationships between the flat surface contact angle and the relevant surface free energies and the variation in the surface free energy with temperature.

$$Cos(\theta_C) = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LV}}$$
 (Equation 1)

$$\gamma(T) = \gamma(T_0) + Tc_{\gamma} * (\Delta T)$$
 (Equation 2)

[0098] Where θ_c : Flat surface contact angle, γ_{LV} : Surface tension of water, γ_{SG} : Surface free energy (SFE) of surface (e.g. PTFR), γ_{SL} : SFE between surface and water, $\gamma(T_0)$: Value of γ at temperature T_0 ., $T_{C_{\gamma}}$: Temperature coefficient of the substance., ΔT : $(T_0 - T)$.

[0099] FIG. 1a illustrates the contact angle on a flat surface; in FIG. 1a θ is equivalent to θ_c in equation 1.

[0100] FIG. 2 shows water surface tension as a function of temperature.

$$Cos(\theta_{int}) = \frac{\gamma_{SG}(T_{int}) - \gamma_{SL}(T_{int})}{\gamma_{LG}(T_{int})}$$
 (Equation 3)

$$\cos(\theta_{crit}) = \frac{\gamma_{SC}(T_{crit}) - \gamma_{SL}(T_{crit})}{\gamma_{LG}(T_{crit})}$$
(Equation 4)

$$Tc_{\gamma_{SL}} = \frac{\gamma_{SL}(T_{crit}) - \gamma_{LV}(T_{int})}{T_{crit} - T_{int}}$$
 (Equation 5)

[0101] Where γ_{SLcrit} : Critical surface tension. Defined as $\cos(\theta_c)=1$ @ γ_{LV} (T_{crit})= γ_{crit} T_{crit} . Temperature where γ_{LV} (T)= γ_{crit} θ_c at T_{int} . Use Equation 2 to solve Equations 3-5 simultaneously. This determines $T_{C_{\gamma SL}}$, γ_{SL} @ $^{25\circ}$, and $T_{C_{\gamma SL}}$. Once these values are known, Equation 1 can be solved at any temperature. Tables 1 and 2 show initial conditions and unknowns related to interfacial energy related parameters and contact angle parameters respectively.

TABLE 1

γ	γ @ 25° C. (mN/m)	$T_{C\gamma} (mN/m*K)$
YLV	72.04	-0.1514
YSG	19.71	-0.0580
YSL	??	??
YSLerit	18.00	N/A

TABLE 2

θ	Angle (°)	T	(° C.)	
θint θcrit	95 0	$\begin{matrix} \mathbf{T}_{int} \\ \mathbf{T}_{crit} \end{matrix}$	25 ??	

[0102] FIG. 1b illustrates a liquid droplet on a rough surface in the Wenzel state. This state may be described by $\cos\theta_w=r\cos\theta$ (Equation 6), where r is the Wenzel roughness factor. FIG. 1c illustrates a liquid droplet on a rough surface in the Cassie-Baxter state, where the droplet sits on top of the surface roughness. This state may be described by $\cos\theta_{CB}=f(\cos\theta+1)-1=f\cos\theta-(1-f)$ (Equation 7) where f is the Cassie roughness factor. For a surface with pitch p, A elements per area p^2 , surface area of element top s, element height h and perimeter of element top L, the Wenzel roughness factor may be described by $r=1+(A/p^2)$ hL (Equation 8). Similarly the Cassie roughness factor may be described by $f=(A/p^2)$ S (Equation 9).

Example 2

Measurements for Water and Oleic Acid

[0103] FIGS. 3A-B and 4A-C schematically illustrate some of the waffle and pillar surface textures fabricated for testing. FIG. 3 is a schematic top view of a hexagonal waffle structure (FIG. 3A) and a grid-like waffle structure (FIG. 3B). FIG. 4 is a schematic top view of different configurations of pillar elements: hexagonal arrangement (FIG. 4A), square arrangement (FIG. 4B), and honeycomb arrangement (FIG. 4C).

