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(54) **MULTIFUNCTIONAL REPELLENT MATERIALS**

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(71) Applicant: **President and Fellows of Harvard College, Cambridge, MA (US)**

Publication Classification

(72) Inventors: **Joanna Aizenberg, Boston, MA (US); Michael Aizenberg, Boston, MA (US); Tak Sing Wong, State College, PA (US); Nicolas Vogel, Cambridge, MA (US); Cicely Shillingford, Waterloo (CA); Philseok Kim, Arlington, MA (US); Benjamin Hatton, Toronto (CA); Stefanie Utech, Cambridge, MA (US); Oktay Uzun, Boston, MA (US); Steffi Sunny, Cambridge, MA (US)**

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B05D 5/08 (2006.01)

B65D 25/14 (2006.01)

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B08B 17/06 (2006.01)

(52) **U.S. Cl.**

CPC **C10M 105/76** (2013.01); **C03C 17/001** (2013.01); **B08B 17/06** (2013.01); **B65D 25/14** (2013.01); **B05D 5/08** (2013.01); **C03C 2217/76** (2013.01); **C03C 2218/31** (2013.01)

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§ 371 (c)(1),

(2) Date: **Jan. 13, 2015**

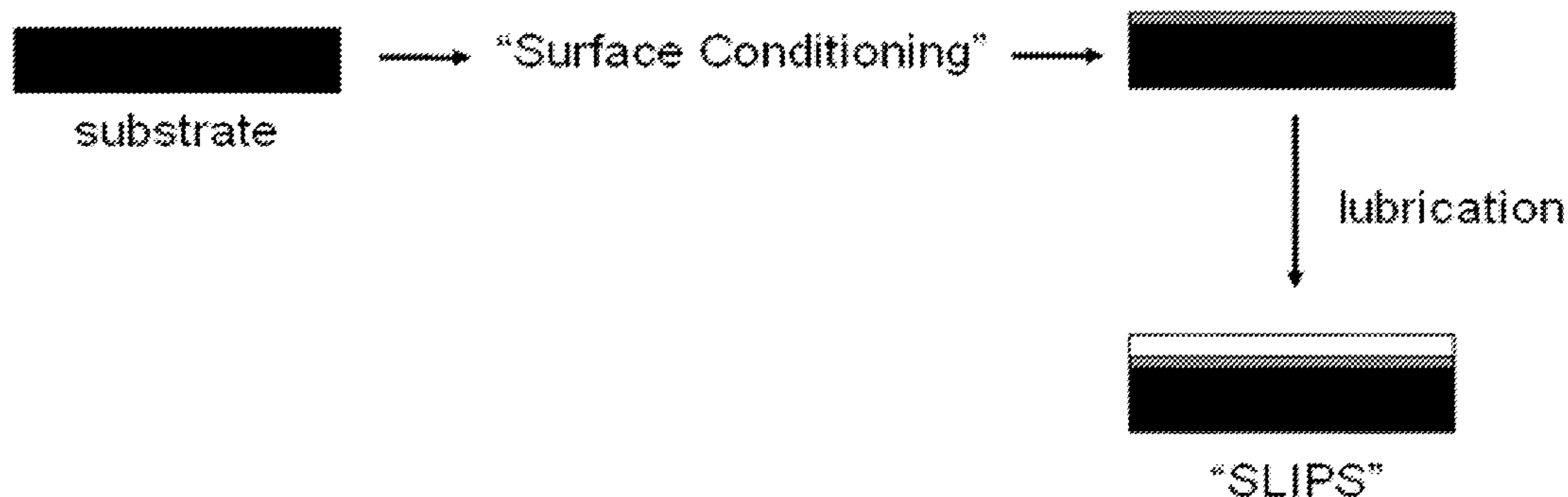
Related U.S. Application Data

(60) Provisional application No. 61/673,705, filed on Jul. 19, 2012, provisional application No. 61/671,442,

(57)

ABSTRACT

Methods and compositions disclosed herein relate to liquid repellant surfaces having selective wetting and transport properties. An article having a repellant surface includes a substrate comprising fabric material and a lubricant wetting and adhering to the fabric material to form a stabilized liquid overlayer, wherein the stabilized liquid overlayer covers the fabric material at a thickness sufficient to form a liquid upper surface above the fabric material, wherein the fabric material is chemically functionalized to enhance chemical affinity with the lubricant such that the lubricant is substantially immobilized on the fabric material to form a repellant surface.



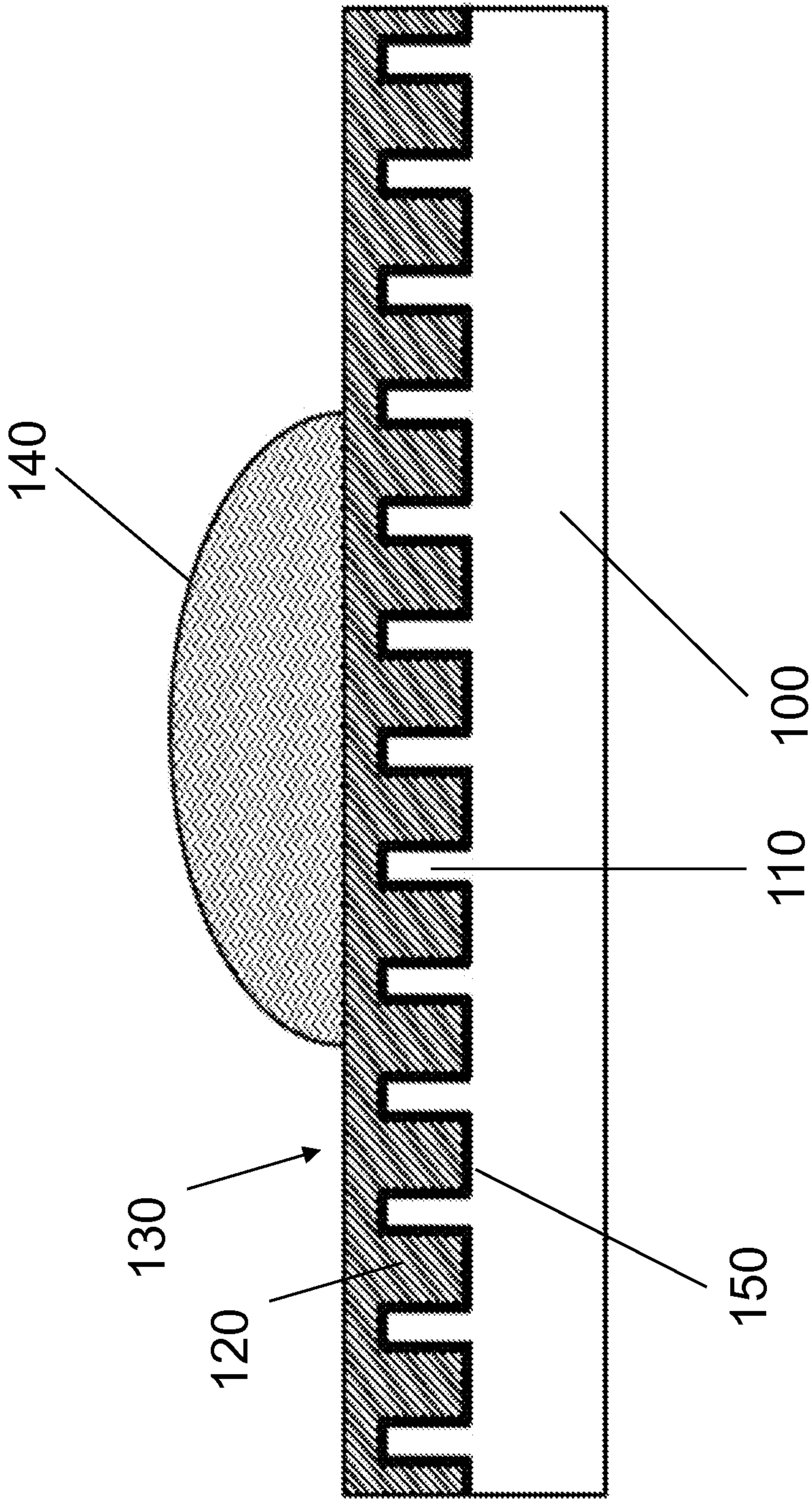


FIG. 1

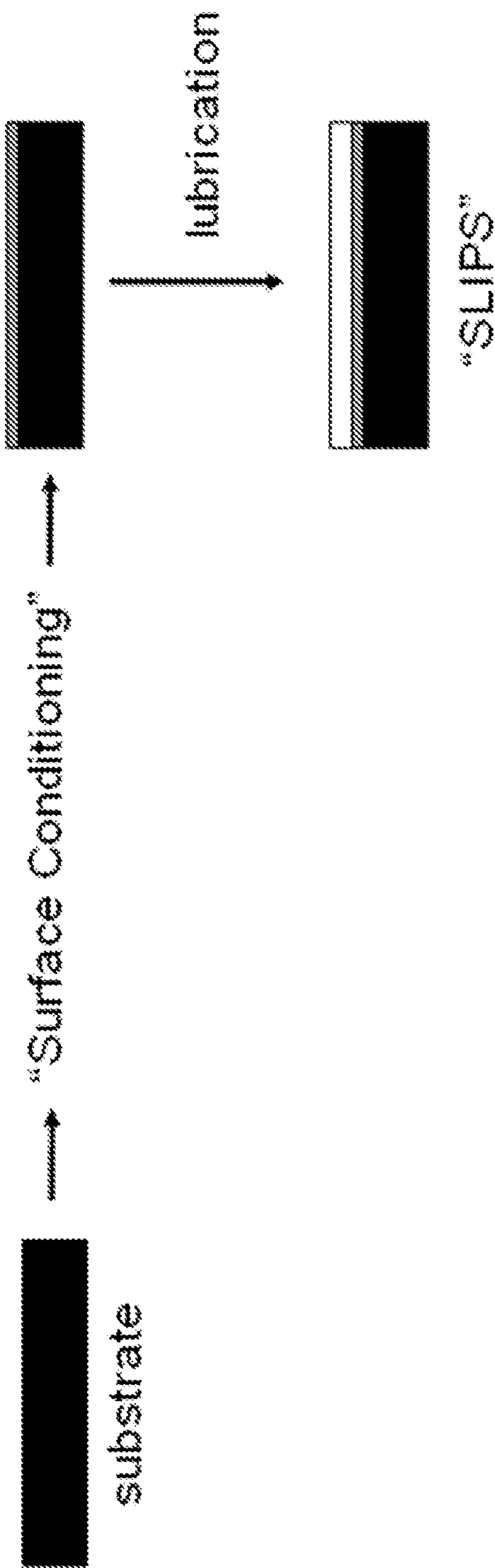
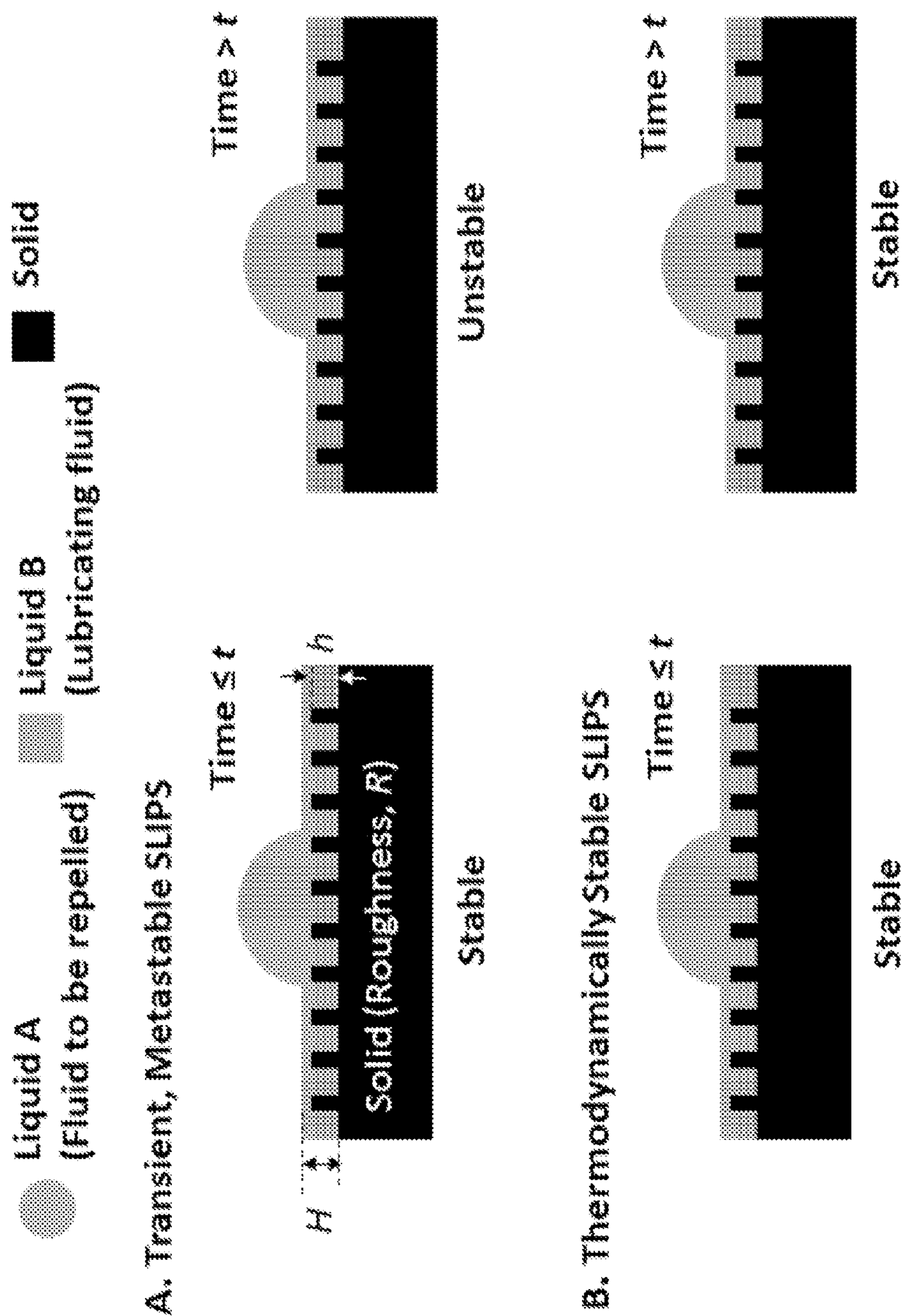


