



US 20240210130A1

(19) **United States**

(12) **Patent Application Publication**
Roehling et al.

(10) **Pub. No.: US 2024/0210130 A1**

(43) **Pub. Date: Jun. 27, 2024**

(54) **INFRARED TRANSPARENT AEROGEL COMPOSITE FOR DEEP SUB-AMBIENT COOLING OF VIRTUALLY ANY SURFACE**

(71) Applicant: **Lawrence Livermore National Security, LLC**, Livermore, CA (US)

(72) Inventors: **John D. Roehling**, Livermore, CA (US); **Michael Bagge-Hansen**, San Leandro, CA (US); **Hannah V. Eshelman**, Dublin, CA (US); **Mariana Desiree Reale Batista**, Livermore, CA (US); **Tien T. Roehling**, Tracy, CA (US); **Alyssa L. Troksa**, Livermore, CA (US)

(21) Appl. No.: **18/600,120**

(22) Filed: **Mar. 8, 2024**

Related U.S. Application Data

(63) Continuation-in-part of application No. 17/935,396, filed on Sep. 26, 2022.

(60) Provisional application No. 63/261,788, filed on Sep. 29, 2021.

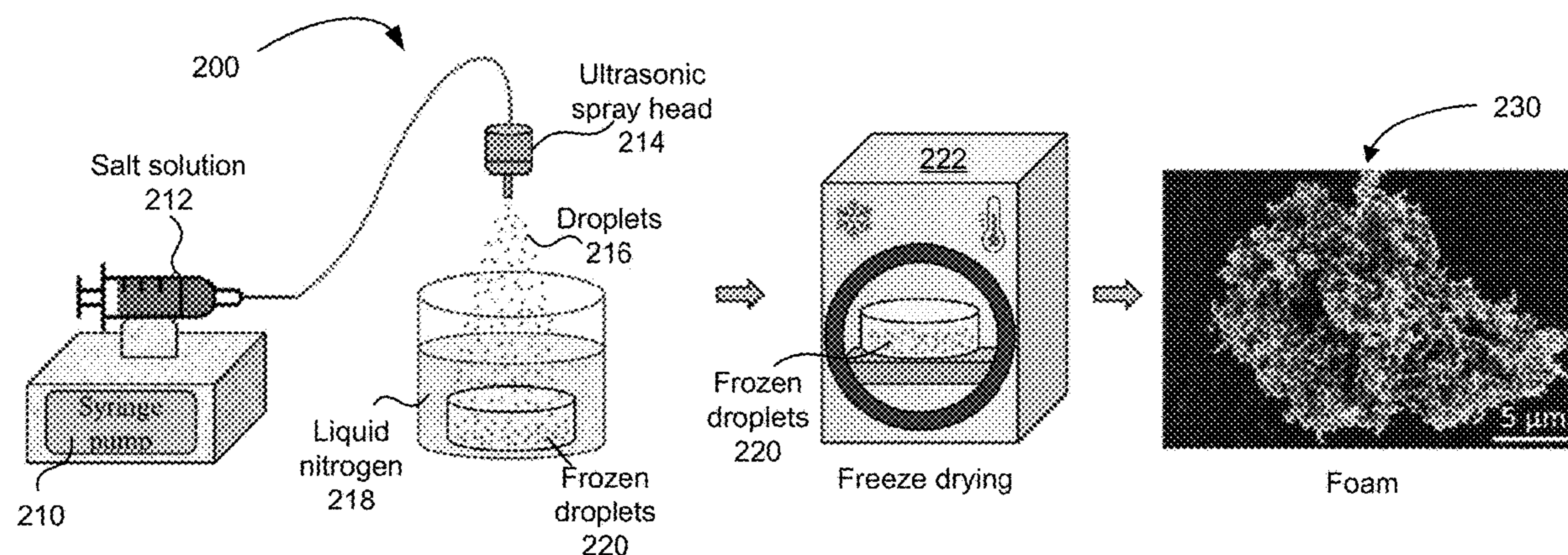
Publication Classification

(51) **Int. Cl.**
F28F 13/00 (2006.01)
F28F 21/04 (2006.01)

(52) **U.S. Cl.**
CPC *F28F 13/003* (2013.01); *F28F 21/04* (2013.01); *F28F 2255/06* (2013.01); *F28F 2270/00* (2013.01)

(57) **ABSTRACT**

An apparatus for cooling a surface includes a composite that includes a porous infrared (IR) transparent material having at least one substance that is transparent to infrared radiation having a wavelength in a range of 8 to 13 μm . In addition, the composite includes a support frame having an opening for exposing a sky-facing surface of the porous IR transparent material and an encapsulant. The encapsulant is positioned on the sky-facing surface of the porous IR transparent material. The composite is configured to be optically reflective to sunlight and is thermally insulating for reducing heating of a surface from surrounding air.