[0104] Tables 3 and 4 respectively provide additional information about waffle and pillar surface textures. In Table 2, h is element height, p is pitch and w is width of square or hexagonal depression. In Table 4, A is elements per area p^2 , d is diameter of the pillar, p is pitch, and h is element height.

TABLE 3

	Square Waffles	
h (µm)	p(µm)	w (µm)
3	22	20
	Hexagonal Waffles	
h (μm)	p(µm)	w (µm)
3	12	10

TABLE 4

Square Pillars					
A	d (µm)	h (µm)	p (µm)		
1	50	50	100		
	Hexagon	al Pillars			
A	d (µm)	h (μm)	p (µm)		
1.57	50	300	100		

[0105] FIG. 5 shows an experimental setup used for contact angle measurements. The apparatus includes a pressure chamber 10, a pump 20, which may be an infusion pump, a camera 30, a light source 40 and data acquisition unit 50.

[0106] Table 5 shows the contact angle (CA) measured for water and oleic acid oil on smooth and microtextured surfaces. The surfaces are either smooth, textured with a waffle pattern of FIG. 3 as either hexagons or squares, or textured with a standard lotus leaf type pattern consisting of dense pillar structures (FIG. 4). w is feature width, d is diameter, p is microstructure period, and h is feature height (or depth of waffles).

TABLE 5

Pattern	w or d μm	р µm	h μm	Water CA°	Oleic Acid CA°
Smooth	_	_	_	118	66
Hexagon Waffles	20	22	0.3	144	135
Hexagon Waffles	20	22	1.0	142	137
Square Waffles	20	22	151	151	139
Square Waffles	20	22	146	146	140
Square Pillars	10	20	148	149	68

[0107] FIG. 6 shows a graph for θ values between 25 and 250° C. Contact angles plotted at the saturation pressure of water for a given temperature for different surface textures (values from model).

[0108] FIG. 7 shows an image of a droplet of distilled water on a waffle patterned Si wafer coated in PTFE inside of pressure vessel. Image taken at 35.8° C. and 62.0 kPa. Vapor is water.

[0109] FIG. 8 shows an image sequence of a droplet of water evaporating on a flat Si wafer coated in PTFE inside of the pressure vessel. Images taken at labeled temperatures and corresponding saturation pressures.

[0110] FIG. 9 shows a plot of temperature dependent contact angle for a textured surface (pillars, d=50 μ m h=50 μ m p=100 μ m) compared to a flat surface and the mathematical model. Vapor is water.

[0111] FIGS. 10a-10b show an image sequence of water droplet on waffle patterned Si wafer coated in PTFE. Droplet heated from 31.7° C. to 54.1° C. Droplet triple line expands outward due to expansion of trapped pockets of water vapor between droplet and surface until reaching a maximum at 46.4° C. Vapor is water. FIG. 10c shows a magnified image of vapor expansion inside of water droplet. (see FIG. 10b) Vapor is water. Waffle pattern 10 micrometer squares, 20 micrometer pitch.

[0112] FIG. 11 shows an image sequence of water droplet on waffle textured (25 μm squares 50 μm pitch). Si wafer coated with PTFE inside pressure vessel. As triple line expands, θ^* decreases from ~90° to ~32° after the trapped water vapor completes expansion inside droplet. Vapor is water.

[0113] FIG. 12 shows a droplet of water on a glass slide with micro textured surfaces coated in silane inside of pressure vessel. Image taken at 22° C. and 100. 3 kPa. Vapor is water. Apparent contact angle 113°.

[0114] FIG. 13 shows a droplet of water on a glass slide with micro textured surfaces without silane coating inside of pressure vessel. Image taken at 22° C. and 100. 3 kPa. Vapor is water. Apparent contact angle 60°.

[0115] FIG. 14 shows an SEM image of microtextures on glass slide (see FIGS. 12 and 13).

[0116] FIG. 15 shows a water droplet on zinc-oxide nano particle coated glass slide. Image taken at 22° C. and 100. 3 kPa. Vapor is water

[0117] FIGS. 16a-b show SEM images of a 2PDMS:1ZnO coating at two different magnifications.