FIG. 2



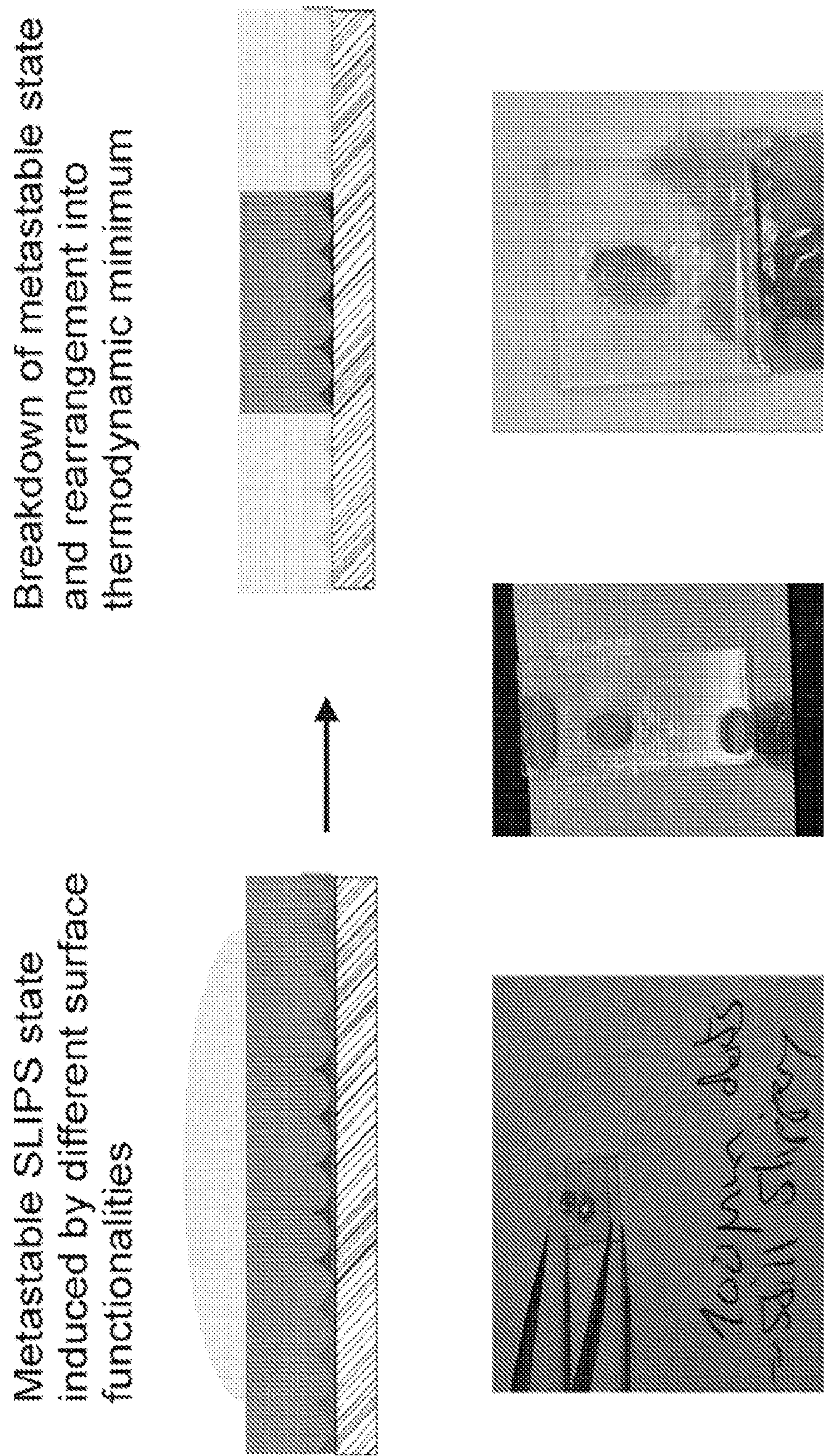


FIG. 3C

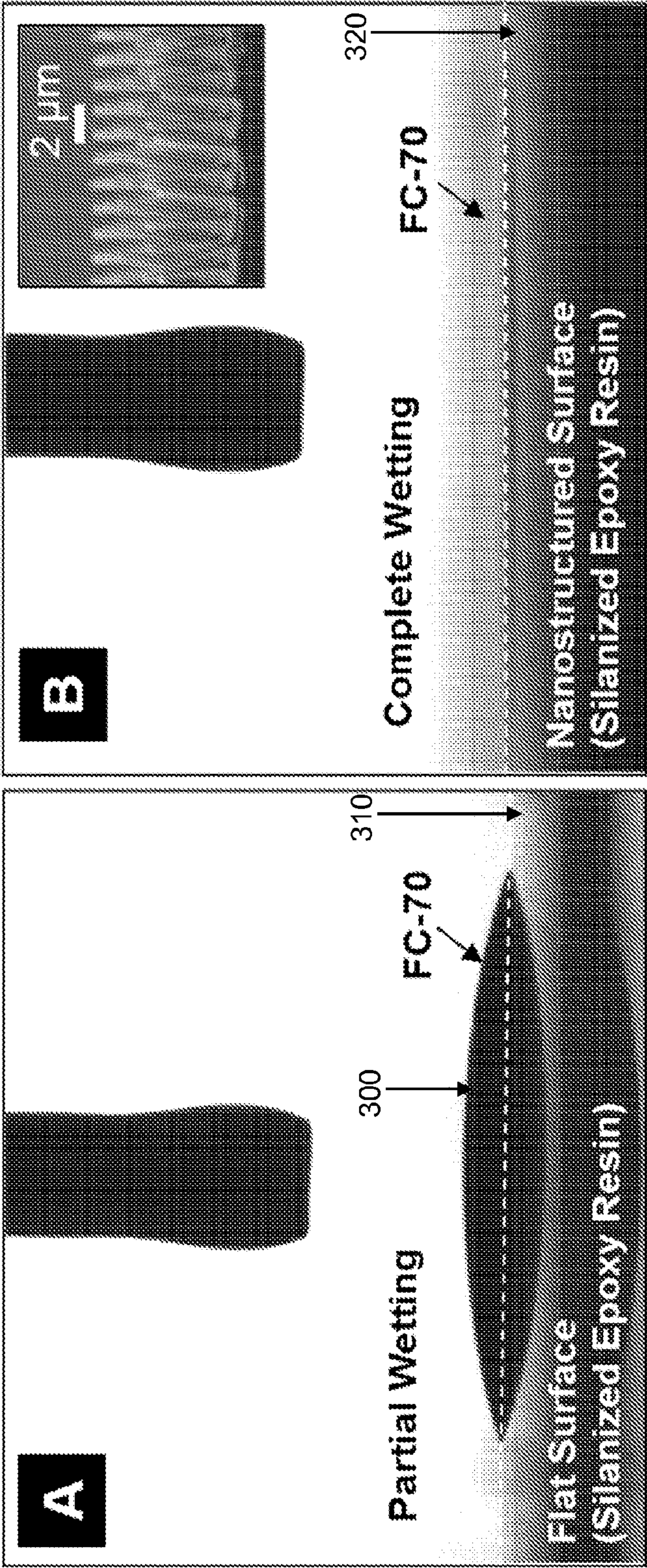


FIG. 4

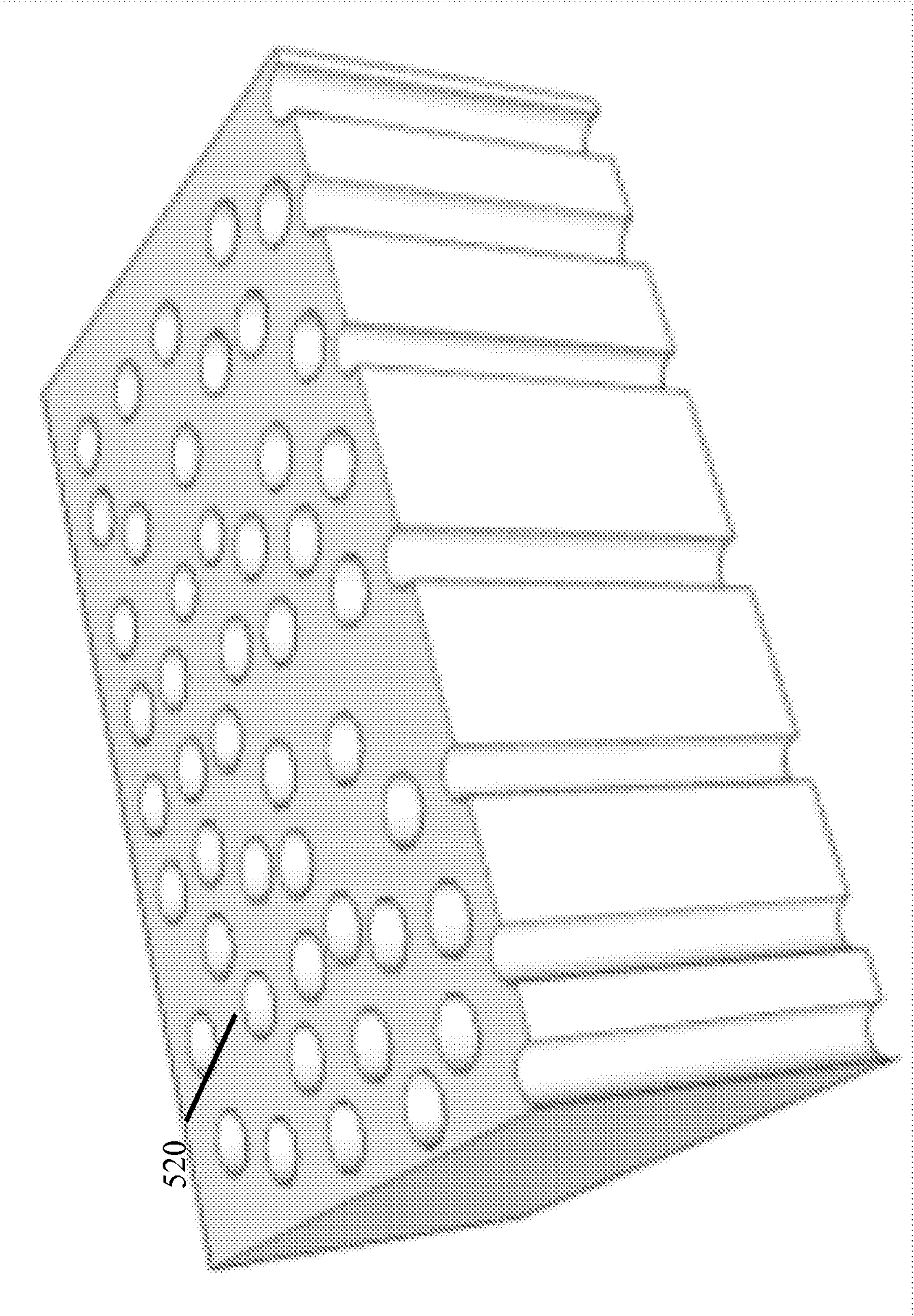


FIG. 5A

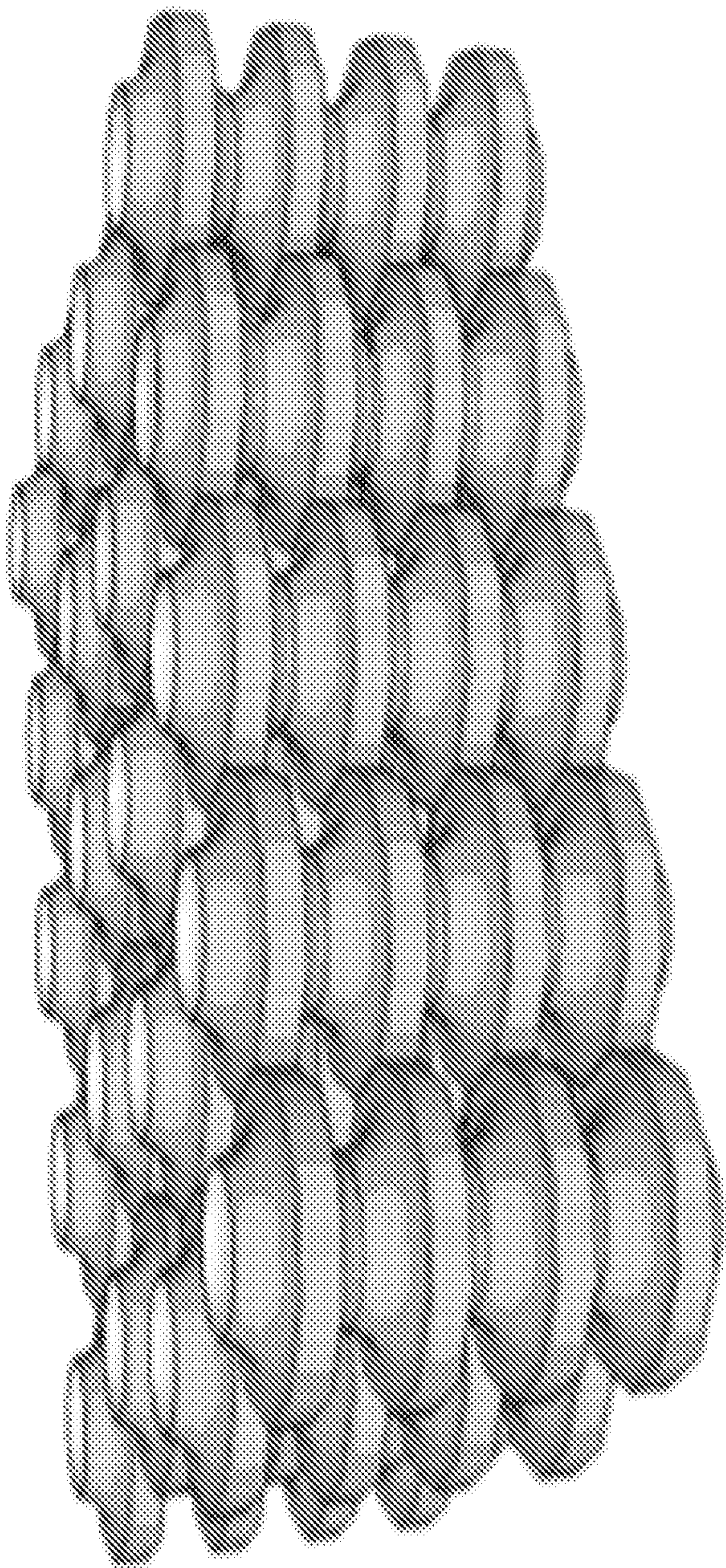


FIG. 5B

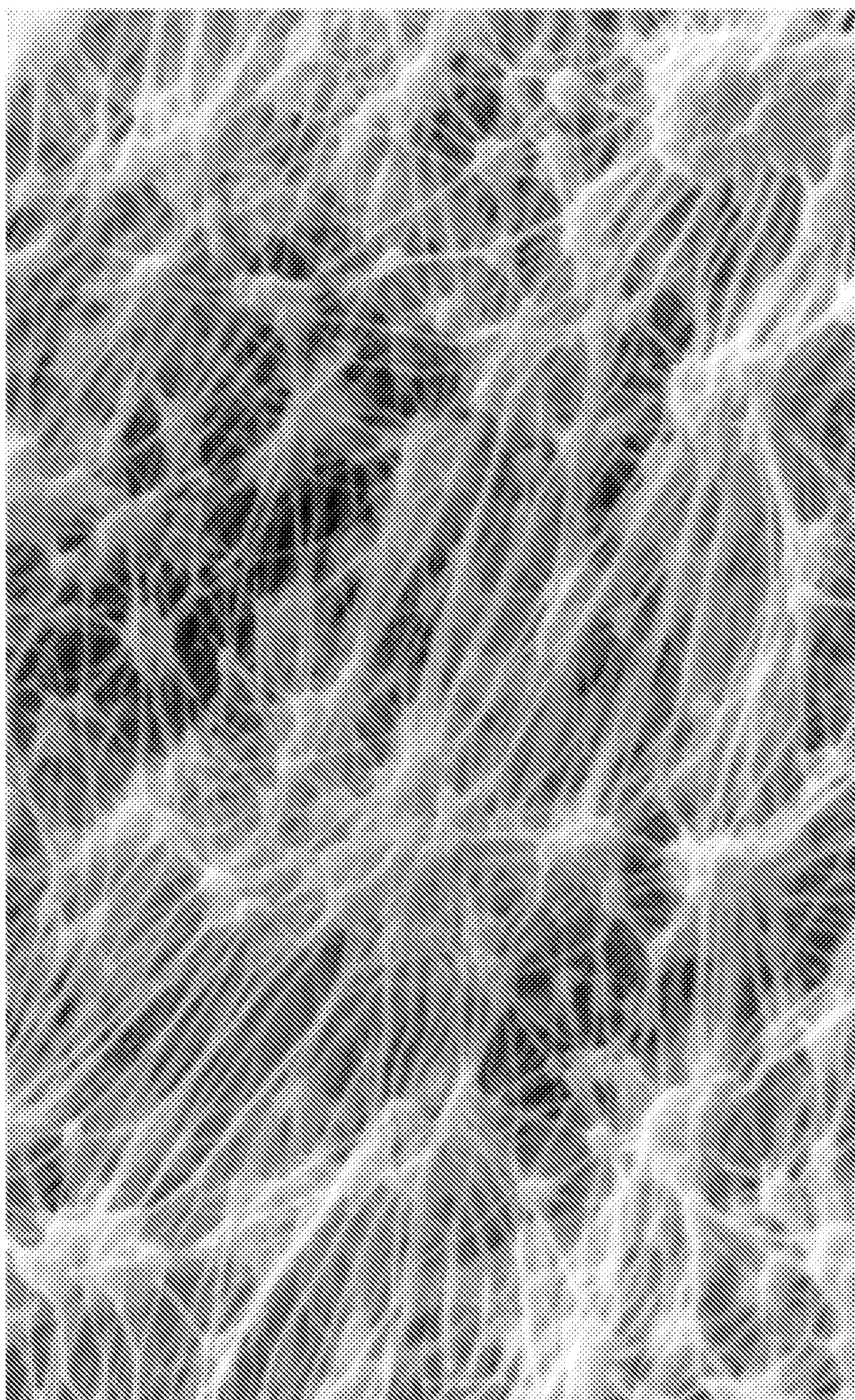


FIG. 5C

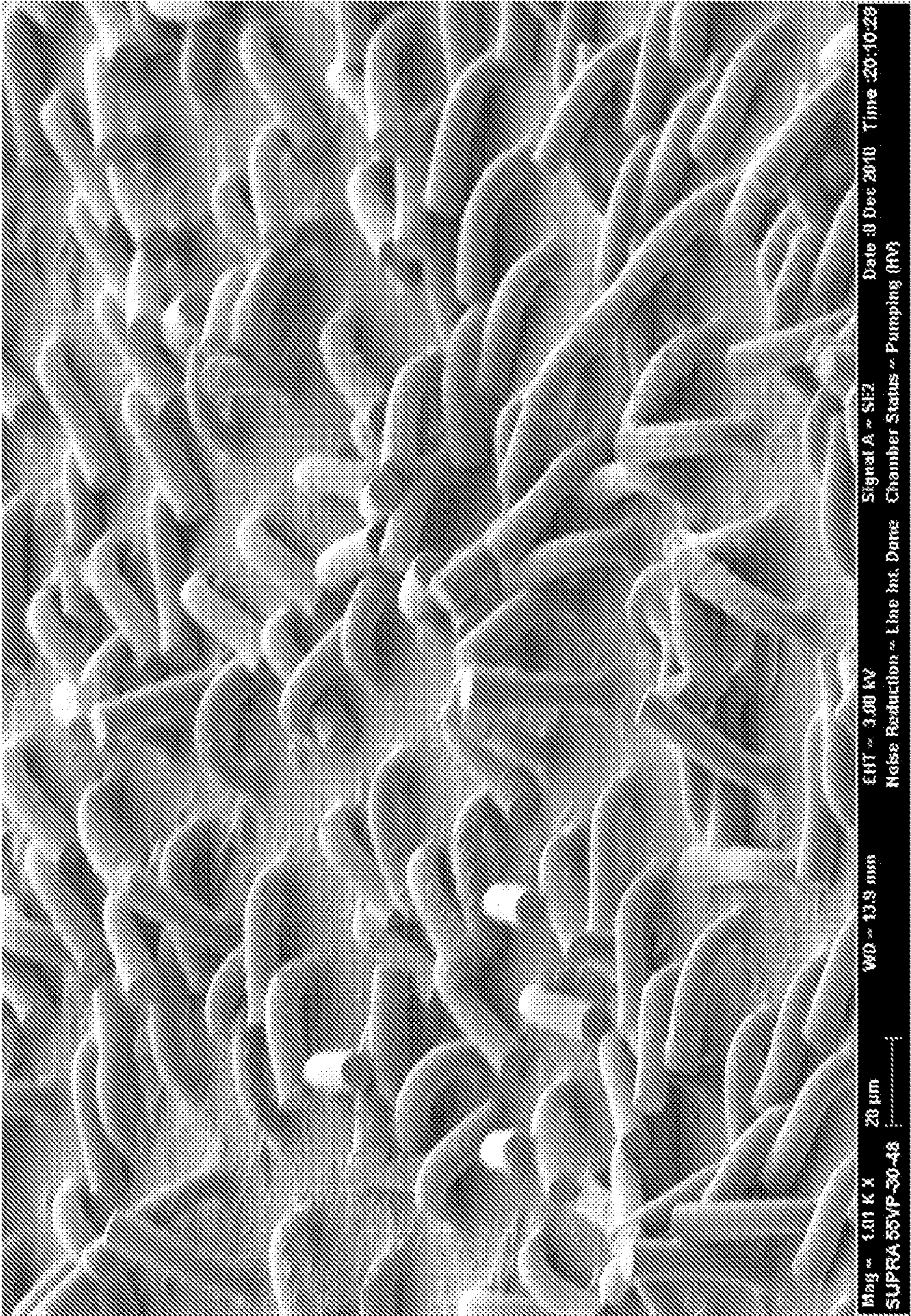


FIG. 5D

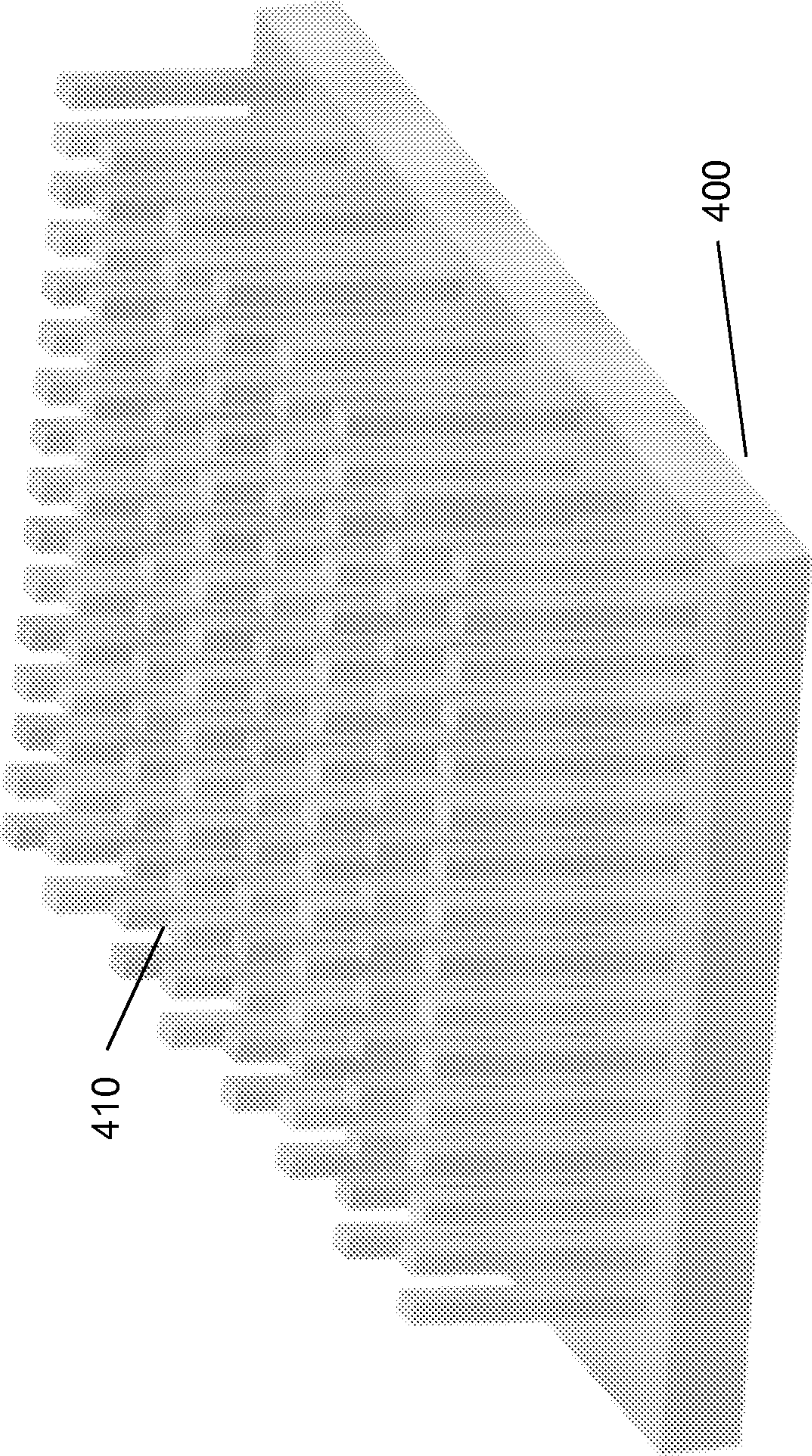


FIG. 5E

FIG. 6

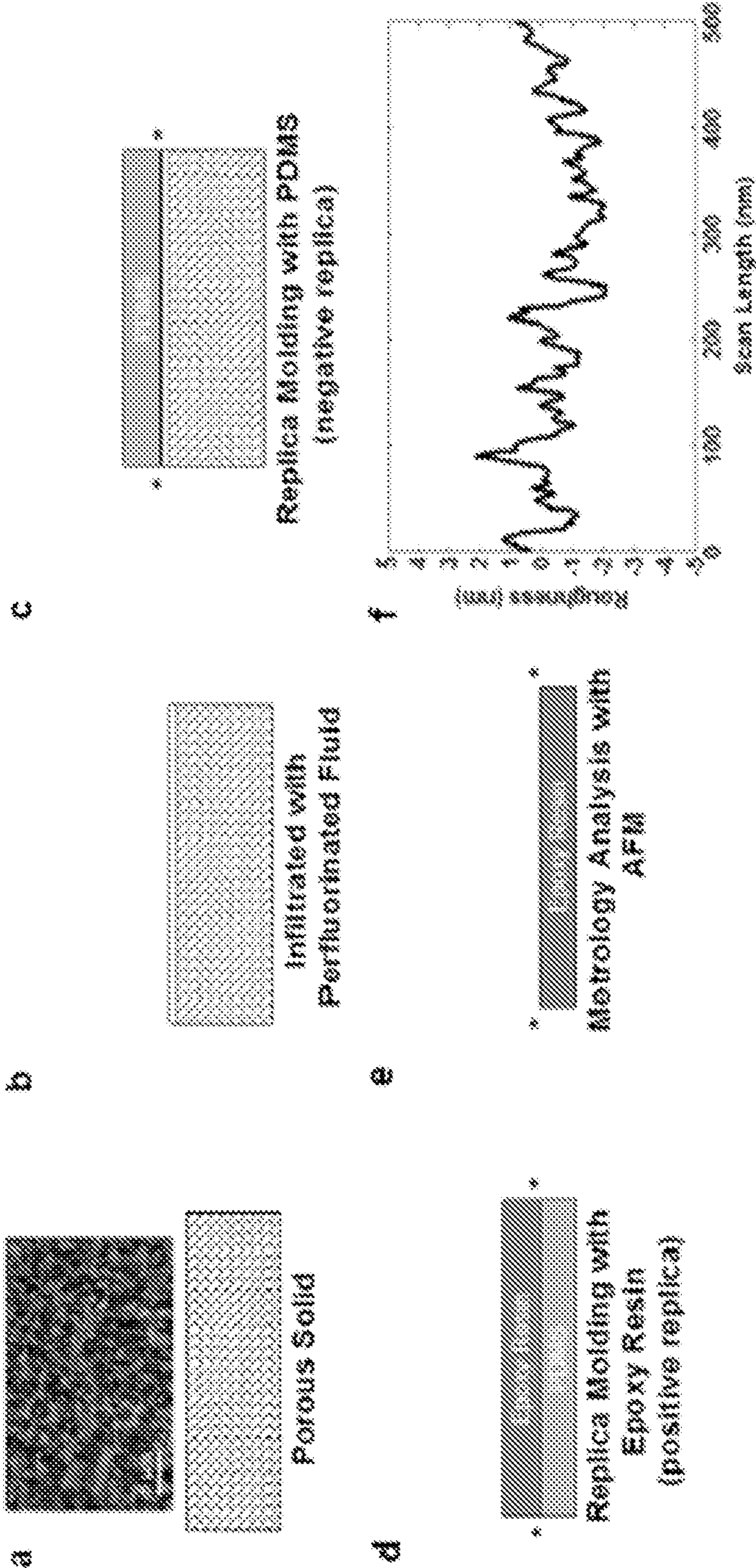


FIG. 7A

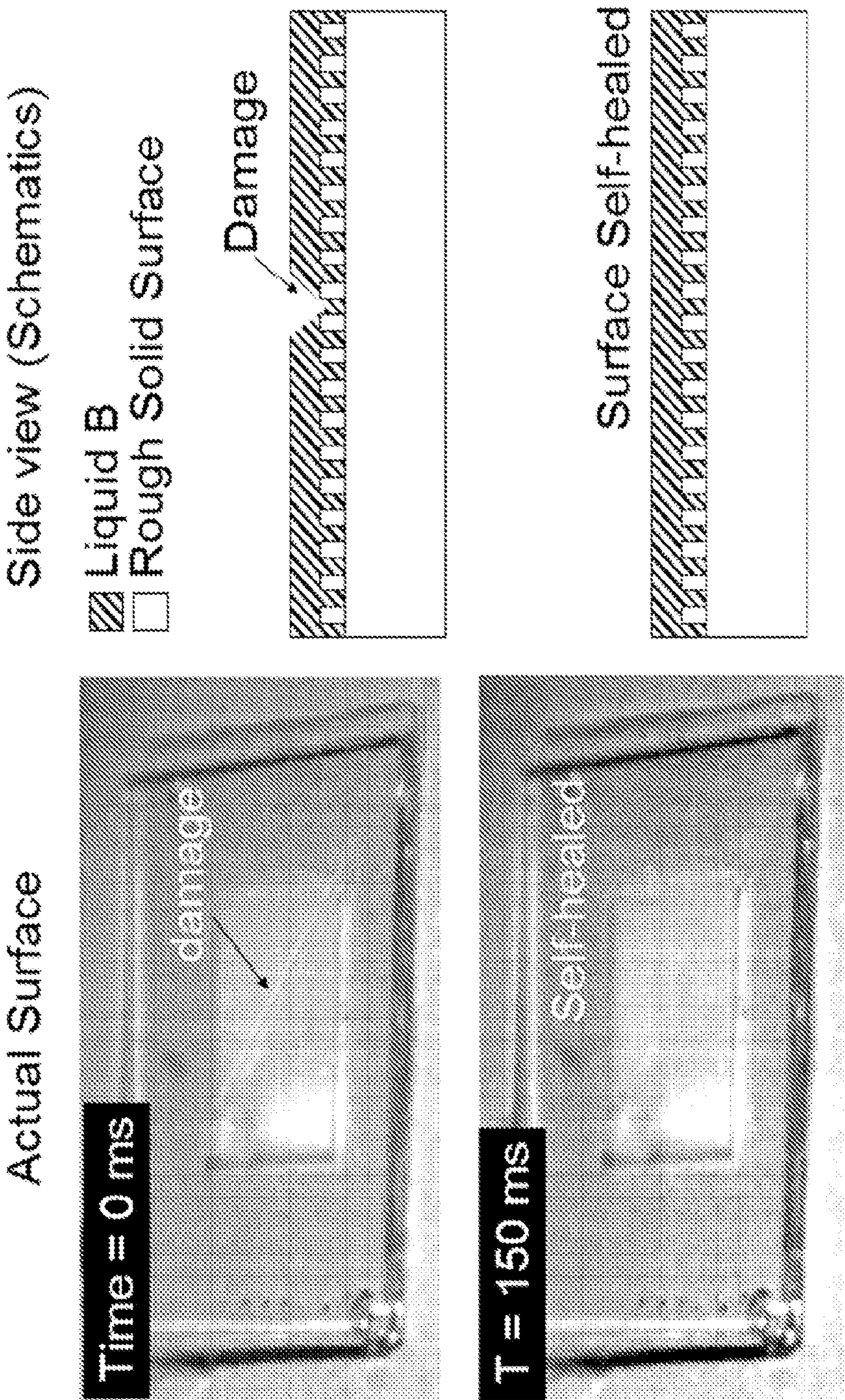


FIG. 7B

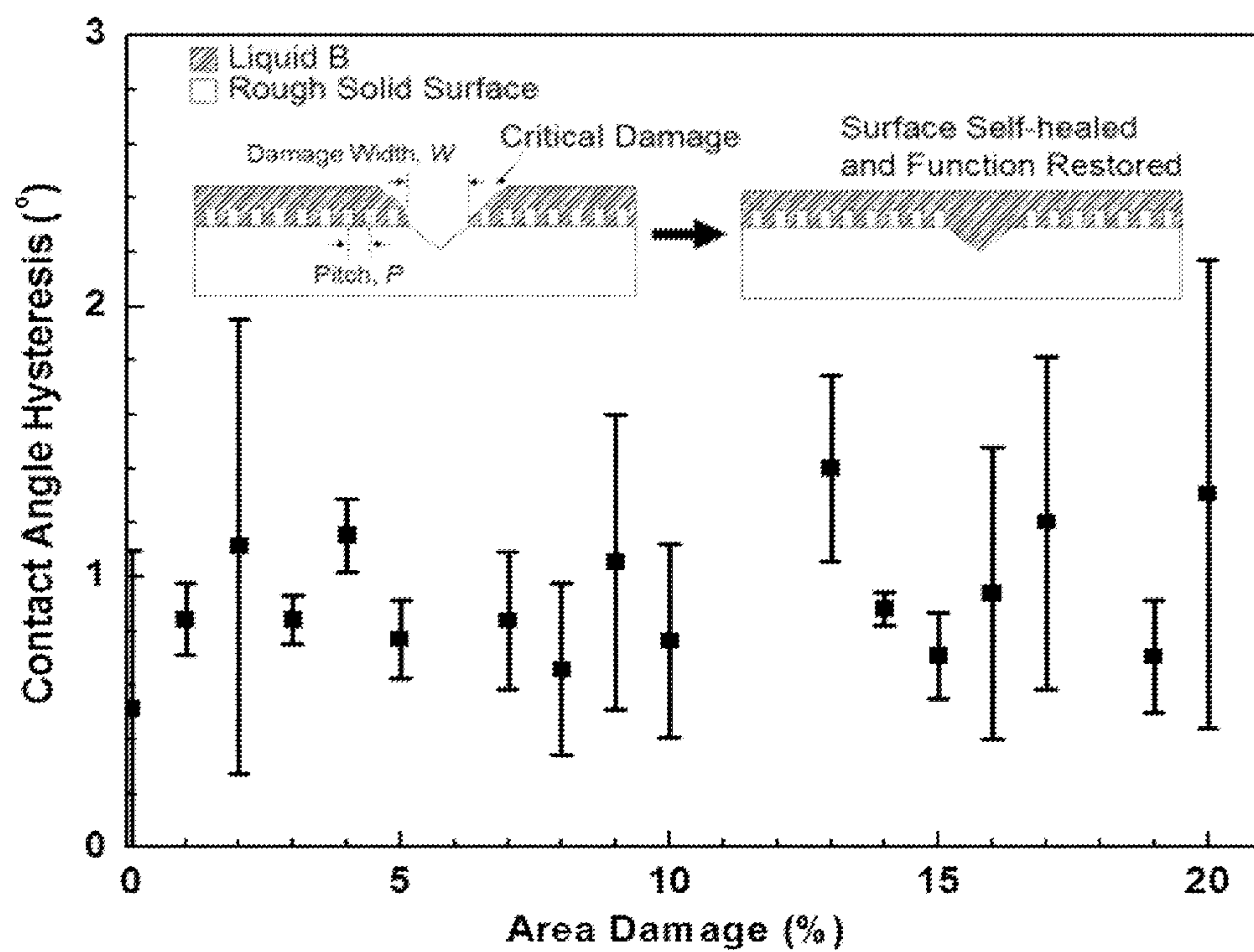
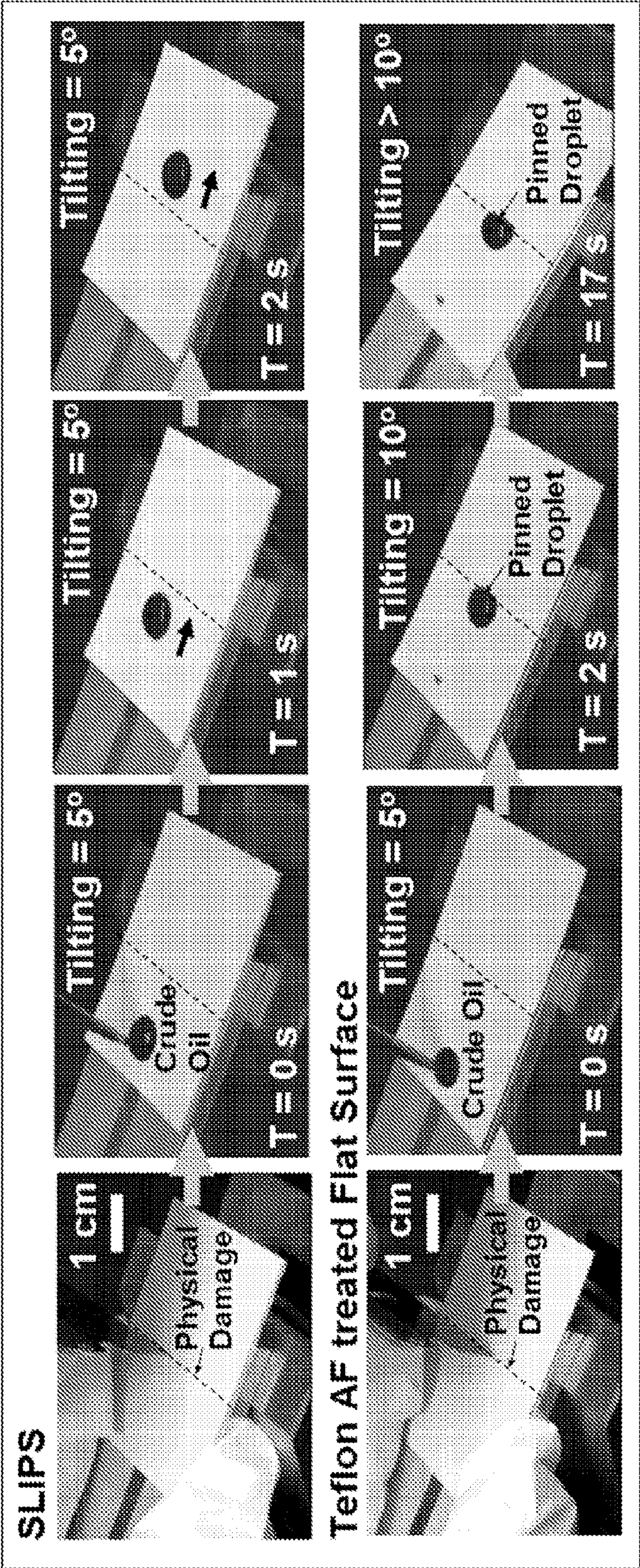


FIG. 7C



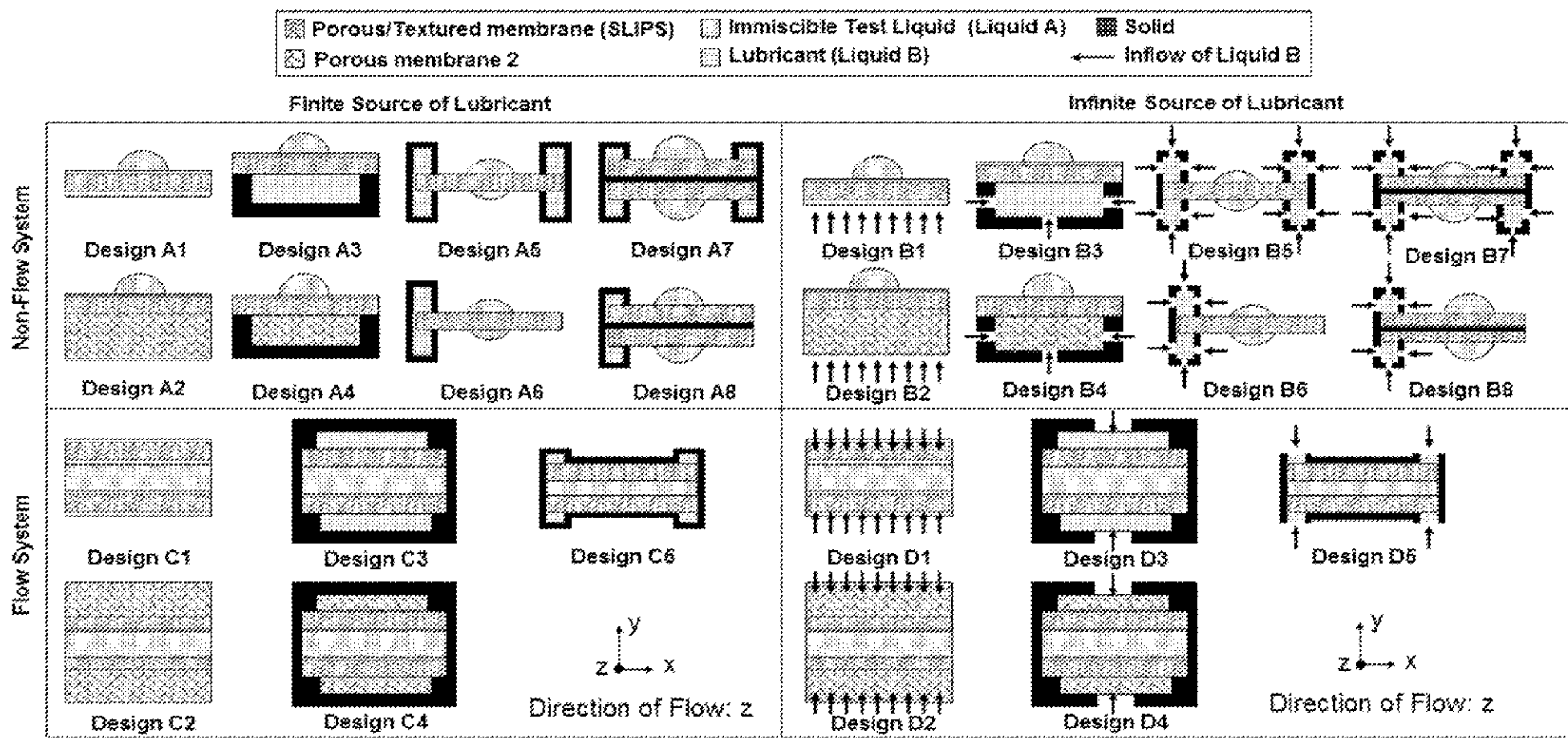


FIG. 7D

FIG. 8

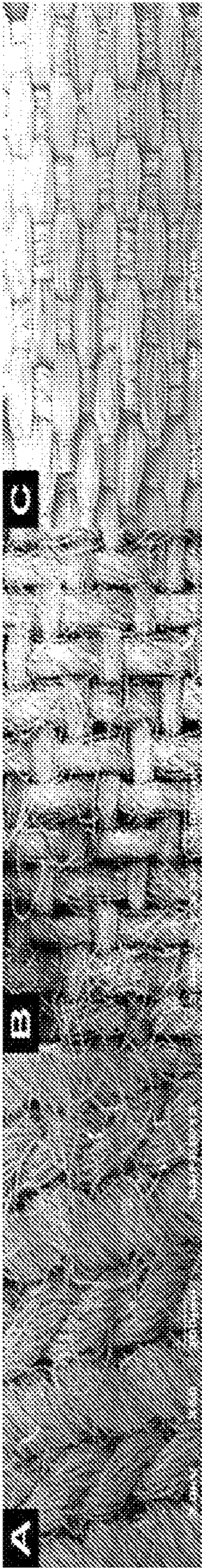
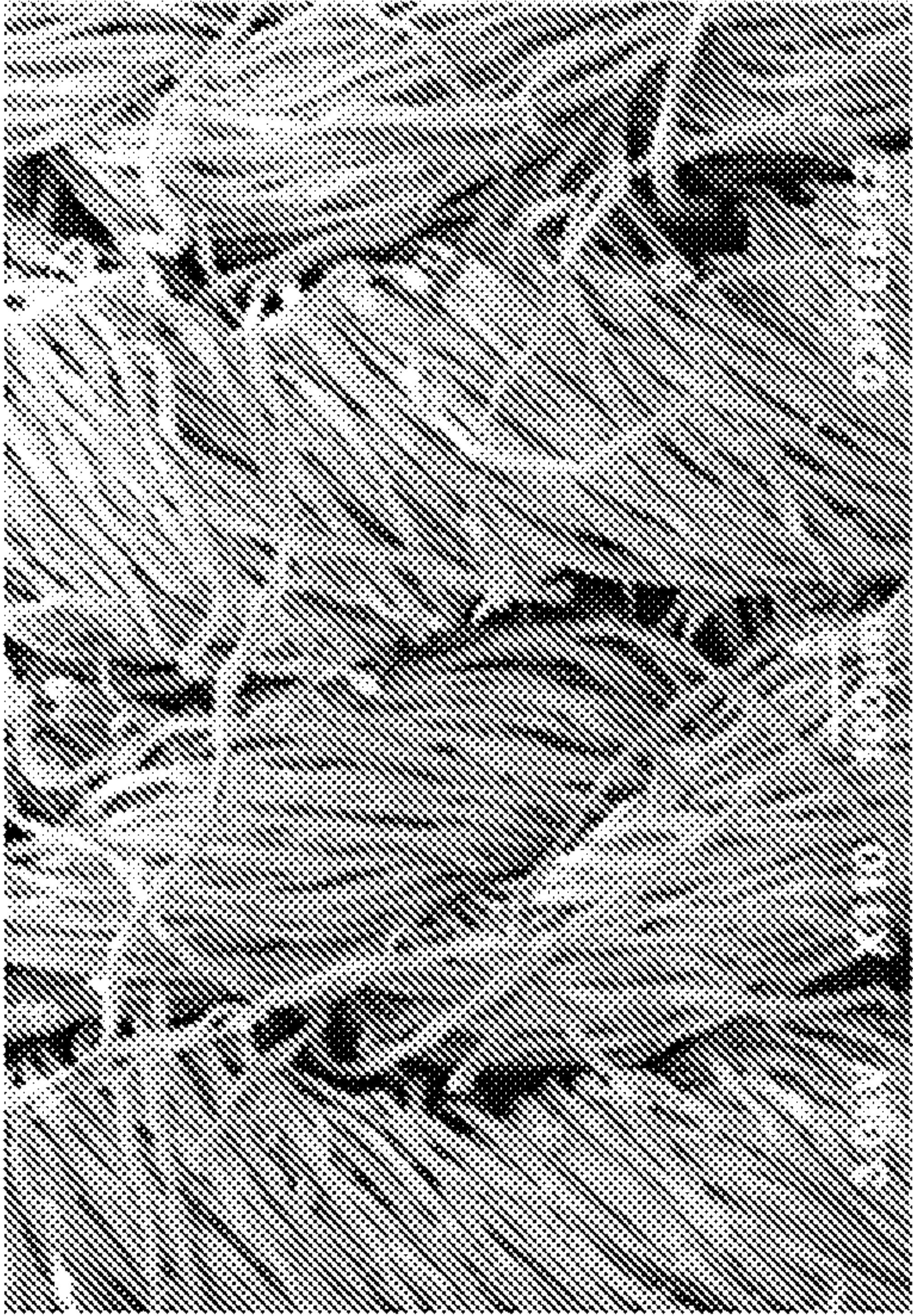


Figure 8. Common natural and synthetic fabrics systems. A) Natural cotton; B) Muslin (Cottonbased); C) Synthetic fabrics.