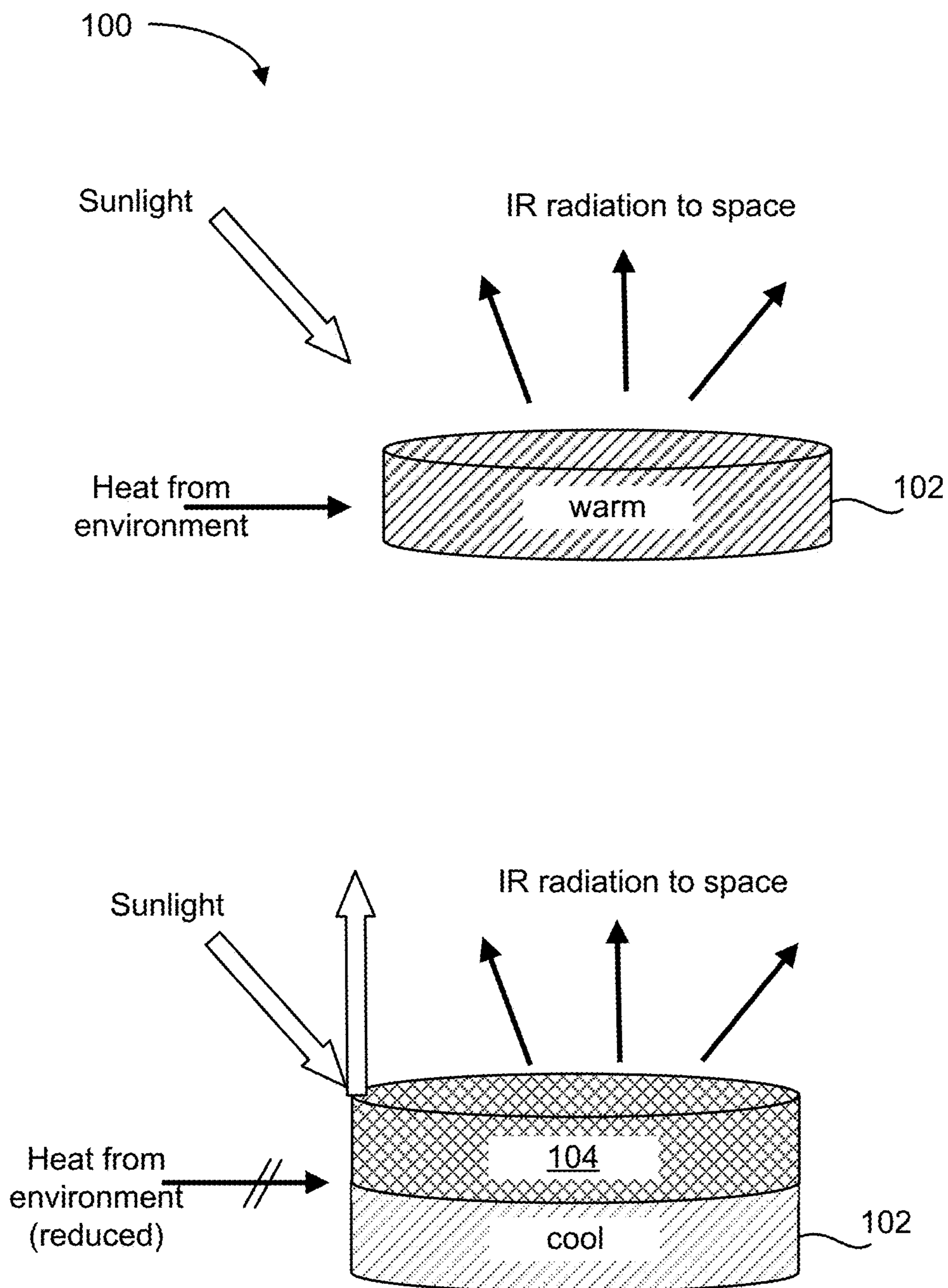


FIG. 1

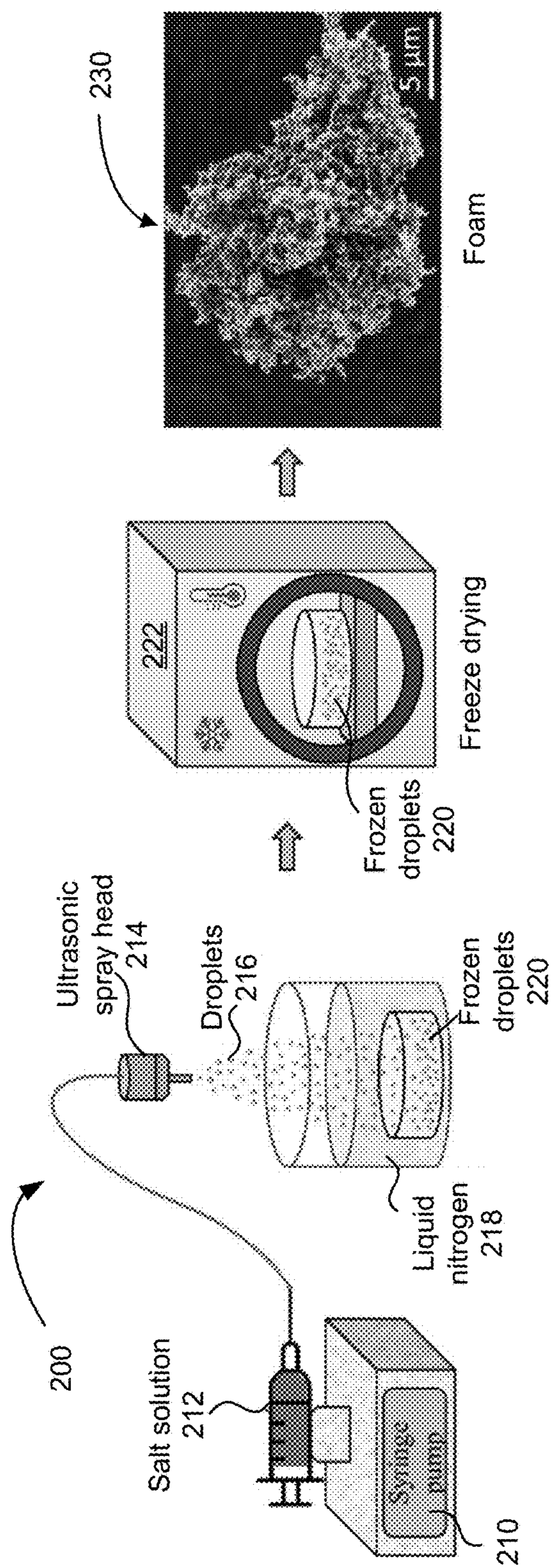


FIG. 2A

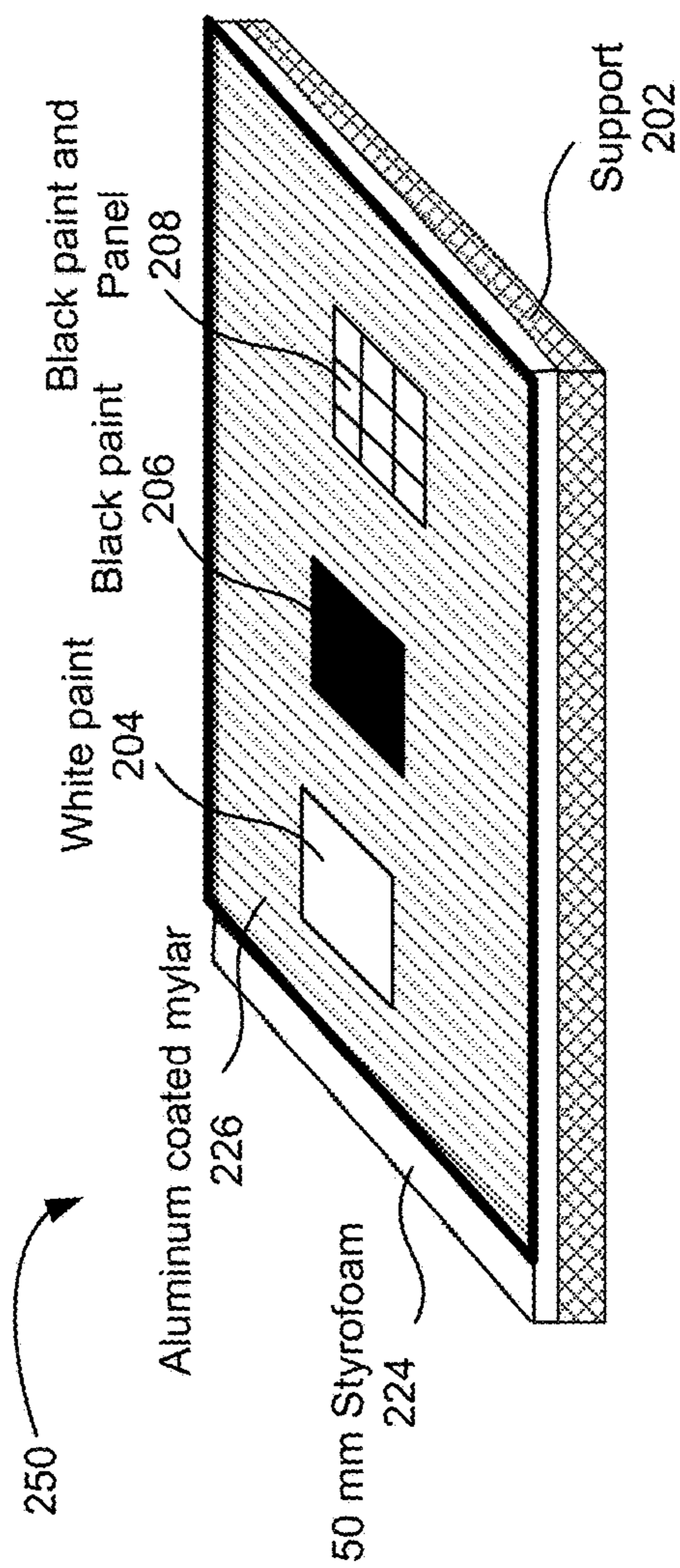


FIG. 2B

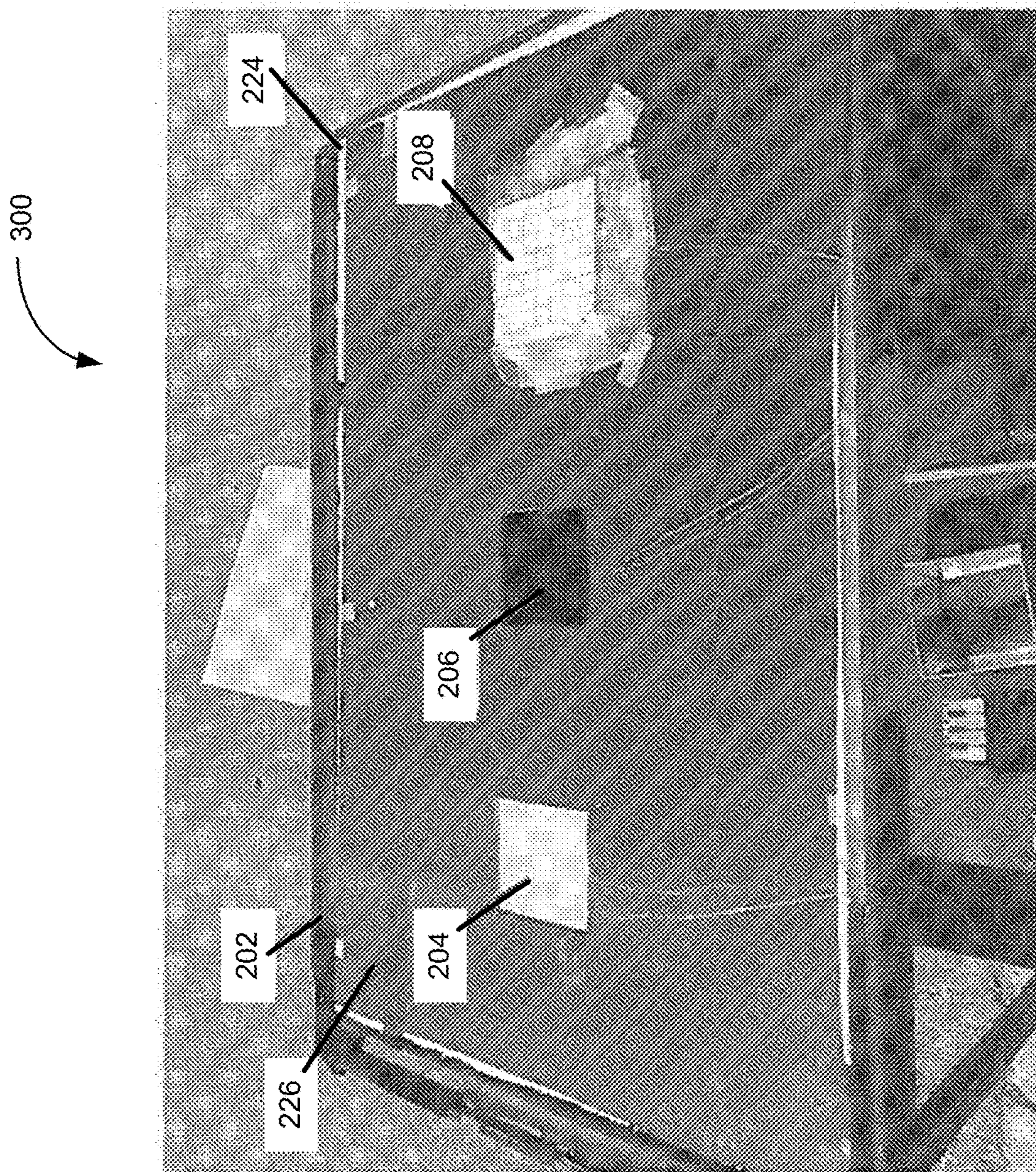


FIG. 3

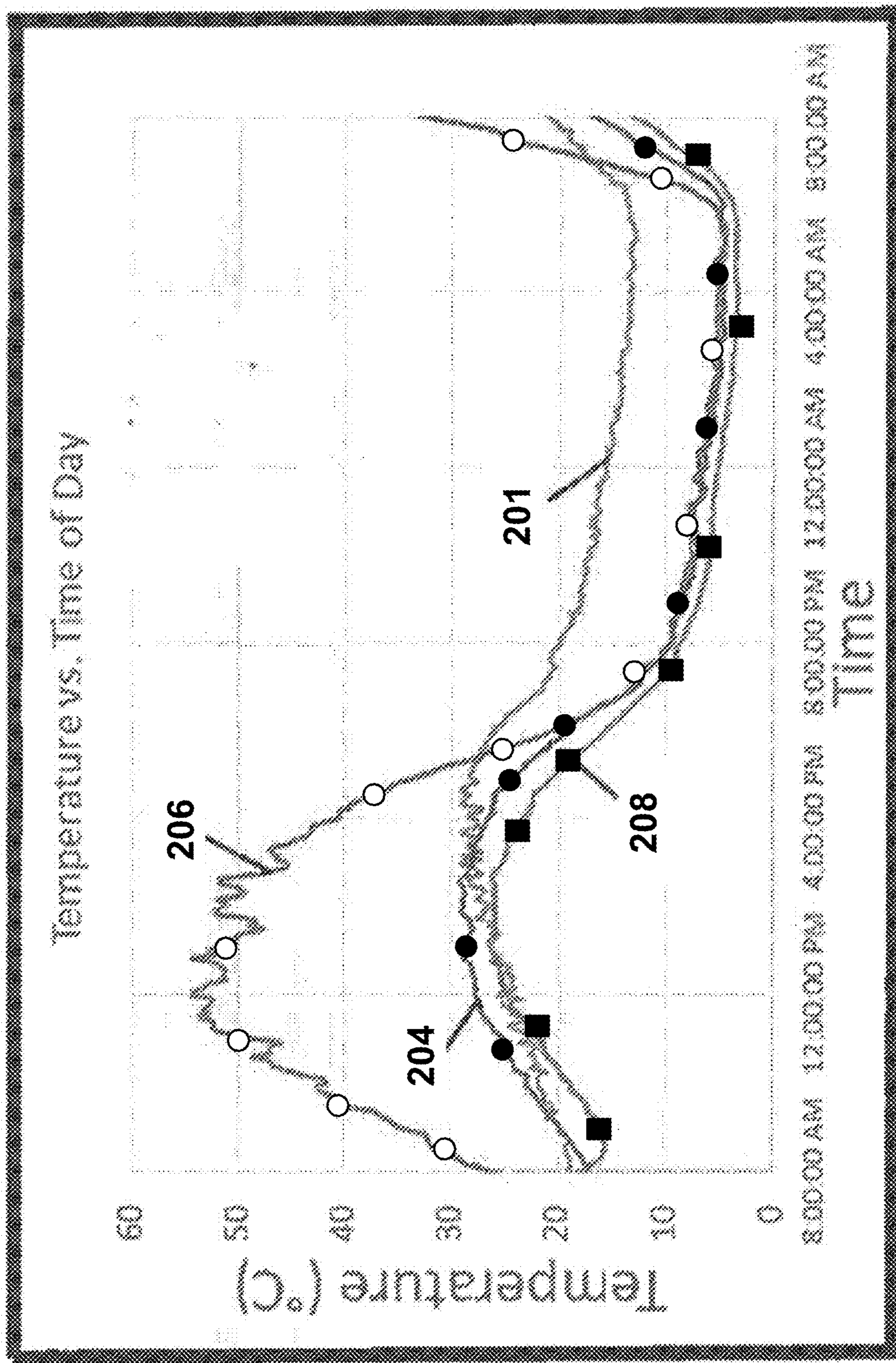


FIG. 4

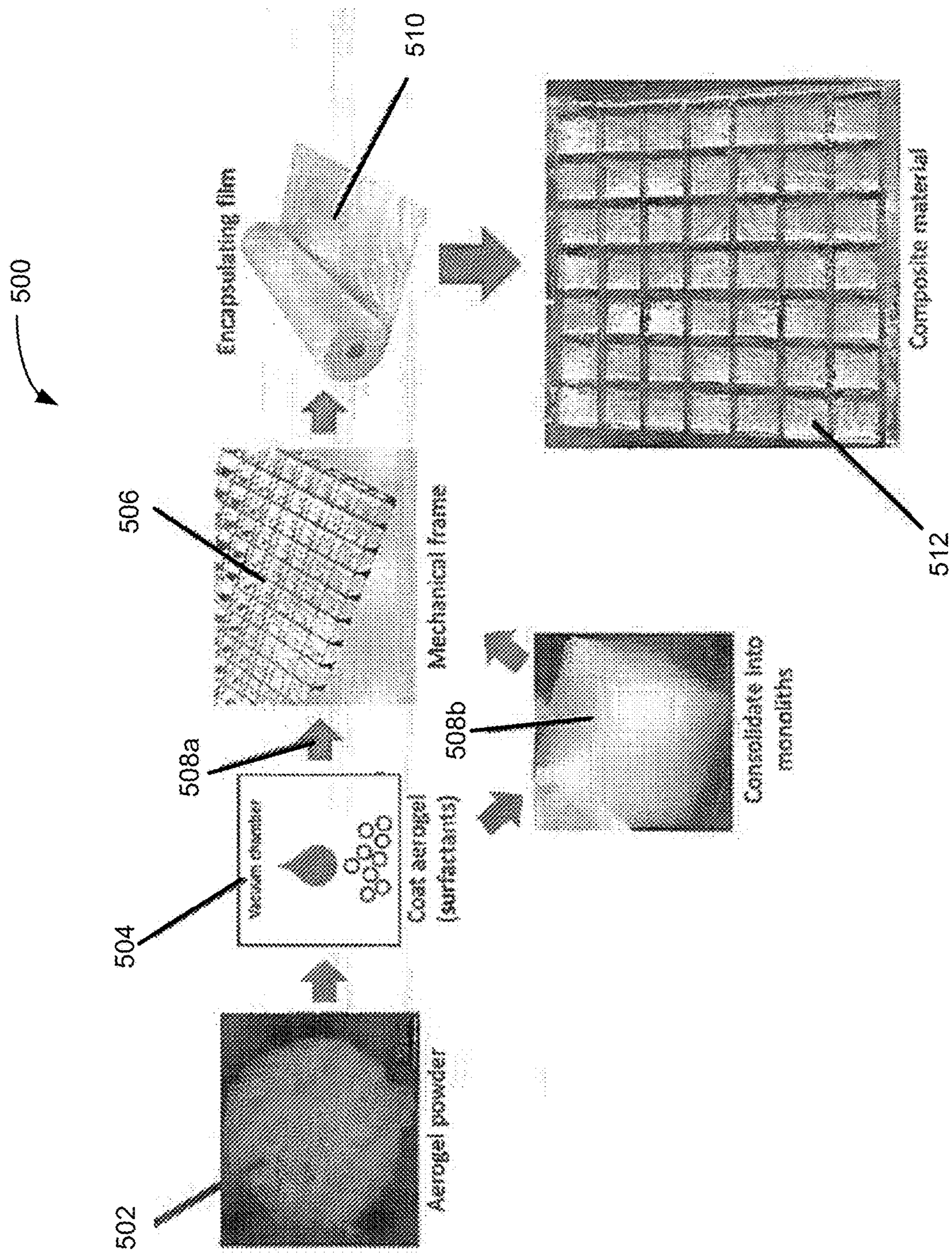


FIG. 5

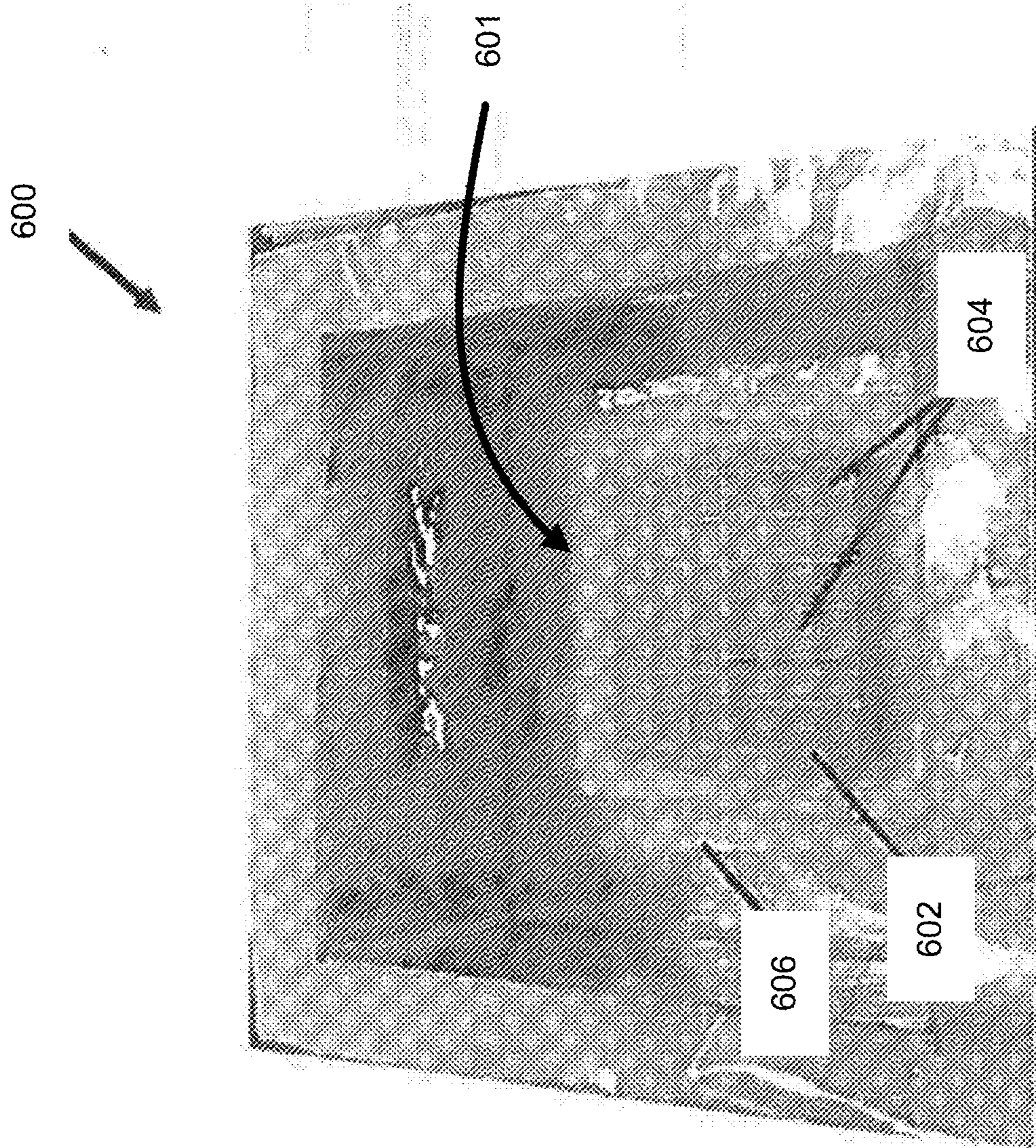