[0118] FIG. 17 shows water droplets on flat and microtextured PTFE coated surfaces, when the surrounding environment is air, low pressure air, or water vapor. The apparent contact angle of the droplets decreased for both the square pillar and square waffle textured surfaces when the vapor phase was changed from air to water vapor. These measurements demonstrate that the vapor environment around the water droplet influences how the water droplet wets the surface (All images taken at 22° C.). FIG. 18a shows apparent contact angles for flat and square pillar textured surfaces while FIG. 18b shows apparent contact angles for flat and square waffle surfaces in saturated water vapor at various temperatures.

[0119] FIG. **19** illustrates relevant dimensions for surface features having a "mushroom" or "micro mushroom" geometry. W is width from the center of the stem to the edge of the cap. R is the radius of the cap. H is the distance between the lower portion of the surface and the bottom of the cap. 2D is the spacing between the edges of the caps. Θ is the characteristic contact angle, ψ is the local geometry angle, h1 is a sagging height and h2 is a pore depth (Tuteja et al., 2008, PNAS, 107(47), 18200-19205). Table 6 lists relevant dimensions for several micromushroom surface textures.

TABLE 6

Sample No.	D (µm)	W (µm)	R (µm)	H (µm)
1	53	66	35	85
2	67.5	58	30	90
3	44	92	28	107
4	55	19	N/A	94

TABLE 6-continued

Sample No.	D	W	R	H
	(µm)	(µm)	(µm)	(µm)
5	48	96	35.7	107
6	60	31.5	30	67

[0120] FIG. 20a shows a SEM image of micromushroom sample texture 1 (see Table 6), FIG. 20b shows an SEM image of micromushroom sample texture 2, FIG. 20c shows a SEM image of micromushroom sample texture 3, FIG. 20d shows an SEM image of micromushroom sample texture 4, FIG. 20e shows a SEM image of micromushroom sample texture 5, and FIG. 20f shows a SEM image of micromushroom sample texture 6 (samples 1-6 as given in Table 6)

[0121] Table 7 lists apparent contact angles measured and calculated for water and oleic acid for the coated and uncoated micromushroom geometries of Table 6.

TABLE 7

GEOMETRY	COATING	LIQUID	θ_{Calc}	$\theta_{Measured}$
Flat	None	Water	N/A	68.5
Flat	Teflon AF	Water	N/A	127.1
Flat	None	Oleic Acid	N/A	28.6
Flat	Teflon AF	Oleic Acid	N/A	45.0
μMushroom - 1	None	Water	153.5	30.7
μMushroom - 1	Teflon AF	Water	172.3	147.5
μMushroom - 1	None	Oleic Acid	150.5	N/A
μMushroom - 1	Teflon AF	Oleic Acid	147.8	132.0
μMushroom - 2	None	Water	158.2	142.3
μMushroom - 2	Teflon AF	Water	170.2	146.5
μMushroom - 2	None	Oleic Acid	155.5	N/A
μMushroom - 2	Teflon AF	Oleic Acid	153.3	147.3
μMushroom - 3	None	Water	147.6	131.1
μMushroom - 3	Teflon AF	Water	171.1	137.8
μMushroom - 3	None	Oleic Acid	143.9	N/A
μMushroom - 3	Teflon AF	Oleic Acid	140.5	147.9
μMushroom - 4	None	Water	167.8	148.2
μMushroom - 4	Teflon AF	Water	172.2	157.7
μMushroom - 4	None	Oleic Acid	166.5	N/A
μMushroom - 4	Teflon AF	Oleic Acid	165.2	147.9
μMushroom - 5	None	Water	148.0	146.7
μMushroom - 5	Teflon AF	Water	173.4	145.7
μMushroom - 5	None	Oleic Acid	144.3	N/A
μMushroom - 5	Teflon AF	Oleic Acid	142.0	139.0
μMushroom - 6	None	Water	163.7	152.9
μMushroom - 6	Teflon AF	Water	171.9	165.9
μMushroom - 6	None	Oleic Acid	161.8	N/A
μMushroom - 6	Teflon AF	Oleic Acid	160.1	126.8

[0122] FIGS. **21***a-d* show sessile drops on micromushroom texture 1. FIGS. **21***a-b* respectively show a drop of water and a drop of oleic acid on the uncoated texture while FIGS. **21***c-d* respectively show a drop of water and a drop of oleic acid on the texture as coated with Teflon® AF.