A. Gray Cotton

FIG. 9A

Before Silica and Silane Treatment



After Silica and Silane Treatment



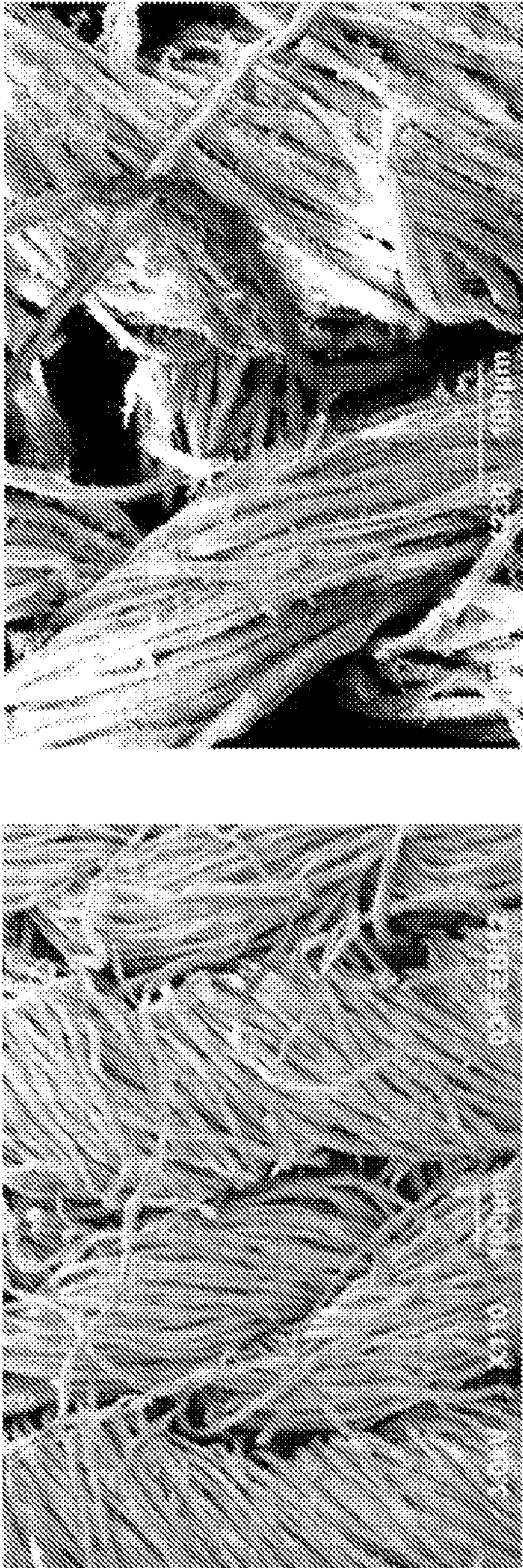
Treatment	Lubricant	Test Liquid	Static	adv	rec	hysteresis
silica modified & silanized, 1%	None	Water	162.8	165.9	140.5	25.4
silica modified & silanized, 1%	K100	Water	135.8	136.2	107.2	29.0

FIG. 9B

B. Muslin (White Cotton)

Before Silica and Silane Treatment

After Silica and Silane Treatment

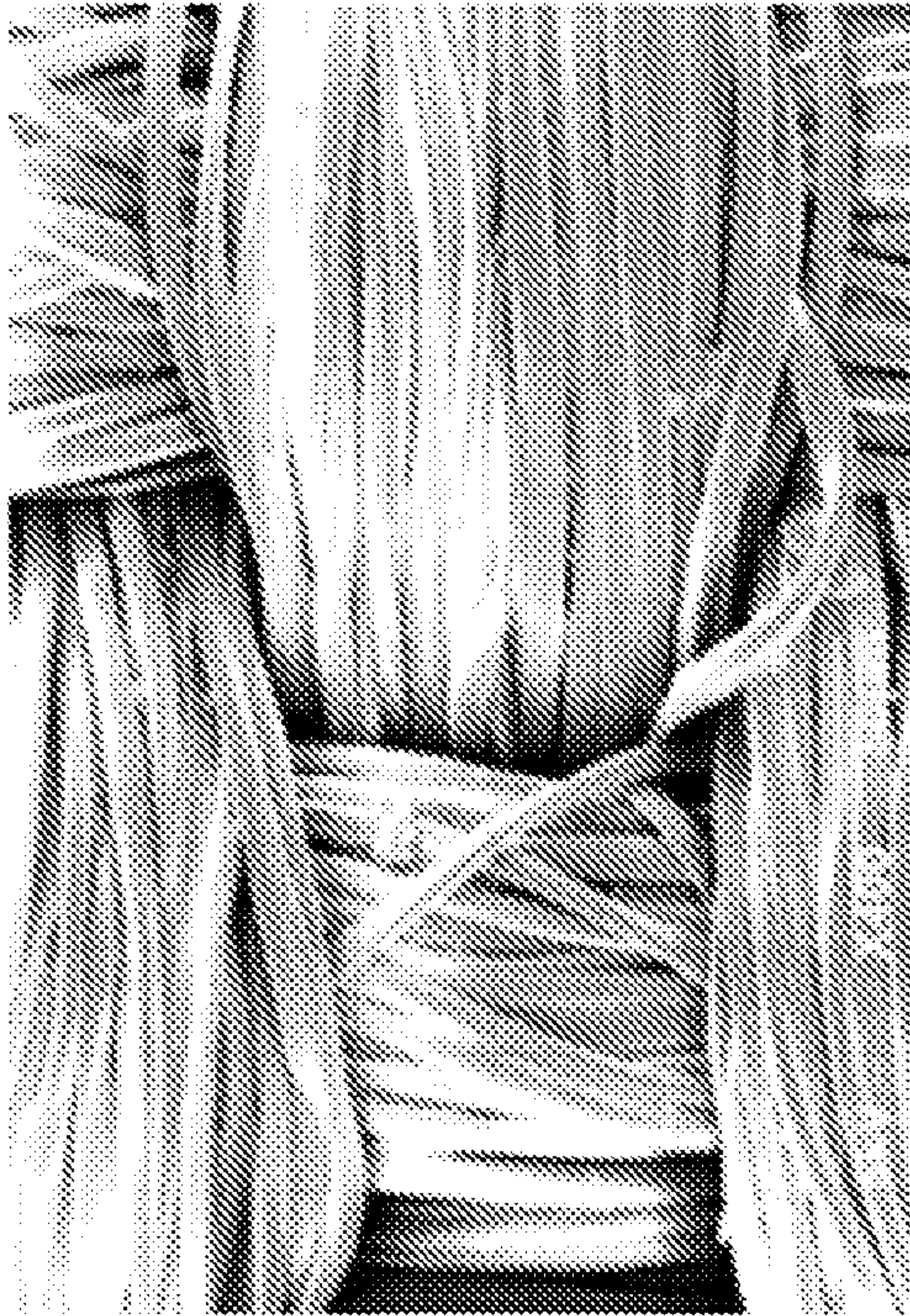


Treatment	Lubricant	Test Liquid	Θ Static	Θ adv	Θ rec	hysteresis
silica modified & silanized, 1%	None	Water	161.2	165.3	137.2	28.1
silica modified & silanized, 1%	K100	Water	112.4	118.7	101.1	17.6
silica modified & silanized, 1%	K103	Water	118.0	127.3	106.5	20.8

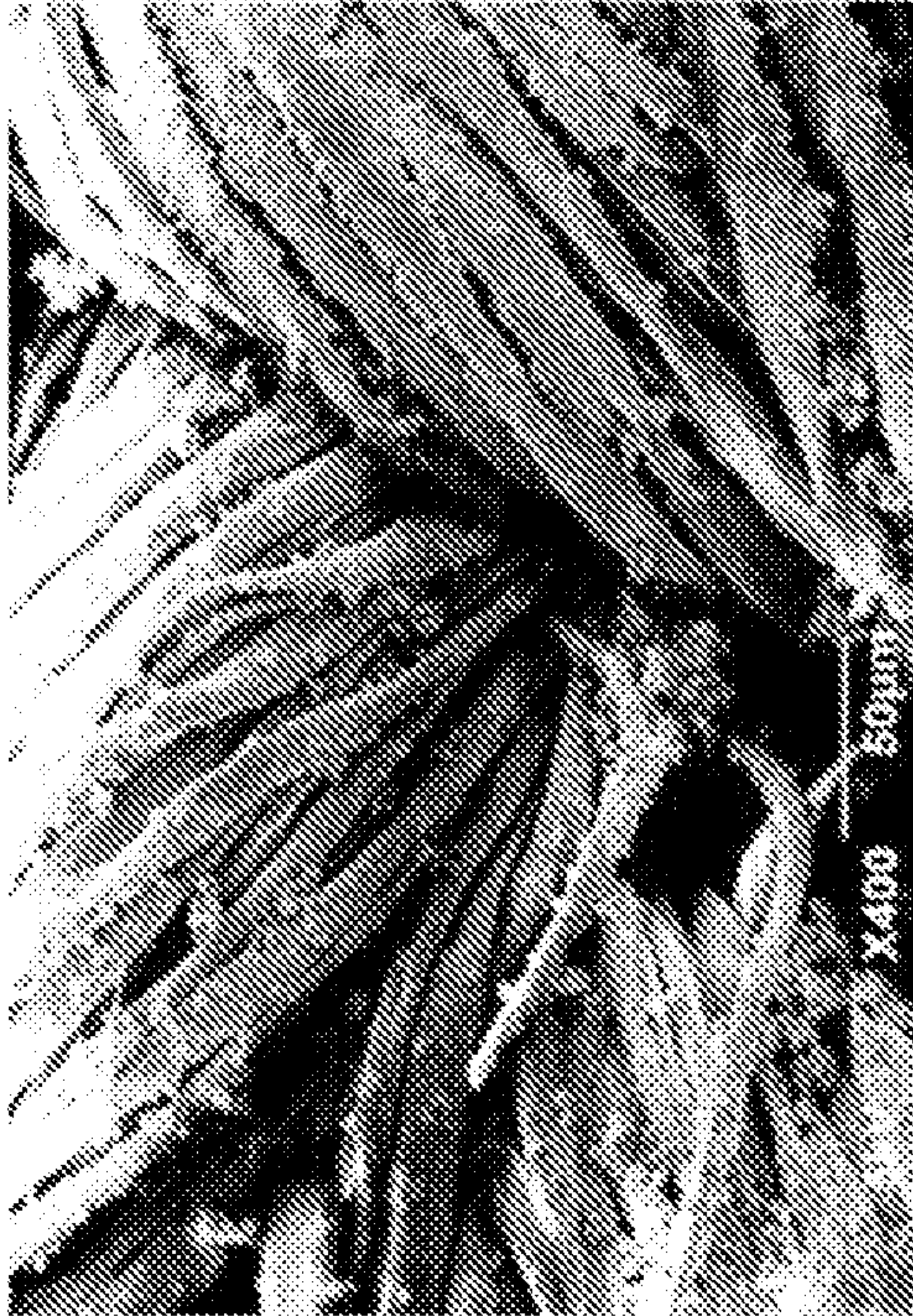
C. Synthetic Fabrics

FIG. 9C

Before Silica and Silane Treatment



After Silica and Silane Treatment



Treatment	Lubricant	Test Liquid	Static	adv	rec	hysteresis
silica modified & silanized, 1%	None	Water	149.9	154.8	134.1	20.7
silica modified & silanized, 1%	K100	Water	115.3	130.2	116.1	14.1

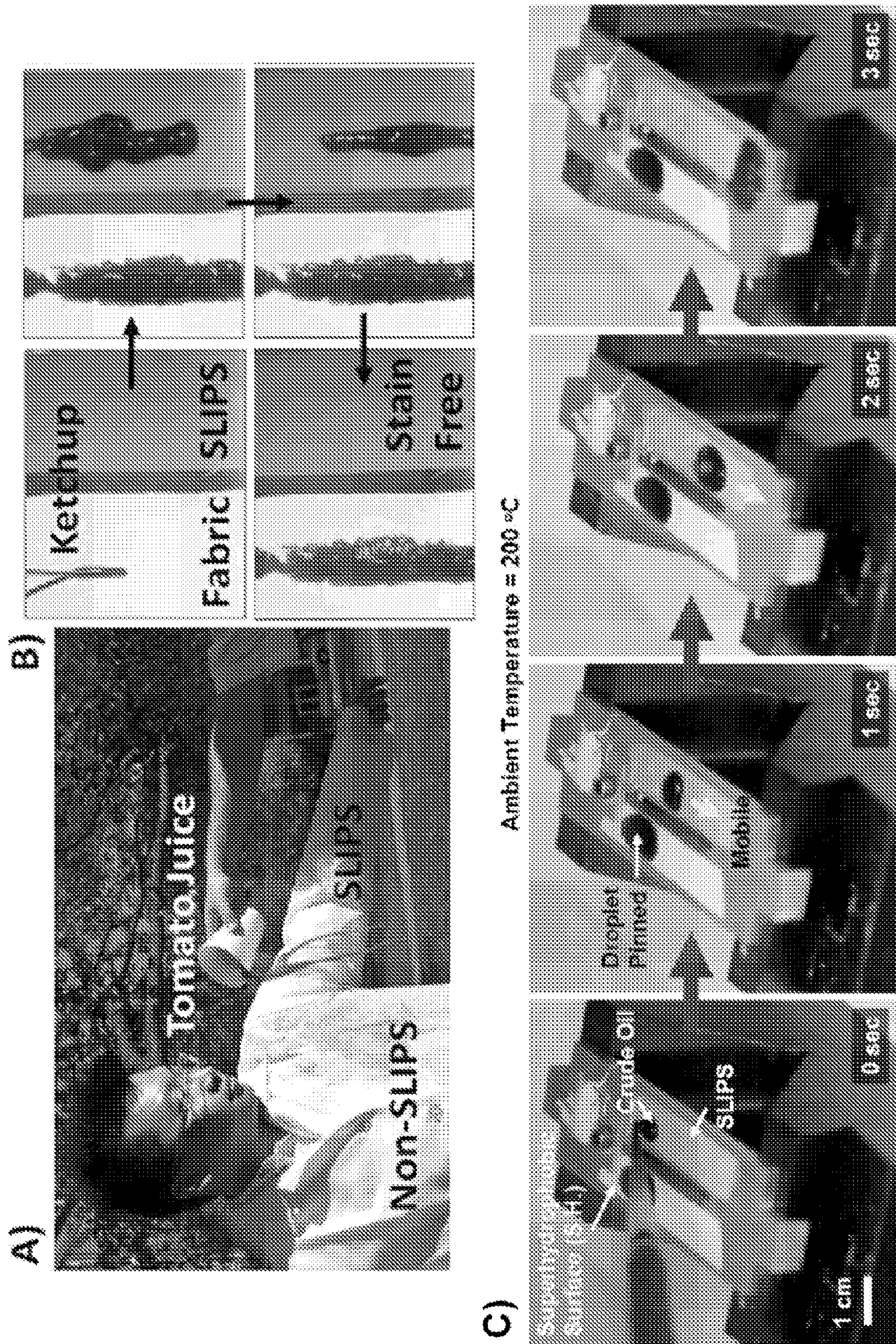


FIG. 10

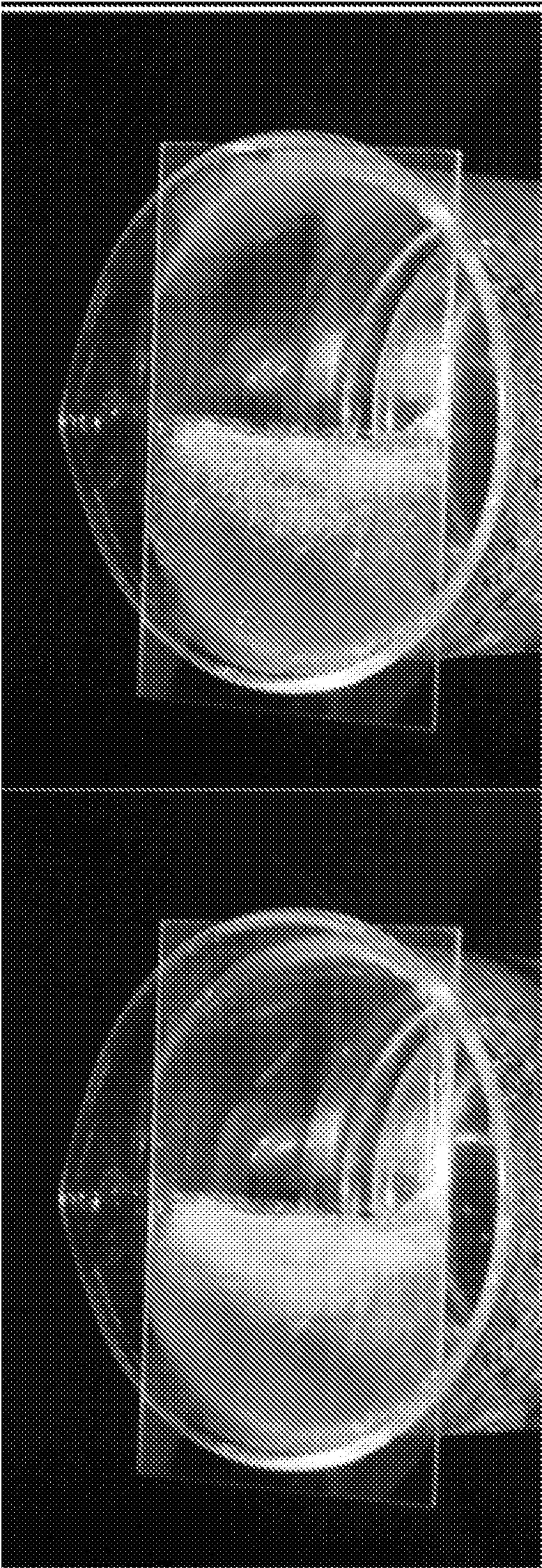


FIG. 11

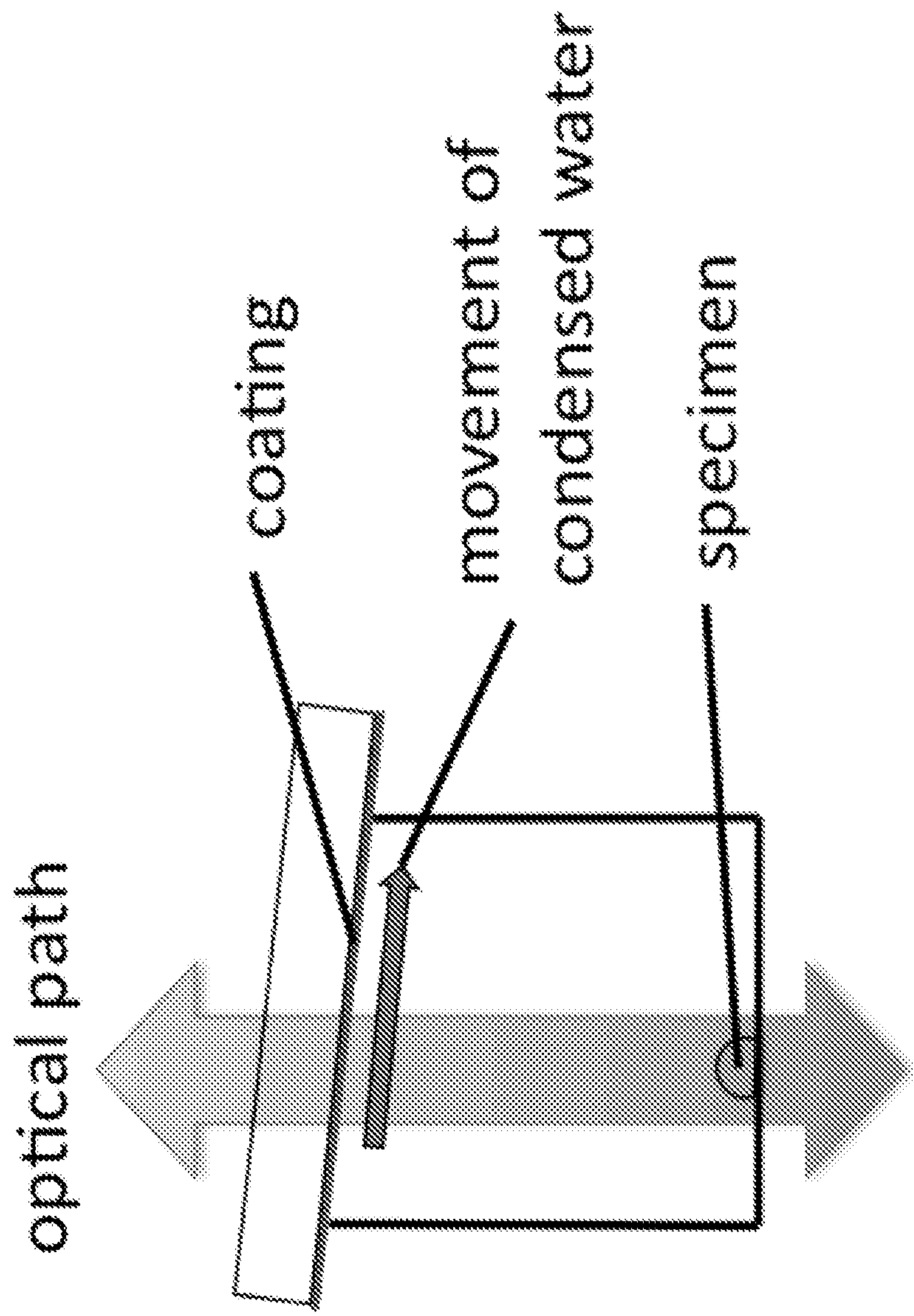


FIG. 12

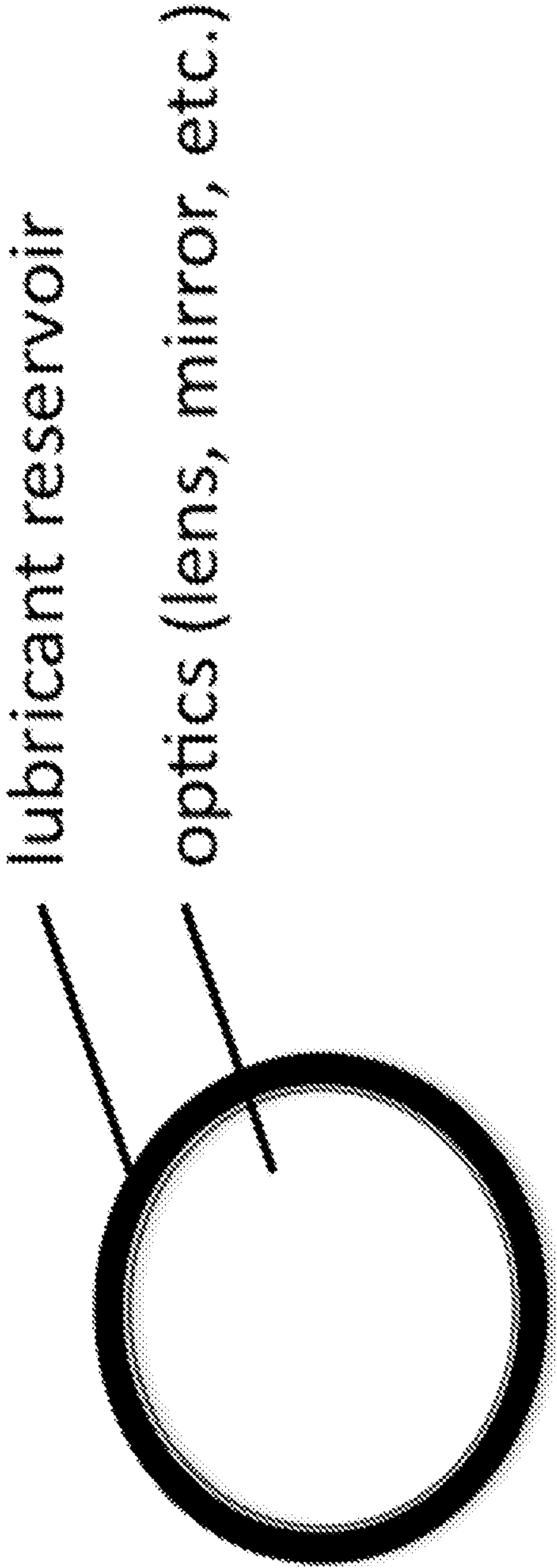


FIG. 13

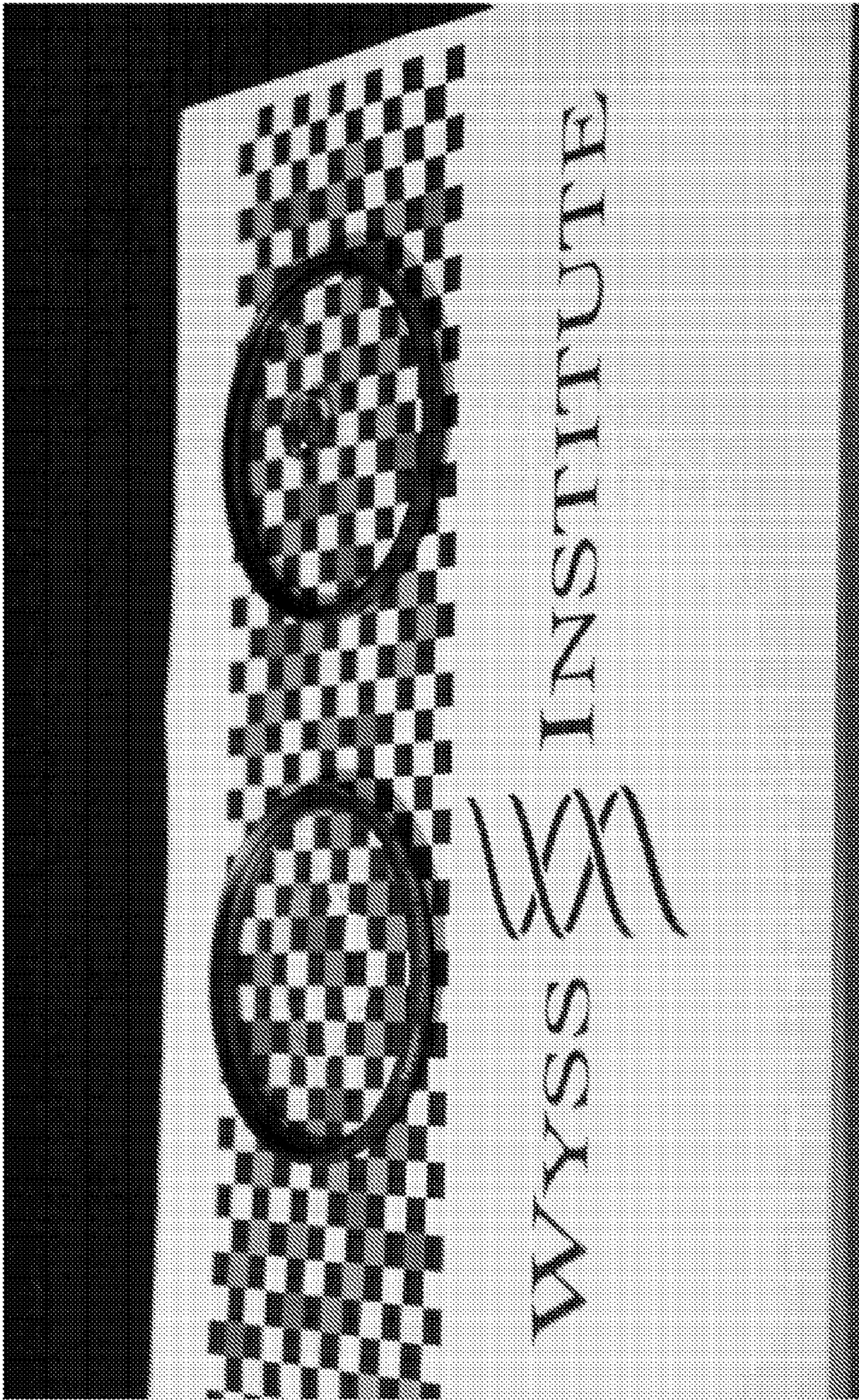


FIG. 14

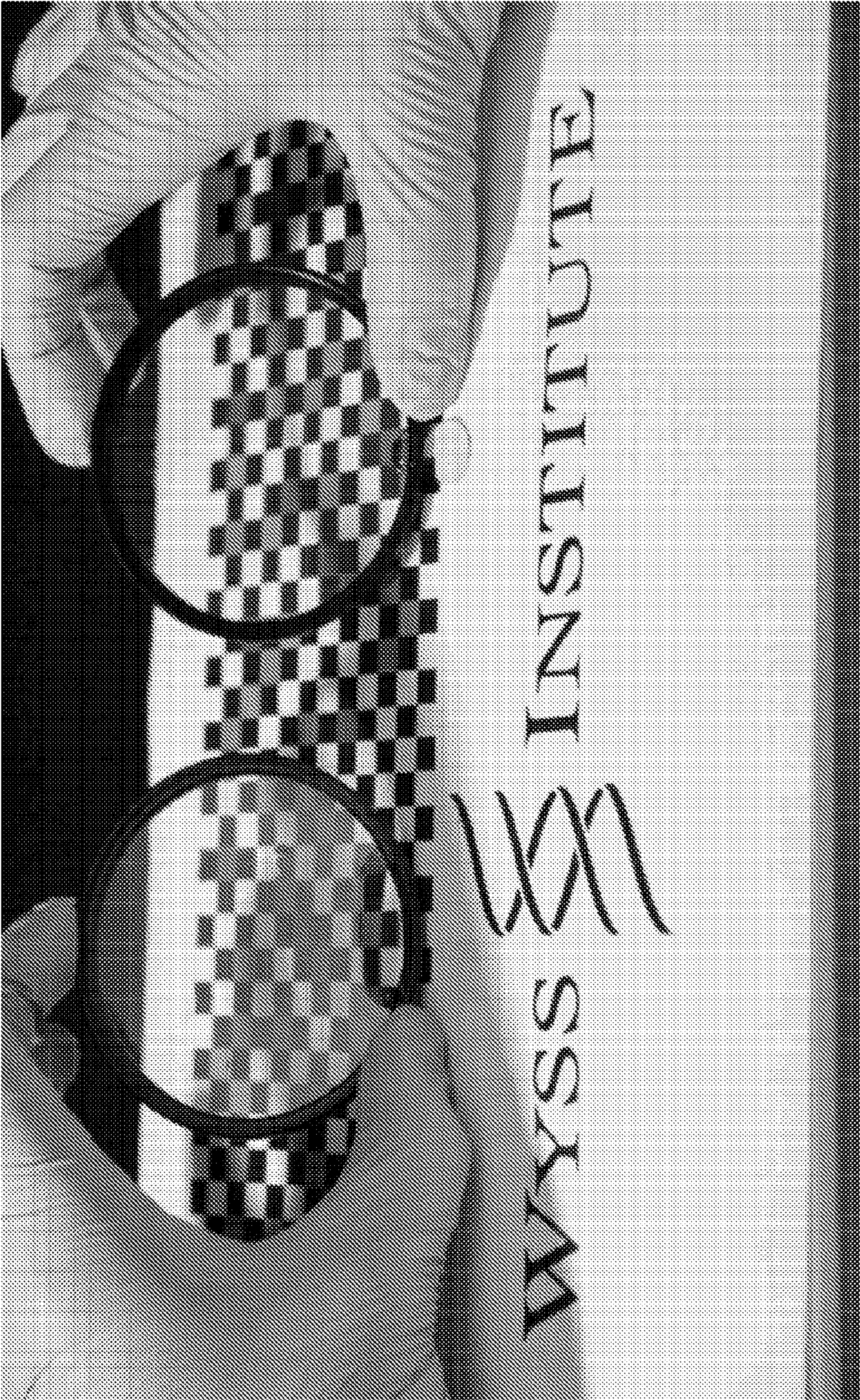


FIG. 15

Regulatory Approval Chart
(all information assumes natural color with no additional additives)

Typical Approvals Only – Confirm with Salesperson at time of Order if a specific approval and certifications are required. Professional Plastics assumes no liability in your specific application.