FIG. 6

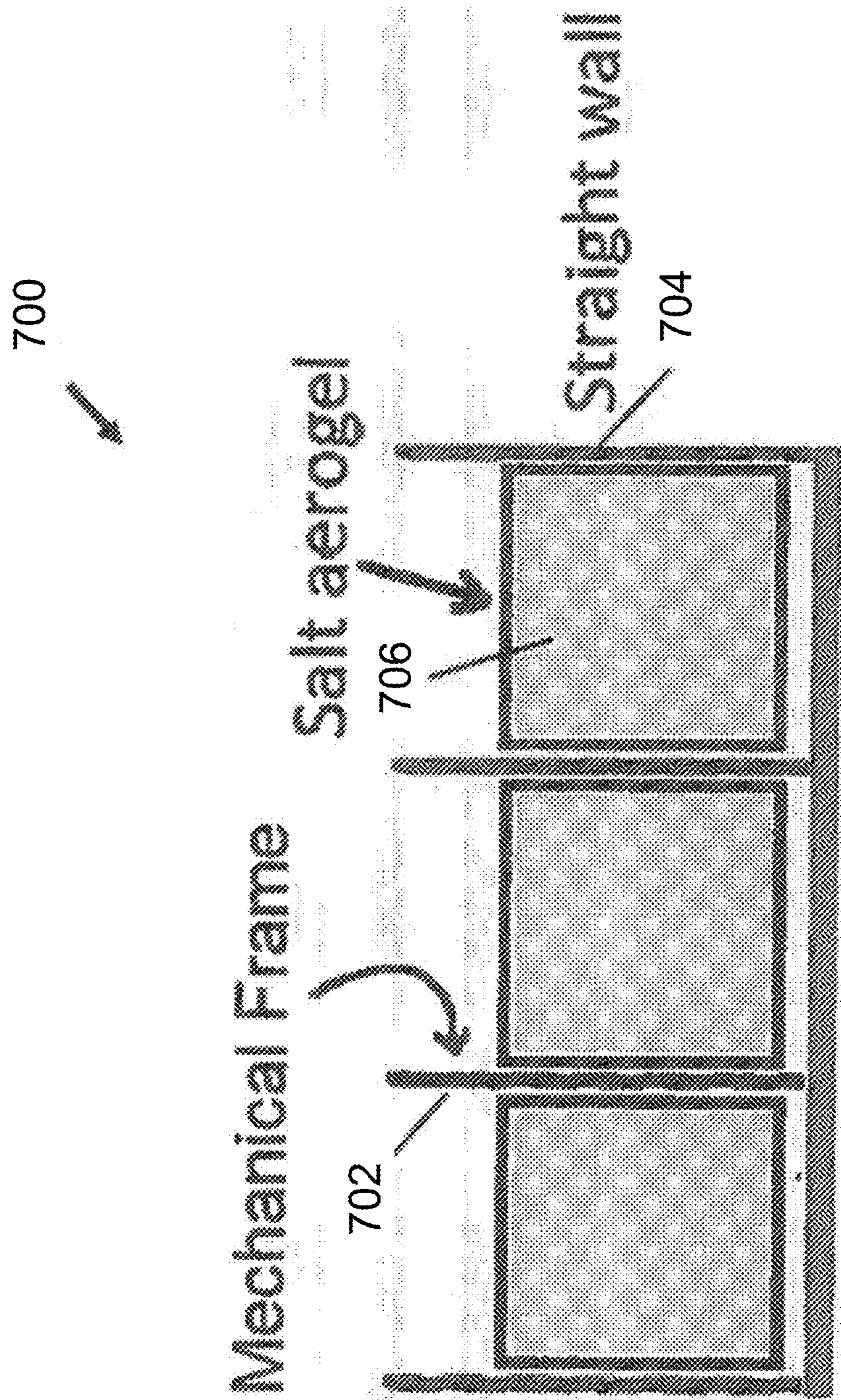


FIG. 7

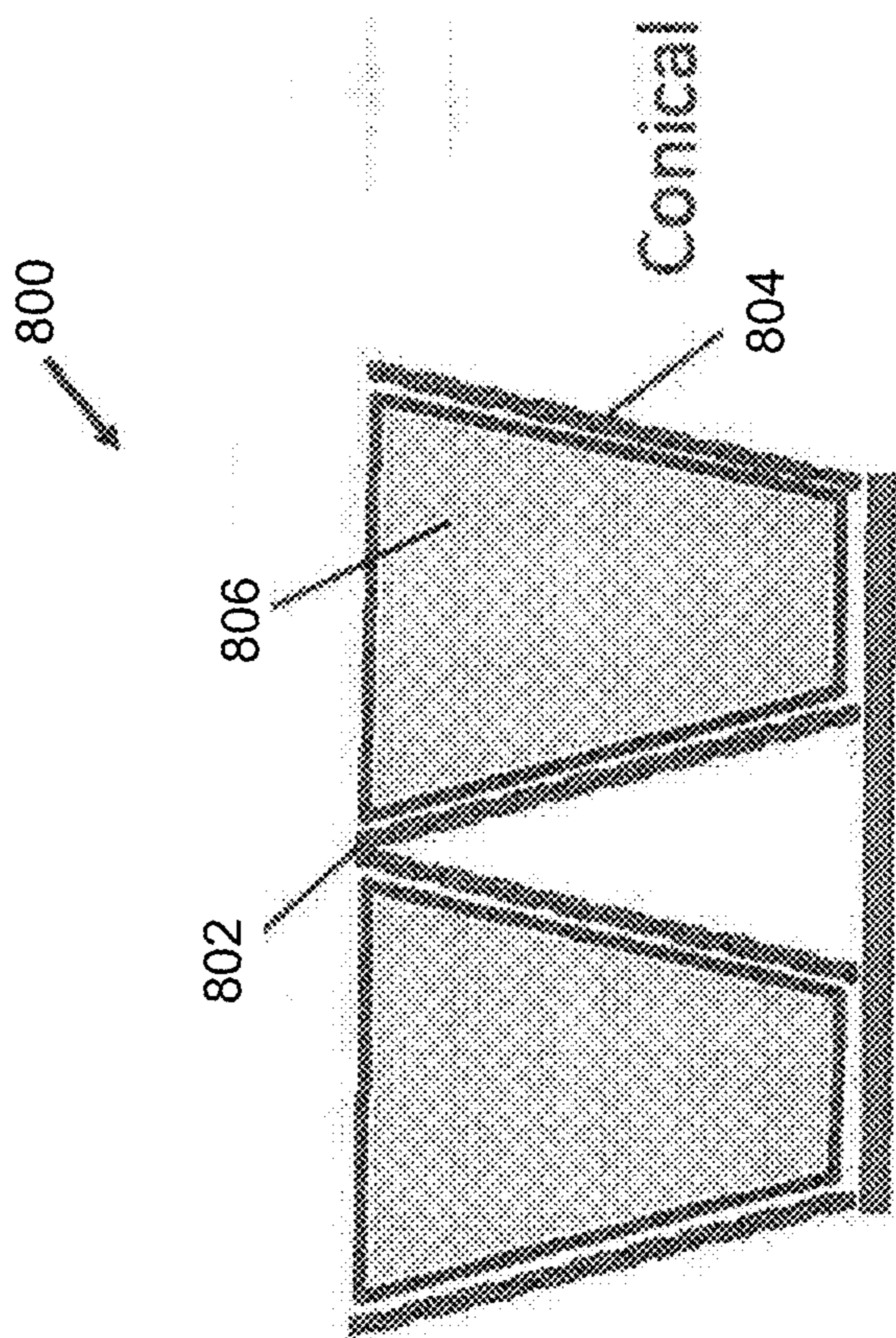


FIG. 8

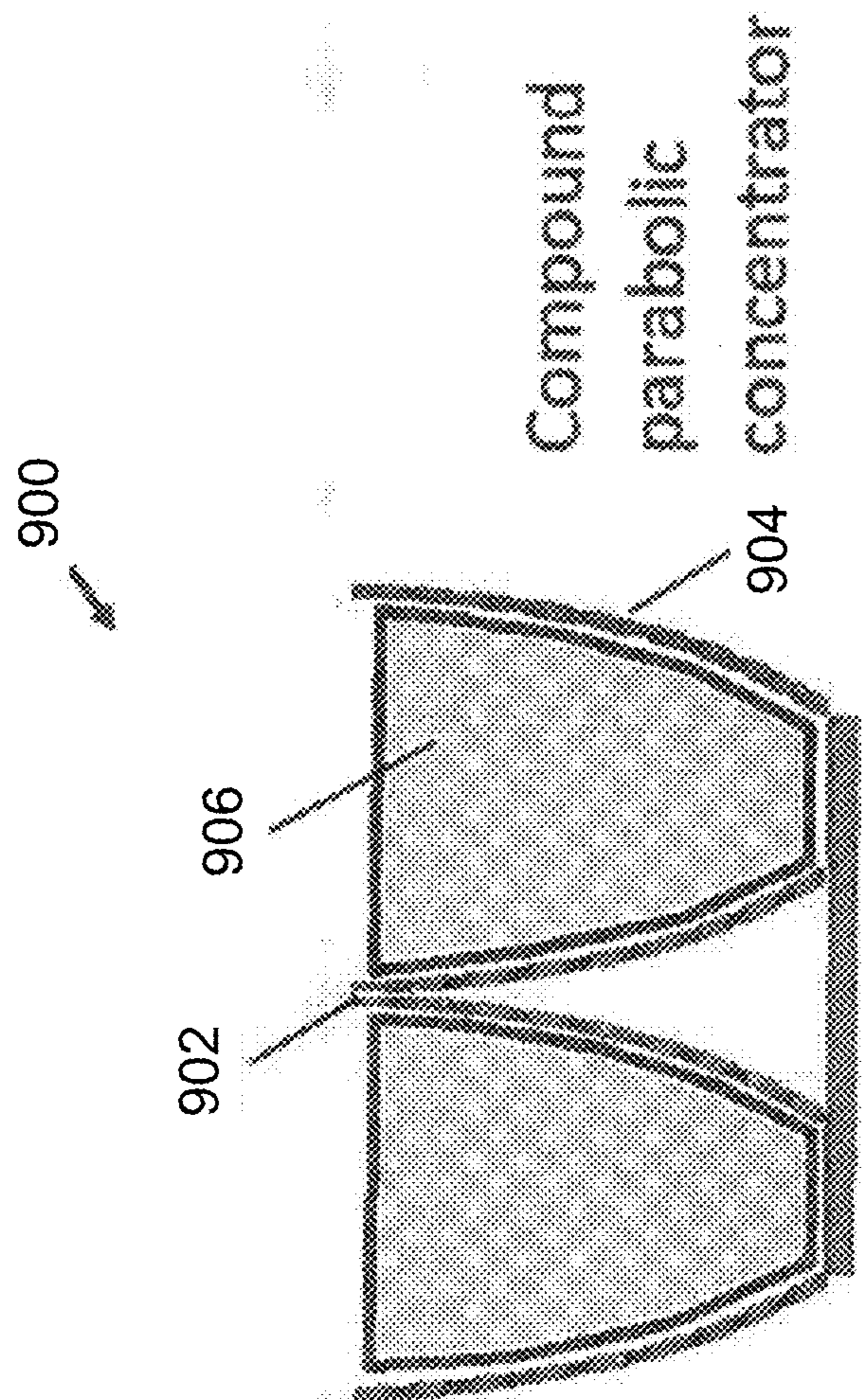


FIG. 9

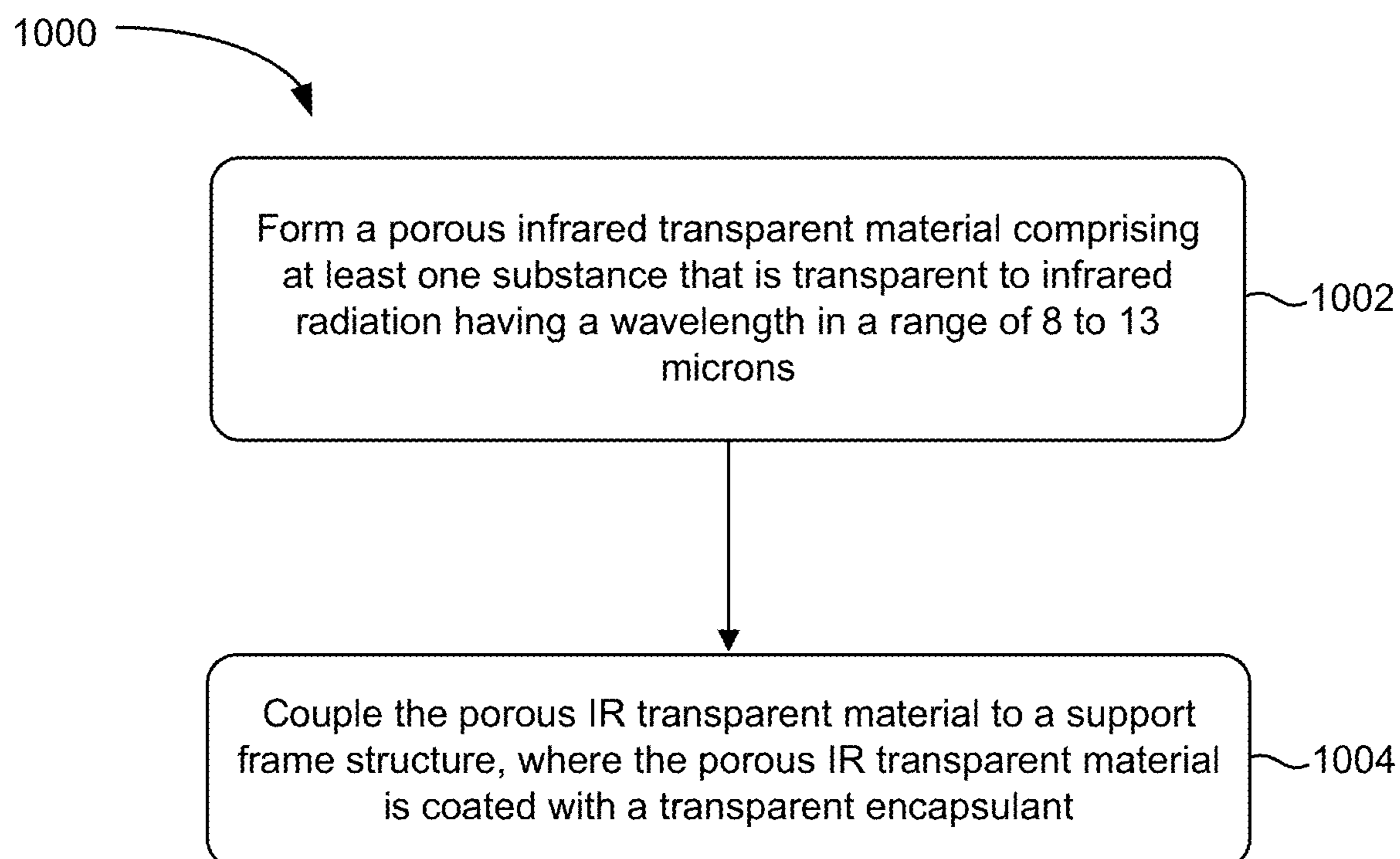


FIG. 10

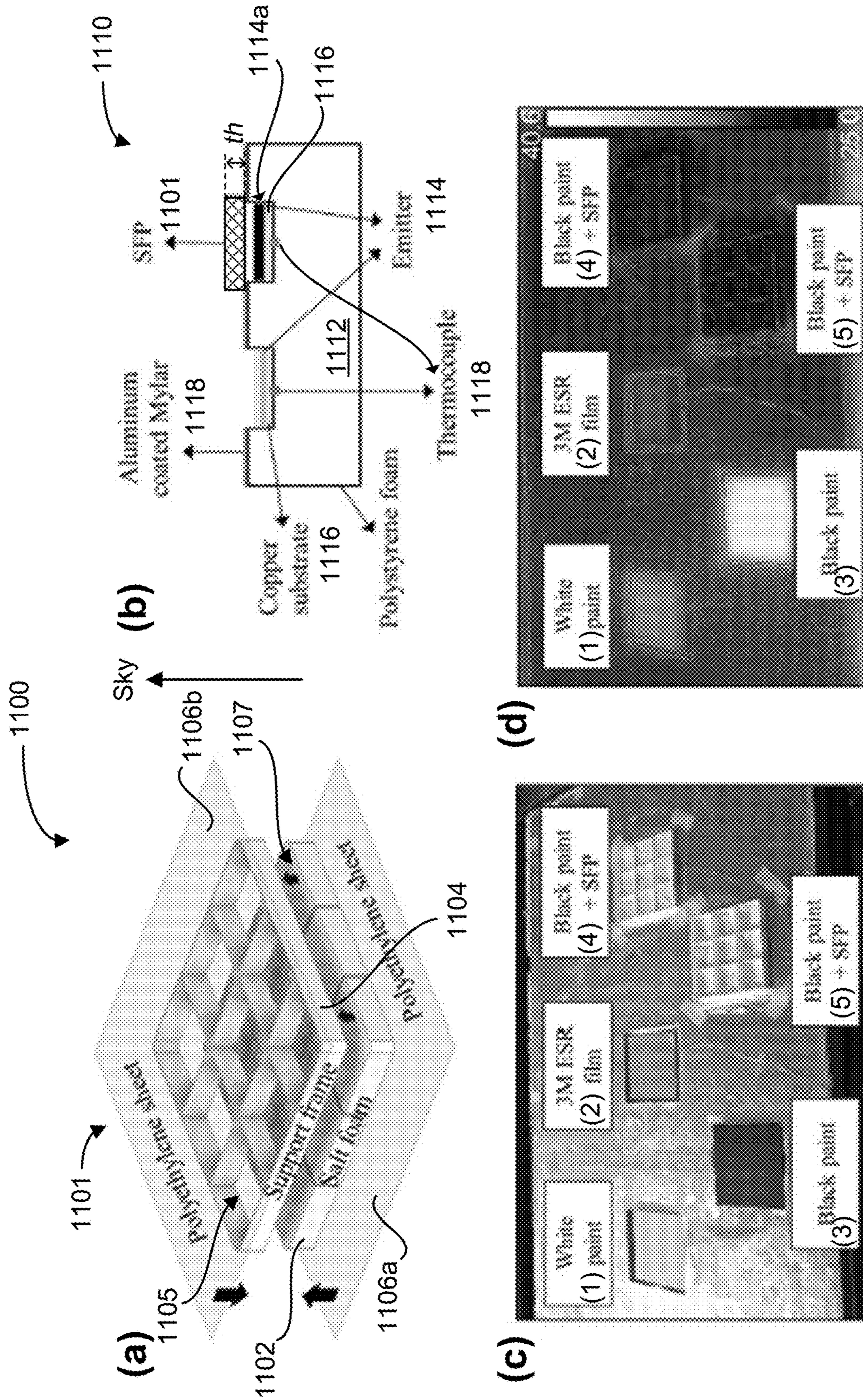


FIG. 11

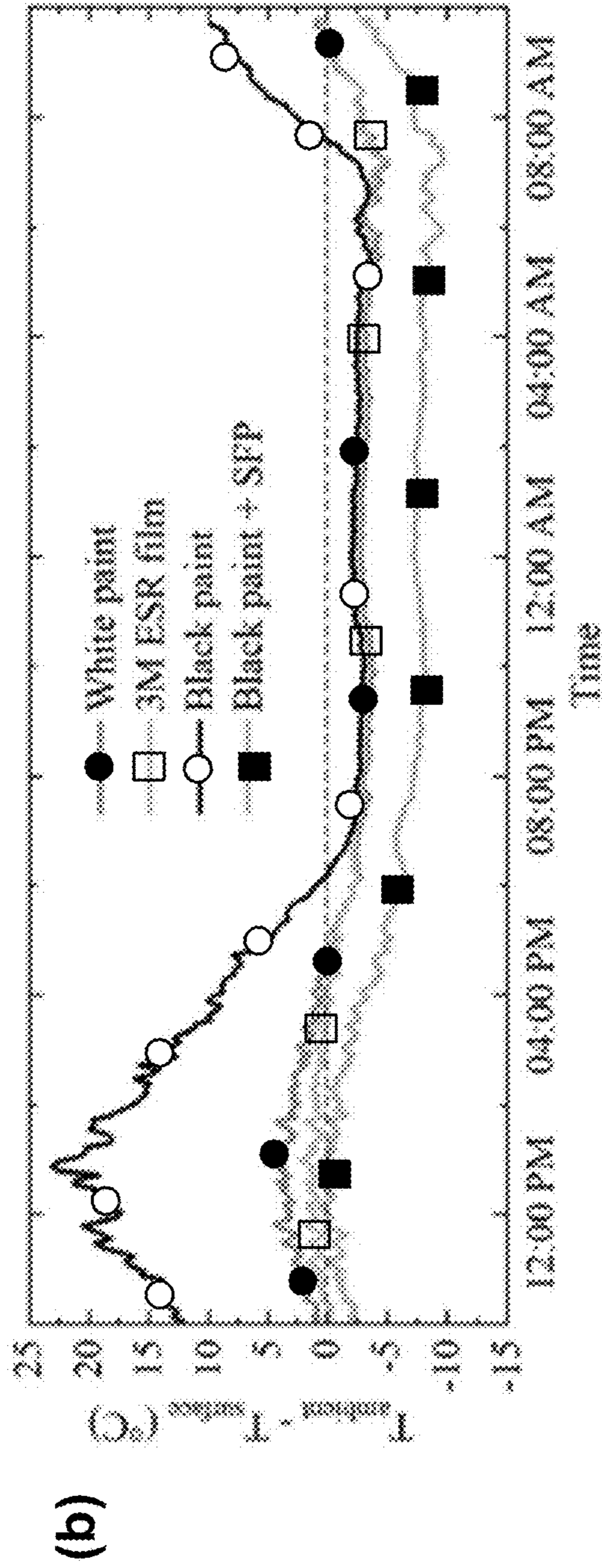
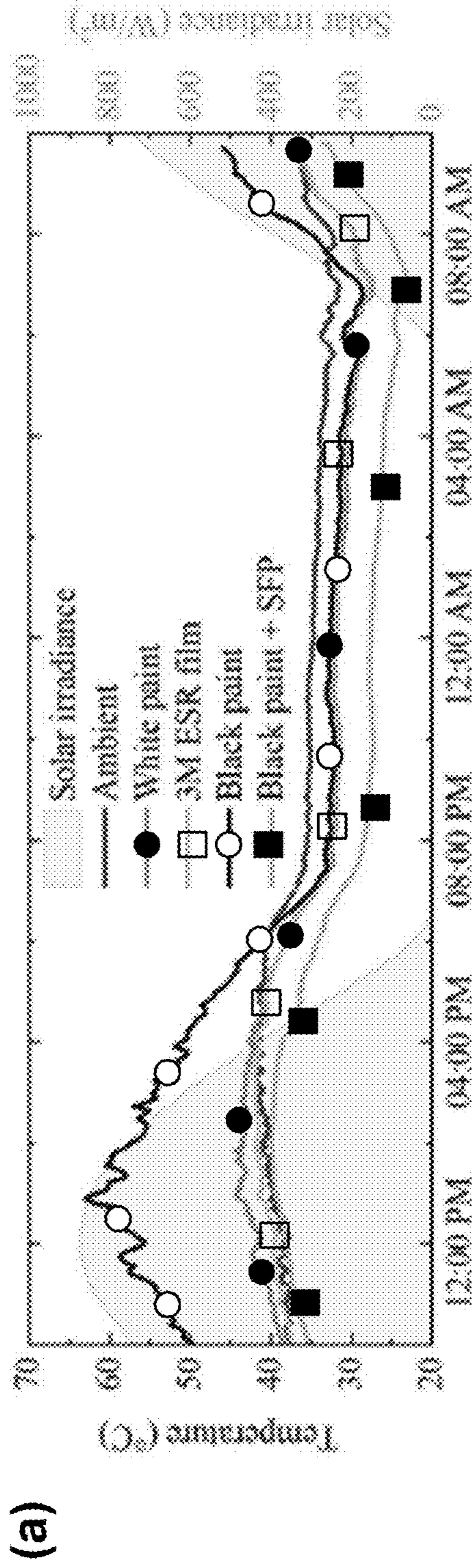