[0123] FIGS. 22*a-d* show sessile drops on micromushroom texture 2. FIGS. 22*a-b* respectively show a drop of water and a drop of oleic acid on the uncoated texture while FIGS. 22*c-d* respectively show a drop of water and a drop of oleic acid on the texture as coated with Teflon® AF.

[0124] FIGS. 23*a-d* show sessile drops on micromushroom texture 3. FIGS. 23*a-b* respectively show a drop of water and a drop of oleic acid on the uncoated texture while FIGS. 23*c-d* respectively show a drop of water and a drop of oleic acid on the texture as coated with Teflon® AF.

[0125] FIGS. 24a-d show sessile drops on micromushroom texture 4. FIGS. 24a-b respectively show a drop of water and a drop of oleic acid on the uncoated texture while FIGS. 24c-d

respectively show a drop of water and a drop of oleic acid on the texture as coated with Teflon® AF.

[0126] FIGS. 25*a-d* show sessile drops on micromushroom texture 5. FIGS. 25*a-b* respectively show a drop of water and a drop of oleic acid on the uncoated texture while FIGS. 25*c-d* respectively show a drop of water and a drop of oleic acid on the texture as coated with Teflon® AF.

[0127] FIGS. 26*a-d* show sessile drops on micromushroom texture 6. FIGS. 26*a-b* respectively show a drop of water and a drop of oleic acid on the uncoated texture while FIGS. 26*c-d* respectively show a drop of water and a drop of oleic acid on the texture as coated with Teflon® AF.

[0128] Advancing and receding contact angles were measured using the sliding angle method. A droplet was deposited on a tilted surface. A camera captures the droplet movement as it slides down the inclined surface.

[0130] FIG. 27 shows images of halocarbon 200 oil on ZnO particle coated slides; these images illustrate the change in contact angle over 20 seconds. Image taken at 22° C. and 100. 3 kPa.

Example 4

Measurements for RL 68H and Mixtures of R134a and RL 68H

[0131] The contact angle of polyol ester oil RL 68H was measured on various textured surfaces. RL 68H is a commonly used oil in pumps for refrigeration systems.

[0132] Sessile drop measurements were obtained for some coatings including zinc oxide nanoparticles. FIG. 28a shows the contact angle obtained for a 5% ZnO, 2:1fPDMS coating.

TABLE 7

Saturated Water Advancing Contact Angles						
Sample					$T_{sat} = 100^{\circ} \text{ C.},$ $P_{sat} = 2.3 \text{ kPa}$	
Flat	87	78	86	89	88	
Pillar (h = $3 \mu m$)	140	149	110	89	84	
Pillar (h = $10 \mu m$)	150	135	127	128	130	
Pillar $h = 20 \mu m$)	154	150	152	138	128	
Waffle (p = $12 \mu m$)	120	123	127	110	19	
Waffle $(p = 12 \mu m)$	133	134	136	110	91	

TABLE 8

Saturated Water Receding Contact Angles					
Sample					$T_{sat} = 100^{\circ} \text{ C.},$ $P_{sat} = 2.3 \text{ kPa}$
Flat	73	65	70	73	78
Pillar (h = $3 \mu m$)	102	105	68	66	75
Pillar (h = $10 \mu m$)	111	106	105	112	106
Pillar (h = $20 \mu m$)	118	110	116	113	110
Waffle (p = $12 \mu m$)	104	102	100	90	90
Waffle (p = $12 \mu m$)	106	108	104	102	71

Example 3

Measurements for HC-200

[0129] The contact angle of halocarbon oil HC-200 was measured on smooth and square waffle patterns. The experimental methods were the same as above, with only the liquid type being different. HC-200 is a liquid polymer oil with the chemical name chlorotrifluoroethylene. HC-200 has a surface tension about 0.025 N/m, which is lower than the surface tension for oleic acid. Table 9 shows the results, where the square waffle patterns are oleophobic, while a smooth surface of the same material is oleophillic. In Table 9, w is feature width, p is microstructure period, and d is feature depth.