Material	FDA	USDA	NSF	3A Dairy	Canada AG
ABS - Engineering Grade	YES	YES	NO	YES	NO
Acetal Copolymer	YES	YES	YES	YES	YES
Acrylic - Cast & Extruded	YES	YES	YES	N/A	N/A
Delrin® Acetal Homopolymer	YES	YES	YES	NO	YES
Ertalite® PET-P	YES	YES	NO	YES	YES
Ertalite® TX (lubricated PET-P)	YES	YES	NO	YES	NO
FEP	YES	NO	NO	NO	NO
Fluorocast® 207 (food grade)	YES	YES	NO	NO	NO
Kalar® ECTFE	YES	NO	NO	NO	NO
Kynar® PVDF	YES	YES	YES	YES	NO
MC 907®	YES	YES	NO	YES	NO
Noryl® PPO	YES	YES	NO	NO	NO
Norprene® Tubing	YES	N/A	YES	YES	N/A
Nylon® Type 6/6 Extruded	YES	YES	YES	YES	NO
Nyloil FG®	YES	YES	NO	YES	NO
PEEK	YES	YES	NO	YES	NO
PFA	YES	NO	NO	NO	NO
Polyethylene - HDPE	YES	YES	NO	NO	NO
Polyethylene - LDPE	YES	NO	NO	NO	NO
Polypropylene - Homopolymer	YES	YES	YES	YES	NO
Polypropylene - Copolymer	YES	YES	N/A	YES	NO
Polysulfone	YES	YES	YES	YES	YES
Sanalite® Cutting Boards	YES	YES	YES	N/A	N/A
Sanatec® Cutting Boards	YES	YES	YES	N/A	N/A
Silbraid® Tubing	YES	N/A	YES	N/A	N/A
Techtron® PPS	YES	YES	NO	NO	NO
Techtron® HPV	YES	NO	NO	NO	NO
Teflon® PTFE	YES	NO	NO	NO	NO
Tygon® S-44-3 Tubing	YES	N/A	YES	YES	N/A
Tygothane® Tubing	YES	N/A	N/A	N/A	N/A
UHMW-PE	YES	YES	N/A	YES	N/A
Utem® 1000 - PEI	YES	NO	NO	NO	NO

Typical Approvals Only – Confirm with Salesperson at time of Order if a specific approval and certifications are required. Professional Plastics assumes no liability in your specific application. Approvals Listed as N/A do not necessarily indicate failure in that particular criteria. This product may not have gone through the testing and approval process. Please contact Professional Plastics technical support for further information or questions.