FIG. 12

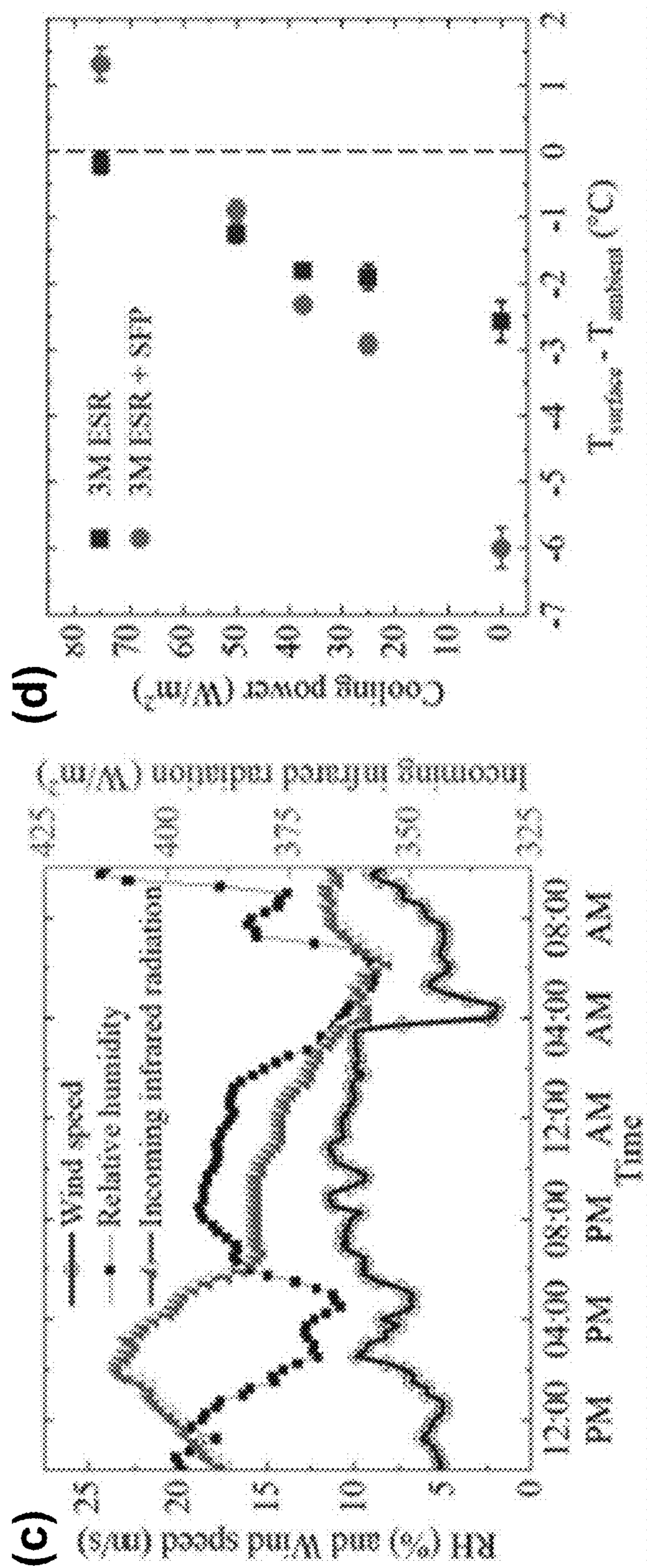


FIG. 12, continued

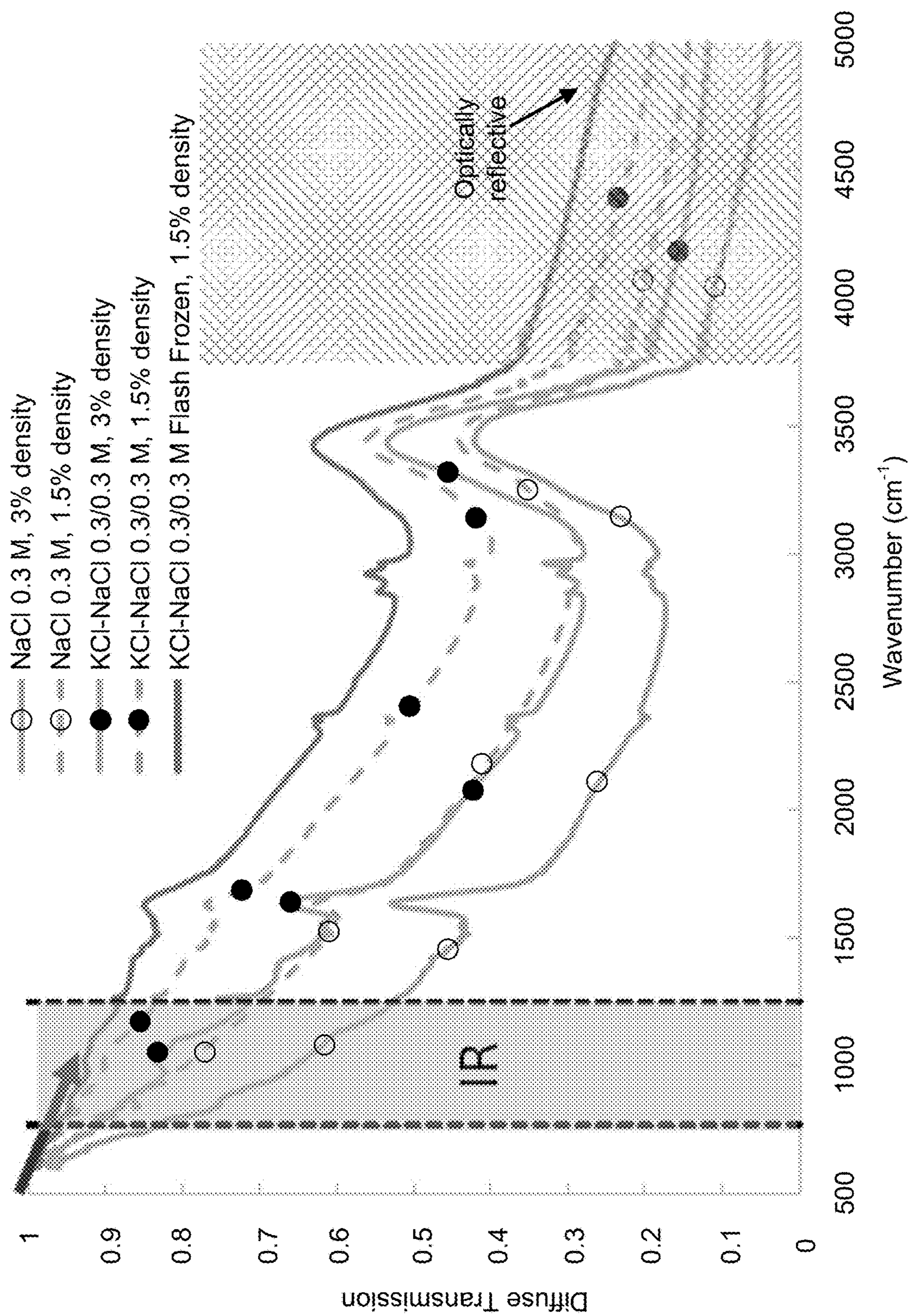


FIG. 13

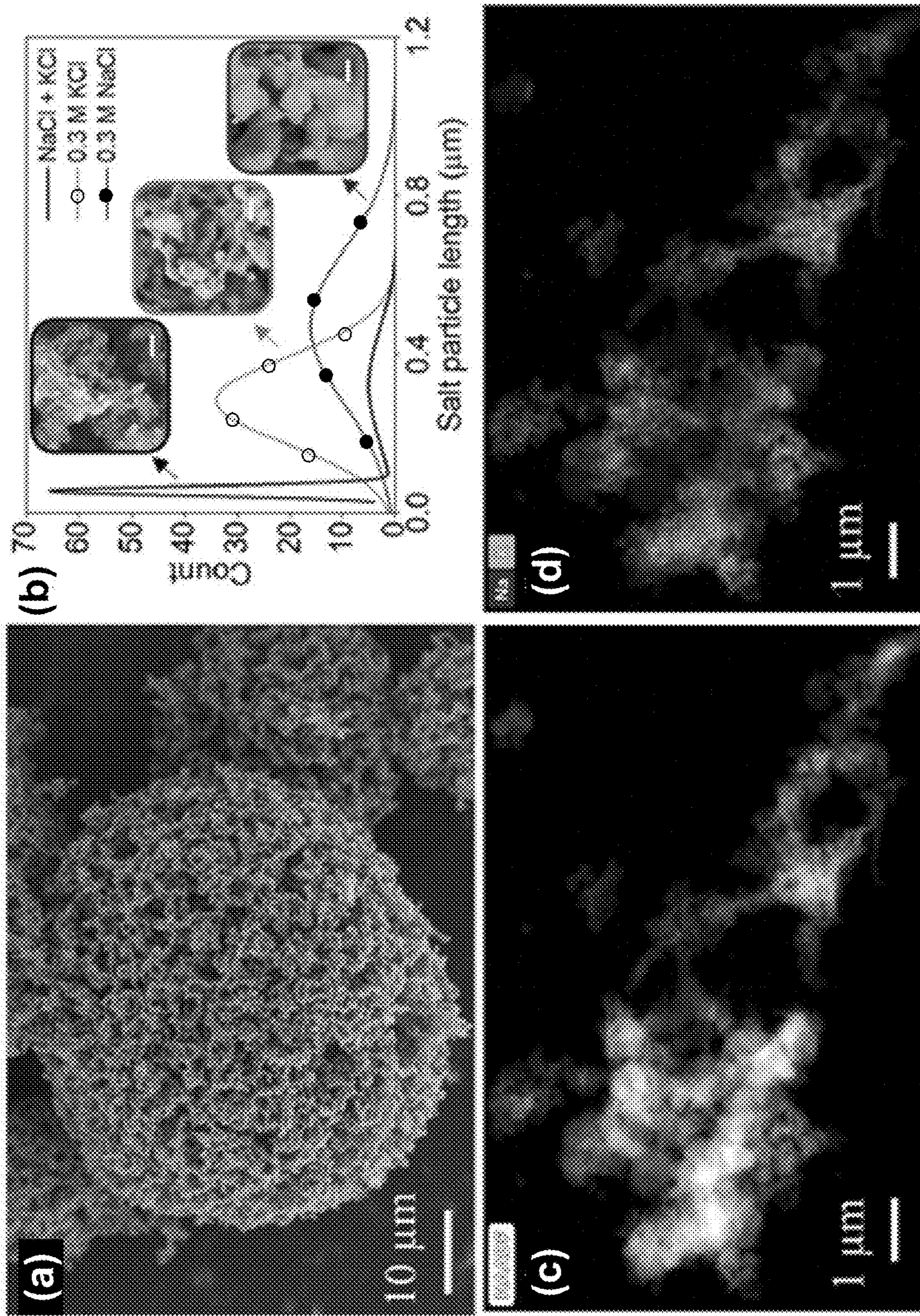


FIG. 14

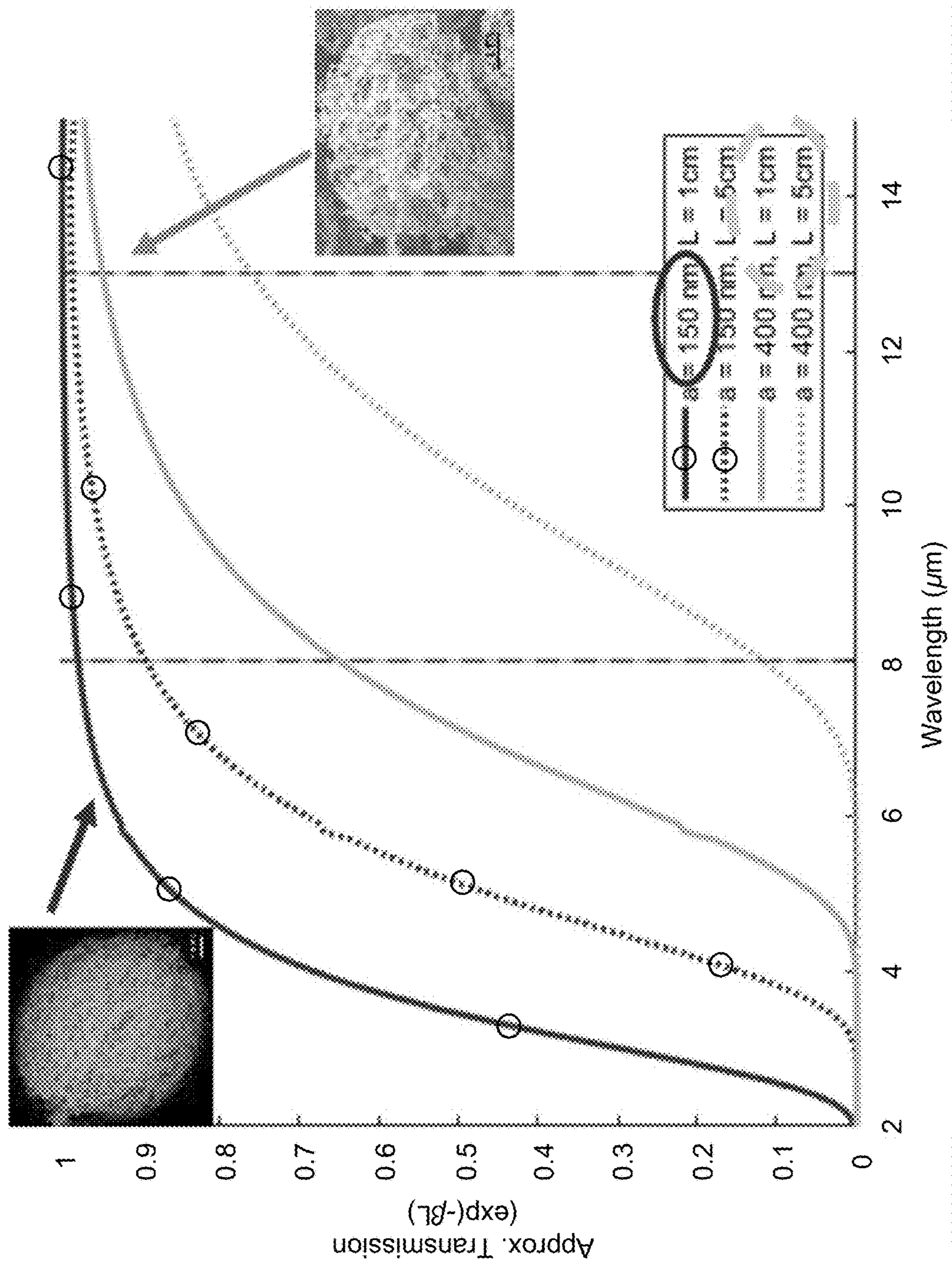


FIG. 15

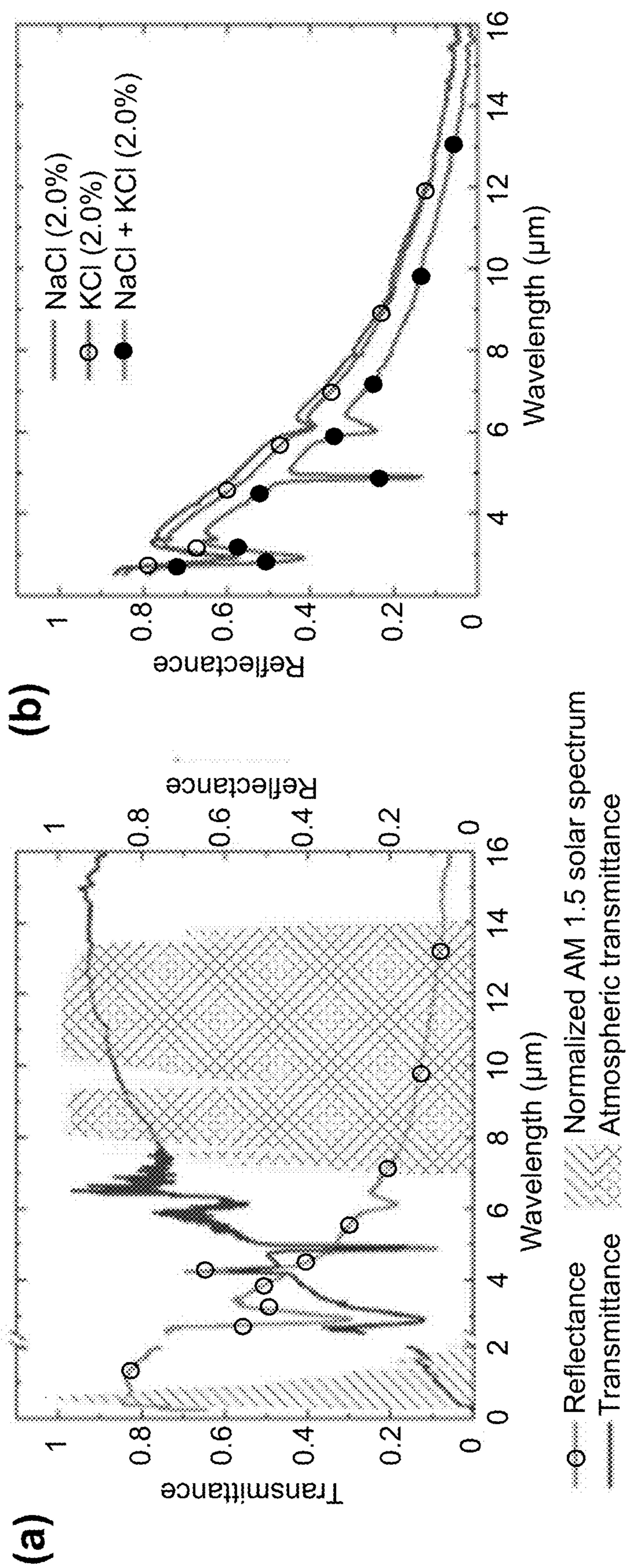


FIG. 16

**INFRARED TRANSPARENT AEROGEL
COMPOSITE FOR DEEP SUB-AMBIENT
COOLING OF VIRTUALLY ANY SURFACE**

RELATED APPLICATIONS

[0001] This application is a Continuation in Part of U.S. patent application Ser. No. 17/935,396, filed on Sep. 26, 2022, which claims priority to U.S. Provisional Patent Application No. 63/261,788 filed Sep. 29, 2021, each of which are herein incorporated by reference.