TABLE 9

Pattern	Liquid	w µm	p μm	d μm	Oil CA°
Smooth Square Waffles	HC 200 HC 200			 0.3	40 122

The apparent contact angle was 25.4°. FIG. **28***b* shows the contact angle obtained for a PDMS:ZnO 2:1 coating at STP. The apparent contact angle obtained was 138.6°. The coating of zinc oxide (ZnO) nanoparticles and PDMS in FIG. **28***b* was formed by mixing the ZnO particles into suspension of Polydimethylsiloxane (PDMS) and spraying the mixture onto a silicon wafer. The particle coated substrate was then coated with polytetrafluoroethylene (PTFE) before measuring contact angles.

[0133] FIG. 28c shows the contact angle of 122.0° obtained on a PTFE coated textured surface (pillars, d=10 μ m h=20 μ m p=22 μ m). FIGS. 29a, 30a, and 31a illustrate drops obtained on micromushroom structures and FIGS. 32a and 33a illustrate drops obtained on waffle structures.

[0134] The mixing process for R-134a and RL 68H was as follows. A quantity of RL 68H was measured to +/-0.5 g. The RL 68H was then added to the pressure vessel. The pressure vessel was then evacuated to 0.15 psi at 22 c to remove air and water vapor. The pressure vessel was then cooled to 10 C. A quantity of R-134a was then measured to within +/-0.5 g and added to the pressure vessel. The mixture was then recovered into a sampling vessel.

[0135] The contact angle of mixtures of R134a and RL 68H was measured for several Teflon coated textured surfaces. Table 10 lists contact angle measurements for several mixtures. For comparison, the contact angle measured on flat surfaces ranged from zero to 70 degrees depending on the mixture

32a: 0% R-134a, Psat=101 kpa, Tsat=10.3° C. FIG. 32b: 25% R-134a, Psat=270 kpa, Tsat=10.1° C. FIG. 32c: 33% R-134a, Psat=363 kpa, Tsat=11.5° C. FIG. 32d: 50% R-134a, Psat=384 kpa, Tsat=11.0° C. FIG. 32e: 60% R-134a, Psat=430 kpa, Tsat=12.3° C. FIG. 32f: 80% R-134a, Psat=441 kpa, Tsat=14.2° C.

TABLE 10

	Psat = 270 kpa, Tsat = 10.1° C.	Psat = 363 kpa, Tsat = 11.5° C.	Psat = 384 kpa, Tsat = 11.0° C.	Psat = 430 kpa, Tsat = 12.3° C.	Psat = 441 kpa, Tsat = 14.2° C.
Sample		θ 33% R-134a, 66% RL 68H			
μμMushroom D = 68 μm W = 58 μm R = 30 μm H = 90 μm	120	59	51	44	12
μMushroom D = 55 μm W = 19 μm R = N/A H = 94 μm	100	58	47	31	25
μMushroom D = 48 μm W = 96 μm R = 35.7 μm H = 107 μm	139	125	111	87	51
Waffle (p = 12 μm)	113	94.5	81	75	19
Waffle (p = 22 μ m)	119	116	112	70	40

[0136] FIGS. 29 *a-f* illustrate sessile drops of mixtures of R134a and RL68H on a micro mushroom patterned surface (D=67.5 micron, W=58 micron, R=30 micron, H=90 micron, see micromushroom texture 2). FIG. 29*a*: 0% R-134a, Psat=101 kPa, Tsat=10.3° C. FIG. 29*b*: 25% R-134a, Psat=270 kPa, Tsat=10.1° C. FIG. 29*c*: 33% R-134a, Psat=363 kPa, Tsat=11.5° C. FIG. 29*d*: 50% R-134a, Psat=384 kPa, Tsat=11.0° C. FIG. 29*e*: 60% R-134a, Psat=430 kPa, Tsat=12.3° C. FIG. 29*f*: 80% R-134a, Psat=441 kPa, Tsat=14.2° C.