FIG. 16A

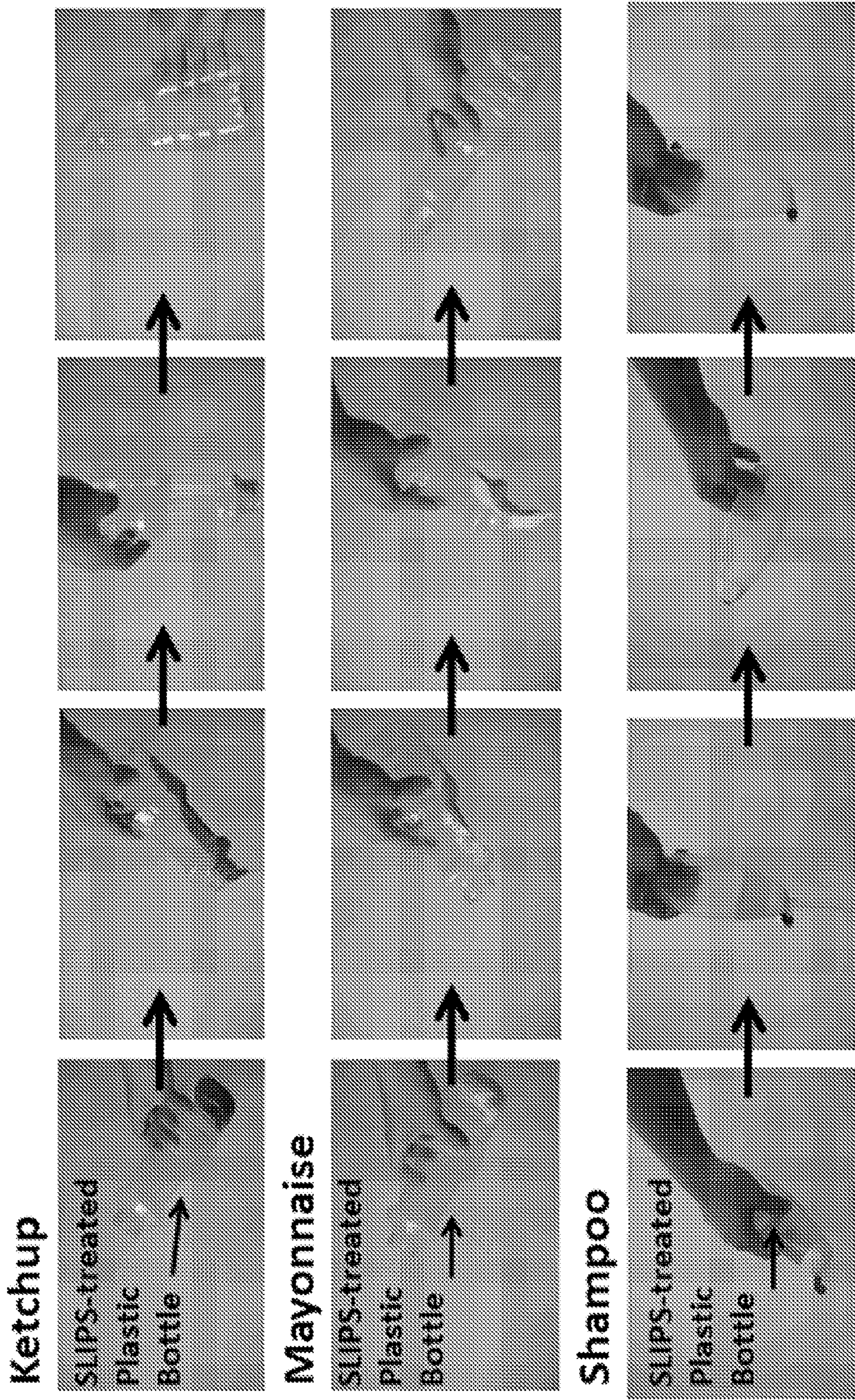


FIG. 16B

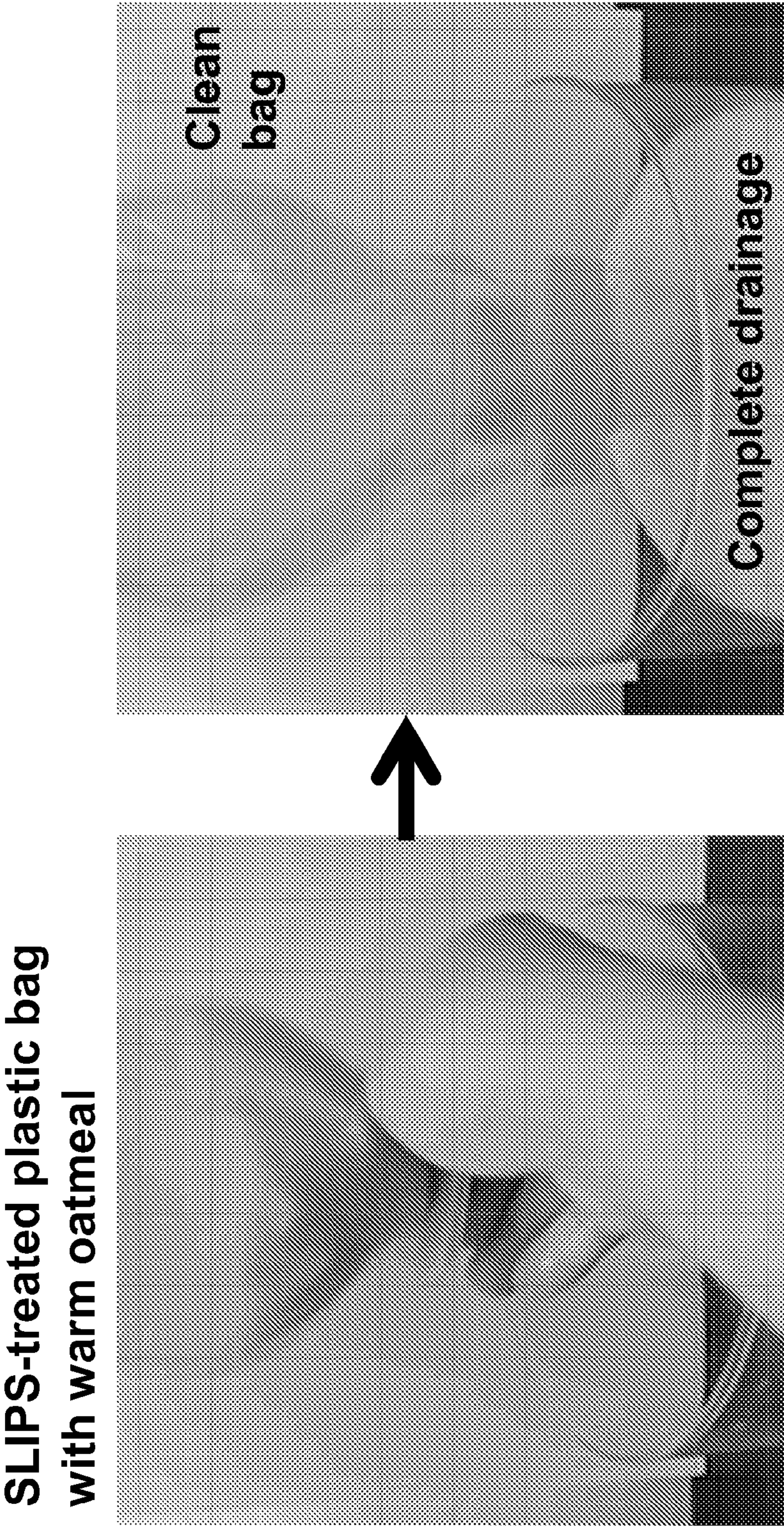


FIG. 16C

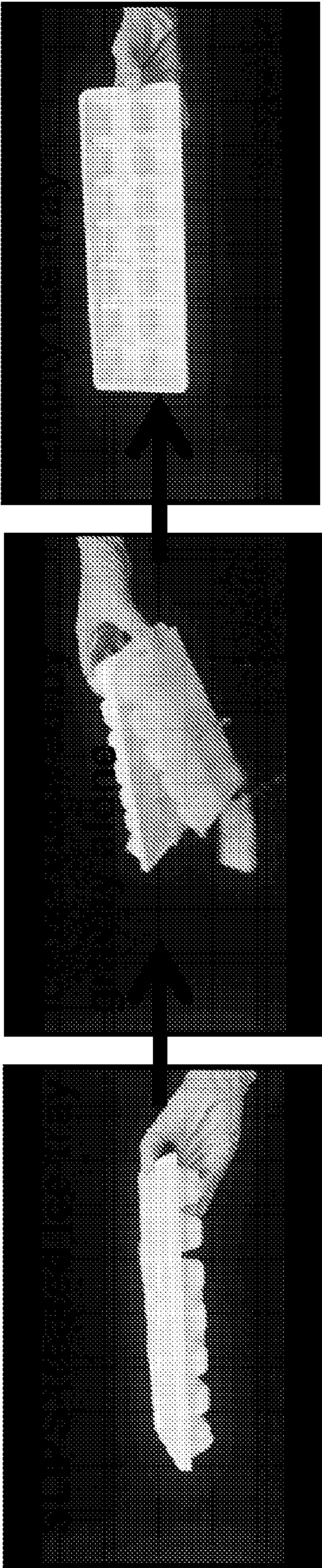


FIG. 16D

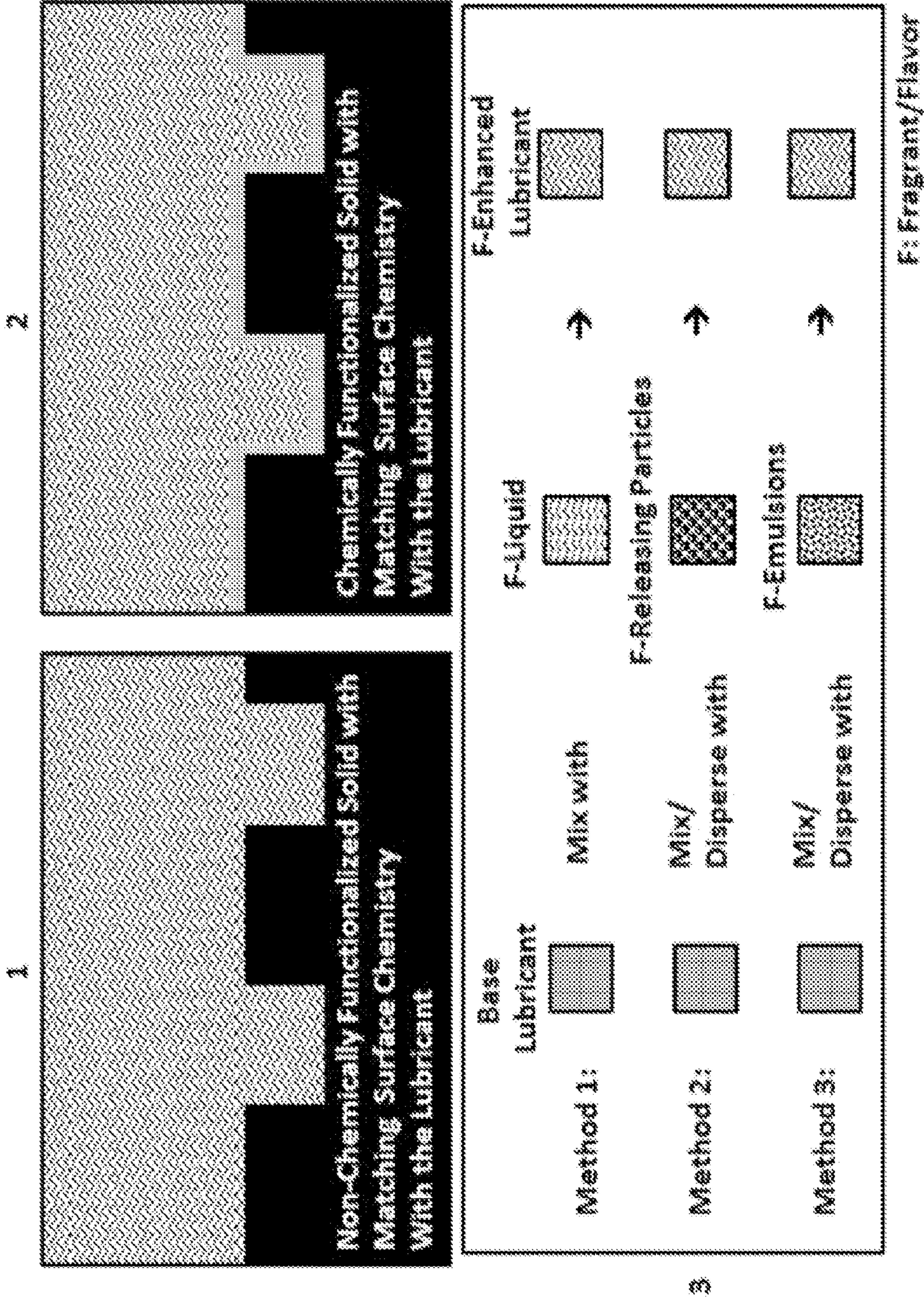


FIG. 17

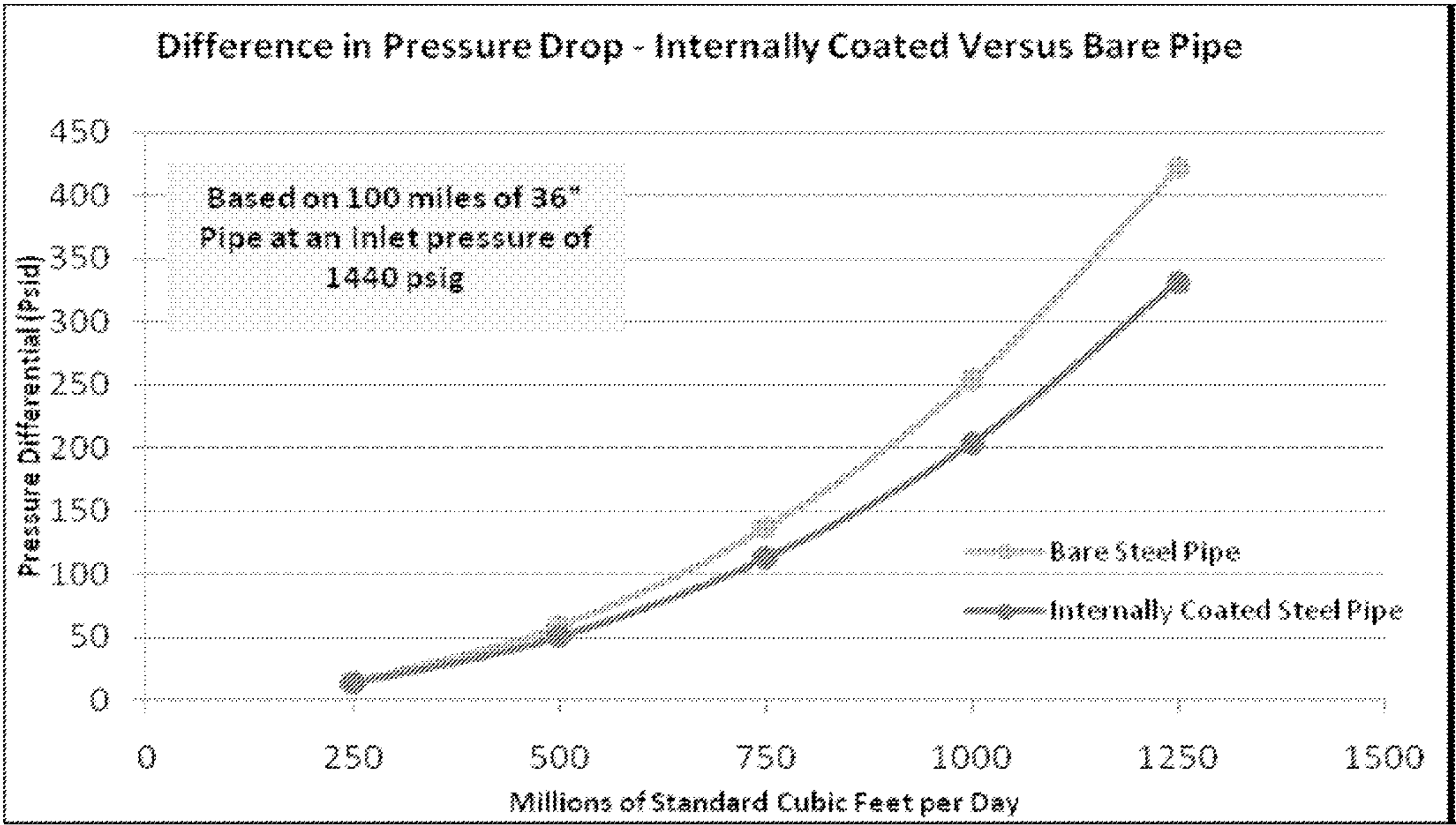


FIG. 18

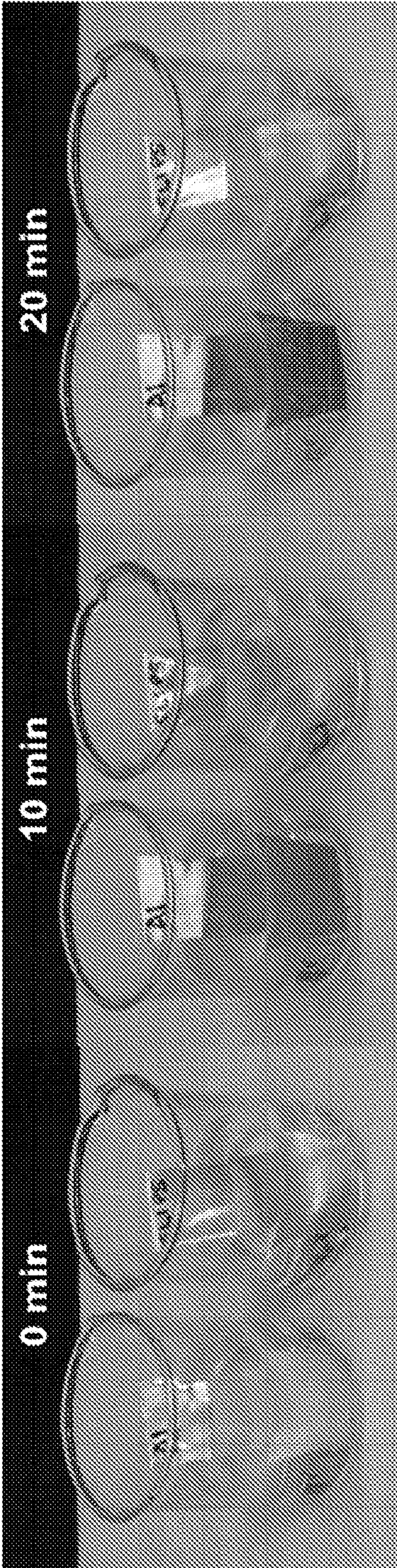


FIG. 19

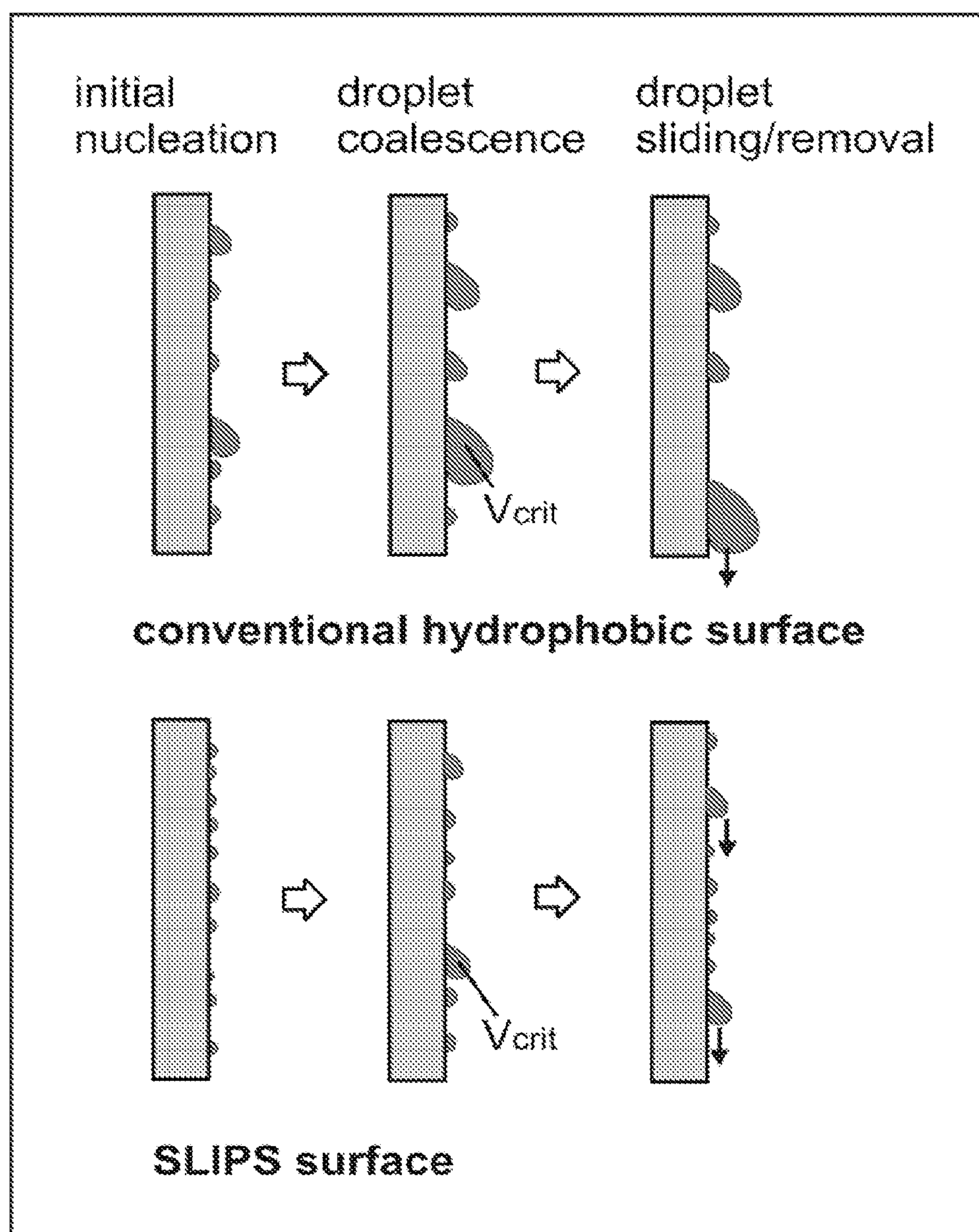


FIG. 20

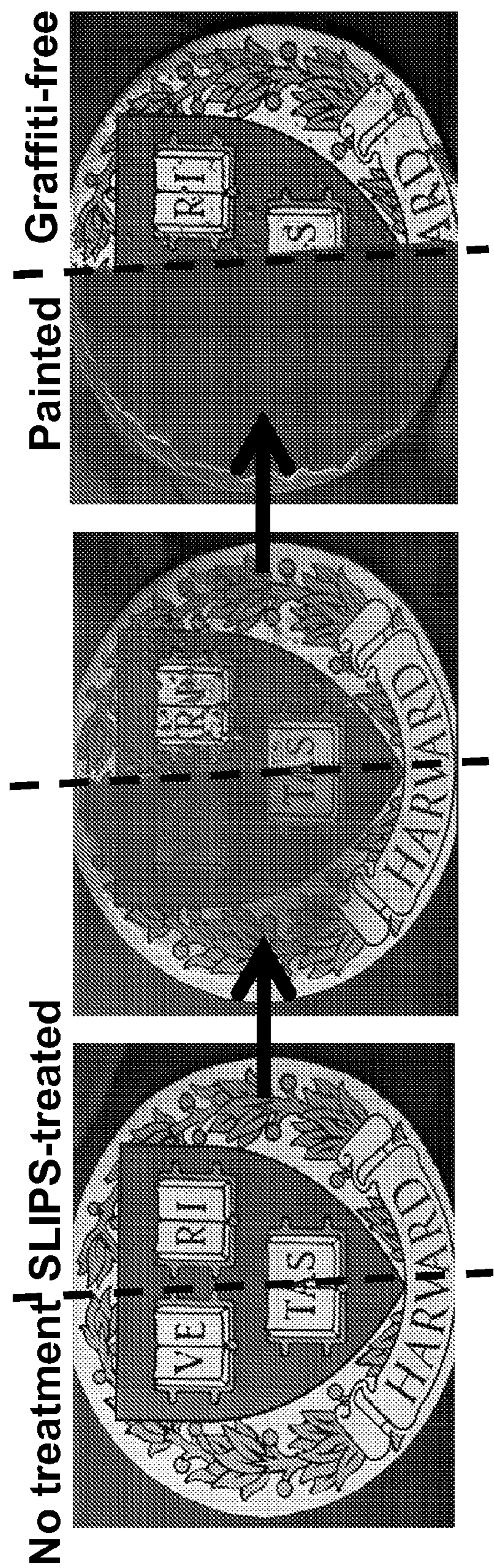


FIG. 21

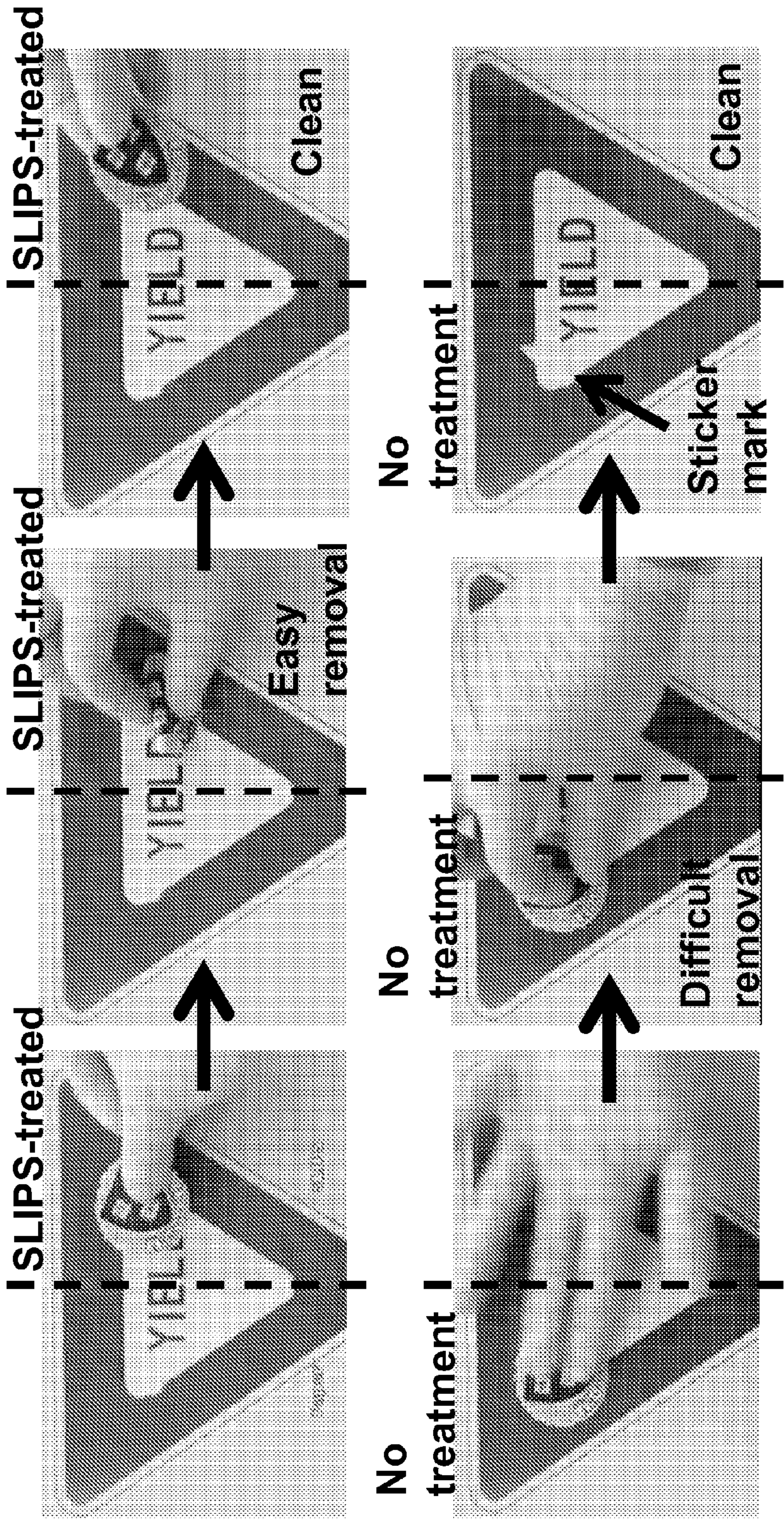


FIG. 22

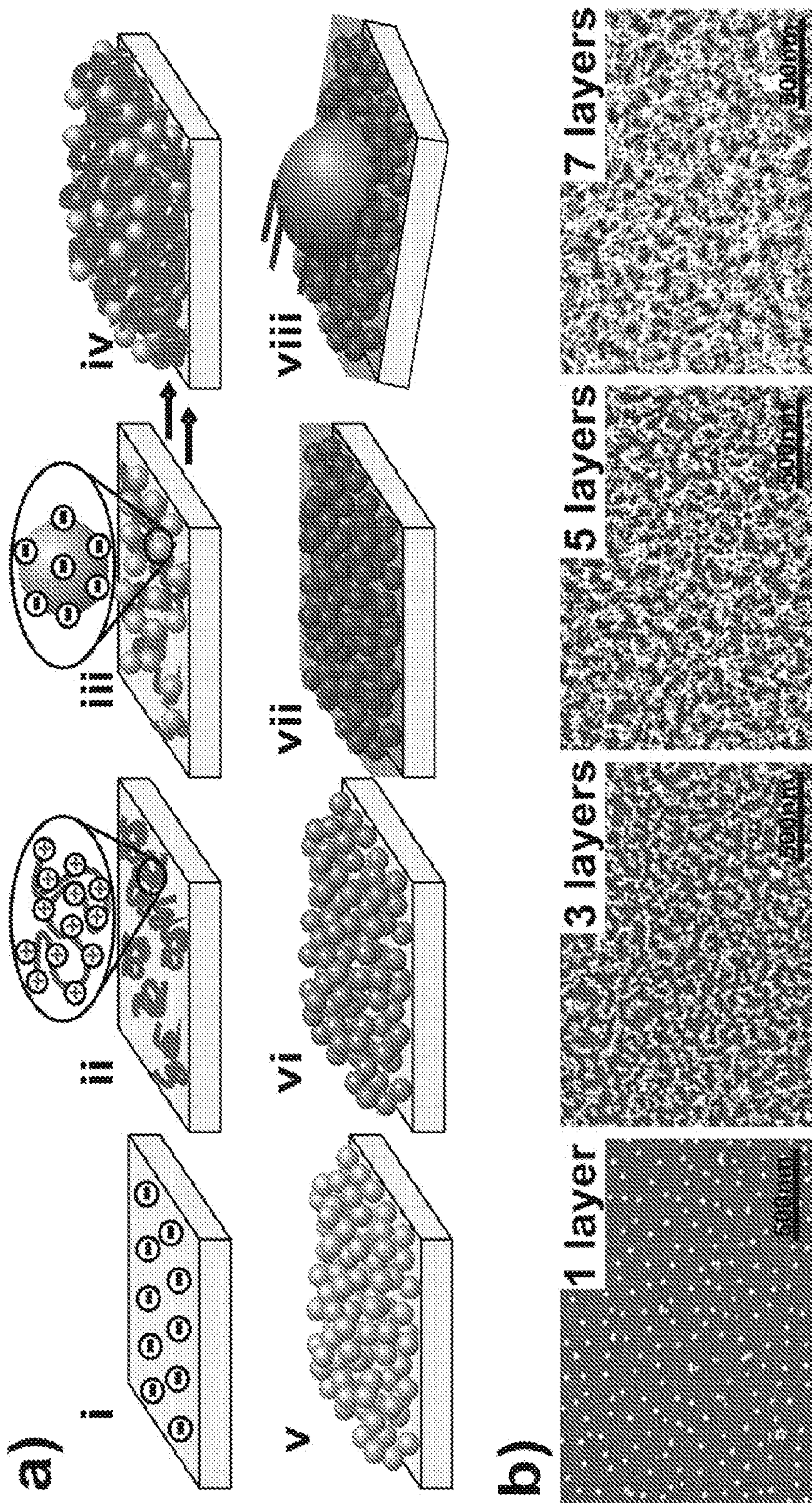


FIG. 23A-23B

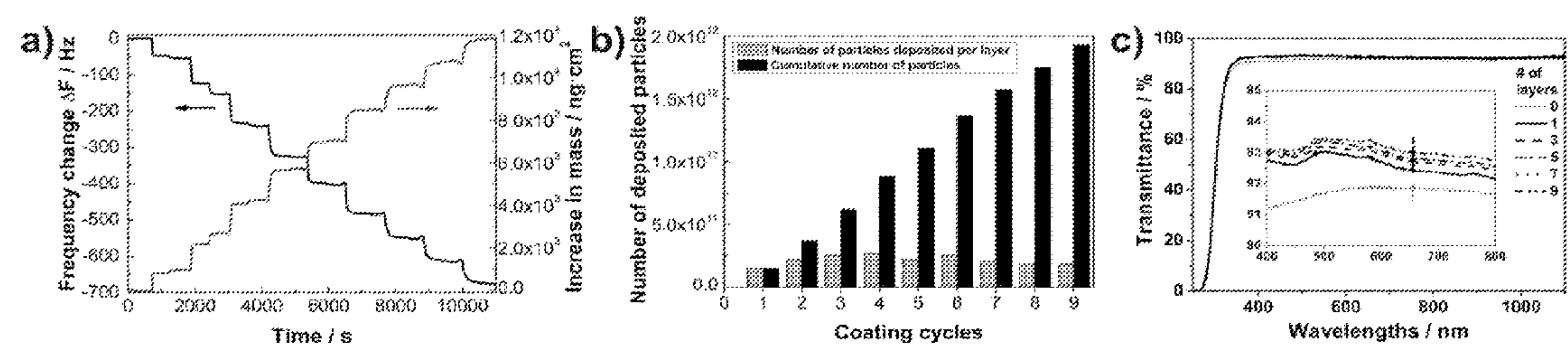
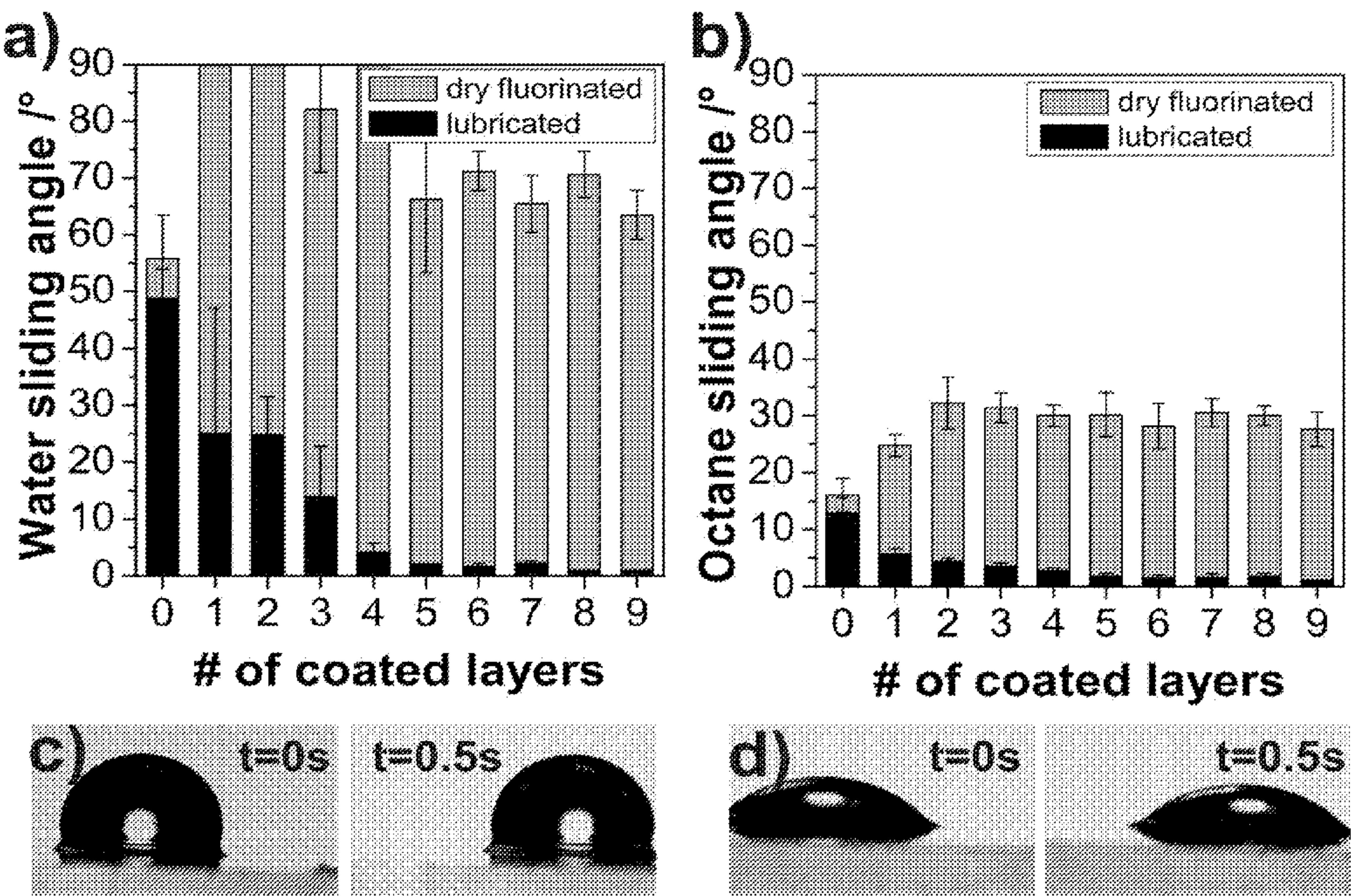
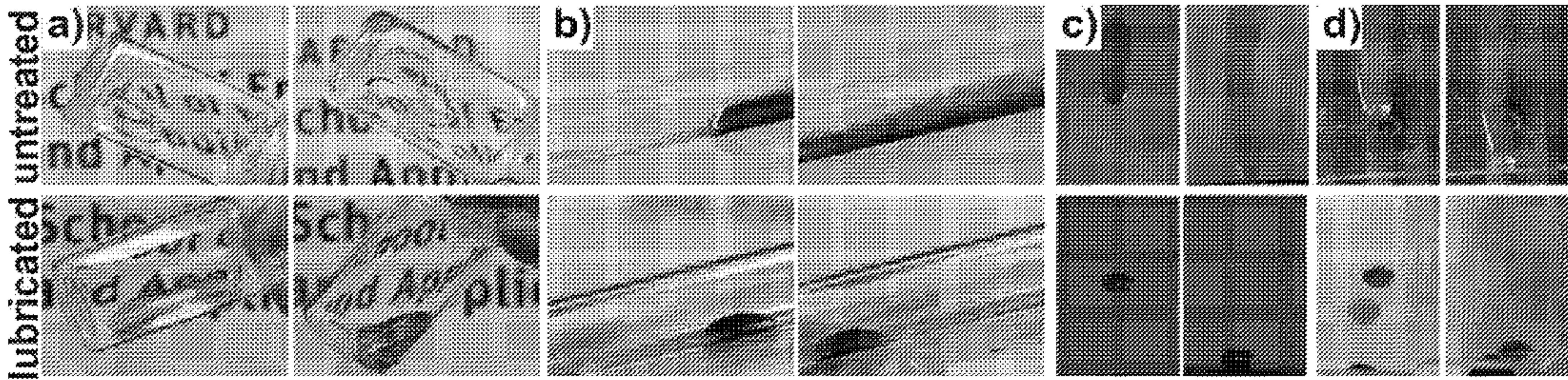
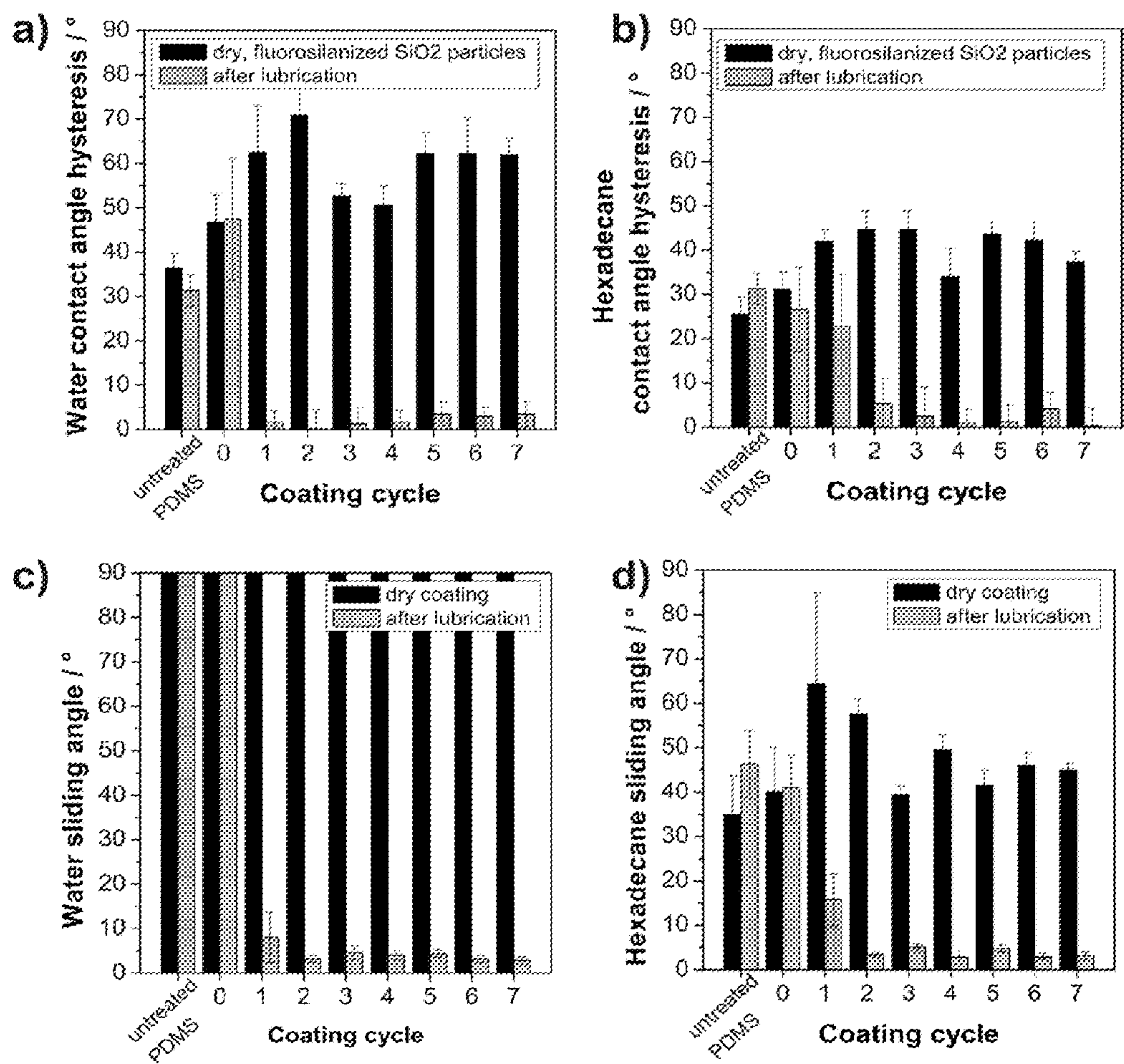


FIG. 24A-24C





FIGS. 26A-26D



FIGS. 27A-27D

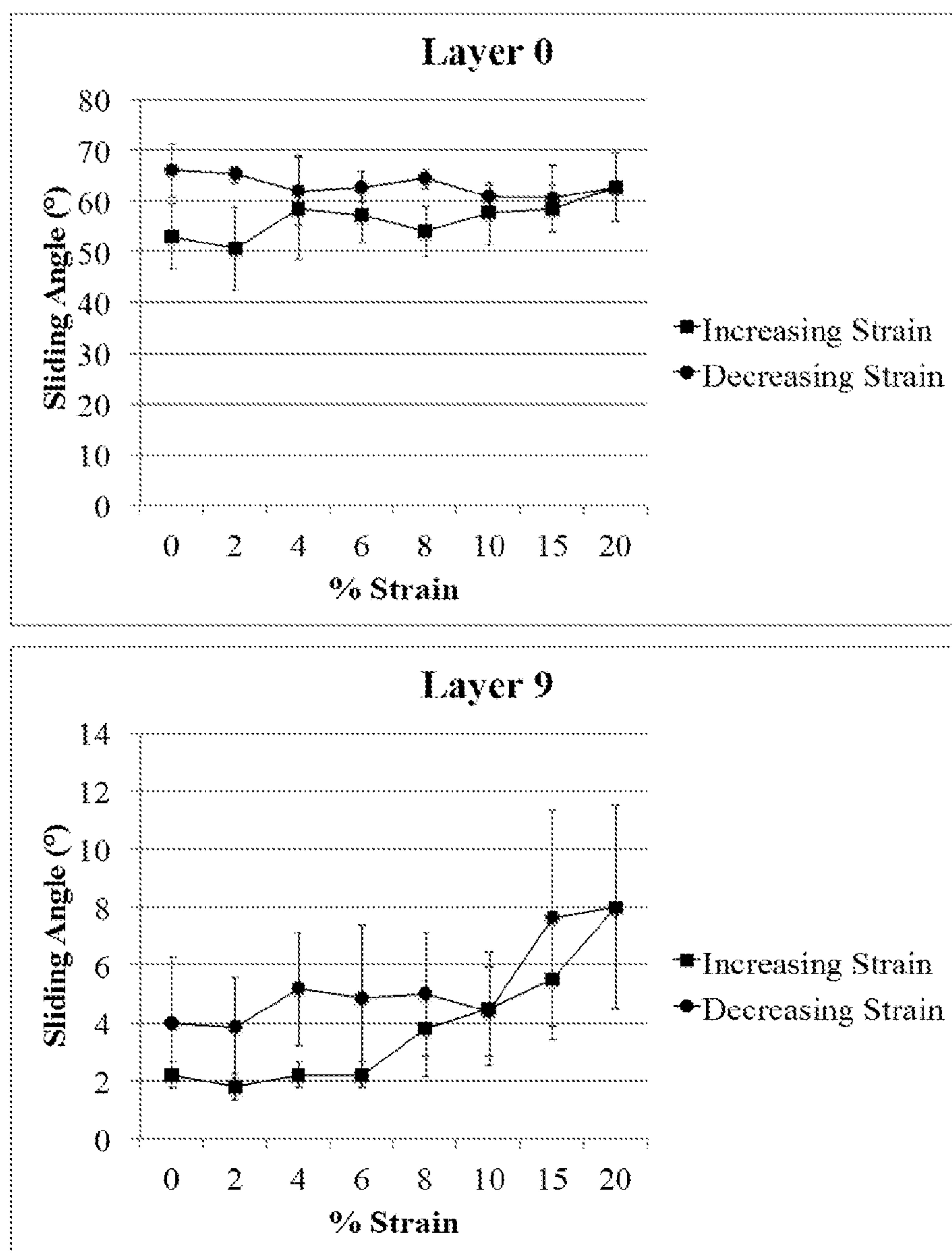
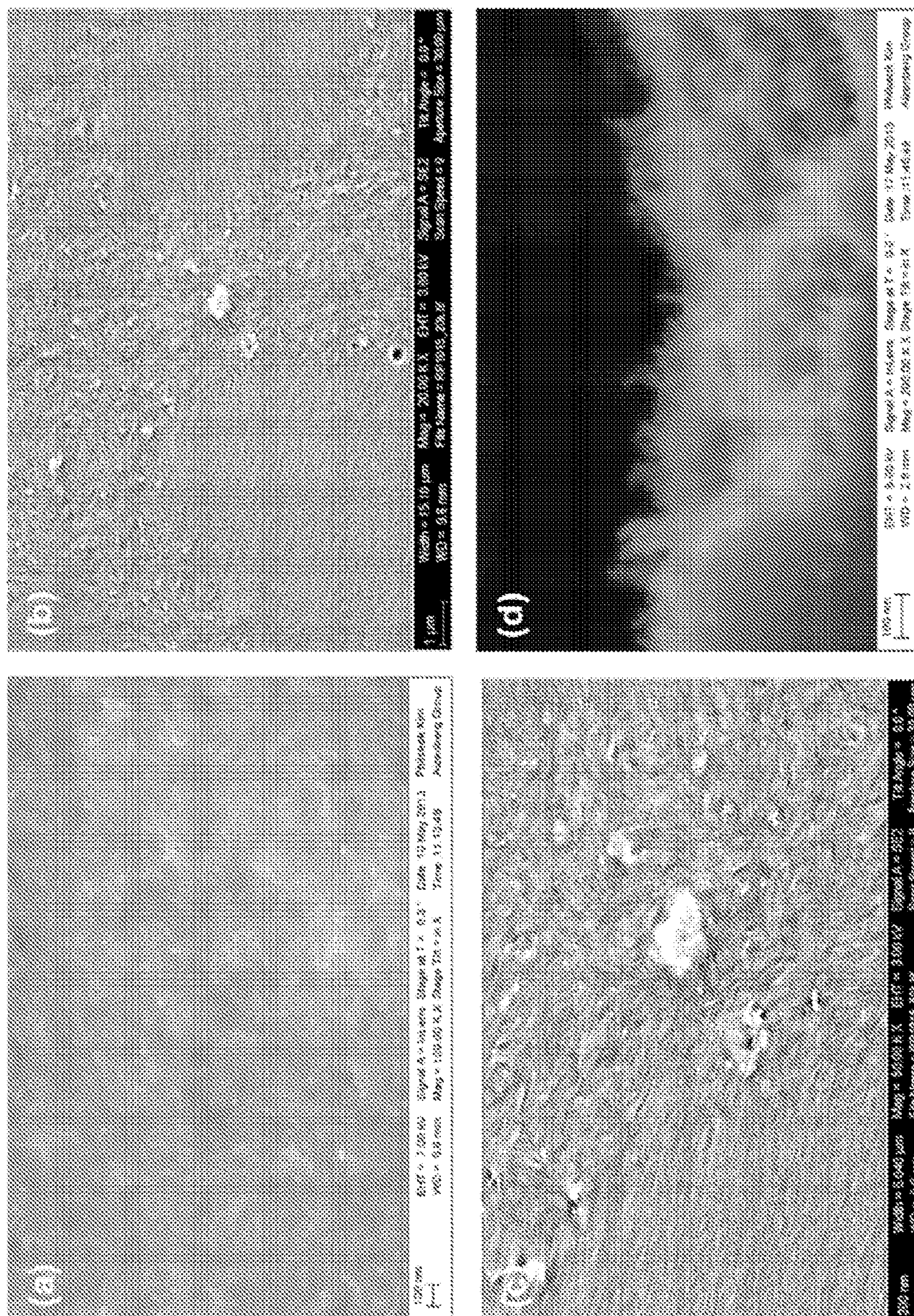
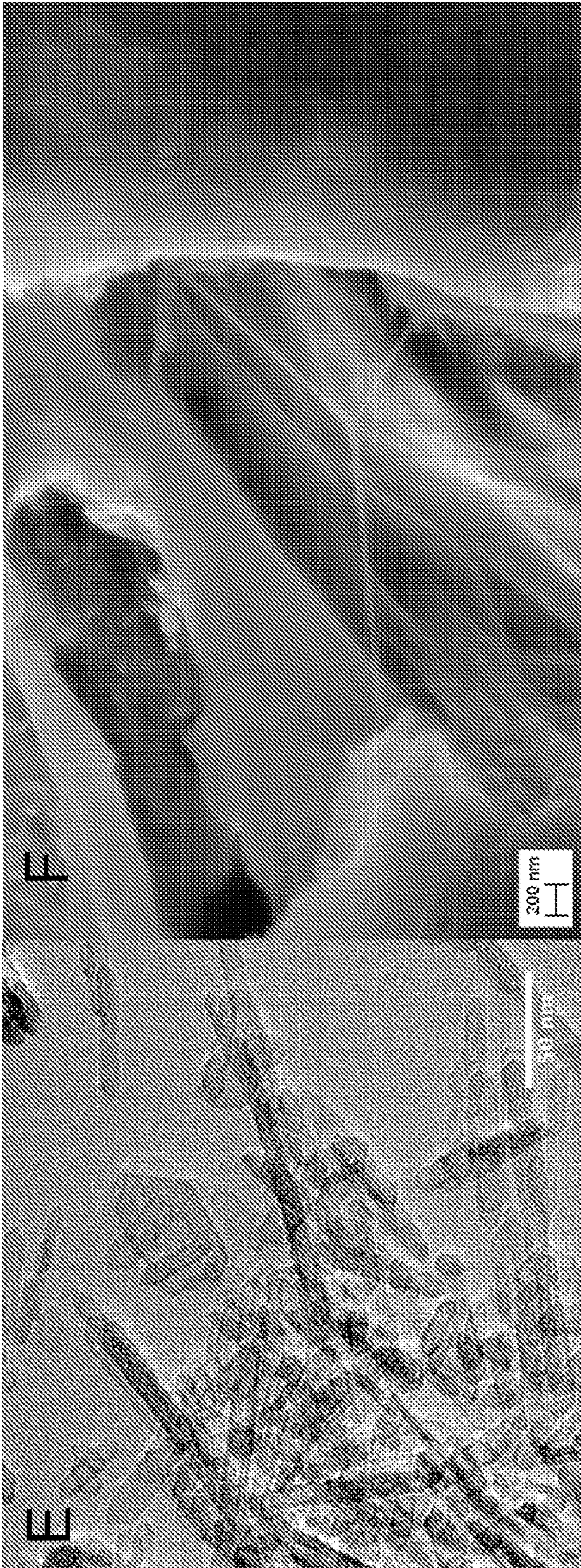