[0002] This invention was made with Government support under Contract No. DE-AC52-07NA27344 awarded by the United States Department of Energy. The Government has certain rights in the invention.

STATEMENT REGARDING PRIOR
DISCLOSURES BY THE INVENTOR OR A
JOINT INVENTOR

[0003] The following disclosure(s) are submitted under 35 U.S.C. 102(b)(1)(A):

[0004] “All-day passive radiative cooling using common salts,” Authorea, Mariana Desiree Reale Batista, Alyssa L. Troksa, Hannah V. Eshelman, Michael Bagge-Hansen, and John D. Roehling. Posted on 10 Mar. 2023, [online 10.22541/au.167845407.79020772/v1].

[0005] “All-day passive radiative cooling using common salts,” Material Horizons, Mariana Desir e Reale Batista, Alyssa L. Troksa, Hannah V. Eshelman, Michael Bagge-Hansen, and John D. Roehling. Accepted on 28 Sep. 2023, [online 10.1039/d3mh01139a].

FIELD OF THE INVENTION

[0006] The present invention relates to cooling a surface, and more particularly, this invention relates to infrared transparent aerogel composite for deep sub-ambient cooling of virtually any surface.

BACKGROUND

[0007] Thermal radiative heat loss occurs continuously for any surface facing the sky. Radiation from a surface can escape to space because the atmosphere is transparent to thermal infrared (IR) radiation having wavelengths between 8 and 13 microns (μm), encompassing the peak of thermal radiation at room temperature. In practice, a surface undergoes radiative heat exchange with the sky having a very low apparent temperature. The cold heat-sink of space can therefore be used to absorb heat generated from a surface without additional energy input. This radiative heat exchange is a radiative cooling effect that occurs on every sky-facing surface and may allow cooling to sub-ambient temperatures.

[0008] In fact, daily ambient temperature swings between night and day are due to (1) surface cooling via infrared (IR) radiation escaping into the cold of space, and (2) surface heating from solar absorption outpacing IR cooling. Therefore, by avoiding the pathway of heating a radiating surface (e.g., avoiding the absorption of sunlight), it may be possible to achieve sub-ambient cooling during the day. Passive day-time radiative cooling (PDRC) is a viable method that can provide 24 hour, electricity-free cooling.

[0009] Sunlight may be reflected from a surface so that the surface may be cooled by redirection (e.g., by reflection) of sunlight and loss of infrared radiation. Two factors have

been the focus of surface cooling: (1) high reflectivity for solar light, (2) high IR emission for cooling. However, there is a theoretical gap. Theoretically, considering only IR radiation and sunlight, a surface should be able to be cooled to 60 to 50° C. to below ambient temperature; however, reports demonstrate only a 5 to 10° C. at maximum reduction.

[0010] Different studies have achieved daytime cooling through engineering the optical and IR properties. This kind of daytime sub-ambient cooling effect has been demonstrated by numerous materials (i.e., emitters) that are highly effective at reflecting and/or blocking to solar radiation resulting in reduced solar absorption, and also highly emissive in the 8-13 μm band (i.e., nearly maximum loss of heat to space). These radiating surfaces typically reach a few degrees below ambient temperature (<2 to 10)° C. Small temperature differences are a typical result because the radiative cooling effect is negated by parasitic heating from the surrounding warmer air (once a surface gets cold, the surface regains heat from the warmer surroundings). Thus, a significant drawback of these studies include parasitic losses from the surrounding air severely limiting the ultimate performance of most engineered surfaces.

[0011] Therefore, if parasitic heat gains are minimized, eliminated, etc. much lower temperatures may be possible with increased cooling power. In fact, theoretical work has shown that cooling up to 60° C. below ambient is possible under optimal conditions. In short, if a cooling surface is sufficiently insulated from its surroundings while still allowing IR radiation to escape to space, much more effective radiative cooling can be realized.

[0012] One recent demonstration engineered to overcome the heat loss included a vacuum chamber with an IR transparent (ZnSe) window that can reach 43° C. below ambient temperature when using a strong IR emitter. However, while this method demonstrated effective cooling, the approach is not scalable to large areas which is an essential aspect for most practical cooling applications, such as air conditioning.

[0013] To reduce costs, an inexpensive IR material is needed that can insulate large areas of cooling emitters. Polyethylene (PE) aerogels have been fabricated to this end for improved performance over un-insulated emitters, and while they are effective, PE aerogels will not survive typical outdoor conditions due to sunlight degradation and they are somewhat costly to produce. PE films only last weeks to months in direct sunlight before completely falling apart. Additionally, ultraviolet (UV) light from the sun degrades the plastic drastically reduces IR transmission within a few days, which reduces the ability to allow an underlying surface to cool.

SUMMARY

[0014] Features and advantages of the disclosed apparatus, systems, and methods will become apparent from the following description. Applicant is providing this description, which includes drawings and examples of specific embodiments, to give a broad representation of the apparatus, systems, and methods. Various changes and modifications within the spirit and scope of the application will become apparent to those skilled in the art from this description and by practice of the apparatus, systems, and methods. The scope of the apparatus, systems, and methods is not intended

to be limited to the particular forms disclosed and the application covers all modifications, equivalents, and alternatives falling within the spirit and scope of the apparatus, systems, and methods as defined by the claims.

[0015] Applicant's apparatus, systems, and methods accomplishes the requirements of: (1) losing heat to space and (2) preventing heating from sunlight and ambient surroundings by being (a) infrared transparent in the 8-13 μm wavelength range, (b) highly optically reflective to reduce heating from sunlight in the 300 nm-2500 nm range (solar spectrum), and (c) thermally insulating to avoid heating from surrounding air. The various embodiments Applicant's apparatus, systems, and methods provides a material composite that enables sub-ambient radiative cooling of virtually any sky-facing surface, when the disclosure is placed on top in close contact. Applicant's apparatus, systems, and methods work similar to a solar heater vacuum tube, but instead of providing heating, it provides cooling by maintaining a temperature difference between a surface and ambient air. In a preferred embodiment Applicant's apparatus, systems, and methods comprises of an IR transparent aerogel or aerogel, made from an inexpensive IR transparent material, such as common table salt (NaCl, KCl), and an optomechanical frame (multiple designs are possible) that physically protect the delicate IR transparent aerogel, and can serve to concentrate emitted radiation to the most transparent part sky (near vertical) to improve the net cooling power and serve as a mechanical support to the aerogel. NaCl and other water soluble salts have many of the desired properties for this application (high transmittance in 8-13 μm band) but are typically not considered for outdoor use. The insulating aerogel contains a certain size distribution and porosity to add optical reflectance and maintain 3 Other aspects and implementations of the presently described inventive concepts will become apparent from the following detailed description, which, when taken in conjunction with the drawings, illustrate by way of example the principles of the invention. strength, while continuing to provide high thermal resistance for insulating power and high IR transparency in the 8-13 μm band. In the preferred embodiment the water-soluble aerogel/aerogel can be coated with a hydrophobic coating and/or anti-caking agents (i.e., potassium ferrocyanide) to minimize moisture absorption and negative effects from outdoor weather. Additionally, a UV-stabilized, IR transparent plastic film with thin-film water-vapor transmission barriers can be used to encapsulate the whole device to serve as an improved moisture barrier, mitigating the issue of water-solubility and hygroscopicity.

[0016] Applicant's apparatus, systems, and methods can be used to cool virtually any surface for such uses as electricity-free air conditioning, remote refrigeration, potable water collection, etc. It could be used to cool buildings or vehicles directly, recycle evaporated process water (cooling towers) and could condense potable water from the air in arid areas and serve for disaster relief when electricity is not available. Coupling it with a heat exchanger and fluid storage, it could be used to supplement and improve the efficiency of HVAC systems, or deep-freezer units by providing a low temperature heat sink for rejecting heat.

[0017] The apparatus, systems, and methods are susceptible to modifications and alternative forms. Specific embodiments are shown by way of example. It is to be understood that the apparatus, systems, and methods are not

limited to the particular forms disclosed. The apparatus, systems, and methods cover all modifications, equivalents, and alternatives falling within the spirit and scope of the application as defined by the claims.

[0018] According to one embodiment, an apparatus for cooling a surface includes a composite that includes a porous infrared (IR) transparent material having at least one substance that is transparent to infrared radiation having a wavelength in a range of 8 to 13 μm . In addition, the composite includes a support frame having an opening for exposing a sky-facing surface of the porous IR transparent material and an encapsulant. The encapsulant is positioned on the sky-facing surface of the porous IR transparent material. The composite is configured to be optically reflective to sunlight and is thermally insulating for reducing heating of a surface from surrounding air.

[0019] According to another embodiment, a method of forming an apparatus for cooling a surface includes forming a porous infrared (IR) transparent material having at least one substance that is transparent to infrared radiation having a wavelength in a range of 8 to 13 μm . The method includes coupling the porous IR transparent material to a support frame structure, where the porous IR transparent material is coated with an IR transparent encapsulant.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The accompanying drawings, which are incorporated into and constitute a part of the specification, illustrate specific embodiments of the apparatus, systems, and methods and, together with the general description given above, and the detailed description of the specific embodiments, serves to explain the principles of the apparatus, systems, and methods.

[0021] FIG. 1 is a schematic drawing of a transparent IR insulator, according to one embodiment.

[0022] FIG. 2A illustrates one embodiment of forming a transparent IR insulator, according to one embodiment

[0023] FIG. 2B illustrates a test apparatus for a transparent IR insulator, according to one embodiment.

[0024] FIG. 3 provides additional details of a test apparatus for a transparent IR insulator, as illustrated in FIG. 2B.

[0025] FIG. 4 is a graph of heat over time of samples obtained from the test apparatus illustrated in FIG. 3.

[0026] FIG. 5 is an illustration of another embodiment of forming a transparent IR insulator, according to one embodiment.

[0027] FIG. 6 is an image depicting a consolidated material positioned on a sky-facing surface, according to one embodiment.

[0028] FIG. 7 is a descriptive illustration of one embodiment of a mechanical frame having straight walls, according to one embodiment.

[0029] FIG. 8 is a descriptive illustration of an embodiment of a mechanical frame having conical walls, according to one embodiment.

[0030] FIG. 9 is a descriptive illustration of an embodiment of a mechanical frame having compound parabolic concentrator walls, according to one embodiment.

[0031] FIG. 10 is a flow chart of a method for forming an apparatus for cooling a surface, according to one embodiment.

[0032] FIG. 11 is an illustration of an apparatus and system associated with a salt aerogel panel, according to one embodiment. Part (a) is a schematic drawing of a salt aerogel

panel assembly, part (b) is an illustration of a testing set up, part (c) is an optical image of a testing set up, and part (d) is a thermal image of a testing set up.

[0033] FIG. 12 is a series of graphs depicting the heating of the samples in the testing set up of part (d) of FIG. 11, according to one embodiment. Part (a) is a graph of the temperature of each tested sample over a 24 hour period, part (b) is a graph of the adjusted $T_{ambient} - T_{surface}$ for each tested sample over the 24 hour period, part (c) is a graph of the wind speed, relative humidity, and incoming infrared radiation during the 24 hour period, and part (d) is a graph of the cooling power of a layer of SFP compared to a layer of 3M ESR.

[0034] FIG. 13 is a plot of the diffuse transmission of different salt aerogels formed with different salt conditions and freezing parameters, according to one embodiment.

[0035] FIG. 14 is a series of images of features and particles of the IR transparent material, according to one embodiment. Part (a) is a scanning electron microscope (SEM) image of a NaCl+KCl aerogel particle, part (b) is a histogram of feature sizes of particles of different materials with inset SEM images of each material, parts (c) and (d) are transmission electron microscopy (TEM) images of crushed NaCl+KCl particles.

[0036] FIG. 15 depicts the approximate IR transmission of salt aerogel samples having different feature sizes and different thickness of the salt aerogel sample, according to one embodiment.

[0037] Part (a) of FIG. 16 depicts the hemispherical transmittance and reflectance of aerogels according to one embodiment.

[0038] Part (b) of FIG. 16 is a plot of reflectance of different aerogels formed from pure salts, NaCl and KCl, according to one embodiment.

[0039] FIG. 17 is a series of images showing the effect of humidity on uncoated salt foam panels and salt foam panels coated with ferrocyanide, according to one embodiment.

DETAILED DESCRIPTION

[0040] The following description is made for the purpose of illustrating the general principles of the present invention and is not meant to limit the inventive concepts claimed herein. Further, particular features described herein can be used in combination with other described features in each of the various possible combinations and permutations.

[0041] Unless otherwise specifically defined herein, all terms are to be given their broadest possible interpretation including meanings implied from the specification as well as meanings understood by those skilled in the art and/or as defined in dictionaries, treatises, etc.

[0042] It must also be noted that, as used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless otherwise specified.

[0043] As also used herein, the term “about” denotes an interval of accuracy that ensures the technical effect of the feature in question. In various approaches, the term “about” when combined with a value refers to plus and minus 10% of the reference value. For example, a length of about 100 nm refers to a length of 100 nm+10 nm, a temperature of about 50° ° C. refers to a temperature of 50° C.±5° C., etc.

[0044] As further used herein, the term “fluid” may refer to a liquid or a gas.

[0045] Further, as used herein, all percentage values are to be understood as percentage by weight (wt. %), unless

otherwise noted. Moreover, all percentages by weight are to be understood as disclosed in an amount relative to the bulk weight of an organic plastic scintillator material, in various approaches.

[0046] Unless expressly defined otherwise herein, each component listed in a particular approach may be present in an effective amount. An effective amount of a component means that enough of the component is present to result in a discernable change in a target characteristic of the ink, printed structure, and/or final product in which the component is present, and preferably results in a change of the characteristic to within a desired range. One skilled in the art, now armed with the teachings herein, would be able to readily determine an effective amount of a particular component without having to resort to undue experimentation.

[0047] The following description includes embodiments of apparatus of an infrared transparent porous material composite for deep sub-ambient cooling of virtually any surface and/or related systems and methods.

[0048] In accordance with one general embodiment, an apparatus for cooling a surface includes a composite that includes a porous infrared (IR) transparent material having at least one substance that is transparent to infrared radiation having a wavelength in a range of 8 to 13 μm . In addition, the composite includes a support frame having an opening for exposing a sky-facing surface of the porous IR transparent material and an encapsulant. The encapsulant is positioned on the sky-facing surface of the porous IR transparent material. The composite is configured to be optically reflective to sunlight and is thermally insulating for reducing heating of a surface from surrounding air.

[0049] In accordance with another general embodiment, a method of forming an apparatus for cooling a surface includes forming a porous infrared (IR) transparent material having at least one substance that is transparent to infrared radiation having a wavelength in a range of 8 to 13 μm . The method includes coupling the porous IR transparent material to a support frame structure, where the porous IR transparent material is coated with an IR transparent encapsulant.

[0050] A list of acronyms used in the description is provided below.

[0051] C Celsius

[0052] CTAB cetyltrimethylammonium bromide

[0053] ESR Enhanced Specular Reflector

[0054] IR infrared

[0055] M molar

[0056] nm nanometer

[0057] PDRC passive day-time radiative cooling

[0058] PE polyethylene

[0059] SEM scanning electron microscopy

[0060] SFP salt foam panel

[0061] TEM transmission electron microscopy

[0062] TBA tert butyl alcohol

[0063] μm micron

[0064] UV Ultraviolet

[0065] Referring to the drawings, to the following detailed description, and to incorporated materials, detailed information about the apparatus, systems, and methods is provided including the description of specific embodiments. The detailed description serves to explain the principles of the apparatus, systems, and methods. The apparatus, systems, and methods are susceptible to modifications and alternative forms. The application is not limited to the particular forms disclosed. The application covers all modifications, equiva-

lents, and alternatives falling within the spirit and scope of the apparatus, systems, and methods as defined by the claims.

[0066] According to various embodiments, an apparatus, a system, and methods have been developed that allow virtually any underlying surface to be cooled to sub-ambient temperatures using materials that are inexpensive, scalable, and robust to sunlight. The essential properties of the apparatus described herein include, 1) materials are highly reflective to solar radiation to reduce heating from sunlight in the 300 nm to 2500 nm range (solar spectrum) (minimizing heat gain during the day), 2) materials are highly thermally insulating to avoid heating from surrounding air (minimizing heat gain, around the clock), and 3) materials are transparent to the 8-13 μm band, allowing radiation to escape to space and effectively cool the surface. These three properties allow the current invention to be placed atop virtually any surface, thereby allowing the surface to cool to sub-ambient temperature.