[0137] FIGS. 30 a-f illustrate sessile drops of mixtures of R134a and RL68H on a micro mushroom patterned surface (D=55 micron, W=19 micron, R=N/A micron, H=94 micron, see micromushroom texture 4). FIG. 30a: 0% R-134a, Psat=101 kPa, Tsat=10.3° C. FIG. 30b: 25% R-134a, Psat=270 kPa, Tsat=10.1° C. FIG. 30c: 33% R-134a, Psat=363 kPa, Tsat=11.5° C. FIG. 30d: 50% R-134a, Psat=384 kPa, Tsat=11.0° C. FIG. 30e: 60% R-134a, Psat=430 kPa, Tsat=12.3° C. FIG. 30f: 80% R-134a, Psat=441 kPa, Tsat=14.2° C.

[0138] FIGS. 31a-f illustrate sessile drops of mixtures of R134a and RL68H on a micro mushroom patterned surface (D=48 micron, W=96 micron, R=35.7 micron, H=107 micron, see micromushroom texture 5). FIG. 31a: 0% R-134a, Psat=101 kpa, Tsat=10.3° C. FIG. 31b: 25% R-134a, Psat=270 kpa, Tsat=10.1° C. FIG. 31c: 33% R-134a, Psat=363 kpa, Tsat=11.5° C. FIG. 31d: 50% R-134a, Psat=384 kpa, Tsat=11.0° C. FIG. 31e: 60% R-134a, Psat=430 kpa, Tsat=12.3° C. FIG. 31f: 80% R-134a, Psat=441 kpa, Tsat=14.2° C.

[0139] FIGS. 32 *a-f* illustrate sessile drops of mixtures of R134a and RL68H on a waffle pattern with a pitch of 12 micrometers (h=10 micrometers, w=10 micrometers). FIG.

[0140] FIGS. 33 *a-f* illustrate sessile drops of mixtures of R134a and RL68H on a waffle pattern with a pitch of 22 micrometers (h=10 micrometers, w=20 micrometers). FIG. 33*a*: 0% R-134a, Psat=101 kpa, Tsat=10.3° C. FIG. 33*b*: 25% R-134a, Psat=270 kpa, Tsat=10.1° C. FIG. 33*c*: 33% R-134a, Psat=363 kpa, Tsat=11.5° C. FIG. 33*d*: 50% R-134a, Psat=384 kpa, Tsat=11.0° C. FIG. 33*e*: 60% R-134a, Psat=430 kPa, Tsat=12.3° C. FIG. 33*f*: 80% R-134a, Psat=441 kPa, Tsat=14.2° C.

Example 5

Measurement for R134a

[0141] FIG. 34. shows an image of R-134a droplet with a relatively high apparent contact angle on PTFE coated textured Si wafer in pressure vessel. Image taken at 24° C. and 645.8 kPa. Vapor is R134a. The surface texture was a waffle pattern, 25 μm squares, 50 μm pitch. The contact angle for R-134a on a flat surface coated with PTFE was less than 10 degrees Surface tension of R-134a is 14.6 mN/m @-20° C.

1. A method for condensation heat transfer comprising condensing a refrigerant vapor on a textured portion of an interior surface of a chamber to form a plurality of refrigerant droplets at a user selected pressure, thereby transferring heat from the refrigerant vapor to the interior surface wherein the user selected pressure is not atmospheric pressure, the textured portion of the interior surface comprises surface features, the surface features comprising a surface material and the apparent contact angle of the refrigerant droplets on the surface features is non-zero and greater than the characteristic contact angle of the refrigerant droplets on the surface material of the surface features.