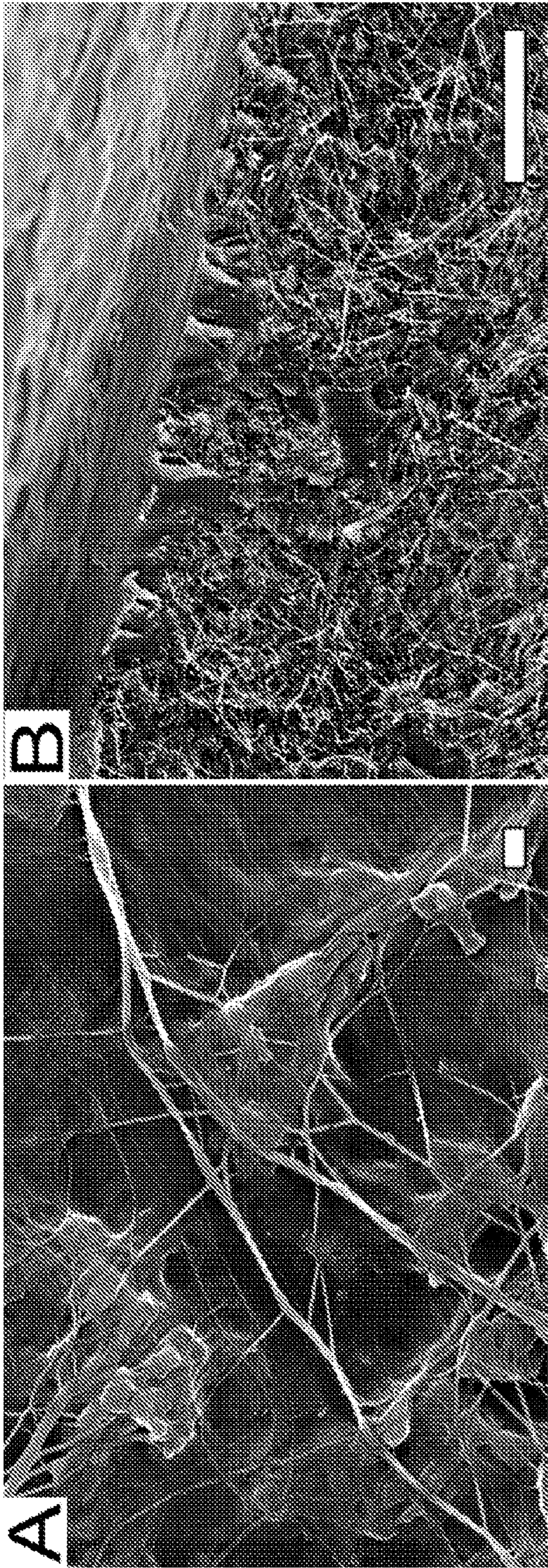
FIG. 28



FIGS. 29A-29D



FIGS. 29E-29F



FIGS. 30A-30B

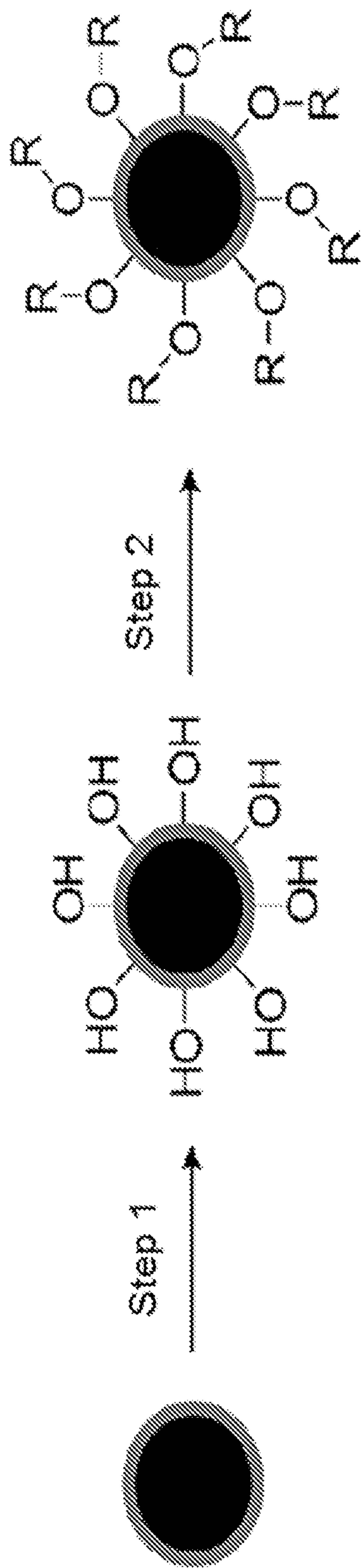


FIG. 31A

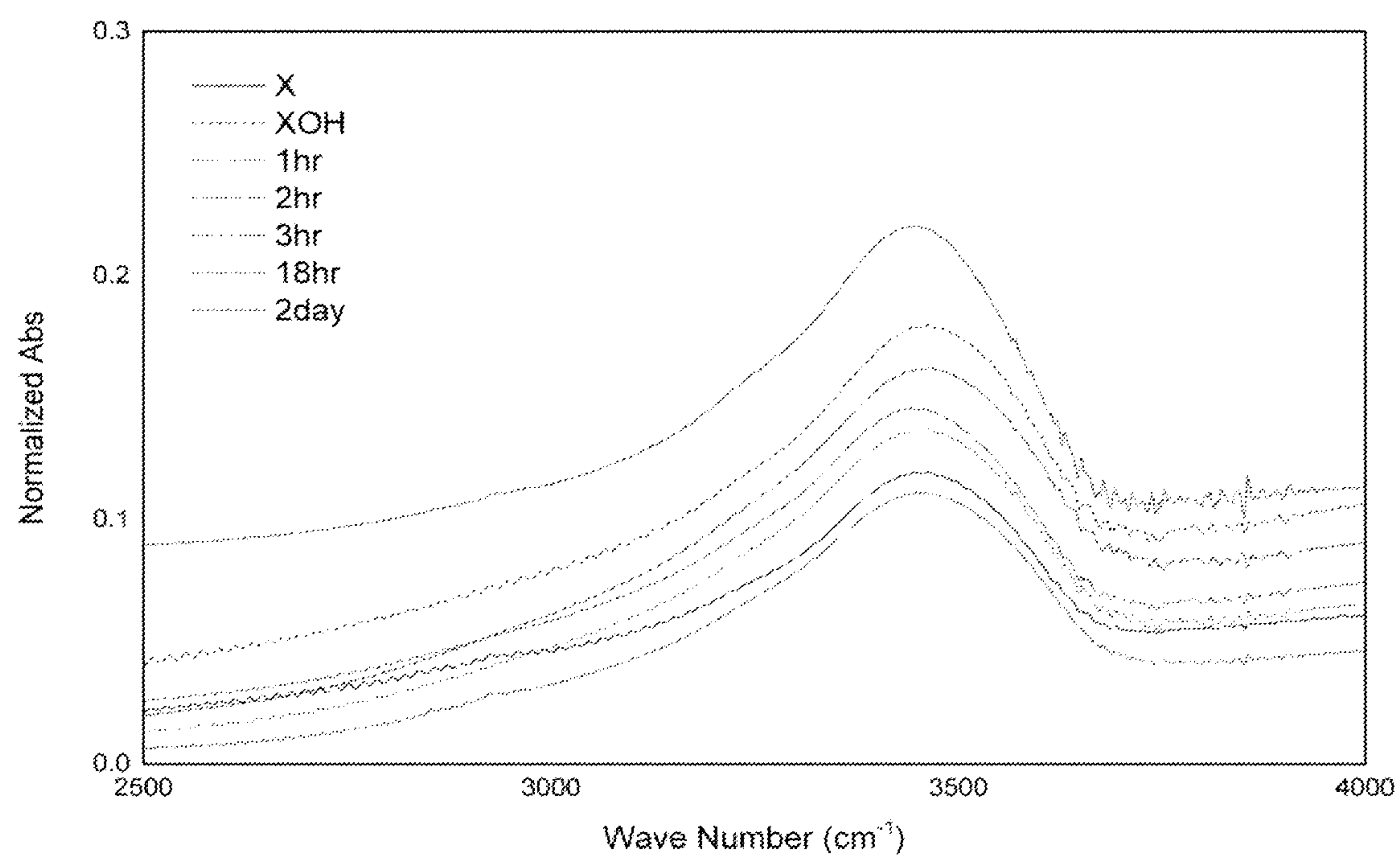


FIG. 31B

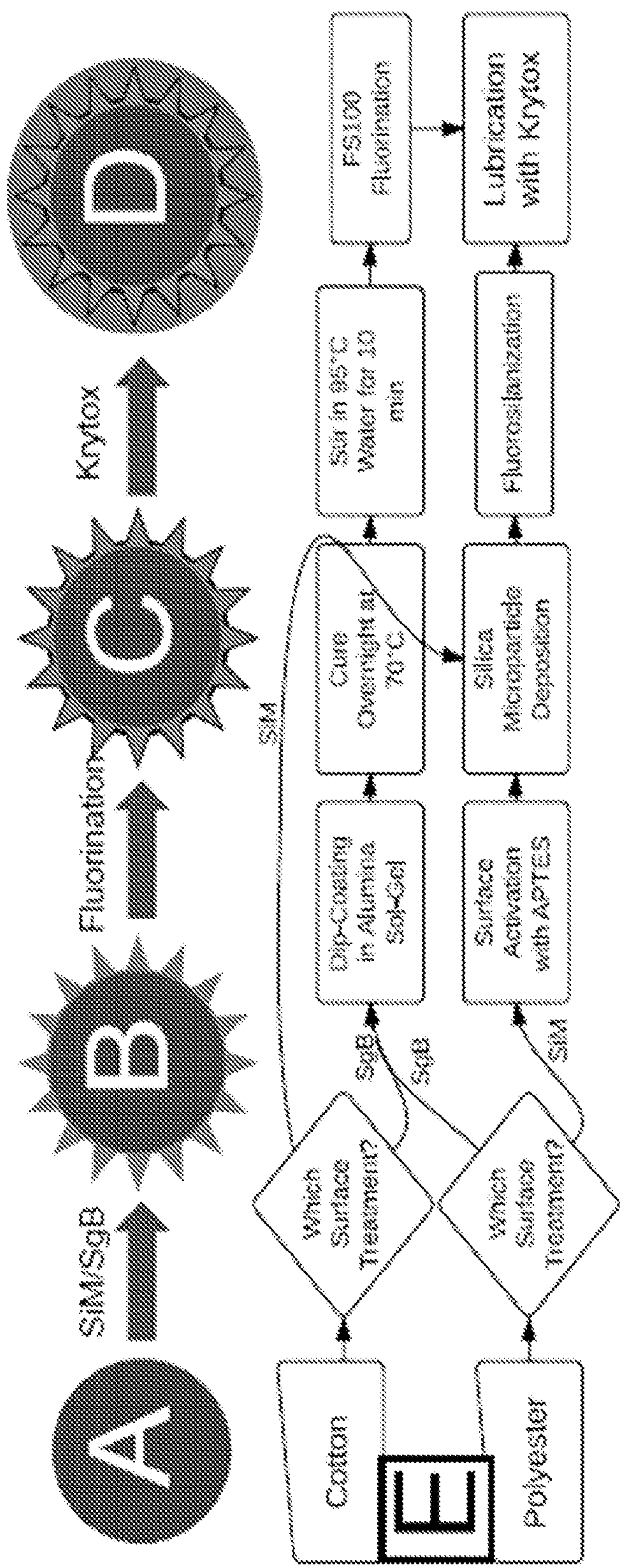


FIG. 32

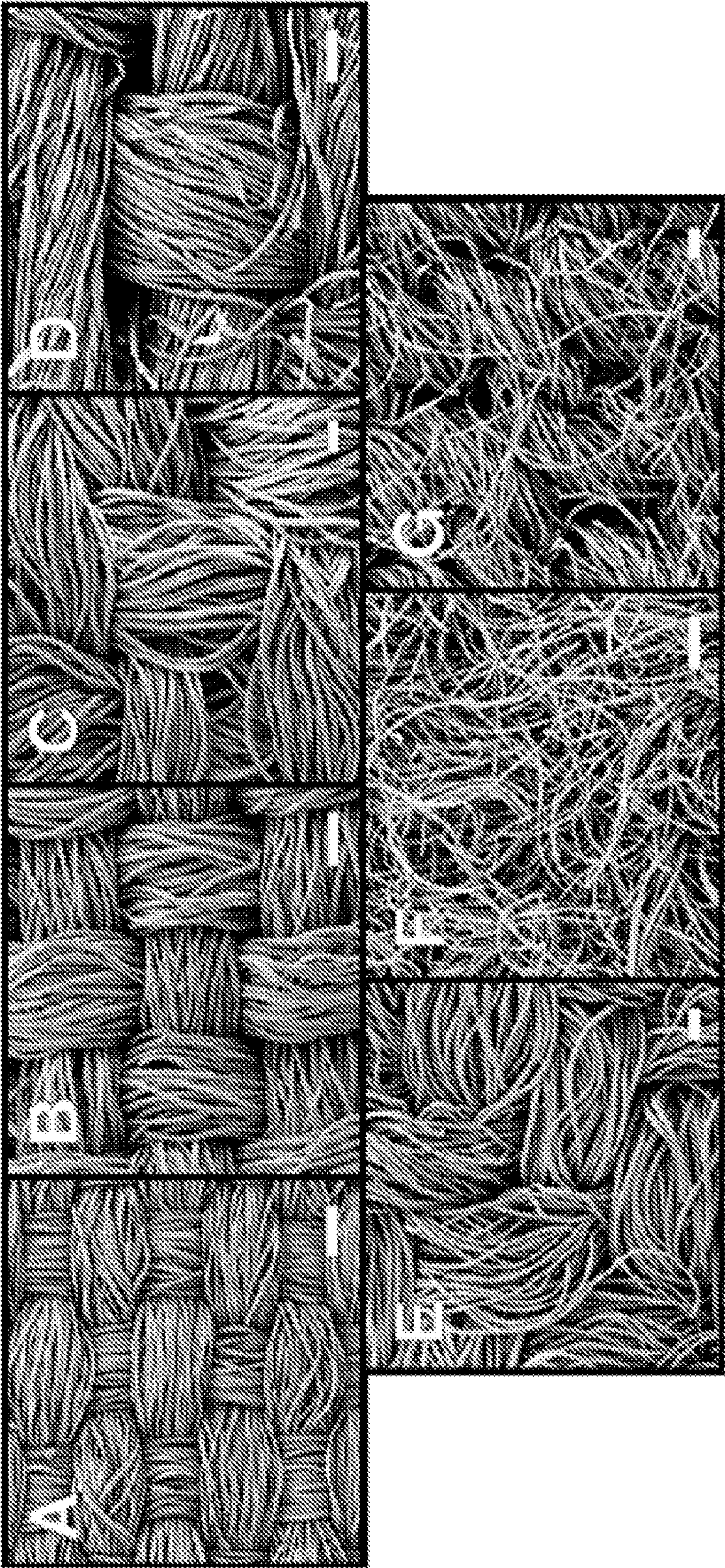


FIG. 33

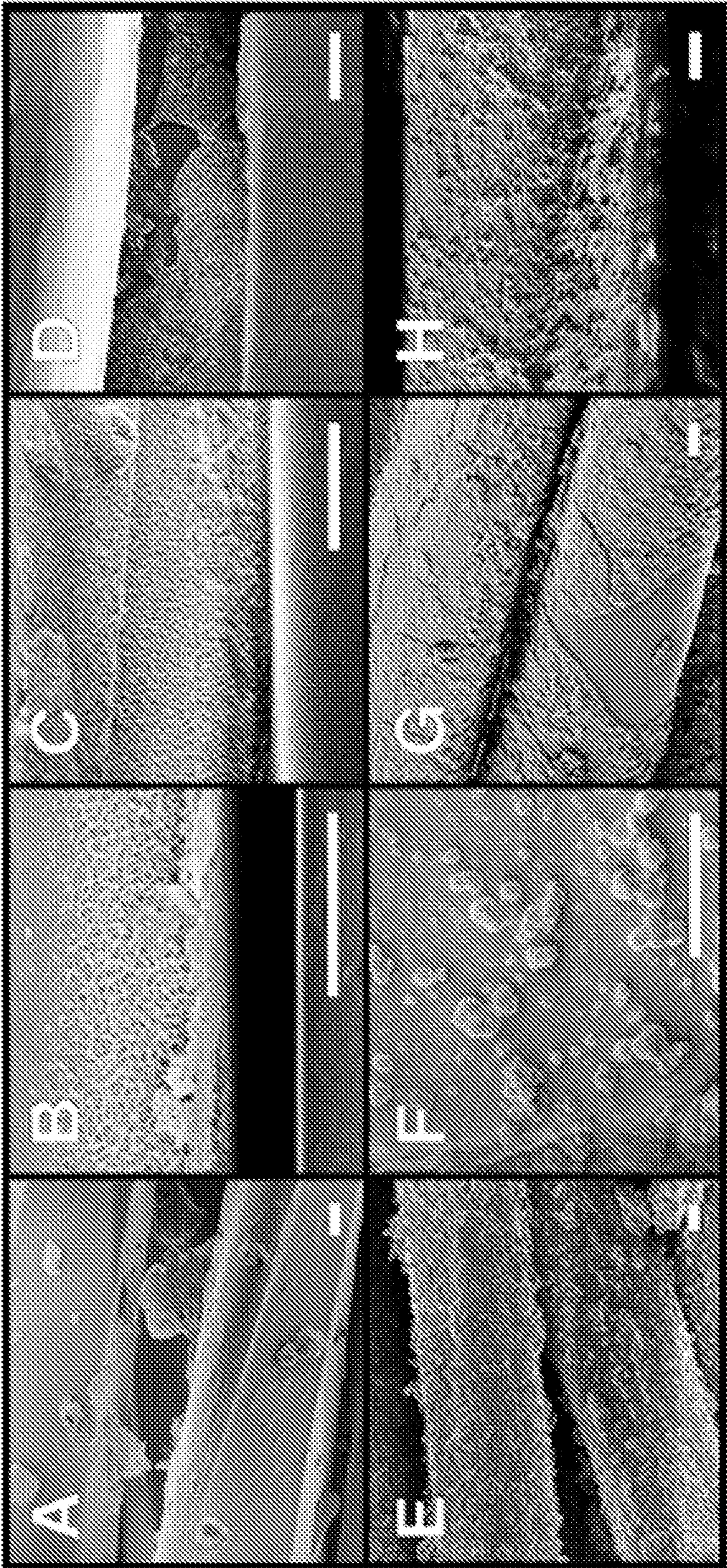


FIG. 34

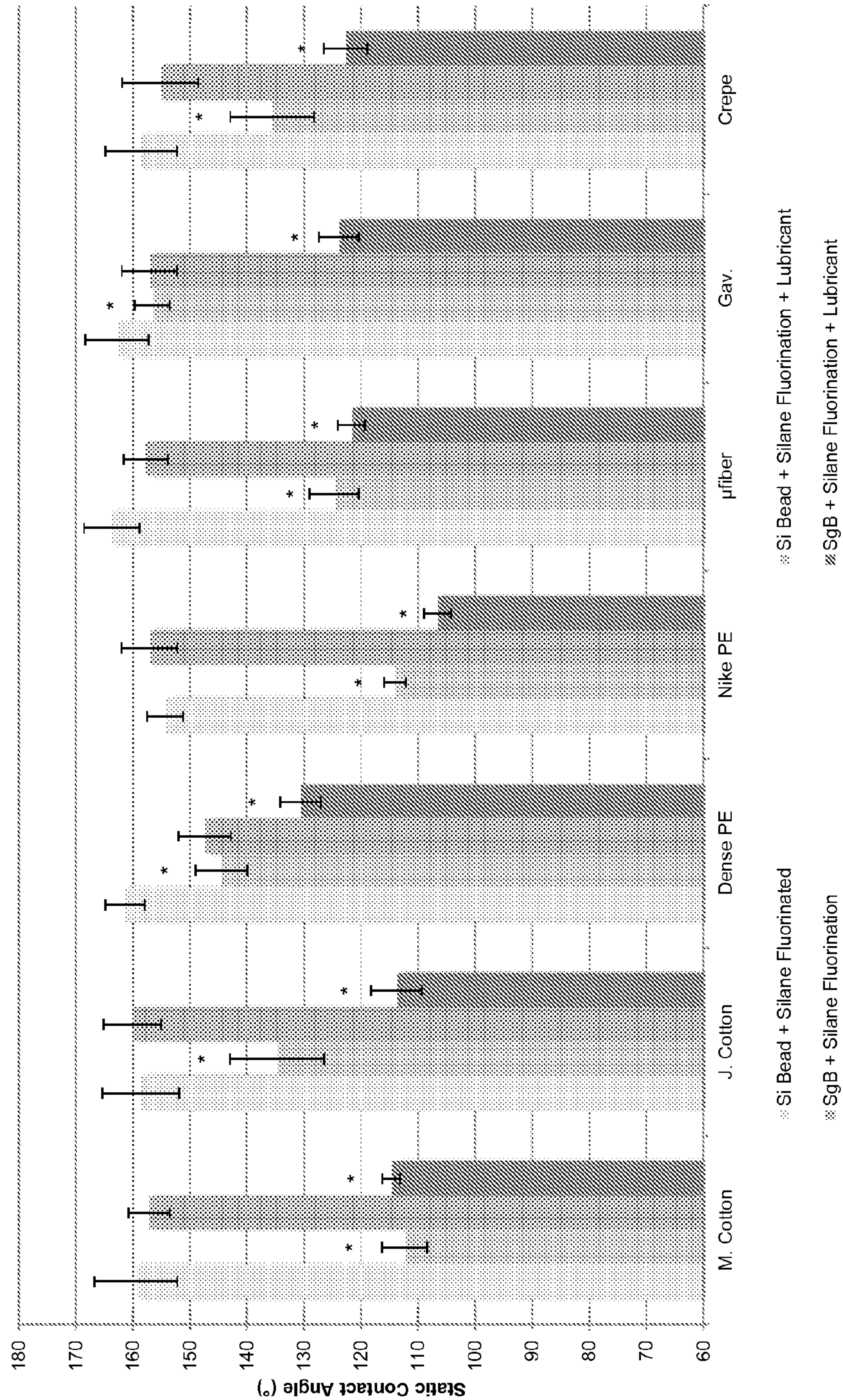


FIG. 35A

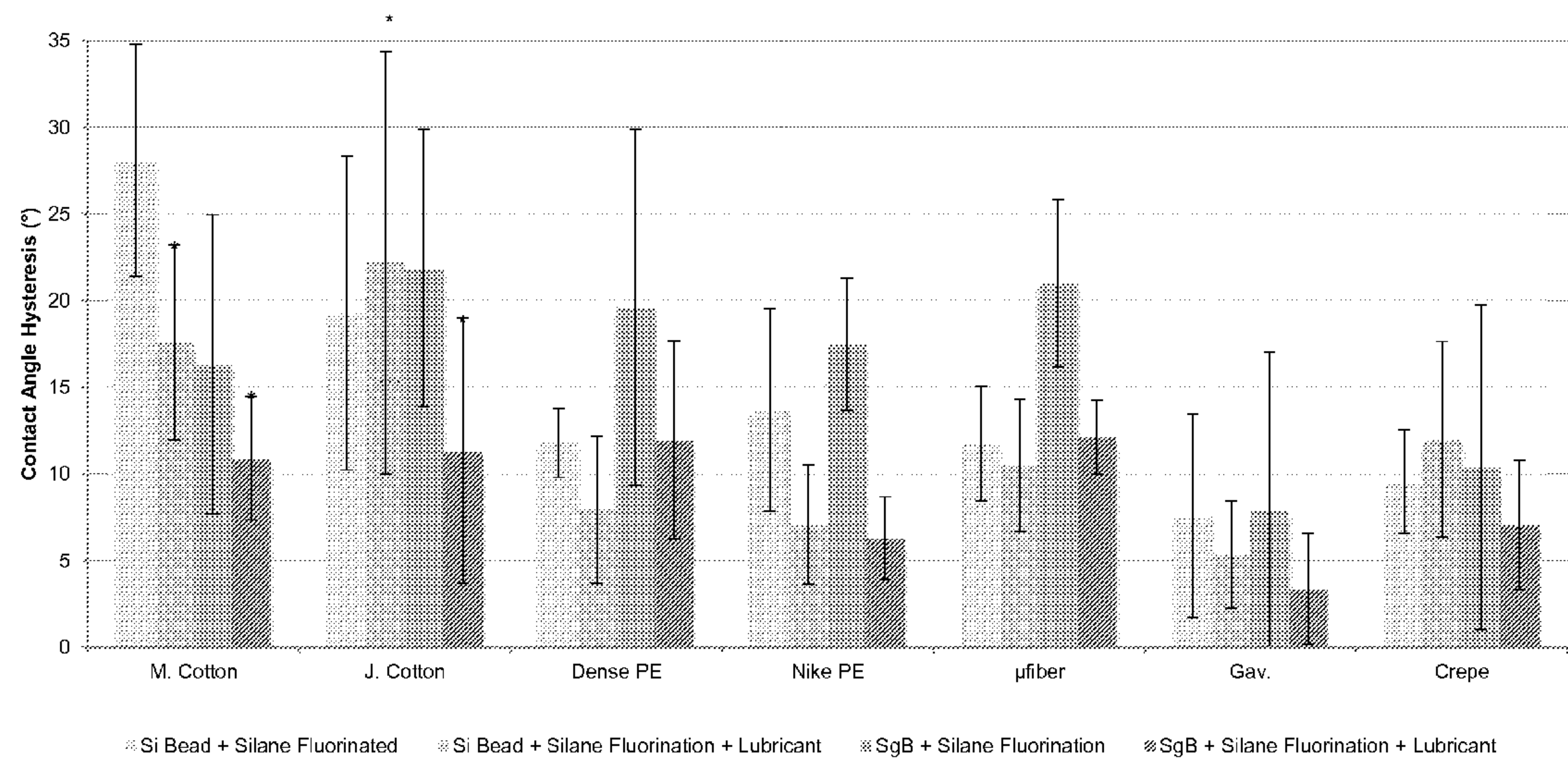


FIG. 35B

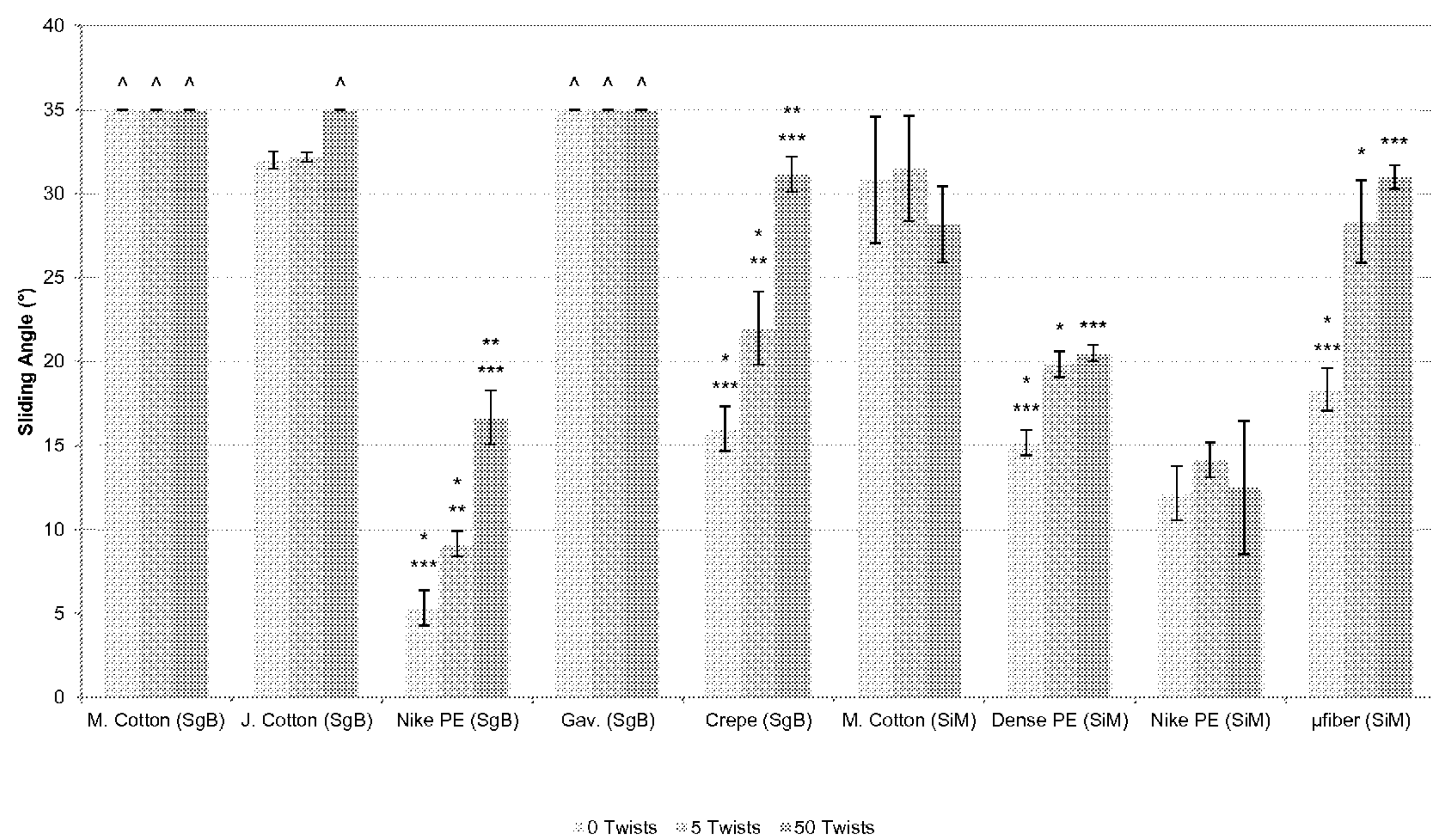


FIG. 36

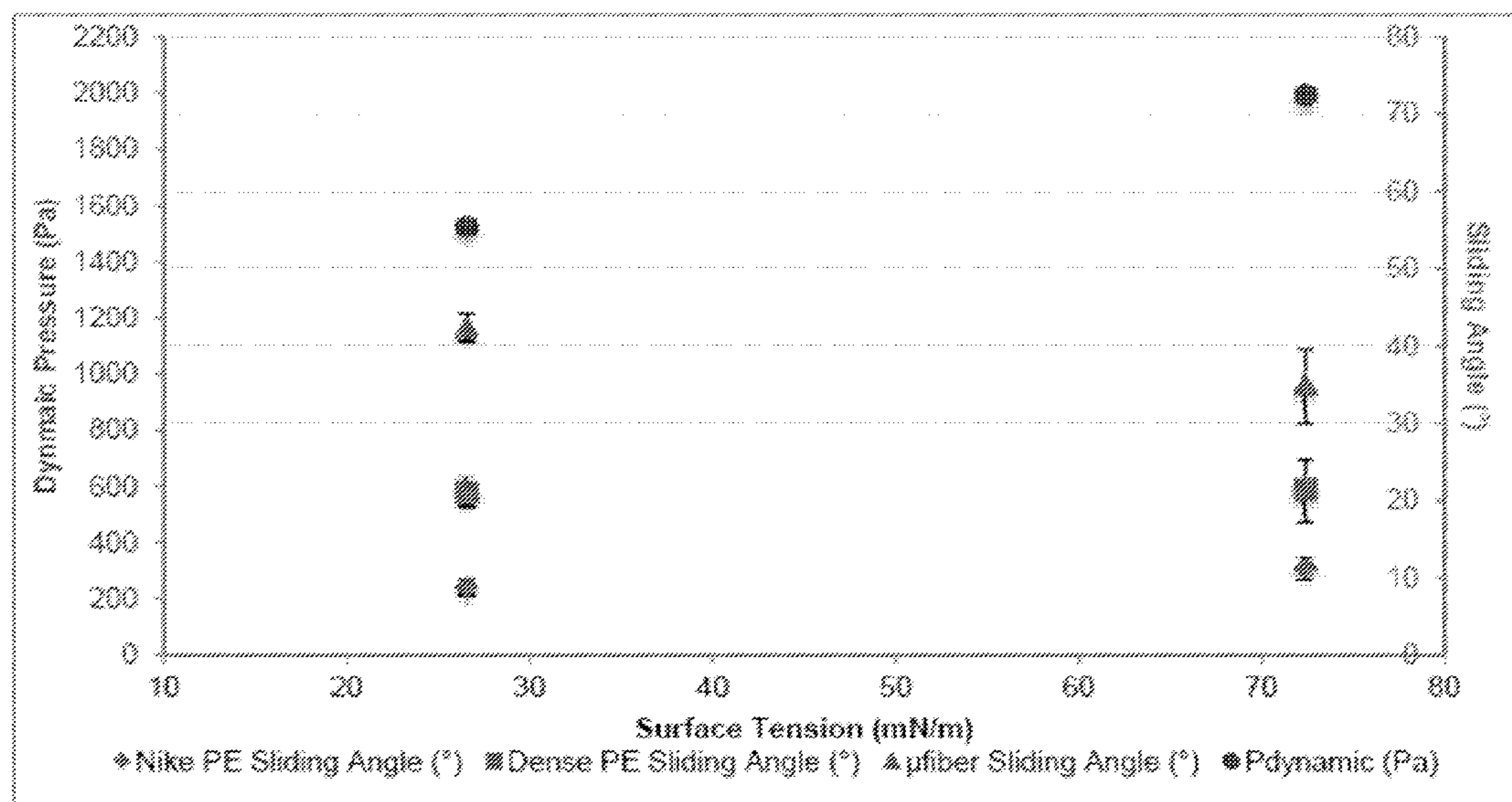


FIG. 37

MULTIFUNCTIONAL REPELLENT MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The application claims the benefit of the earlier filing date of U.S. Patent Application No. 61/671,442, filed on Jul. 13, 2012; U.S. Patent Application No. 61/671,645, filed on Jul. 13, 2012; and U.S. Patent Application No. 61/673,705, filed on Jul. 19, 2012, the contents of which are incorporated by reference herein in their entirety.

[0002] The present application related to the following co-pending applications filed on even date herewith:

[0003] International Application entitled SELECTIVE WETTING AND TRANSPORT SURFACES, filed on even date herewith;

[0004] International Application entitled SLIPS SURFACE BASED ON METAL-CONTAINING COMPOUND, filed on even date herewith;

[0005] International Application entitled MULTIFUNCTIONAL REPELLENT MATERIALS, filed on even date herewith;

the contents of which are incorporated by reference herein in their entirety.

STATEMENT CONCERNING GOVERNMENT RIGHTS IN FEDERALLY-SPONSORED RESEARCH

[0006] This invention was made with government support under FA9550-09-1-0669-DOD35CAP awarded by the U.S. Air Force and under DE-AR0000326 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

TECHNICAL FIELD

[0007] The field of this application generally relates to slippery surfaces, methods for forming them, and their uses.

BACKGROUND

[0008] Current development of liquid-repellent surfaces is inspired by the self-cleaning abilities of many natural surfaces on animals, insects, and plants. Water droplets on these natural surfaces roll off or slide off easily, carrying the dirt or insects away with them. The presence of the micro/nanostructures on many of these natural surfaces has been attributed to the water-repellency function. These observations have led to enormous interests in manufacturing biomimetic water-repellent surfaces in the past decade, owing to their broad spectrum of potential applications, ranging from water-repellent fabrics to friction-reduction surfaces.

SUMMARY

[0009] Liquid repellant surfaces having selective wetting and transport properties and their applications in a variety of fields are described. In certain embodiments, such liquid repellant surfaces have additional functionalities, in addition to the wetting and transport properties.

[0010] Disclosed subject matter includes, in one aspect, an article having a repellant surface, which includes a substrate comprising fabric material having a weave density that is greater than 100 threads/cm² and a lubricant wetting and adhering to the fabric material to form a stabilized liquid

overlayer, wherein the stabilized liquid overlayer covers the fabric material at a thickness sufficient to form a liquid upper surface above the fabric material, wherein the fabric material is chemically functionalized to enhance chemical affinity with the lubricant such that the lubricant is substantially immobilized over the fabric material to form a repellant surface.

[0011] Disclosed subject matter includes, in another aspect, an optical article having a repellant surface, which includes a substrate comprising transparent or translucent material with a surface, a housing that holds the substrate, and a lubricant wetting and adhering to the surface to form a stabilized liquid overlayer, wherein the stabilized liquid overlayer covers the surface at a thickness sufficient to form a liquid upper surface above the surface, wherein the surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, wherein the housing is infiltrated with the lubricant to replenish the lubricant onto the substrate.