[0067] As illustrated in FIG. 1, a system 100 may be implemented to cool a surface 102. A surface 102 warms from exposure to sunlight and heat from the surrounding environment that is not counterbalanced by heat loss from IR radiation to space. Adding an IR transparent insulator 104 above the surface 102, where the IR transparent insulator 104 faces the direction of sunlight, blocks heating while allowing heat loss from IR radiation. The IR transparent insulator 104 allows reflection of incoming sunlight and as an insulator reduces heat from surrounding environment. The transparency of the IR transparent insulator 104 allows heat loss from IR radiation. Additionally, as described herein, the method of manufacture and the materials used are low-cost and scalable thereby realizing large-scale daytime radiative cooling.

[0068] Improved cooling has been shown to occur by limiting the radiative exchange with the sky to the most transparent regions (45° to the zenith). This angular selectivity effectively reduces radiative exchange with the warmer parts of the sky (angles toward the horizon) and improves the net cooling power from an emitting surface. This is usually accomplished with geometrically placed reflecting materials that surround the emitting surface, such as a conical reflector, but can be accomplished by other means such as photonic-crystal, where the surface emission does not follow the typical Lambert's cosine law.

[0069] According to various embodiments, an apparatus, systems, and methods use solution-processed, freeze-dried aerogels/foams from common salts to produce an insulating material that is optically reflective, thermally insulating, and infrared transparent. The utility of using common salts to produce these materials is three-fold, 1) they are inexpensive materials and the methods described herein make the materials inexpensive to produce, 2) the materials are robust to UV light and long-term exposure to UV does not degrade their performance, and 3) they can be packaged into mechanical frames that can further improve cooling performance through angular selectivity of the frame (i.e. geometrical reflectors built into the frame).

[0070] Sodium chloride, potassium chloride, etc. are very highly transparent to the IR, in addition to being stable under UV. If they are sitting out in sunlight, they will not be degraded from sunlight. The reason for that choice is a lot of work with polyethylene (plastic bags) degrades rapidly in sunlight unless it has some sort of UV stabilizer. IR trans-

parent aerogel are typically made from polyethylene and polyethylene is not stable and if ever directly rained on, it would collapse. The liquid tension in the polyethylene aerogel would collapse during exposure to water (e.g., rain). Aerogels are light, fluffy solids that are dried by removing the solvent by conversion from a solid to a gas, from a non-liquid state without surface tension, resulting in a dense network (e.g., super critical CO₂ drying). Freeze-drying does the same process. NaCl and KCl may be used as thick window for IR optics, a vacuum chamber with a KCl chamber, etc. NaCl and KCl have not been used in an aerogel.

[0071] Referring now to FIG. 2A, an exemplary method 200 of forming a salt aerogel panel (e.g., an IR transparent insulator, such as those disclosed herein) is shown, according to one inventive concept. As an option, the present method 200 may be implemented in conjunction with features from any other inventive concept listed herein, such as those described with reference to the other FIGS. Of course, the method 200 and others presented herein may be used in various applications and/or in permutations, which may or may not be specifically described in the illustrative inventive concept listed herein. Moreover, more or less operations than those shown in FIG. 2A may be included in method 200, according to various inventive concept. Furthermore, while exemplary processing techniques are presented with respect to FIG. 2A, other known processing techniques may be used for various steps.

[0072] According to one embodiment, the following description includes steps of an apparatus, systems, and methods. According to one embodiment, fabricating an electricity-free, around-the-clock, deep sub-ambient radiative cooling is described. In one approach, a thermally insulating material, e.g., a salt foam panel, an IR transparent aerogel, foam, etc. is packaged into panels. In a one approach, the thermally insulating material is an aerogel. Aerogels are the optimal size to scatter visible light (solar reflective), but small enough not to scatter infrared radiation (IR transparent). Aerogels are also the most thermally insulating solid currently known. Superhydrophobic coatings are commonly applied to some types of aerogels and can provide stability against moisture and rain. Additional encapsulation with a suitable IR transparent material can provide additional protection against moisture.

[0073] As illustrated in FIG. 2A, a syringe pump 210 provides a salt solution 212 to an ultrasonic spray head 214. The ultrasonic spray head 214 provides droplets 216 that are immersed in liquid nitrogen 218. The process allows fine control of droplet size according to the ultrasonic spray head 214 and syringe pump 210. This forms frozen droplets 220. The frozen droplets 220 are transferred to a freeze drying unit 122. The freeze drying unit 222 transforms the frozen droplets 220 to an aerogel 230.

[0074] FIG. 2B illustrates a placement of samples for testing thermal cooling on a surface. The aerogel 230 formed in FIG. 2A may be assembled into a panel 208 that is placed above black paint. Samples include white paint 204, black paint 206, and a panel 208 above black paint. The samples are transferred to an Aluminum coated mylar material surface 226 that rests on a 50 mm Styrofoam material 224 that is supported by a support or substrate 202. The support or substrate 202 also supports a panel of white paint 204 and a panel of black paint 206. The material composite of black

paint and panel **208**, the panel of white paint **204**, and the panel of black paint **206** are positioned on sky-facing surface.

[0075] Referring now to FIG. 2, additional details of Applicant's apparatus, systems, and methods shown in FIG. 1 are provided. The inventors prepared a test apparatus **250** and obtained test data. As illustrated in FIG. 2, the test apparatus **250** includes a support or substrate **202** that supports a panel of white paint **204**, a panel of black paint **206**, and a material composite of black paint and panel **208**.

[0076] Now referring to FIG. 3, in one example, a test apparatus **300** provides cooling for virtually any surface. A test apparatus **300** includes a panel of white paint **204**, a panel of black paint **206**, and the composite of black paint and panel **208**. Applicant's test apparatus **300** includes a support or substrate **202** with a 50 mm Styrofoam material support **224** and an Aluminum coated mylar material support **226**. The composite of black paint and panel **108** includes an IR transparent aerogel or foam made from an IR transparent material. The panel of white paint **204**, the panel of black paint **206**, and the composite of black paint and panel **108** are positioned on a sky-facing surface.

[0077] Referring now to FIG. 4, in one example, a graph provides test data of an apparatus and a system depicted in FIG. 3 that provides cooling for virtually any surface. The graph of FIG. 4 charts temperature vs time over a 24 hour period (8 am to 8 am). The ambient **201** curve (solid line) represents ambient temperature. The white paint **204** curve (●) represents the temperature of the white paint **204** sample. The black paint **206** curve (○) represents the temperature of the black paint **206** sample. The panel **208** curve (■) show the temperature of the composite of black paint and panel. The graph of FIG. 4 shows that composite of panel **208** (with black paint) provides better cooling over a 24 hour period.

[0078] Referring now to FIG. 5, an illustrative diagram provides a descriptive illustration of another embodiment of an apparatus, systems, and methods. According to one embodiment, an aerogel powder **502** is obtained. In one approach, an aerogel powder **502** is formed using methods described herein. The aerogel powder **502** is coated in a vacuum chamber **504**. In one approach, an aerogel powder may be coated with a surfactant. A mechanical frame **506** is provided. Alternatively, in one approach **508a**, the coated aerogel powder may be (1) transferred directly into the mechanical frame **506**. In another approach **508b**, the coated aerogel powder may be (2) initially consolidated into monoliths and then the consolidated monoliths are transferred into the mechanical frame **506**. An encapsulating film **510** may be used to encapsulate the aerogel and mechanical frame. The aerogel and mechanical frame encapsulated in a film provides a composite material **512**. The composite material **512** forms a mechanically robust, weather-stable panel that will enable deep, sub-ambient cooling from any surface in a cheap and scalable manner.

[0079] Referring now to FIG. 6, one example of a consolidated material is shown positioned on a sky-facing surface as designated by an image of an apparatus **600**. As illustrated in FIG. 6, the consolidated material **601** is positioned in a support or substrate **606**. The aerogel **604** is contained in the mechanical frame **602**. As described herein the apparatus **600** provides a material composite **601** that enables sub-ambient radiative cooling of virtually any sky-facing surface, when the disclosure is placed on top in close

contact. Applicant's apparatus, systems, and methods work similar to a solar heater vacuum tube, but instead of providing heating, it provides cooling by maintaining a temperature difference between a surface and ambient air.

[0080] FIG. 7 is a descriptive illustration of one embodiment of a mechanical frame. Initially, a mechanical frame **702** is provided. The mechanical frame **702** has a straight wall **704**. A salt aerogel **706** is contained in the mechanical frame **702**.

[0081] FIG. 8 is a descriptive illustration of another embodiment of a mechanical frame. Initially, the mechanical frame **802** is provided. The mechanical frame **802** in this embodiment has a conical wall **804**. The salt aerogel **806** is contained in the mechanical frame **802**.

[0082] FIG. 9 is a descriptive illustration of yet another embodiment of a mechanical frame. Initially, the mechanical frame **902** is provided. The mechanical frame **902** in this embodiment has a compound parabolic concentrator wall **904**. The salt aerogel is contained in the mechanical frame **902**.

[0083] One of the goals for a practical radiative cooler is to achieve 20 to 25° C. below ambient for a highly emissive surface. Preferably, the cooling apparatus achieves 60 W/m² at 10° C. below ambient temperature. For example, a radiative cooler may keep at 10' by 12' insulated building 10° C. below ambient temperature with 2 to 3 people inside. Preferably, the practical radiative cooler is capable of cooling any surface.

[0084] FIG. 10 shows a method **1000** for forming an apparatus for cooling a surface, in accordance with one aspect of one inventive concept. As an option, the present method **1000** may be implemented to construct structures such as those shown in the other FIGS. described herein. Of course, however, this method **1000** and others presented herein may be used to form structures for a wide variety of devices and/or purposes which may or may not be related to the illustrative embodiments listed herein. Further, the methods presented herein may be carried out in any desired environment. Moreover, more or less operations than those shown in FIG. 10 may be included in method **1000**, according to various embodiments. It should also be noted that any of the aforementioned features may be used in any of the embodiments described in accordance with the various methods.

[0085] Method **1000** begins with operation **1002** of forming a porous infrared (IR) transparent material that includes at least one substance that is transparent to infrared radiation having a wavelength in a range of 8 to 13 μm. In one approach, the substance may be a common salt. In another approach, the substance may be an element known to be transparent to IR radiation. In yet another approach, the substance may be a compound that is transparent to IR radiation.

[0086] According to one embodiment, an IR transparent material is a porous solid having low density, reflective to sunlight, and is thermal insulating for reducing heating of a surface. The IR transparent material is at least 70% to 90% transparent to IR between 8 to 13 μm. In preferred approaches, the IR transparent material has a density in a range of 0.5% to 2.0% of a maximum theoretical density. In one approach, the porous IR transparent material has a porosity in a range of 98% to 99% porosity. In one approach, density is calculated according to the mass of the material

divided by the volume of the material. Preferably, the IR transparent material is porous and low density for favorable insulating properties.

[0087] According to one approach, an IR transparent material may be an IR transparent foam. According to another approach, an IR transparent material is an IR transparent aerogel. In one approach, the IR transparent material is in the form of an aerogel powder. In another approach, the IR transparent material is in the form of an aerogel monolith.

[0088] In various approaches, the substance transparent to IR radiation may include a salt. In one approach, the substance may be a common salt. In one approach, the IR transparent material may be formed with a solution of a salt and a solvent. The solution may be an aqueous solution. The solution may include an organic solvent, e.g., TBA. In various approaches, common salts may include sodium chloride (NaCl), potassium chloride (KCl), sodium bromide (NaBr), potassium bromide (KBr), cesium iodide (CsI), etc.

[0089] In some approaches, the substance transparent to IR radiation may include one or more of the following: germanium (Ge), zinc selenide (ZnSe), zinc sulfide (ZnS), barium fluoride (BaF₂), etc.

[0090] In one approach, a process of forming an IR transparent material may include spraying a solution of salt and solvent to form droplets. The solution may include at least one salt that is transparent to infrared radiation having a wavelength in the range of 8 to 13 μm . One approach of the process of the method is illustrated in part (a) of FIG. 2. A flash freezing process of the droplets may include spraying the droplets into liquid nitrogen, spraying the droplets onto a cold surface, etc. The frozen droplets are then dried to form a porous material.

[0091] The solubility of the salts with water and the phase diagram of the salt mixtures strongly controls the feature sizes of the resulting aerogel/foam when the ice is freezing. In some approaches, smaller structures may be formed during freeze drying salts, so a mixture of salts may be preferable and may behave differently than single salts.

[0092] According to one embodiment, the structure of the IR transparent material (e.g., aerogel, foam, etc.) is responsible for the cooling properties of the material. In various approaches, the concentration of the substance may be tuned to result in predefined sizes of finer features of the IR transparent material. For example, lower concentrations of a precursor salt result in finer features of the porous material. The feature sizes provide an IR transparent material favorable optical and IR properties, while the low density and porosity provide the favorable thermal properties.

[0093] Moreover, controlling the freezing conditions of the salt solution and the salt composition, the features size of the structure of the IR transparent material (e.g., aerogel, foam, etc.) may be controlled. In some approaches, scattering calculations reveal that features smaller than approximately 500 nm achieve a desired IR transmission for effective PDRC (~70% transmission over atmospheric IR window).

[0094] In some approaches, a porous IR transparent material may be formed with at least one substance that is transparent to IR radiation using methods for forming aerogel, foam, etc. In one approach, a porous IR transparent material may be formed using gelation techniques for forming an aerogel. In another approach, a porous IR transparent material may be formed using a freeze-drying process that

uses super critical drying. In another approach, a porous IR transparent material may be formed by plasma spraying.

[0095] In exemplary approaches, an IR transparent material may be formed having predefined small fine features for optimal reflection of sunlight, transparency to IR radiation, and optimal insulating properties. A material having features larger than a micron may strongly reflect, e.g., scatter solar light, strongly, as well as scatter IR thereby reducing the transmission of IR radiation. It is generally well understood that finer the features, then the higher the IR transmission increases with a material having finer features. In some approaches, an average diameter of the features of the IR transparent material (e.g., foam, aerogel, etc.) is in a range of greater than 10 nm to about 500 nm. In preferred approaches, an average diameter of the features of the IR transparent material (e.g., foam, aerogel, etc.) is in a range of greater than 20 nm to about 300 nm. In one approach, an insulating material has fine features having a size that scatters optical sunlight and is transparent to IR radiation. In one approach, the IR transparent material is effective at scattering optical light having a wavelength less than one micron. In a preferred approach, the IR transparent material is optically reflective to sunlight.

[0096] In some approaches, a concentration of the precursor salt at about 3 M to 6 M forms a material having features with an average diameter in a range of greater than 0.7 μm to greater than 1 μm . Preferably, a concentration of the precursor salt is in a range of 0.01 M up to about 2 M for forming a material with features having an average diameter in a range of less than 100 nm up to 500 nm. In preferred approaches, a mixture of precursor salts forms a material with features having an average diameter in a range of around 50 nm to 200 nm. Preferably, a concentration of the at least one salt is in a range of 0.1 M to about 0.4 M. For a solution having a combination of salts, each salt has a concentration in a range of 0.1 M to about 0.4 M. In one approach, the concentration of each salt is the same in a solution having a combination of salts.

[0097] A total salt concentration may affect the overall feature size as well as the material density. The eutectic composition is known to result in finer feature sizes due to eutectic-mode solidification. In the NaCl and H₂O solution, hypereutectic concentrations (>5.1 M) resulted in larger feature sizes than hypoeutectic concentrations (<5.1 M). For hypereutectic concentrations, the salt crystals freeze first, and the eutectic structure follows, leaving large proeutectic salt crystals. For hypoeutectic concentrations, H₂O crystals form first, followed by the eutectic structure, leaving only the finely formed eutectic salt crystals. Since the H₂O is removed upon freeze drying, this leaves a highly porous network from the missing large proeutectic ice crystals making hypoeutectic solutions more favorable for these lower density materials.

[0098] A mixture of salts in solution may also result in smaller feature sizes since ternary eutectics can form very fine features (e.g., NaCl+KCl+H₂O is a ternary eutectic forming mixture). Similar to the case with NaCl+H₂O, the hypoeutectic concentration forced proeutectic H₂O crystals to form first, followed by NaCl+KCl in the eutectic ratio.

[0099] In some approaches, combining two different precursor salts results in an IR transparent material having finer features. For example, a combination of NaCl+KCl with each having a concentration of 0.3 M, the features of the resulting a material may be finer than a material formed with

each precursor salt at the same concentration (0.3 M). In preferred approaches, features are smaller 250 nm. In some approaches, an optimized NaCl+KCl particle may be created by changing the salt concentration within the solution, mixing different salts, and adding a cosolvent such as TBA. The size of fine features of the aerogels, foams, etc. (SEM histograms of the materials) may have a bimodal range, where a plurality of features have an average diameter of about 50 nm and then a plurality of features have an average diameter of about 300 nm. In a preferred approach, a mixture of NaCl and KCl in a particular ratio which forms a ternary eutectic may form the finest structures.

[0100] In some approaches, an addition of a cosolvent such as TBA into the salt solution may cause further refinement and even distribution of the features of the material. In some reports, TBA may be included in the solution for freeze-casting to refine microstructures in freeze-cast materials. The eutectic freezing of ice and TBA causes small domains of TBA, and H₂O ice to freeze, distributing small liquid domains of liquid H₂O (with dissolved salt) around the freezing droplet. This is the aforementioned proeutectic freezing of H₂O and drives the concentration of salt up to the eutectic point in the liquid H₂O regions. Subsequently, eutectic freezing of H₂O/salt and any remaining liquid TBA occurs, leaving the fine structures seen in the image of part (a), FIG. 14.

[0101] In another approach, the porous material (e.g., salt aerogel, salt foam) having desired fine features, may be sintered to form a monolith structure having particles immobilized within the monolith structure. Approaches for sintering the porous material may include application of heat, exposure to a predefined humidity (e.g., a high moisture content of a humidity chamber).

[0102] Moreover, the composite preferably includes a coating to protect the salt-based material from humidity. In some approaches, a coating is included in addition to the encapsulant, such that a coating is added onto the encapsulant. In one example, a coating may be added to the surface of PE film that encapsulates the composite.