- 2. The method of claim 1, wherein the characteristic contact angle for the refrigerant droplets on the surface material is less than 50° .
- 3. The method of claim 2 wherein the characteristic contact angle is less than or equal to 20° .
- **4**. The method of claim **1**, wherein the apparent contact angle of the refrigerant droplets on the surface features is greater than 90°.
- 5. The method of claim 1 wherein the difference between the apparent contact angle and the characteristic contact angle is greater than 45°.
- **6**. The method of claim **1** wherein the atmosphere in the chamber substantially comprises refrigerant vapor.
- 7. The method of claim 1 wherein the refrigerant comprises a component selected from the group consisting of halocarbon, hydrofluorocarbon (HFC), hydrofluoroolefin (HFO) and a hydrocarbon (HC).
- 8. The method of claim 7, wherein the refrigerant further comprises a lubricant.
- 9. The method of claim 8, wherein the refrigerant comprises less than or equal to 50% lubricant by mass.
- 10. The method of claim 7 wherein the refrigerant has a molecular mass from 50 to 125.
- 11. The method of claim 7 wherein the component is selected from the group consisting of tetrafluoroethane (R134a) and 2,3,3,3-tetrafluoroprop-1-ene (HFO 1234yf)
- 12. The method claim 1 wherein the surface features provide a re-entrant geometry.
- 13. The method of claim 12, wherein the surface features are micro mushrooms.
- **14.** The method of claim **13**, wherein the micro mushrooms are characterized by the parameters D, W, R and H as shown in FIG. **19** and D=40-70, W=20-100, R=25-40 and H=65-110
- 15. The method of claim 1 wherein the surface features form a network or grid pattern.
- 16. The method of claim 1, wherein the surface material is a polymer coating.
- 17. The method of claim 16 wherein the polymer is a fluoropolymer.
- **18**. The method of claim **1** wherein the surface material is a silane coating.
- 19. The method of claim 1 wherein the user selected pressure is greater than atmospheric pressure and less than or equal to 5 MPa.

- 20. The method of claim 1 wherein the surface tension of the refrigerant is from 5 mN/m to 25 mN/m.
- 21. A heat exchanger system for condensation heat transfer through condensation of a refrigerant vapor into droplets of the refrigerant, the heat exchanger system comprising: a chamber comprising an interior hollow portion and an interior surface, the interior surface comprising a textured portion, the textured portion of the surface comprising surface features, the surface features comprising a surface material
 - wherein the apparent contact angle of the refrigerant droplets on the surface features is greater than the characteristic contact angle of the refrigerant droplets on the surface material of the surface features.
- 22. The system of claim 21 wherein the surface features provide a re-entrant geometry.
- 23. The system of claim 22 wherein the surface features are micro mushrooms.
- 24. The system of claim 23 wherein the micro mushrooms are characterized by the parameters D, W, R and H as shown in FIG. 19 and D=40-70, W=20-100, R=25-40 and H=65-110
- 25. The system of claim 21 wherein the surface features form a network or grid pattern.
- 26. The system of claim 21 wherein the surface material is a polymer coating.
- 27. The system of claim 26 wherein the polymer is a fluoropolymer.
- 28. The system of claim 21 wherein the surface material is a silane coating.
- **29**. The system of claim **21**, further comprising a refrigerant positioned in the hollow portion of the chamber, the refrigerant comprising a component selected from the group consisting of halocarbon, hydrofluorocarbon (HFC), hydrofluoroolefin (HFO) and hydrocarbon (HC).
- **30**. The system of claim **29** wherein the refrigerant is selected from the group consisting of tetrafluoroethane (R134a) and 2,3,3,3-tetrafluoroprop-1-ene (HFO 1234yf)
- 31. The system of claim 21 wherein the characteristic contact angle is less than or equal to 20° .
- 32. The system of claim 21 wherein the difference between the apparent contact angle and the characteristic contact angle is greater than 45° .

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