[0012] Disclosed subject matter includes, in another aspect, an article having a repellant inner surface, which includes a container comprising an inner surface to contain a complex fluid; and a complex fluid having a liquid and one or more other components within said container; wherein the liquid wets and adheres to the inner surface to form a stabilized liquid overlayer, wherein the stabilized liquid overlayer covers the inner surface at a thickness sufficient to form a liquid surface on the inner surface, wherein the inner surface and the liquid have an affinity such that the liquid is substantially immobilized on the inner substrate to form a repellant surface, the repellant surface repelling other components within said complex fluid.

[0013] Disclosed subject matter includes, in another aspect, a membrane-like article, which includes a membrane substrate comprising a top surface, a bottom surface, and a plurality of through-holes and a low-surface tension fluid wetting and adhering the top surface, the bottom surface, and inner walls surrounding the plurality of through-holes, forming a pre-conditioning layer and a fluid deposited over the pre-conditioning layer to form a protective layer, the protective layer providing a repellant surface to the membrane substrate, wherein the membrane substrate, the pre-conditioning layer, and the protective layer have an affinity to each other such that the protective layer is substantially immobilized on the membrane substrate to form the repellant surface.

[0014] Disclosed subject matter includes, in another aspect, an article for carrying fluid flow, which includes a substrate comprising a roughened surface and a lubricant wetting and adhering to the roughened surface to form a stabilized liquid overlayer, wherein the stabilized liquid overlayer covers the roughened surface at a thickness sufficient to form a liquid upper surface on top of the roughened surface, wherein the roughened surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a slippery surface, the slippery surface reducing drag and friction of the fluid flow.

[0015] Disclosed subject matter includes, in another aspect, a method for protecting metal or metalized surfaces from corrosion, which includes providing a metal or metalized surface, introducing roughness, and chemically functionalizing the metal or metalized surface to enhance affinity of the metal surface with a lubricant and introducing the lubricant to wet and adhere to the metal or metalized surface to form an overlayer, wherein the metal or metalized surface and the

lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, providing anti-corrosion to the metal or metalized surface.

[0016] Disclosed subject matter includes, in another aspect, a method for protecting surfaces from scaling, which includes providing a surface, introducing roughness, and chemically functionalizing the surface to enhance affinity of the surface with a lubricant, and introducing the lubricant to wet and adhere to the surface to form an overlayer, wherein the surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, providing anti-scaling to the metal surface.

[0017] Disclosed subject matter includes, in another aspect, an article having a repellant surface, which includes a substrate comprising a roughened surface; a lubricant wetting and adhering to the roughened surface to form a stabilized liquid overlayer, wherein the liquid covers the roughened surface at a thickness sufficient to form a liquid upper surface above the roughened surface; and a fragrance enhancer located within said substrate and/or said lubricant; wherein the roughened surface and the lubricating liquid have an affinity for each other such that the lubricating liquid is substantially immobilized on the substrate to form a repellant surface.

[0018] In certain embodiments, the roughened surface and/or the liquid possess more than one chemical state that can be switched to enhance or diminish the affinity between the surface and the lubricating liquid.

[0019] Disclosed subject matter includes, in another aspect, an article having a repellant surface, which includes a substrate comprising a roughened surface and a lubricant wetting and adhering to the roughened surface to form a stabilized liquid overlayer, wherein the liquid covers the roughened surface at a thickness sufficient to form a liquid upper surface above the roughened surface, wherein the roughened surface and the lubricating liquid have an affinity for each other such that the lubricating liquid is substantially immobilized on the substrate to form a repellant surface, wherein the roughened surface includes a microscale or nanoscale structure.

[0020] In certain embodiments, the substrate includes a plurality of nanofibers or nanotubes embedded in an epoxy medium.

[0021] Disclosed subject matter includes, in another aspect, an article having a repellant surface, which includes a substrate comprising an at least partially roughened surface and a lubricant wetting and adhering to the roughened surface to form a kinetically stabilized liquid overlayer, wherein the liquid covers the roughened surface at a thickness sufficient to form a liquid upper surface above the roughened surface, wherein the roughened surface or parts of the roughened surface and the lubricating liquid have an affinity for each other such that the lubricating liquid is substantially immobilized on the substrate to form a repellant surface. The metastability prevents thermodynamically favorable displacement of the liquid for at least a certain amount of time.

[0022] Disclosed subject matter includes, in another aspect, a method for vapors collection, which includes providing a solid surface, introducing roughness, chemically functionalizing the solid surface to enhance affinity of the surface with a lubricant, introducing the lubricant to wet and adhere to the solid surface to form an overlayer, wherein the solid surface and the lubricant have an affinity for each other such that the

lubricant is substantially immobilized on the substrate to form a repellant surface, and condensing condensate droplets on the repellant surface for liquid collection.

[0023] Disclosed subject matter includes, in another aspect, an article having a repellant surface, which includes a substrate comprising a roughened surface and a lubricant wetting and adhering to the roughened surface to form a stabilized liquid overlayer, wherein the liquid covers the roughened surface at a thickness sufficient to form a liquid upper surface above the roughened surface, wherein the roughened surface and the lubricating liquid have an affinity for each other such that the lubricating liquid is substantially immobilized on the substrate to form a repellant surface, wherein the substrate is a component of a ski, a luge, a surf board, a hovercraft, a winter sports item, or a water sports item.

[0024] Disclosed subject matter includes, in another aspect, a method for protecting plastic, glass, ceramic, and composite surfaces from scaling, which includes providing a said solid surface, introducing roughness, chemically functionalizing the said surface to enhance affinity of the said surface with a lubricant, and introducing the lubricant to wet and adhere to the said surface to form an overlayer, wherein the surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, providing anti-scaling to the said surface.

[0025] Disclosed subject matter includes, in another aspect, a method for protecting plastic, glass, ceramic, and composite surfaces from graffiti, which includes providing a said solid surface, introducing roughness, chemically functionalizing the said surface to enhance affinity of the said surface with a lubricant, and introducing the lubricant to wet and adhere to the said surface to form an overlayer, wherein the said surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, providing anti-graffiti properties to the said surface.

[0026] Disclosed subject matter includes, in another aspect, method for forming a repellent surface, which includes providing a substrate having a surface, depositing a first material having a charge to said surface; depositing a second material having a charge that is opposite to the charge of the first material; sequentially repeating said depositing a first material and said depositing a second material to provide a roughened surface; and introducing a lubricant to wet and adhere to said roughened surface to form an overlayer, wherein said roughened surface and said lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellent surface.

[0027] Disclosed subject matter includes, in another aspect, a method to reduce friction against fluids and solids, which includes providing a said solid surface, introducing roughness, chemically functionalizing the said surface to enhance affinity of the said surface with a lubricant, and introducing the lubricant to wet and adhere to the said surface to form an overlayer, wherein the said surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, providing anti-graffiti properties to the said surface.

[0028] Disclosed subject matter includes, in another aspect, a method to reduce adhesion against fluids and solids, which includes providing a said solid surface, introducing roughness, chemically functionalizing the said surface to enhance affinity of the said surface with a lubricant, and introducing

the lubricant to wet and adhere to the said surface to form an overlayer, wherein the said surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, providing anti-graffiti properties to the said surface.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The following figures are provided for the purpose of illustration only and are not intended to be limiting.

[0030] FIG. 1 shows a schematic of a self-healing slippery liquid-infused porous surface (SLIPS) in accordance with certain embodiments of the present disclosure;

[0031] FIG. 2 illustrates a general scheme of creating SLIPS in accordance with certain embodiments of the present disclosure;

[0032] FIGS. 3A-3B illustrates the comparison between a thermodynamically stable SLIPS with a kinetically stable (meta-stable) SLIPS) in accordance with certain embodiments of the present disclosure;

[0033] FIG. 3C further illustrates an exemplary meta-stable SLIPS state;

[0034] FIG. 4A-4B shows the wetting behaviors of an exemplary fluorinated liquid B on (A) a flat surface and (B) nanostructured surface;

[0035] FIG. 5A shows a schematic of an exemplary columnar porous material over which the slippery surface is formed;

[0036] FIG. 5B shows a schematic of an exemplary inverse opal porous material over which the slippery surface is formed;

[0037] FIG. 5C shows an image of an exemplary random network porous material over which the slippery surface is formed;

[0038] FIG. 5D shows an image of exemplary self-assembled polymeric microstructures induced by solvent drying in accordance with certain embodiments of the present disclosure;

[0039] FIG. 5E shows a schematic of an exemplary structured surface over which the slippery surface is formed;

[0040] FIG. 6 shows a replication process to reproduce the morphology of the SLIPS surface, where the corresponding surface characterization indicates ultra-smoothness of the SLIPS, in accordance with certain embodiments;

[0041] FIG. 7A shows images of SLIPS demonstrating self-healing properties, where the self-healing time scale is on the order of 100 ms, in accordance with certain embodiments;

[0042] FIG. 7B is a chart showing restoration of liquid repellency function after critical physical damages (Test liquid=decane, $\gamma_{LV}=23.6\pm0.1$ mN/m) in accordance with certain embodiments;

[0043] FIG. 7C shows time-lapse images demonstrating the restoration of liquid repellency of a SLIPS after physical damage, as compared to a typical hydrophobic flat surface on which oil remains pinned at the damage site, in accordance with certain embodiments;

[0044] FIG. 7D illustrates a self-refilling mechanism in accordance with certain embodiments;

[0045] FIGS. 8, 9A-9C show some exemplary common natural and synthetic fabrics systems.

[0046] FIGS. 10A-10C demonstrates SLIPS fabrics for functional clothing against various complex fluids and high temperature fluids in accordance with certain embodiments;

[0047] FIG. 11 demonstrates photographs of a fog test on a 60 C water.

[0048] FIG. 12 shows a schematic illustration of a fog-free optical viewing cover for microscope.

[0049] FIG. 13 contains a schematic illustration of a circular optics encased in a lubricant-containing O-ring serving as a reservoir in accordance with certain embodiments.

[0050] FIG. 14 demonstrates a photograph of camera lens protectors in accordance with certain embodiments.

[0051] FIG. 15 further demonstrates a photograph of anti-reflective camera lens protectors in accordance with certain embodiments.

[0052] FIG. 16A shows a regulatory approval chart of various materials.

[0053] FIGS. 16B and 16C illustrate SLIPS-treated bottles and containers repelling complex food products, such as ketchup, mayonnaise, and oatmeal, in accordance with certain embodiments.

[0054] FIG. 16D illustrates SLIPS-treated ice tray repelling ice, in accordance with certain embodiments.

[0055] FIG. 17 is a schematic showing different methods to produce slippery surfaces using fragrance/flavor-enhanced lubricants in accordance with certain embodiments.

[0056] FIG. 18 illustrates pressure drop on internally coated pipe as a function of flow in accordance with certain embodiments.

[0057] FIG. 19 illustrates the time lapse of untreated Al (left) and SLIPS-coated Al (right) immersed in 1 M KOH solution at room temperature showing rapid degradation of untreated aluminum while coated Al essentially remains unchanged.

[0058] FIG. 20 shows the steps involved in the nucleation, coalescence and sliding of water droplets on a conventional hydrophobic surface and a SLIPS in accordance with certain embodiments.

[0059] FIGS. 21 and 22 show SLIPS-treated surfaces that can function as anti-graffiti surfaces in accordance with certain embodiments.

[0060] FIG. 23A shows a schematic illustration of the layer-by-layer deposition process to form porous, lubricant-infused coatings in accordance with certain embodiments.

[0061] FIG. 23B shows SEM images of the silica coating show the increase in deposited particles with increasing coating cycles in accordance with certain embodiments.

[0062] FIG. 24A shows a plot demonstrating the increase in deposited mass for each consecutive layer-by-layer adsorption cycle, calculated using Sauerbrey's equation from the frequency drop measured by Quartz Crystal Microbalance in accordance with certain embodiments.

[0063] FIG. 24B shows a plot of number of silica nanoparticles deposited onto the substrate during each adsorption cycle (gray) and as cumulative during the complete process (black line) calculated from QCM-D data. A near-linear increase in deposited particles with increasing coating cycles is visible in accordance with certain embodiments.

[0064] FIG. 24C shows UV-Vis-NIR transmittance spectra of lubricated samples after calcination and fluorosilanization of the silica nanoparticle coating. With increasing numbers of deposited layers, an increase in light transmittance is observed for all coatings as compared to a normal glass slide in accordance with certain embodiments.

[0065] FIGS. 25A and 25B show repellency of a 10 μ l droplet of water (a) and octane (b) in dry and lubricated state for coatings with up to 9 deposited layers. The lubricated samples drastically outperform both uncoated (0 layers) and

dry, coated substrates and feature extremely small sliding angles for both liquids in accordance with certain embodiments.

[0066] FIGS. 25C and 25D show time-lapse pictures of a water (c) and octane (d) droplet sliding under an angle of 2° on a lubricated substrate with 5 deposited silica nanoparticle layers without getting pinned to the substrate in accordance with certain embodiments.

[0067] FIGS. 26A through 26D compares time-lapsed images taken from for untreated (upper row) and lubricated layer-by-layer assembled SiO_2 nanoparticle coated surfaces (lower row) using a) honey in the inside of a glass vial, b) crude oil in a glass tube; c) octane sliding down a stainless steel surface; d) octane sliding down a poly methylmethacrylate surface in accordance with certain embodiments.

[0068] FIGS. 27A through 27D shows contact angle hysteresis and sliding angles for water and hexadecane for SLIPS formed over PDMS substrate using a layer-by-layer assembly approach in accordance with certain embodiments.

[0069] FIG. 28 shows sliding angles as a function of applied strain in accordance with certain embodiments.

[0070] FIGS. 29A-29D show SEM images of a porous "paper" produced from boehmite nanofibers in accordance with certain embodiments.

[0071] FIG. 29E shows a TEM image of individual solvothermal boehmite nanofibers with some agglomerated particles in accordance with certain embodiments.

[0072] FIG. 29F shows SEM image of bundled boehmite nanofibers drop cast on a copper conductive tape in accordance with certain embodiments.

[0073] FIGS. 30A and 30B show a (A) top view and (B) cross section HR-SEM images of multi wall carbon nanotubes dispersed in epoxy resin matrix prior plasma etching in accordance with certain embodiments.

[0074] FIG. 31A shows an exemplary method to generate surface functionalized alumina nanoparticles (AINPs) for use as filler material in nanocomposites in accordance with certain embodiments.

[0075] FIG. 31B shows the normalized FTIR absorbance spectra of O—H stretching mode recorded from AINPs taken at different treatment times with Fenton chemistry in accordance with certain embodiments.

[0076] FIG. 32 shows a schematic design principles of lubricated nanostructured fabrics (SLIPS-fabrics) in accordance with certain embodiments.

[0077] FIG. 33 shows SEM images of the weave pattern of different fabrics in accordance with certain embodiments.

[0078] FIG. 34 shows SEM images of the fabrics after various different treatments in accordance with certain embodiments.

[0079] FIG. 35A shows static contact angle data for all the different functionalized fabrics in accordance with certain embodiments.

[0080] FIG. 35B shows contact angle hysteresis data for all the different functionalized fabrics in accordance with certain embodiments.

[0081] FIG. 36 shows twisting test results to determine robustness for a set of functionalized fabrics in accordance with certain embodiments.

[0082] FIG. 37 shows drop impact characterization of SLIPS-treated fabrics in accordance with certain embodiments.

DETAILED DESCRIPTION

[0083] The patent and scientific literature referred to herein establishes knowledge that is available to those of skill in the art. The issued U.S. patents, allowed applications, published foreign applications, and references, that are cited herein are hereby incorporated by reference to the same extent as if each was specifically and individually indicated to be incorporated by reference.

[0084] For convenience, certain terms employed in the specification, examples and claims are collected here. Unless defined otherwise, all technical and scientific terms used in this disclosure have the same meanings as commonly understood by one of ordinary skill in the art to which this disclosure belongs. The initial definition provided for a group or term provided in this disclosure applies to that group or term throughout the present disclosure individually or as part of another group, unless otherwise indicated.

[0085] The present disclosure describes slippery surfaces referred to herein as Slippery Liquid-Infused Porous Surfaces (SLIPS). In certain embodiments, the slippery surfaces of the present disclosure exhibit substance-repellent, drag-reducing, anti-adhesive and anti-fouling properties. The slippery surfaces of the present disclosure are able to prevent adhesion of a wide range of materials. Exemplary materials that do not stick onto the surface include liquids, solids, and gases (or vapors). For example, liquids such as water, oil-based paints, hydrocarbons and their mixtures, organic solvents, complex fluids such as crude oil, fluids containing complex biological molecules (such as proteins, sugars, lipids, etc) and biological cells and the like can be repelled. The liquids can be both pure liquids and complex fluids. In certain embodiments, SLIPS can be designed to be omniphobic, where SLIPS exhibit both hydrophobic and oleophobic properties. As another example, solids such as bacteria, insects, fungi and the like can be repelled or easily cleaned. As another example, solids such as ice, paper, sticky notes, or inorganic particle-containing paints, dust particles can be repelled or cleaned. SLIPS surfaces are discussed in International Patent Application Nos. PCT/US2012/21928 and PCT/US2012/21929, both filed Jan. 19, 2012, and U.S. Provisional Patent Applications 61/671,442 and 61/671,645, both filed Jul. 13, 2012, the contents of which are hereby incorporated by reference in their entireties.

[0086] Such materials that can be prevented from sticking to the slippery surfaces disclosed herein are referred to herein as "Object A." Object A that is in liquid form is referred to as "Object A in liquid form," or "liquefied Object A," or "Liquid A." Object A that is in solid form is referred to as "Object A in solidified form," or "solidified Object A" or "Solid A." Object A that is in gaseous/vapor form is referred to as "Object A in gaseous form", or "gaseous Object A". In certain embodiments, Object A can contain a mixture of both solids and fluids (i.e., gas/vapor/liquid mixed with a solid; eg particles in air, or particles in liquids). In certain embodiments, Object A can contain a mixture of both gas/vapors and liquids.

[0087] A wide range of materials can be repelled by the slippery surfaces of the present disclosure. For example, Object A can include polar and non-polar Liquids A, their mixtures, and their solidified forms, such as hydrocarbons and their mixtures (e.g., from pentane up to hexadecane and mineral oil, paraffinic extra light crude oil; paraffinic light crude oil; paraffinic light-medium crude oil; paraffinic-naphthenic medium crude oil; naphthenic medium-heavy crude oil; aromatic-intermediate medium-heavy crude oil; aromatic-naphthenic heavy crude oil, aromatic-asphaltic crude

oil, etc.), ketones (e.g., acetone, etc.), alcohols (e.g., methanol, ethanol, isopropanol, higher alcohols, propylene glycol, dipropylene glycol, ethylene glycol, and glycerol, etc.), water (with a broad range of salinity, e.g., containing sodium chloride or bromide from 0 to 6.1 M; potassium chloride or bromide from 0 to 4.6 M, water with high affinity to scaling, such as having high concentration of Mg and Ca ions, etc.), acids (e.g., concentrated hydrofluoric acid, hydrochloric acid, nitric acid, etc.) and bases (e.g., potassium hydroxide, sodium hydroxide, etc.), and ice, etc. Object A can include biological objects, such as insects, small animals, protozoa, bacteria, viruses, fungi, bodily fluids and fecal matter, tissues, biological molecules (such as proteins, sugars, lipids, etc.), and the like. Object A can include gasses, such as natural gas, air or water vapors. Object A can include solid particles suspended in liquid. Object A can include solid particles suspended in gas. Object A can include non-biological objects, such as dust, colloidal suspensions, spray paints, food items, common household materials, and the like. Object A can include adhesives and adhesive films. The list is intended to be exemplary and the slippery surfaces of the present disclosure are envisioned to successfully repel numerous other types of materials and materials combinations.

[0088] In certain embodiments, the slippery surface of the present disclosure has a coefficient of friction that is lower than that of polytetrafluoroethylene (PTFE or Teflon™) surface. In certain embodiments, the coefficient of friction may be less than 0.1, less than 0.05, or even less than 0.04. In certain embodiments, the coefficient of friction can be measured by sliding two different surfaces against each other. The value of the coefficient of friction should be load-independent. The friction force can depend on the load applied onto the surface, the sliding velocity, and the materials of the surfaces. For example, a reference surface, such as a polished steel, could be used to slide against the target surfaces, such as Teflon, or the SLIPS of the present disclosure could be used to slide against itself (e.g., SLIPS/SLIPS) to obtain the coefficients of friction (both static and dynamic).

[0089] A schematic of the overall design of Slippery Liquid-Infused Porous Surfaces (SLIPS) is illustrated in FIG. 1. As shown, the article includes a solid surface **100** having surface features **110** that provide a certain roughness (i.e. roughened surface) with Liquid B **120** applied thereon. Liquid B wets the roughened surface, filling the hills, valleys, and/or pores of the roughened surface, and forming an ultra-smooth surface **130** over the roughened surface. Due to the ultra-smooth surface resulting from wetting the roughened surface with Liquid B and forming a flat liquid overlayer, Object A **140** does not adhere to the surface.

[0090] In certain embodiments, the surface features **110** can be functionalized with one or more functional moieties **150** that further promote adhesion of the Liquid B **120** to the surface features **110**. In certain embodiments, the functional moieties **150** can resemble the chemical nature of Liquid B **120**. In certain embodiments, the surface features **110** can be functionalized with one or more functional moieties **150** that are hydrophobic.

[0091] In some embodiments, the Liquid B follows the topography of the roughened surface (e.g., instead of forming a smooth layer that overcoats all the textures). For example, Liquid B may follow the topography of the roughened surface if the equilibrium thickness of the overlayer is less than the height of the textures.

[0092] SLIPS can be designed based on the surface energy matching between a lubricating fluid and a solid (i.e. formation of a stable lubricating film which is not readily displaced by other, immiscible fluids). In some embodiments, SLIPS can be designed based on at least the following three factors: 1) the lubricating liquid (Liquid B) can infuse into, wet, and stably adhere within the roughened surface, 2) the roughened surface can be preferentially wetted by the lubricating liquid (Liquid B) rather than by the Object A, complex fluids or undesirable solids to be repelled (Object A), and 3) the lubricating fluid (Liquid B) and the object or liquid to be repelled (Object A) can be immiscible and may not chemically interact with each other. These factors can be designed to be permanent or lasting for time periods sufficient for a desired life or service time of the SLIPS surface or for the time till a reapplication of the partially depleted infusing liquid is performed.

[0093] The first factor (a lubricating liquid (Liquid B) which can infuse into, wet, and stably adhere within the roughened surface) can be satisfied by using micro- and/or nanotextured, rough substrates whose large surface area, combined with chemical affinity for Liquid B, facilitates complete wetting by, and adhesion of, the lubricating fluid. More specifically, the roughness of the roughened surface, R , can be selected such that $R \geq 1/\cos \theta_{BX}$, where R is defined as the ratio between the actual and projected areas of the surface, and θ_{BX} is the equilibrium contact angle of Liquid B on a flat solid substrate immersed under medium X (X =water/air/other immiscible fluid medium). R factor can vary between 1 and infinity. In certain embodiments, R may be any value greater than or equal to 1, such as 1 (flat, smooth surface), 1.5, 2, 5, or even higher.

[0094] The stable adhesion of the liquid B to the underlying solid is often achieved through chemical functionalization or applications of a coating that has a very high affinity to both Liquid B and the solid, thus producing a stable chemical or physical bonding between the liquid B and the solid.

[0095] To satisfy the second factor (that the roughened surface can be preferentially wetted by the lubricating liquid (Liquid B) rather than by the liquid, complex fluids or undesirable solids to be repelled (Object A)), a determination of the chemical and physical properties required for working combinations of substrates and lubricants can be made. This relationship can be qualitatively described in terms of affinity; to ensure that the Object A to be repelled (fluid or solid) remains on top of a stable lubricating film of the lubricating liquid, the lubricating liquid must have a higher affinity for the substrate surface than materials to be repelled, such that the lubricating layer cannot be displaced by the liquid or solid to be repelled. This relationship can be described as a “stable” region. As stated above, these relationships for a “stable” region can be designed to be satisfied permanently or for a desired period of time, such as lifetime, service time, or for the time till the replenishment/reapplication of the partially depleted infusing liquid is performed. In order to create a stable (or energetically favorable) Liquid B-solid interface, the following condition has to be satisfied:

$$\Delta E_0 = \gamma_{AS} - \gamma_{BS} = \gamma_{BX} \cos \theta_{RB} - \gamma_{AX} \cos \theta_{AX} > 0 \quad (\text{eq. 0})$$

where γ_{AS} and γ_{BS} are the interfacial tension of solid-liquid A and solid-liquid B interfaces respectively; γ_{BX} and γ_{AX} are the interfacial tension of lubricating fluid (Liquid B) and other immiscible fluid (Liquid A) with medium X; θ_{BX} and θ_{AX} are the contact angle of Liquid B and Liquid A on the solid under

medium X, where X can be air or other immiscible phases with the solid, Liquid A, and Liquid B. The condition includes both kinetically stable and thermodynamically stable SLIPS. Also, see FIGS. 3A and 3B.

[0096] Kinetically-stable SLIPS will form for certain combinations that do not satisfy eq. 0, where either (i) the Liquid B-solid interface may be gradually replaced by that of the Liquid A-solid interface over time, t, if Liquid A has a higher affinity to the solid surface than Liquid B (in other words, if an additional energy penalty is required to form Liquid B-Liquid A interface); or (ii) if Liquid A and B show some reactivity or miscibility over time degrading the slippery interface quality. These kinetically stable SLIPS would still show improved performance over existing surfaces, if the SLIPS need to keep their properties only within a limited period of time.

[0097] In order to create a stable (or energetically/thermodynamically favorable) SLIPS materials that are not degraded over time and where Liquid B is not being replaced by an Object A, the following criteria must be satisfied. A comparison of the total interfacial energies between textured solids that are completely wetted by either an arbitrary immiscible liquid (E_A), or a lubricating fluid with (E_1) or without (E_2) a fully wetted immiscible test liquid floating on top of it can be calculated. This can ensure that Object A remains on top of a stable lubricating film of Liquid B. In order to ensure that the solid is wetted preferentially by the lubricating fluid, both $\Delta E_1 = E_A - E_1 > 0$ and $\Delta E_2 = E_A - E_2 > 0$ should be true. The equations can be expressed as:

$$\Delta E_1 = R(\gamma_{BX} \cos \theta_{BX} - \gamma_{AX} \cos \theta_{AX}) - \gamma_{AB} > 0 \quad (\text{eq. 1})$$

$$\Delta E_2 = R(\gamma_{BX} \cos \theta_{BX} - \gamma_{AX} \cos \theta_{AX}) + \gamma_{AX} - \gamma_{BX} > 0 \quad (\text{eq. 2})$$

where R is the roughness factor (i.e. the ratio between the actual and projected surface areas of the textured solids).

[0098] This relationship can also be qualitatively described in terms of affinity; to ensure that Object A remains on top of a stable lubricating film of Liquid B, Liquid B must have a higher affinity for the substrate than Object A. For example, a solid functionalized or coated with hydrophilic molecules and infiltrated with polar Liquids B, will provide a functional oleophobic SLIPS for repelling oils; a solid functionalized or coated with hydrophobic moieties and infiltrated with hydrocarbons as Liquid B will provide a functional hydrophobic surface for repelling polar, hydrophilic materials, such as water; a solid functionalized or coated with fluorinated molecules and infiltrated with fluorinated oils will work as functional SLIPS that are both hydrophobic and oleophobic; etc. For patterned SLIPS, this relationship can be described as a “stable” region. Conversely, where Object A has a higher affinity for the substrate (for example, an unfunctionalized region of the substrate) than Liquid B, Object A will displace Liquid B in that region. This relationship can be described as an “unstable” region.

[0099] To satisfy the third factor (that the lubricating fluid (Liquid B) and the object or liquid to be repelled (Object A) can be immiscible and may not chemically interact with each other), the enthalpy of mixing between Object A and Liquid B should be sufficiently high (e.g., water/oil; insect/oil; ice/oil, etc.) that they phase separate from each other when mixed together, and/or do not undergo substantial chemical reactions between each other. In certain embodiments, Object A and Liquid B are substantially chemically inert with each other so that they physically remain distinct phases/materials without substantial mixing between the two. For excellent immiscibility between Liquid A and Liquid B, the solubility

in either phase should be <500 parts per million by weight (ppmw). For example, the solubility of water (Liquid A) in perfluorinated fluid (Liquid B, e.g., 3M Fluorinert™) is on the order of 10 ppmw; the solubility of water (Liquid A) in polydimethylsiloxane (Liquid B, MW=1200) is on the order of 1 ppm. In some cases, SLIPS performance could be maintained transiently with sparingly immiscible Liquid A and Liquid B. In this case, the solubility of the liquids in either phase is <500 parts per thousand by weight (ppthw). For solubility of >500 ppthw, the liquids are said to be miscible. For certain embodiments, an advantage can be taken of sufficiently slow miscibility or mutual reactivity between the infusing liquid and the liquids or solids or objects to be repelled, leading to a satisfactory performance of the resulting SLIPS over a desired period of time.

[0100] In some embodiments, a spatially heterogeneous pattern on a liquid-coated surface is created by first functionalizing a solid surface with spatially defined surface energy. When a given lubricant is wetted on a solid surface, the surface can be designed such that part of the region can form a stable lubricant film owing to the matching in surface energies between the solid and lubricant (i.e. $\Delta E_1 > 0$ and $\Delta E_2 > 0$), where the rest of the regions remain unstable (i.e. $\Delta E_1 < 0$ and/or $\Delta E_2 < 0$). When a suitable immiscible liquid encounters the unstable lubricating region, it can displace the lubricant and remain trapped within the patterned region.

[0101] Potential applications of patterned SLIPS include spatially defined patterning of cells for tissue engineering, mechano-biology, and single cell study, patterning of biological fluids, as well as high sensitivity biological sensors. Other applications include microfluidics, controlled placement of molecules or material without cross-contamination, etc.

[0102] Heterogeneous topologies or spatially-defined patterns of selective wettability can be formed on a liquid-coated or liquid-infiltrated solid substrate (SLIPS). The regions or holes that allow selective wetting (e.g., of an aqueous phase) can allow, by way of non-limiting example, local culture of cells, bacteria patterning for single cell study. DNA/RNA patterning for genomic sequencing and identification, protein patterning, fluid condensation and collection, ice nucleation, or transport of liquid through a SLIPS layer for sensing or drainage functions. The combination of these ultra-low adhesion and selective wetting (or wicking) properties can be used for applications for patterning of biological and non-biological substances, printing of characters, creating liquid adhesives, or permeable/non-permeable solid support, or for the design of bandage or ‘breathing skin layer’ biomedical materials.

General Scheme of Creating SLIPS

[0103] FIG. 2 illustrates a general scheme of creating SLIPS in accordance with certain embodiments of the present disclosure. Some of these steps illustrated in FIG. 2 can be combined and repeated; but in some cases these steps can be skipped (e.g., porous Teflon does not require the conditioning step at all, just lubrication; if the solid is already roughened, only functionalization might be required before lubrication; etc.). In one example, the scheme can be Original substrate → Surface conditioning steps → Lubrication to make SLIPS. In another example, the scheme can be Original surface → Surface roughening → Surface functionalization → Lubrication. In yet another example, the scheme can be Original surface → Coating with a layer of a

different material→Roughening of the additive layer→Surface functionalization→Lubrication.