[0103] NaCl and KCl are both hygroscopic materials that can easily be recrystallized by ambient humidity resulting in macroscopic shrinkage of the material and microscopic coarsening of the crystallites. Structural changes induced by humidity may reduce the ability of the material to insulate and may drastically reduce IR transmission, rendering the IR transparent material ineffective at cooling. Even with encapsulant PE sheets, humidity may easily penetrate the SFP and interact with the IR transparent material since PE has a high water vapor transmission rate. With recent PDRC works demonstrating continued optimal performance of emitter materials in outdoors environments, longevity of IR transparent material (e.g., aerogel, foam, etc.) is desired.

[0104] In some approaches, an anti-caking agent may be included in the forming of an IR transparent material to prevent the small features in the salt from growing larger in ambient humidity. Examples of an anti-caking agent include a surfactant, ferrocyanide, CTAB, a common surfactant cation, etc. which may be included with the salt during formation of the material. Being hygroscopic, the salt components such as NaCl and KCl, have a net positive charge that attracts atmospheric water. The relative humidity in the air will absorb the surface of the porous material (e.g., aerogel, foam, etc.). The absorption of water will cause the salt to diffuse along the water at the surface and form

crystalline bridges, growing the salt crystals and coarsening features. Preferably, the composite includes a means of protecting the porous IR transparent material from the absorption of water to prevent the formation of undesirable coarsened features that reduces IR transparency of the material. In one approach, a surfactant such as cetyltrimethylammonium bromide (CTAB) may be used as a hydrophobic coating on the porous material to mitigate water uptake and improve lifetime of the porous material.

[0105] In one approach, addition of known anti-caking agents might protect the porous material from humidity induced damage. Anti-caking agents include surfactants, surface tension modifiers, etc. In one example, sodium ferrocyanide Na₄Fe(CN)₆ is a well-known anti-caking agent known to stop coarsening of salts from ambient moisture. In one approach, adding the anti-caking component ferrous cyanide (Na₄Fe(CN)₆) to the salt components may adhere to the surface of salt to prevent movement of the salt on the surface of the porous material, and thereby prevent crystallization of the salt-based porous material. In preferred approaches, the presence of ferrocyanide in the salt-based porous material allows the salt in the material to resist forming crystal structures during exposure to very high humidity. Another preferred approach is to use a process of coating the porous material (e.g., aerogel, foam, etc.) using vacuum evaporation of PDMS. This process coats the aerogel surface and does not allow moisture to attach to the surface. A combination of approaches is also possible to minimize moisture uptake and coarsening.

[0106] In one example, an IR transparent composite (e.g., salt foam panel) may be fabricated in part from an aqueous solution containing NaCl, KCl, sodium ferrocyanide (Na₄Fe(CN)₆) and tert-butyl alcohol (TBA) sprayed directly into a bath of liquid nitrogen to flash-freeze the solution. The frozen droplets may be freeze dried overnight, yielding highly porous powder particles with nanoscale features. The rapid solidification using liquid nitrogen may be necessary to achieve the desired small feature size. The solvent TBA may be included to refine the features of the porous material and the Na₄Fe(CN)₆ may be added to minimize coarsening from moisture.

[0107] According to one approach, the features of a porous material may be optimized by improving the flash freeze process. As described in part (a) of FIG. 2 flash freezing the droplets into liquid nitrogen followed by drying results in porous material with fine features. Another approach includes a flash freezing apparatus for continuous flash freezing on a cold surface. For example, flash freezing onto an 80K Cu plate may result in smaller features of around 100 nm. Moreover, the process may allow for a scale-up fabrication process to kilogram quantities of fine features porous salt material. Freezing droplets on a cold surface may allow smaller features of the material to form quicker than freezing droplets on in liquid nitrogen. Moreover, freezing droplets on a cold surface may improve heat transfer rates and allow a higher continuous freezing on a solid substrate.

[0108] Looking back to method 1000 of FIG. 10, after the formation of porous IR transparent material, operation 1004 includes coupling the porous IR transparent material to a support frame structure. The support frame structure may function as an optomechanical frame. An optomechanical frame is a frame that may be designed to hold the porous IR transparent material against a surface for cooling and to

align the sky-facing side of the IR transparent material with the sky. Moreover, the frame contains the IR transparent material to protect the structure of the material from movement so that the material's original macrostructure and microstructure are maintained during the lifetime of the apparatus. In preferred approaches, the porous IR transparent material is coated with an IR transparent encapsulant as described herein.

[0109] As described herein, in one approach, the process may fabricate batches of 5 to 10 grams of foam at once (enough material for one or two cooling panels), and the process may be completed within 24 hours. In one approach, the production method may be scaled to kg quantities of foam. In sharp contrast, supercritical CO₂ drying may take up to 3 days for the necessary solvent exchanges and drying processes to complete.

[0110] Referring now to FIG. 11, part (a), an apparatus 1100 is described according to one embodiment. As an option, the apparatus 1100 may be implemented in conjunction with features from any other aspect listed herein, such as those described with reference to the other FIGS. Of course, the apparatus 1100 and others presented herein may be used in various applications and/or in permutations which may or may not be specifically described in the illustrative aspects listed herein. For instance, the apparatus 1100 may be used in any desired environment and/or include more or less features, layers, etc. than those specifically described in FIG. 11.

[0111] In one approach, part (a) of FIG. 11 illustrates an assembly of an infrared (IR) transparent composite 1101 of an apparatus 1100 for cooling a surface. An IR transparent material 1102 (e.g., aerogel, foam, etc.) is formed that includes at least one substance transparent to IR radiation having a wavelength in a range of 8 to 13 μm . The extent of transparency to IR radiation may be 70% to 90% transparent to IR radiation. The porous IR transparent material 1102 is placed into a support frame 1104 to protect it from mechanical disruption (e.g., aerogel powders are brittle and easily crushed by applied pressure). The support frame 1104 contains the IR transparent material 1102. The IR transparent material 1102 has a sky-facing surface 1107 that is exposed to the sky.

[0112] According to some approaches, the support frame includes a plurality of sections (e.g., compartments) for containing the IR transparent material. The support frame has an opening for exposing the sky facing surface of the IR transparent material to its surroundings, and preferably the sky so as to maximize radiative transmission of heat. Preferably, the support frame has an opening for exposing the entirety of the sky-facing surface of the IR transparent material.

[0113] The support frame provides a confined sections, space, compartments, etc. for particles of the IR transparent material to be immobilized. Without a support frame, material that is composed of particle spheres having an average diameter of 10 to 20 μm would tumble, rock, shift, etc. in response to environmental factors, and this movement results in a compaction of the particles and material. Preferably each compartment 1105 of the support frame 1104 is filled with the material 1102 so that the particles do not move and collapse.

[0114] One example of a mechanical support frame may have dimensions of 110 mm w \times 110 mm/x 10 mm h, with each compartment having dimensions of about 35 mm \times 35

mm \times 10 mm. As illustrated in part (a), arrows indicate the mechanical support frame 1104 and the material 1102 are in the same plane, each compartment 1105 of the support frame 1104 is filled with the material 1102. The support frame may function as an optomechanical frame, where the frame holds the material on the surface to be cooled and aligns the material in the direction of the IR radiation from the sky.

[0115] The composite includes an encapsulant to protect the IR transparent material (e.g., aerogel, foam, etc.) from humidity of the environment. In one approach, the composite may include a coating for inhibiting water vapor transmission to the IR transparent material. In one approach, the coating may be applied to the encapsulant. As illustrated in part (a), the encapsulant 1016a is positioned on the sky-facing surface of the IR transparent material 1102. The encapsulant 1016a, 1016b may cover the composite. In one approach, the encapsulant may be in the form of a transparent film. In one approach, the composite is encapsulated by a thin sheet of polyethylene (PE). As shown in part (a), in one example, the IR transparent material 1102/mechanical support frame 1014 may be encapsulated with thin polyethylene (PE) sheets 1016a, 1016b to prevent the porous material being blown away by wind currents. The encapsulant may be a commercially available film that is transparent to IR radiation in a range of 8 to 13 μm . The thickness of the encapsulant (measured from the surface of the porous IR transparent material to the outer surface of the encapsulant) may be a thickness that maintains an IR transparency of the encapsulant. For example, a thickness of the encapsulant, e.g., PE sheets, may be about 12.5 μm . In another approach, a portion of an IR transparent material in the shape of a compartment of the support frame is encapsulated with PE film thereby forming packets of the IR transparent material that are placed in each compartment of the support frame to immobilize the encapsulated IR transparent material.

[0116] Part (b) of FIG. 11 illustrates a testing apparatus for testing one example of an IR transparent composite 1111 (shown as a salt foam panel (SFP)). The schematic diagram illustrates the placement of the IR transparent composite 1111 on a surface to be cooled (in this case, the surface includes an emitter 1114 and thermocouple 1118 to measure cooling). A thickness th of the composite may be defined as the length from a bottom surface of the composite to the sky-facing surface of the composite, where the thickness th is in a range of greater than 0.5 cm to about 5 cm. Preferably, the bottom surface of the composite is placed in contact with a surface for cooling when in use. In one approach, an IR transparent material having features in the range of 150 nm range allows a thickness th of a salt foam to be in a range of 1 up to 5 cm, and preferably up to 2 to 3 cm.

[0117] In a preferred approach, the composite is thermally insulating for reducing heating of a surface from surrounding air. The composite may function as an insulation layer without sacrificing IR transmission or optical reflectance. In some approaches, a thickness of the IR transparent composite (e.g., salt foam panel, aerogel composite, etc.) may contribute to increased solar reflectance. The configuration of the dimensions of the composite includes considerations of adding more material to gain reflectance that may result in reduced IR transmission where the particles are not completely transparent and scatter IR radiation. There are considerations of the interplay between thickness for insu-

lation, optical reflectance, and IR transmission to determine the optical feature size of the IR transparent material (e.g., foam, aerogel, etc.).

[0118] As illustrated in part (b), a diagram of one example of an outdoor testing apparatus **1110** including the composite **1101** (e.g., salt foam panel (SFP)). The cooling ability of the SFP was demonstrated by outdoor testing on a hot, clear day. Emitters **1114** were affixed to polished Cu substrates **1116** with thermocouples **1118** attached to the bottom of the substrates **1116**. Since the cooling performance of an emitter is greatly affected by non-radiative (conductive and convective) heat gains from the surroundings, the bottom of emitters **1114** were insulated by polystyrene foam **1112**.

[0119] As illustrated in parts (c) and (d), several emitting surfaces may be tested for comparative thermal performance; (1) white reflective TiO₂ paint, (2) 3M Enhanced Specular Reflector (ESR) film, and (3) black paint, etc. As illustrated in part (b), the composite **1101** may be placed on top of black paint **1114a**. In part (c), two emitting surfaces include a composite **1101** (SFP) placed on top of black paint (4) and (5) to serve as a worst-case scenario, where any sunlight transmitted through the IR composite would be absorbed and heat the emitter. The two black painted substrates+SFP represent two salt aerogel panels formed with different Na₄Fe(CN)₆ concentrations. (4) black paint+SFP with higher Na₄Fe(CN)₆ concentration, and (5) black paint+SFP with higher Na₄Fe(CN)₆ concentration.

[0120] In one example, a testing was performed on 2022 September 8-9 near Livermore, California (peak solar irradiance of 872 W m⁻²) with the ambient temperature peaking at 42° C. (one of the hottest days of the year). A full 24 hour cycle was measured to demonstrate the uninterrupted cooling capabilities of the SFP. Conditions on the testing day included high wind speeds of up to 10 m s⁻¹, which increases parasitic heating, and high downwelling atmospheric radiation with an average of 381 W m⁻².

[0121] Part (c) depicts an optical image of the emitting surfaces tested for comparative thermal performance. Part (d) depicts an IR thermal image of the emitting surfaces. Sample (4) SFP with the higher Na₄Fe(CN)₆ concentration demonstrates the lowest thermal energy compared to sample (3) black paint (only) that demonstrates the brightest IR thermal image. Sample (2), the metal-backed 3M ESR film, which has been reported as a sub-ambient cooling film in multiple publications, did not remain sub-ambient in these adverse conditions, and demonstrates a similar IR thermal image to white paint (1). The difference in temperature can be clearly seen in the IR thermal images of the emitters during outdoor test.

[0122] Graphs of the cooling performance of the emitters are illustrated in FIG. 12. Part (a) illustrates emitter surface temperatures (y-axis) over a 24 hour period (x-axis). Part (b) illustrates a temperature difference between each surface and ambient temperature. Shadings indicate the solar irradiance between 10 AM to 6 PM on the left side of the graph and 6 AM to 10 PM on the right side of the graph (scale on right axis). Ambient temperature is depicted by the solid line. The SFP (■) maintains the underlying black paint below ambient temperature throughout the day, even at solar noon, with a maximum reduction of 10° C. below ambient temperature. Moreover, during the period of highest solar irradiance (from 10:30 AM to 04:00 PM PST), the SFP (■) covered substrate was the only emitter that remained below ambient temperature, consistently maintaining significantly lower

temperatures than the other emitters throughout the day. The SFP (■) reduced the temperature of the black paint (relative to the uncovered paint (○)) by 24° C. during the daytime (12:53 PM) and by 5° C. during the night (12:00 AM).

[0123] The SFP (■) also outperformed highly reflective TiO₂ white paint (●), and the state-of-the-art 3M ESR film (□) which has been commercially used for radiative cooling applications. Compared to the 3M ESR film (□), the SFP (■) demonstrated 2.1° C. cooler at solar noon and an average temperature drop below ambient of 5.5° C. throughout the day while the average temperature drop for 3M ESR film (□) was 1.7° C.

[0124] According to one embodiment, performance advantages of SFP may be attributed to a reduction of parasitic heating from the environment. Although the presence of the SFP decreases the overall IR transmission from the emitter surface, at low temperatures the insulating properties may outweigh transmission losses. Part (c) of FIG. 12 is a graph of the wind speed, relative humidity, and incoming infrared radiation during the time duration of the test of part (a).

[0125] In one example, part (d) of FIG. 12 depicts the cooling power as a function of the temperature drop ($T_{surface} - T_{ambient}$) of an uncovered emitter (3M ESR) (■) and a SFP covered emitter (SFP on 3M ESR) (●). The graph depicts an improvement in cooling power performance due to covering the 3M ESR with SFP (●). Two identical 3M ESR films, affixed to aluminum substrates and backed with resistive heaters were tested. One film was left uncovered, and the other was covered with the SFP. These were tested under identical conditions, at the same time and location to ensure performance differences observed could be directly attributed to the presence of the SFP. The SFP begins to outperform an uncovered surface at approximately 1.5° C. below ambient. Below this temperature, the SFP provides higher cooling power than the uncovered surface. The SFP also had a greater maximum temperature drop. The uncovered surface (■) was limited to <3° C. while the SFP (●) achieved up to 6° C. below ambient, due to the decrease in parasitic heating by the insulating SFP.

EXPERIMENTS

Materials and Methods

[0126] NaCl (ACS, 99.0%) was purchased from Alfa Aesar, Thermo Fisher Scientific, and KCl (ACS) was supplied by LabChem. TBA was obtained from Millipore-Sigma. Sodium ferrocyanide decahydrate (Na₄Fe(CN)₆·10H₂O) was also supplied by Millipore-Sigma.

Aerogel Synthesis

[0127] To prepare the salt aerogels, an aqueous solution of salt was made with 20.83 g of NaCl to 9.19 g KCl, to 1069.80 g of deionized H₂O (added 1000 g H₂O to ternary eutectic composition). Other additives such as Na₄Fe(CN)₆ (1 mM, H₂O basis) or TBA (18 wt % with respect to H₂O) were also added at this point and the solutions were mixed well for several minutes. Next, the solution was pumped through an ultrasonic spray head vibrating at 180 kHz (4.5 W) via a Sono-Tek syringe pump to disperse the solution into 5-50 mm droplets. The droplets were sprayed directly into a bath of liquid nitrogen to rapidly freeze. A feed rate of 8 mL min⁻¹ was used to minimize build-up of salt on the

liquid nitrogen surface. The resulting ice was then kept at -196.2°C . (77 K) until it was transferred into a freeze drier and was lyophilized in a Harvest Right Scientific Freeze dryer with a temperature profile set to -23.2°C . (250 K) for 8 hours, -18.2°C . (255 K) for 6 hours, -9.2°C . (264 K) for 4 hours and -1.2°C . (272 K) for 2 hours and lastly to room temperature until the sample was removed. This profile ensured that the ice was removed while frozen, avoiding any local melting of the salt. Every freeze-dried batch consisted of several containers full of frozen droplets, 25 mL of solution per container was used to ensure that the layer of frozen droplets was thin enough to completely dry in the 20-hour lyophilization cycle.

Device Fabrication

[0128] The SFPs fabricated consisted of 3D printed frames of 3×3 squares (each square was $35\text{ mm}\times 35\text{ mm}\times 10\text{ mm}$) printed with acrylonitrile butadiene styrene (ABS) and painted with barium sulfate (BaSO_4) to minimize solar absorption. The frame was filled with salt aerogel powder (0.350 g per square, 1.4% relative density) and encapsulated in a thin clear PE sheet (food wrap, 12.5 mm thick) to prevent wind blowing the aerogel away. The PE sheets were sealed with a heat sealer to make the devices were air-tight. The SFPs were fabricated in a N_2 -filled glove box to minimize any initial moisture exposure.

Outdoor Testing

[0129] The emitters were mounted in 75 mm polystyrene aerogel covered with aluminum coated mylar to minimize solar absorption (part (b), FIG. 11). The temperatures of the samples were recorded every 1 minute by type-K thermocouples connected to an Omega RDXL6SD-USB data logger. An onsite weather station was used to determine relative humidity, wind speed and incoming IR radiation. IR thermal radiation images were captured with a FLIR ONE Pro thermal camera.

[0130] Parasitic heat transfer coefficients were calculated using a National Instruments 9210 Temperature input module with type-K thermocouples (to monitor temperature) and a USB controlled power supply with a proportional-integral-derivative (PID) controller implemented in LabView to control heater power. $10\text{ cm}\times 10\text{ cm}$ silicone encapsulated surface heaters were attached to the bottom of aluminum heat spreader substrates. 3M ESR emitters were affixed to the top of the Al heat spreaders. The test was conducted at night with minimal wind ($<0.5\text{ m s}^{-1}$) using identical 3M SR films and identical SFPs.

Characterization

[0131] The aerogel microstructure was investigated by SEM in an Apreo S Lo Vac at an accelerating voltage of 2 kV. Fourier Transform Infrared (FTIR) spectroscopy was performed in a Bruker's VERTEX 70 spectrometer equipped with a PIKE Technologies mid-IR integrating sphere. UV-Vis-NIR reflectance/transmittance was measured with a PerkinElmer Lambda 950 with an integrating sphere. Thermal conductivity of an encapsulated support frame without aerogel, and a SFP packaged with aerogel at varying relative density was measured in a Hot Disk TPS 3500 Thermal Constants Analyzer (ThermTest Inc). TEM images were collected in a Thermo Fisher Scientific Titan equipped with a SuperX x-ray energy dispersive spectrometer. Particle

sizes histograms from SEM images were analyzed by manual measurements in ImageJ.

Humidity Testing

[0132] Miniature SFPs (1.5% density) were placed in a Memmert AtmoCONTROL climate chamber. Two SFPs (coated and uncoated aerogel samples) were held in succession at 55%, 65%, and 75% RH for 30 minutes each and photographed after each exposure. SEM imaging was performed before and after the final moisture exposure.

Parameters of Salt Aerogel Formation

[0133] FIG. 13 is a plot of the diffuse transmission of different salt aerogels formed with different salt concentrations and freezing parameters. A combination of NaCl and KCl, each at 0.3 M, and flash frozen (solid line) at the lower relative density 1.5% had the highest IR transparency (IR, left shaded portion) and the highest transmission in the optical reflective region (right cross-hatched portion). The salt aerogel comprised of NaCl at 0.3 M concentration (●) frozen to a relative density of 3% and 1.5% and frozen according to conventional method performed lowest. The combination of NaCl and KCl salts, each at 0.3 M, for a relative density at 3% and 1.5% and frozen using conventional methods (○) demonstrated improved diffuse transmission with the lower density of 1.5% (dashed line) having a better diffuse transmission.

[0134] To test how density affects thermal conductivity, miniature SFPs at two different densities were measured using the hot-disk method. As shown in Table 1, the thermal conductivity exhibited a minimum value of $0.037\text{ W m}^{-1}\text{ K}^{-1}$ at 1.5% relative density. This conductivity value is similar to other commonly used insulating materials, such as cotton and fiberglass. The measurements suggest that increasing density further may increase the thermal conductivity. Therefore, SFPs packed at low density between 1.4-1.5% relative density (0.03 g cm^{-3}) minimizes the thermal conductivity, maximizes the IR transmission, and fills any voids after packing the SFP (1% was the lowest self-supporting density possible, but typically results in unfilled regions).

TABLE 1

Thermal conductivity of salt aerogel panels and different insulating materials	
Sample	Thermal conductivity [$\text{W m}^{-1}\text{ K}^{-1}$]
^a Empty support frame (air)	0.026 ± 0.001
^a SFP at 1.5% relative density	0.037 ± 0.002
^a SFP at 2.5% relative density	0.043 ± 0.002
^b Cotton	(0.035-0.060)
^b Fiberglass insulation	(0.33-0.040)

^aError values shown are the standard deviation in the hot-disk measurement value.

^bRange of values

Optimize Feature Size, Thickness of Aerogel Layer

[0135] Part (a) of FIG. 14 shows a scanning electron microscope (SEM) image of an optimized NaCl+KCl aerogel particle made from NaCl+KCl with TBA and 1 mM $\text{Na}_4\text{Fe}(\text{CN})_6$.

[0136] Part (b) shows a histogram of feature sizes measured via SEM from different aerogels. The insets depict

SEM images of each aerogel having a scale bar of 500 nm: NaCl+KCl (top)(solid line), 0.3 M KCl (middle)(○), and 0.3 M NaCl (bottom) (●). The distribution of feature sizes in each aerogel, with a bimodal distribution, may be centered around 50 and 300 nm. The inset SEM images illustrate the features of the particles from the aerogels made from only hypoeutectic NaCl solutions (●) bottom inset, or hypoeutectic KCl solutions (○) middle inset. These aerogels did not result in sufficiently small features (e.g., 500 and 300 nm average features, respectively) whereas the mixed salt formed much finer features (solid line, top inset). The molar ratio of salt to water was around 1%, resulting in approximately 1% dense aerogel particles as the final density of the loose powder with no packing was approximately 0.02 g cm⁻³.

[0137] Parts (c) and (d) depict images of transmission electron microscope (TEM) energy dispersive spectroscopy (EDS) map of a crushed NaCl+KCl particle (made with TBA and 1 mM Na₄Fe(CN)₆). The images reveal the mixture of NaCl and KCl resulted in small crystallites of each component. Chemical mapping showed larger NaCl features measuring approximately 400 nm and mixture of small KCl features <100 nm. This is consistent with proeutectic H₂O crystals forming first, followed by ternary eutectic formation.

[0138] FIG. 15 depicts the approximate IR transmission of salt aerogel samples having different feature sizes and different thicknesses of the salt aerogel sample. Samples having features with the average size of 150 nm (○) demonstrated high IR transmission for samples 1 cm thick (solid line) and 5 cm thick (dotted line). In contrast, samples having features with an average size of 400 nm demonstrated lower IR transmission at both thicknesses (1 cm and 5 cm).

[0139] To quantify the reduction in the parasitic heating rate, the parasitic heat transfer coefficients were measured with and without the SFP. In this method, the cooling power at ambient temperature and the maximum temperature drop are measured simultaneously with two identical devices. The uncovered 3M ESR surface was found to have a parasitic heat transfer coefficient of $h=8.1 \text{ W m}^{-2} \text{ K}^{-1}$. Covering the 3M ESR film with the SFP reduced the parasitic heat transfer rate by more than 50%, to $h=3.6 \text{ W m}^{-2} \text{ K}^{-1}$.

[0140] An aerogel with large average feature sizes (B1 mm) may scatter optical light (i.e., sunlight), and may also scatter IR light (due to Mie scattering) leading to low IR transmission. An optimized salt aerogel with its small feature sizes (B100 nm) may be able to scatter optical light while minimizing IR scattering. In one example, reflectance and transmission of the salt aerogels were measured by packing the aerogel into a holder at 2.0% relative density to ensure no gaps. The hemispherical transmittance and reflectance of the aerogels are shown in part (a) of FIG. 16 for a 2.5 mm thick aerogel layer having 2.05 relative density in a wavelength range of 0.25 μm and 16 μm. The normalized air mass 1.5 (AM 1.5) solar spectrum (U.S. Standard Atmosphere 1976) and the atmospheric transmittance were plotted as a reference. The aerogel had a weighted optical reflectivity (○) of 83% throughout the solar band (weighted by the AM 1.5 spectrum, 0.3 to 2.5 mm) and 86% average transmittance (solid line) in the atmospheric transparency window (8 to 13 mm). The reported 83% optical reflectance was for a 2.5 mm thick aerogel layer, while the salt aerogel panel (SFP) used a 10 mm thick layer, which resulted in the higher

reflectance required for PDRC of 490%. An advantage of using NaCl and KCl is that they have reduced UV absorption relative to other materials such as PE or ZnSe (which absorb UV below 400 nm).

[0141] Additionally, the IR transmission of the NaCl and KCl do not possess any absorption peaks within the atmospheric transmission window. The peak near 3 mm corresponds to the —OH absorption of water that is present on the surface of the NaCl and KCl. As the measurements were done in ambient air, moisture was present on the surface of the salt.

[0142] Part (b) of FIG. 16 is a plot of reflectance of different aerogels formed from pure salts (NaCl, KCl) and the optimized mixed salt aerogel (NaCl+KCl). The effect of larger feature sizes are observed in the reflectance results of part (b). NaCl aerogels (●) and KCl aerogels (○) have larger feature sizes than the optimized NaCl+KCl aerogel (solid line). The reflectance was the highest for the NaCl (largest features) (●) and lowest for the optimized NaCl+KCl (smallest features) (solid line).

Optimize Components to Resist Humidity

[0143] In one approach, Na₄Fe(CN)₆ may be included in salt aerogels to mitigate coarsening. A desired concentration of Na₄Fe(CN)₆ may be added to the salt solution before spray freezing. In one example, aerogel samples were prepared as uncoated SFP samples and “Na₄Fe(CN)₆-coated” SFP samples and placed in a humidity chamber for 30 minutes, removed, photographed, then exposed to the next humidity step. FIG. 17 is a series of images of uncoated SFP (upper row) and 1 mM Na₄Fe(CN)₆-coated SFP (lower row) at different humidity conditions at varying relative humidity (RH) (e.g., no humidity, 55% RH, 65% RH, and 75% RH). For the uncoated SFP, coarsening can easily be seen by macroscale shrinkage of the aerogel within the frame of the samples exposed to humidity compared to no humidity (upper row, FIG. 17). The macroscale shrinkage is indicative of microscale coarsening as seen in the inset SEM images of uncoated—no humidity compared to uncoated—75% RH.

[0144] Addition of 1 mM Na₄Fe(CN)₆ to the SFP aerogel samples reduced the propensity of the coated aerogels to coarsen from exposure to moisture at RH as high as 75% compared to no humidity (lower row, FIG. 17). There is no noticeable macroscale shrinkage of the coated SFP at 55 or 65% RH. Comparing the inset SEM images of the Na₄Fe(CN)₆-coated SFP samples showed only localized coarsening after exposure to 75% RH compared to no humidity. In sharp contrast, the uncoated samples coarsened extensively after being exposed to 75% RH. The humidity testing clearly indicates that Na₄Fe(CN)₆ preserves the aerogel structure and allows the material to be placed outside in local ambient conditions (e.g., RH>60%) without the microscale or macroscale structure being changed drastically. In various examples, testing SFP outdoors for multiple days resulted in minimal reduction of performance despite humidities up to 75% RH.

[0145] Therefore, it will be appreciated that the scope of the present application fully encompasses other embodiments which may become obvious to those skilled in the art. In the claims, reference to an element in the singular is not intended to mean “one and only one” unless explicitly so stated, but rather “one or more.” All structural and functional equivalents to the elements of the above-described preferred embodiment that are known to those of ordinary skill in the

art are expressly incorporated herein by reference and are intended to be encompassed by the present claims. Moreover, it is not necessary for a device to address each and every problem sought to be solved by the present apparatus, systems, and methods, for it to be encompassed by the present claims. Furthermore, no element or component in the present disclosure is intended to be dedicated to the public regardless of whether the element or component is explicitly recited in the claims. No claim element herein is to be construed under the provisions of 35 U.S.C. 112, sixth paragraph, unless the element is expressly recited using the phrase “means for.”

[0146] While the apparatus, systems, and methods may be susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and have been described in detail herein. However, it should be understood that the application is not intended to be limited to the particular forms disclosed. Rather, the application is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the application as defined by the following appended claims.

[0147] Moreover, any of the structures and/or steps may be implemented using known materials and/or techniques, as would become apparent to one skilled in the art upon reading the present specification.

In Use

[0148] Various embodiments may be used to cool virtually any surface for such uses as electricity-free air conditioning, remote refrigeration, potable water collection, etc. One embodiment may be used to cool buildings or vehicles directly, recycle evaporated process water (cooling towers) and could condense potable water from the air in arid areas and serve for disaster relief when electricity is not available. In one approach, coupling the apparatus with a heat exchanger and fluid storage may be useful to supplement and improve the efficiency of HVAC systems, deep-freezer units, etc. by providing a low temperature heat sink for rejecting heat.

[0149] The inventive concepts disclosed herein have been presented by way of example to illustrate the myriad features thereof in a plurality of illustrative scenarios, aspects, and/or implementations. It should be appreciated that the concepts generally disclosed are to be considered as modular, and may be implemented in any combination, permutation, or synthesis thereof. In addition, any modification, alteration, or equivalent of the presently disclosed features, functions, and concepts that would be appreciated by a person having ordinary skill in the art upon reading the instant descriptions should also be considered within the scope of this disclosure.

[0150] While various aspects have been described above, it should be understood that they have been presented by way of example only, and not limitation. Thus, the breadth and scope of an aspect of the present invention should not be limited by any of the above-described exemplary aspects but should be defined only in accordance with the following claims and their equivalents.

What is claimed is:

1. An apparatus for cooling a surface, the apparatus comprising:

a composite comprising:

- a porous infrared (IR) transparent material comprised of at least one substance that is transparent to infrared radiation having a wavelength in a range of 8 to 13 microns;
- a support frame having an opening for exposing a sky-facing surface of the porous IR transparent material; and
- an encapsulant, wherein the encapsulant is positioned on the sky-facing surface of the porous IR transparent material,

wherein the composite is configured to be optically reflective to sunlight,

wherein the composite is thermally insulating for reducing heating of a surface from surrounding air.

2. The apparatus as recited in claim 1, wherein the at least one substance is selected from the group consisting of: sodium chloride (NaCl), potassium chloride (KCl), sodium bromide (NaBr), potassium bromide (KBr), cesium iodide (CsI), germanium (Ge), zinc selenide (ZnSe), zinc sulfide (ZnS), barium fluoride (BaF₂), and a combination thereof.

3. The apparatus as recited in claim 2, wherein the IR transparent material is comprised of a combination of NaCl and KCl.

4. The apparatus as recited in claim 1, wherein the IR transparent material is comprised of a plurality of features, the features having an average diameter of greater than 10 nanometers to less than 500 nanometers.

5. The apparatus as recited in claim 4, wherein the IR transparent material is effective at scattering optical light having a wavelength less than one micron.

6. The apparatus as recited in claim 1, wherein the IR transparent material has a density in a range of 0.5 to 2.0 of the maximum theoretical density.

7. The apparatus as recited in claim 1, wherein the IR transparent material has a porosity in a range of 98 to 99.5% porosity.

8. The apparatus as recited in claim 1, wherein the porous IR transparent material is an IR transparent aerogel.

9. The apparatus as recited in claim 1, wherein the porous IR transparent material is an IR transparent foam.

10. The apparatus as recited in claim 1, wherein the support frame is functional as an optomechanical frame.

11. The apparatus as recited in claim 1, wherein a length from a bottom surface of the composite to the sky-facing surface is in a range of greater than 0.5 centimeters to 5 centimeters.

12. The apparatus as recited in claim 1, wherein the IR transparent material is in the form of an aerogel powder.

13. The apparatus as recited in claim 1, wherein the IR transparent material is in the form of an aerogel monolith.

14. The apparatus as recited in claim 1, wherein the encapsulant is in the form of an IR transparent film.

15. The apparatus as recited in claim 1, wherein the composite further comprises a coating for inhibiting water vapor transmission to the IR transparent material.

16. The apparatus as recited in claim 1, wherein the IR transparent material further comprises an anti-caking agent.

17. The apparatus as recited in claim 16, wherein the anti-caking agent is selected from the group consisting of: sodium ferrocyanide, CTAB, and a cationic surfactant.

18. A method of forming an apparatus for cooling a surface, the method comprising forming a porous infrared (IR) transparent material comprising at least one substance

that is transparent to infrared radiation having a wavelength in a range of 8 to 13 microns; and

coupling the porous IR transparent material to a support frame structure,

wherein the porous IR transparent material is coated with an IR transparent encapsulant.

19. The method as recited in claim **18**, wherein the at least one substance is selected from the group consisting of: sodium chloride (NaCl), sodium bromide (NaBr), potassium chloride (KCl), potassium bromide (KBr), cesium iodide (CsI), germanium (Ge), zinc selenide (ZnSe), zinc sulfide (ZnS), barium fluoride (BaF₂), and a combination thereof.

20. The method as recited in claim **18**, wherein the at least one substance is a combination of NaCl and KCl.

21. The method as recited in claim **18**, wherein the at least one substance is at least one salt selected from the group consisting of: NaCl, KCl, and a combination thereof,

wherein forming the porous IR transparent material comprises:

spraying a solution to form droplets, the solution comprising the at least one salt and a solvent;

freezing the droplets; and

drying the droplets to form a porous material.

22. The method as recited in claim **21**, wherein a concentration of the at least one salt is in a range of 0.1 M to about 0.4 M.

23. The method as recited in claim **18**, wherein a density of the porous IR transparent material is in a range of 0.5 to 2.0 relative density.

24. The method as recited in claim **18**, wherein a porosity of the porous IR transparent material is in a range of 98-99.5% porosity.

25. The method as recited in claim **18**, wherein the IR transparent material further comprises an anti-caking agent.

26. The method as recited in claim **25**, wherein the anti-caking agent is selected from the group consisting of: sodium ferrocyanide, CTAB, and a cation surfactant.

27. An apparatus for cooling a surface, comprising:

a composite that is

an infrared (IR) transparent aerogel or foam that is transparent in the 8-13 micron wavelength range,

that is optically reflective to reduce heating from sunlight,

and that is thermally insulating to avoid heating from surrounding air.

28. The apparatus for cooling of claim **27**, wherein said composite comprises an IR transparent aerogel or foam and a frame that holds said IR transparent aerogel or foam.

29. The apparatus for cooling of claim **27**, wherein said composite comprises a frame that holds said IR transparent aerogel or foam, wherein said IR transparent aerogel or foam is configured to concentrate emitted radiation, and wherein said frame is positioned to concentrate said emitted radiation to the sky to improve cooling.

* * * * *