[0104] A list of exemplary surface conditioning methods is provided below:

[0105] 1. Additive surface conditioning methods

[0106] bonding solid phase material (SLIPS or SLIPS-ready sheet, tape, or laminate)

[0107] application of material using liquid phase coating (paint or ink, spray, spin, dip, air brush, screen printing, inkjet printing, electrospinning, rotary jet printing)

[0108] deposition or reaction of gas phase material (CVD, plasma, corona, ALD, PVD, iCVD, oCVD)

[0109] sputtering or evaporation of metal or metal oxide, sulfides, nitrides, mixed oxides, oxo/hydroxo compounds, silica

[0110] evaporation or gas phase deposition of organic small molecules (parylene), polymers and other carbon-based materials (CNT, graphite, amorphous carbon, soot, graphene, buckminsterfullerene, diamond)

[0111] composite phase material deposition (particle or sacrificial particle+binder)

[0112] electrodeposition or other solution phase growth of material (conducting polymer, electroplated metal, electroless deposition, electrophoretic deposition of particles, surface-initiated polymerization, electrostatic assemblies, surface chemistry reactions, mineralization)

[0113] gas phase growth of material (nanoparticles, nanofibers, nanowires, nanotubes, microparticles, microfibers, microwires, microtubes)

[0114] multiple layer deposition (repeated coating, layer-by-layer deposition)

[0115] self-assembly of precursor material (minerals, small molecules, biomolecules, polymers, nano/microparticles, colloids)

[0116] growth of layers by oxidation

[0117] fouling-based deposition (using fouling as the nanostructure itself, e.g. bacterial biofilm, scaling, marine fouling)

[0118] transfer coating and printing (contact printing, pattern transfer, LB film)

[0119] a polymer foam deposition onto the substrate, with or without an optional promoter/adhesive layer by spraying of a polymer/prepolymer mixture/solution/emulsion/suspension/reagent or comonomer mixture that forms a porous/contiguous porous/open cell-type structured porous surface. The polymer can be chosen from a number of commercially available polymers and their mixtures, non-exhaustive examples including polyurethane, polystyrene, latex foams, etc.

[0120] accordingly, the appropriately chosen lubricating liquids can be spray-coated onto these polymer foams with or without additional conditioning of the polymer surface.

[0121] 2. Subtractive surface conditioning methods

[0122] mechanical/physical etching (sanding, sand and bead blasting, machining, sputtering)

[0123] chemical etching (acid, base, solvent, gas, anodization, parkerizing, black oxide formation)

[0124] chemical mechanical etching

[0125] 3. Surface conditioning by shape change (deformation)

[0126] wrinkle, crack, crease, ridge, fold formation by mechanically or acoustically induced change

[0127] swelling by solvent or lubricant or a solution containing chemical additives (oligomers, polymers, gels, etc.)

[0128] imprinting

[0129] 4. Chemical surface conditioning methods

[0130] formation of covalent bonding

[0131] formation of ionic bonding

[0132] formation of complex/dative bonding

[0133] formation of self-assembled monolayers through the formation of sulfide bonds, oxide bonds, silane, phosphate, phosphonate, carboxylate, sulfonate, amine, etc.)

[0134] formation of non-specific adsorption and van der-Waals interactions

[0135] change of chemical affinity by physisorbed material-change of chemical affinity by oxidation or reduction, electrochemical reactions

[0136] growth (grafting from) of material

[0137] attachment (graft to) of material

[0138] growth and attachment (grafting through) of material

[0139] homogeneous chemicals

[0140] bi- or multi-functional chemical modifiers (zwitter ionic, block co-polymer, switchable molecules) and their solutions

[0141] chemical structural transformation, recrystallization (e.g. Boehmitization)

[0142] 5. Physical surface conditioning methods

[0143] thermal (heating or cooling in air, inert gas, water, steam, solvents, vapors, supercritical fluids, annealing, sintering, melting, crystallization, phase transformation, carbonization)

[0144] mechanical (compression, tension, shear, expansion, aeration, foaming)

[0145] optical and energetic particles (laser ablation, gamma irradiation, electron beam, charged particles beams, UV, particle bombardment)

[0146] electrical (joule heating, electrochemistry)

[0147] acoustic (surface acoustic wave localization)

[0148] 6. Biological surface conditioning methods

[0149] growth or alteration of surfaces using biomolecules

Kinetically Stable SLIPS

[0150] As described above, SLIPS are a class of materials which typically meet the following three requirements:

[0151] 1) the lubricating liquid (Liquid B) must imbibe into, wet, and stably adhere within the substrate (Solid);

[0152] 2) the solid must be preferentially wetted by the lubricating liquid rather than by the liquid one wants to repel (Liquid A); and

[0153] 3) the lubricating and impinging test liquids must be immiscible.

[0154] SLIPS meeting the above three requirements are generally considered thermodynamically stable, meaning its SLIPS state does not tend to change considerably over time.

[0155] These factors can be designed to be permanent or lasting for time periods sufficient for a desired life or service time of the SLIPS surface or for the time till a reapplication of the partially depleted infusing liquid is performed. In some situations, kinetically stable SLIPS, which are stable for a limited period of time and/or for limited number of exposures to the liquid(s) being repelled, can still offer performance substantially better than that of conventional materials. The

kinetic stability can be due to various factors (e.g., high viscosity, slow mixing of liquids having limited but still appreciable mutual solubility, timescale of dewetting of lubricant slower than timescale of wetting and replacement of lubricant by liquid A etc.), while some relations described in the rigorous thermodynamics-based equations (i.e., equations 1 and 2) are not satisfied. FIGS. 3A and 3B illustrate the comparison between a thermodynamically stable SLIPS with a kinetically stable (i.e., meta-stable) SLIPS in accordance with certain embodiments of the present disclosure. There can be many liquid/liquid/(functionalized) solid combinations that fall into this category of kinetically stable (a.k.a., meta-stable) SLIPS. Many of these meta-stable SLIPS can offer cost-effective solutions with performance exceeding that of known in the art materials. The imbining liquid/solid surface functionalization methods can be chosen from a range offering not thermodynamically best, but kinetically adequate combinations that are at the same time compatible with other requirements of the application in question, e.g. biocompatible, biodegradable, food-compatible and the like.

[0156] To maintain high immiscibility between Liquid A and Liquid B, the solubility in either phase should preferably be <500 parts per million by weight (ppmw). For example, the solubility of water (Liquid A) in perfluorinated fluid (Liquid B, e.g., 3M Fluorinert™) is on the order of 10 ppmw; the solubility of water (Liquid A) in polydimethylsiloxane (Liquid B, MW=1200) is on the order of 1 ppm. SLIPS performance could be maintained transiently with sparingly immiscible Liquid A and Liquid B. In this case, the solubility of the liquids in either phase is <500 parts per thousand by weight (ppthw). For solubility of >500 ppthw, the liquids can be considered miscible. The following Table 1 contains examples of kinetically stable combinations of SLIPS. “Y” indicates that Liquid B forms a stable lubricating film, and does not get displaced by Liquid A; whereas “N” indicates that Liquid B is displaced by Liquid A over time. The equilibrium angles, θ_A and θ_B , are estimated from the respective averages of the measured advancing and receding angles on flat substrates from at least three individual measurements. R, γ_A , γ_B represent the roughness factor of the substrate and the surface tensions of Liquid A and B, respectively.

TABLE 1

Solid	Liquid A	Liquid B	R	γ_A	γ_B	θ_A	θ_B	ΔE_0	Stable Film?	
									Theory	Exp
Epoxy	H ₂ O	FC-70	2	72.6	17.1	83.7	28.1	7.1	Y	Y
Epoxy	H ₂ O	FC-70	1	72.6	17.1	83.7	28.1	7.1	Y	N
Silicon	C ₁₆ H ₃₄	H ₂ O	1	27.2	72.6	9.8	7.2	45.2	Y	N
Silicon	C ₁₀ H ₂₂	H ₂ O	1	23.6	72.6	4.2	7.2	48.5	Y	N
Silicon	C ₈ H ₁₈	H ₂ O	1	21.4	72.6	0	7.2	50.6	Y	N
Silicon	C ₆ H ₁₄	H ₂ O	1	18.6	72.6	0	7.2	53.4	Y	N
Silicon	C ₅ H ₁₂	H ₂ O	1	17.2	72.6	0	7.2	54.9	Y	N

[0157] A meta-stable state is created when the lubricant's low surface tension wets the surface but a “lock in”, that is, the energetical minimum situation is not supported by the surface chemistry. As a result, the SLIPS state will eventually break down upon addition of a second liquid. However, this may take time, so a meta-stable slips surface can be created even though the conditions for thermodynamic stability are not satisfied. A meta-stable state could also be created by damaging the surface to an extent that the supporting roughness is not high enough to allow for a lock in. FIG. 3C further

illustrates an exemplary meta-stable SLIPS state that is created by patterning the structured solid in a way that thermodynamically stable SLIPS surfaces are coexisting with surface regions that do not favor lubricant lock in. The upper part shows a scheme; the lower parts show photographs of fluorinated surfaces (support SLIPS) patterned with hydrophilic patches (do not support SLIPS) consisting of 100 μ m dot arrays (left), 500 μ m dot arrays (middle) and 1 mm dot arrays (right). The latter two clearly show pinning (i.e. the thermodynamically stable situation as shown in the scheme is reached in the course of the time the droplet needs to pass the surface) while the first one shows SLIPS conditions in a meta-stable case (i.e. the hydrophilic parts are not wetted by octane in the timescale of the droplet sliding down even though it would be thermodynamically favorable).

Object A

[0158] As noted previously, a wide range of materials can be repelled by the slippery surfaces of the present disclosure. For example, Object A can include polar and non-polar Liquids A, their mixture, and their solidified forms, such as hydrocarbons and their mixtures (e.g., from pentane up to hexadecane and mineral oil, aromatic liquids such as benzene, toluene, xylene, ethylbenzene, aromatic liquids such as benzene, toluene, xylene, ethylbenzene, paraffinic extra light crude oil; paraffinic light crude oil; paraffinic light-medium crude oil; paraffinic-naphthenic medium crude oil; naphthenic medium-heavy crude oil; aromatic-intermediate medium-heavy crude oil; aromatic-naphthenic heavy crude oil, aromatic-asphaltic crude oil, etc. and their oligomers and polymers), ketones (e.g., acetone, etc.), alcohols (e.g., methanol, ethanol, isopropanol, higher alcohols, propylene glycol, dipropylene glycol, ethylene glycol, and glycerol, etc.), water (with a broad range of salinity, e.g., containing sodium chloride or bromide from 0 to 6.1 M; potassium chloride or bromide from 0 to 4.6 M, water with high affinity to scaling, such as having high concentration of Mg and Ca ions, etc), acids (e.g., concentrated hydrofluoric acid, hydrochloric acid, nitric acid, etc) and bases (e.g., potassium hydroxide, sodium hydroxide, etc), ionic liquids, supercritical fluids, solutions of

pure or mixed solutes, complex mixture of fluids and solids such as wine, soy sauce and the like, ketchup and the like, olive oils and the like, honey and the like, candle soot and paraffin, grease, soap water, surfactant solutions, and frost or ice, etc. Object A can include biological objects, such as insects, blood, small animals, protozoa, bacteria (or bacterial biofilm), viruses, fungi, bodily fluids and fecal matter, tissues, biological molecules (such as proteins, sugars, lipids, etc.), and the like. Object A can include gasses, such as natural gas, air or water vapors. Object A can include solid particles (e.g.,

dust, smog, dirt, etc.) suspended in liquid (e.g., rain, water, dew, etc.) or gas. Object A can include non-biological objects, such as dust, colloidal suspensions, spray paints, fingerprints, food items, common household items, and the like. Object A can include adhesives and adhesive films. The list is intended to be exemplary and the slippery surfaces of the present disclosure are envisioned to successfully repel numerous other types of materials and materials combinations.

[0159] In certain embodiments, more than one different Object A can be repelled. In certain embodiments, the combination of two or more Objects A may together be more readily repelled as compared to just one Object A.

Liquid B

[0160] Liquid B (alternatively referred to as the “lubricant” through the specification) can be selected from a number of different materials, and is chemically inert with respect to the Object A. Liquid B flows readily into the surface recesses of the roughened surface and generally possesses the ability to form an ultra-smooth surface overcoat when provided over the roughened surface. In certain embodiments, Liquid B possesses the ability to form a substantially molecularly flat surface when provided over a roughened surface. The liquid can be either a pure liquid, a mixture of liquids (solution), or a complex fluid (i.e., a liquid+solid components such as lipid solutions). For instance, FIG. 6 shows a replication process to reproduce the morphology of the SLIPS surface. First, a porous solid was infiltrated with Liquid B (e.g., perfluorinated fluid). Then polydimethylsiloxane (PDMS) was cured over the Liquid B layer to obtain a negative replica of the SLIPS surface. Then, epoxy resin (e.g., UVO 114, Epotek) was used to obtain a positive replica using the PDMS negative replica. Then metrology analysis was carried out with an atomic force microscope. As shown, the average roughness of the positive replica surface was less than 1 nm, where the roughness represents an upper bound for the actual roughness of Liquid B as this reaches the physical roughness limits for flat PDMS and UVO 114 epoxy resin. Nonetheless, it is evident from the roughness analysis that Liquid B overcoats the surface topographies of the porous solid, forming a nearly molecularly smooth surface.

[0161] In certain other embodiments, Liquid B possesses the ability to form a substantially molecularly or even atomically flat surface when provided over a roughened surface.

[0162] In other embodiments, the lubricant layer follows the topography of the structured surface and forms a conformal smooth coating (e.g., instead of forming a smooth layer that overcoats all the textures). For example, the lubricant may follow the topography of the structured surface if the thickness of the lubricant layer is less than the height of the textures. In certain embodiments, conformal smooth lubricant coating, which follows the topography of the structured surface and can show significantly better performance than the underlying substrate that was not infused with the lubricant.

[0163] Liquid B can be selected from a number of different liquids. For example, perfluorinated or partially fluorinated hydrocarbons or organosilicone compound (e.g., silicone elastomer) or long chain hydrocarbons and their derivatives (e.g., mineral oil, vegetable oils) and the like can be utilized. In particular, the tertiary perfluoroalkylamines (such as perfluorotri-n-pentylamine, FC-70 by 3M, perfluorotri-n-butylamine FC-40, etc), perfluoroalkylsulfides and perfluoroalkylsulfoxides, perfluoroalkylethers, perfluorocycloethers

(such as FC-77) and perfluoropolyethers (such as Krytox family of lubricants by DuPont, Fomblin family of lubricants by Solvay), perfluoroalkylphosphines and perfluoroalkylphosphineoxides as well as their mixtures can be used for these applications, as well as their mixtures with perfluorocarbons and any and all members of the classes mentioned. In addition, long-chain perfluorinated carboxylic acids (e.g., perfluorooctadecanoic acid and other homologues), fluorinated phosphonic and sulfonic acids, fluorinated silanes, and combinations thereof can be used as Liquid B. The perfluoroalkyl group in these compounds could be linear or branched and some or all linear and branched groups can be only partially fluorinated. In addition, organosilicone compounds such as linear or branched polydimethylsiloxane (PDMS) (e.g. Momentive Element family silicone lubricants, Siltech silicone lubricants), polydiethylsiloxane (PDES), methyltris (trimethoxysiloxy) silane, phenyl-T-branched polysilsex-yquioxane, and copolymers of side-group functionalized polysiloxanes (e.g. Pecosil silicone lubricants) and combinations thereof can be used as Liquid B. In addition, various low molecular weight (up to C14) hydrocarbons (e.g. smokeless paraffin, Isopar™), long-chain (C15 or higher) alkyl petroleum oils or “white oils” (e.g. paraffin oils, linear or branched paraffins, cyclic paraffins, aromatic hydrocarbons to petroleum jelly and wax), and raw or modified vegetable oils and glycerides and combinations thereof can be used as Liquid B.

[0164] In certain embodiments, Liquid B has a high density. For example, Liquid B has a density that is more than 0.5 g/cm³, 1.0 g/cm³, 1.6 g/cm³, or even 1.9 g/cm³. In certain embodiments, the density of Liquid B is greater than that of Object A to enhance liquid repellency. High density fluids reduce the tendency of any impacting liquid to ‘sink’ below the surface of Liquid B and to become entrained therein. For Object A that is smaller than its capillary length (assume Object A is in liquid form), it is possible that the Liquid B has a density lower than that of the Object A, where the SLIPS formed by Liquid B can remain functional.

[0165] In certain embodiments, Liquid B has a low freezing temperature, such as less than −5° C., −25° C., or even less than −80° C. Having a low freezing temperature will allow Liquid B to maintain its slippery behavior at reduced temperatures and to repel a variety of liquids or solidified fluids, such as ice and the like, for applications such as anti-icing surfaces.

[0166] In certain embodiments, Liquid B can have a low evaporation rate, such as less than 1 nm/s, less than 0.1 nm/s, or even less than 0.01 nm/s of the thickness of the lubricant per a given area. Taking a typical thickness of Liquid B to be about 10 μm and an evaporation rate of about 0.01 nm/s, the surface can remain highly liquid-repellant for a long period of time without any refilling mechanisms.

[0167] FIGS. 7A to 7C demonstrates the self-healing features of SLIPS. In certain embodiments, the lifetime of the surface can be further extended by using a self-refilling mechanism as illustrated in FIG. 7D.

[0168] Experimentally, it is observed that Liquid A can become highly mobile on the surface of Liquid B when the kinematic viscosity of Liquid B is less than 1 cm²/s. Since liquid viscosity is a function of temperature (i.e., liquid viscosity reduces with increasing temperature), choosing the appropriate lubricant that operates at the aforementioned viscosity (i.e. <1 cm²/s) at specific temperature range is desirable. Particularly, various different commercially available

Liquid B can be found at the specified viscosity, such as perfluorinated oils (e.g., 3M™ Fluorinert™ and DuPont™ Krytox® oils), at temperatures ranging from less than -80°C . to greater than 260°C . For example, the temperature dependence of liquid viscosity of DuPont Krytox oils is shown in Table 2 as a specific example (note: data is provided by the manufacturer of DuPont Krytox oils).

TABLE 2

Temperature dependence of liquid viscosity of DuPont Krytox Oils.								
Temperature ($^{\circ}\text{C}$.)	Viscosity (cm^2/s)							
	Krytox 100	Krytox 101	Krytox 102	Krytox 103	Krytox 104	Krytox 105	Krytox 106	Krytox 107
20	0.124	0.174	0.38	0.82	1.77	5.22	8.22	15.35
40	0.055	0.078	0.15	0.30	0.60	1.60	2.43	4.50
100	—	0.02	0.03	0.05	0.084	0.18	0.25	0.42
204	—	—	—	—	—	0.031	0.041	0.06
260	—	—	—	—	—	—	0.024	0.033

[0169] Liquid B can be deposited to any desired thickness. A thickness of Liquid B which is on the order of the surface roughness peak-to-valley distance of the porous substrate provides good liquid-solid interaction between the substrate and Liquid B. When the solid substrate is tilted at a position normal to the horizontal plane, liquid layer with thickness below a characteristic length scale can maintain good adherence to the roughened surface, whereas liquid layers above the characteristic length can flow, creating flow lines (surface defects) and disrupting the flatness of the fluid surface. For example, non-limiting thicknesses for the fluid layer (as measured from the valleys of the roughened surface are on the order of $5\text{--}20\text{ }\mu\text{m}$ when the peak to valley height is $\sim 5\text{ }\mu\text{m}$).

[0170] In certain embodiments, Object A (i.e., the test liquid) and Liquid B (i.e., the functional liquid layer) may be immiscible. For example, the enthalpy of mixing between Object A and Liquid B may be sufficiently high (e.g., water and oil) that they phase separate from each other when mixed together.

[0171] In certain embodiments, Liquid B can be selected such that Object A has a small or substantially no contact angle hysteresis. Liquid B of low viscosity (i.e., $<1\text{ cm}^2/\text{s}$) tends to produce surfaces with low contact angle hysteresis. For example, contact angle hysteresis less than about 5° , 2.5° , 2° , or even less than 1° can be obtained. Low contact angle hysteresis encourages test Object A sliding at low tilt angles (e.g., $<5^{\circ}$), further enhancing liquid repellent properties of the surface. The mechanics of SLIPS surfaces are discussed in International Patent Application Nos. PCT/US2012/21928 and PCT/US2012/21929, both filed Jan. 19, 2012, the contents of which are hereby incorporated by reference in their entireties.

Roughened Surface

[0172] As used herein, the term “roughened surface” includes both the surface of a three-dimensionally porous material (such as a fibrous net) as well as a solid surface having certain topographies, whether they have regular, quasi-regular, or random patterns, or largely smooth surfaces with very small surface features.

[0173] In certain embodiments, the roughened surface may have a roughness factor, R , greater than or equal to 1, where

the roughness factor is defined as the ratio between the real surface area and the projected surface area. For complete wetting of Liquid B to occur, it is desirable to have the roughness factor of the roughened surface to be greater or equal to that defined by the Wenzel relationship (i.e. $R \geq 1/\cos \theta$ where θ is the contact angle of Liquid B on a flat solid surface). For example, if Liquid B has a contact angle of 50°

on a flat surface of a specific material, it is desirable for the corresponding roughened surface to have a roughness factor greater than ~ 1.5 . It is noteworthy that the “slipperiness” of the surface generally increases with the increase of R for the same material.

[0174] In certain embodiments, the presence of a roughened surface can promote wetting and spreading of Liquid B over the roughened surface, as is demonstrated in FIG. 4. FIG. 4(A) shows a droplet 300 of Liquid B (FC-70, a high boiling point, water-insoluble perfluorinated trialkylamine) on a flat, unstructured surface 310 prepared from a silanized epoxy resin. The dashed line represents the location of the upper surface of the substrate. While the droplet spreads on the surface, it retains its droplet shape and has a finite contact angle. FIG. 4(B) shows the same Liquid B on an exemplary roughened surface 320 of the same composition (silanized epoxy resin). The presence of the roughened surface promotes the spreading out and filling in of the droplet into the valleys of the roughened surface. As shown, the nanostructures greatly enhance the wetting of the Liquid B on the surface, creating a uniformly-coated slippery functional layer over the topographies.

[0175] In certain embodiments, the roughened surface can be manufactured from any suitable materials. For example, the roughened surface can be manufactured from polymers (e.g., epoxy, polycarbonate, polyester, nylon, Teflon, polysulfone, polydimethylsiloxane, etc.), metals (e.g., aluminum, steel, stainless steel, copper, bronze, brass, titanium, metal alloys, iron, tungsten), plastics (e.g., high density polyethylene (HDPE); low density polyethylene (LDPE); polypropylene (PP); polystyrene (PS); polyethylene terephthalate (PET))), sapphire, glass, carbon in different forms (such as diamond, graphite, carbon black, etc.), ceramics (e.g., alumina, silica, titania, zirconia, etc.), and the like. For example, fluoropolymers such as polytetrafluoroethylene (PTFE), polyvinylfluoride, polyvinylidene fluoride, Viton, fluorinated ethylene propylene, perfluoropolyether, and the like can be utilized. In addition, roughened surface can be made from materials that have functional properties such as conductive/non-conductive, and magnetic/non-magnetic, elastic/non-elastic, light-sensitive/non-light-sensitive materials. A broad range of functional materials can make SLIPS.

[0176] In certain embodiments, the roughened surface may be the porous surface layer of a substrate with arbitrary shapes and thickness. The porous surface can be any suitable porous network having a sufficient thickness to stabilize Liquid B, for example a thickness 50+ nm, or the effective range of intermolecular force felt by the liquid from the solid material. The substrates can be considerably thicker, however, such as metal sheets and pipes. The porous surface can have any suitable pore sizes to stabilize the Liquid B, such as from about 10 nm to about 2 mm. Such a roughened surface can also be generated by creating surface patterns on a solid support of indefinite thickness.

[0177] Many porous materials are commercially available, or can be made by a number of well-established manufacturing techniques. For example, PTFE filter materials having a randomly arranged three-dimensionally interconnected network of holes and PTFE fibrils are commercially available. FIGS. 5A to 5E illustrate some non-limiting exemplary embodiments of suitable porous materials.

[0178] The roughened surface material can be selected to be chemically inert to Liquid B and to have good wetting properties with respect to Liquid B. In certain embodiments, Liquid B (and similarly Object A) may be non-reactive with the roughened surface. For example, the roughened surface and Liquid B (or Object A) can be chosen so that the roughened surface does not dissolve upon contact with Liquid B (or Object A). In particular, perfluorinated liquids (Liquid B) work exceptionally well to repel a broad range of Liquids A and their solidified forms, such as polar and non-polar Liquids A, their mixtures, and their solidified forms, such as hydrocarbons and their mixtures (e.g., from pentane up to hexadecane and mineral oil, aromatic liquids such as benzene, toluene, xylene, ethylbenzene, paraffinic extra light crude oil; paraffinic light crude oil; paraffinic light-medium crude oil; paraffinic-naphthenic medium crude oil; naphthenic medium-heavy crude oil; aromatic-intermediate medium-heavy crude oil; aromatic-naphthenic heavy crude oil, aromatic-asphaltic crude oil, etc. and their oligomers and polymers), ketones (e.g., acetone, etc.), alcohols (e.g., methanol, ethanol, isopropanol, higher alcohols, propylene glycol, dipropylene glycol, ethylene glycol, and glycerol, etc.), water (with a broad range of salinity, e.g., sodium chloride from 0 to 6.1 M; potassium chloride from 0 to 4.6 M, etc.), acids (e.g., concentrated hydrofluoric acid, hydrochloric acid, nitric acid, etc) and bases (e.g., potassium hydroxide, sodium hydroxide, etc), ionic liquids, supercritical fluids, solutions of pure or mixed solutes, complex mixture of fluids and solids such as wine, soy sauce and the like, ketchup and the like, olive oils and the like, honey and the like, grease, soap water, surfactant solutions, etc. Object A can include biological objects, such as insects, blood, small animals, protozoa, bacteria (or bacterial biofilm), viruses, fungi, bodily fluids and tissues, lipids, proteins and the like. Object A can include solid particles (e.g., dust, smog, dirt, etc.) suspended in liquid (e.g., rain, water, dew, etc.). Object A can include non-biological objects, such as dust, colloidal suspensions, spray paints, fingerprints, food items, common household items, frost, ice and the like. Object A can include adhesives and adhesive films. The list is intended to be exemplary and the slippery surfaces of the present disclosure are envisioned to successfully repel numerous other types of materials.

[0179] In addition, the roughened surface topographies can be varied over a range of geometries and size scale to provide the desired interaction, e.g., wettability, with Liquid B. In

certain embodiments, the micro/nanoscale topographies underneath the Liquid B can enhance the liquid-wicking property and the adherence of Liquid B to the roughened surface. As a result, the Liquid B can uniformly coat the roughened surface and get entrapped inside at any tilting angles.

[0180] In addition to the desired topography, the roughened surface can be conditioned, modified or functionalized to acquire necessary properties (e.g., affinity, wettability) towards lubricating Liquid B. For example, the surface can be modified to expose hydrophilic/polar/charged chemical groups, including but not limited to hydroxyl, amine, carboxyl, sulfate, sulfonate, phosphate, phosphonate, carboxylate, ammonium, making it compatible with wetting by polar liquids, such as water and aqueous solutions of different pH and ionic strength, ionic liquids and their mixtures. Imbibing the thus modified roughened surface with polar liquids will result in oleophobic SLIPS. In another example, the surface can be modified to expose hydrophobic/non-polar/non-charged chemical groups or chains, including but not limited to alkyl, cycloalkyl, aryl, aralkyl, alkene, substituted silyl, that can be linear, branched or cyclic, making it compatible with wetting by non-polar liquids, such as hydrocarbons, natural, mineral or silicone oils, petroleum fractions, molecules containing aromatic, cycloaliphatic, paraffinic chains of various molecular weight, length and branching and their mixtures. Imbibing the thus modified roughened surface with non-polar liquids will result in hydrophobic SLIPS. In yet another example, the surface can be modified to expose fluorinated chemical groups or chains, including but not limited to partially or fully fluorinated hydrocarbon chains, perfluoropolyethers and other fully or partially fluorinated liquids described in more detail in the description below. Imbibing the thus modified roughened surface with fluorinated liquids will result in omniphobic (both hydrophobic and oleophobic) SLIPS. General types and principles of surface conditioning, modification, and functionalization are classified in the description in this document. Depending on the material of the roughened surface, the applicable conditioning and functionalization methods can include physical, chemical treatment as well as a combination of any number of physical and chemical steps detailed in the following sections. In addition, a combination of not perfectly matched surface functionalization and lubricant can also be used. For example, a robust ice-repellent SLIPS can be made by application of silicone lubricant on fluorinated surface.

Applications

[0181] Numerous different applications for SLIPS can be envisioned where surface that repels a wide range of materials is desired. Some non-limiting exemplary applications are described below.

Example 1

Protective Fabric Materials

[0182] A slippery surface can be applied in functional protective fabrics/gloves/blankets/towels/laboratory-clothing, roofs, domes and windows—in architecture, tent, swim-suits, wet suits, rain-coats, tactical gear, military clothing, fire-fighter clothing, and the like. These functional fabric materials can serve as physical barriers and used to repel a broad range of hazardous fluids/solids, such as acid, base, oxidiz-

ing/reducing agents, toxic substances, highly flammable liquids, high temperature fluids, burning oils, fire/flame, low temperature fluids, ice, and frost.

[0183] SLIPS can be applied onto common fabric materials, such as natural cotton, and synthetic fabrics (e.g., polytetrafluoroethylene (PTFE), polyethylene terephthalate (PET), polypropylene, polyester, acrylic, nylon, latex, rayon, acetate, olefin, spandex, kevlar). In this exemplary application, the lubricating fluids can be chosen from a broad range of perfluorinated fluids (including but not limiting to the tertiary perfluoroalkylamines (such as perfluorotri-n-pentylamine, FC-70 by 3M, perfluorotri-n-butylamine FC-40, etc), perfluoroalkylsulfides and perfluoroalkylsulfoxides, perfluoroalkylethers, perfluorocycloethers (like FC-77) and perfluoropolyethers (such as KRYTOX family of lubricants by DuPont), perfluoroalkylphosphines and perfluoroalkylphosphineoxides as well as their mixtures can be used for these applications); polydimethylsiloxane and their functional modifications; food compatible liquids (including but not limiting to olive oil, canola oil, coconut oil, corn oil, rice bran oil, cottonseed oil, grape seed oil, hemp oil, mustard oil, palm oil, peanut oil, pumpkin seed oil, safflower oil, sesame oil, soybean oil, sunflower oil, tea seed oil, walnut oil, and a mixtures of any of the above oils).

[0184] Depending on the chemical affinity of the solid to the lubricants with respect to the fluids one want to repel, chemical functionalization and roughening of the solid can further enhance the chemical affinity. Most of the natural cottons and synthetic fibers are woven into highly textured, porous surfaces (e.g., see FIG. 8), in which the solid support can provide enough surface area for the adherence of the lubricating fluids. When these materials are converted into SLIPS, appropriate chemical functionalization schemes can enhance the chemical affinity with the lubricants. The following are a few examples of the chemical functionalization schemes for materials where further chemical treatments can be applied.

[0185] 1) Fluorosilanization of PET: To fluorosilanize PET to create a highly fluorinated surface, one could start with amines (e.g., 3-aminopropyltrialkoxysilanes) which can react readily with PET to activate the ester linkages on the surface. Amine functionalized PET can react with tetraethylorthosilicate (TEOS) to create surface hydroxyl groups which can condense with silanes (e.g., tridecafluoro-1,1,2,2-tetrahydrooctyl)-trichlorosilane). Protocols to achieve the aforementioned steps can be referred to A. Y. Fadeev and T. J. McCathy, *Langmuir* 14, 5586-5593 (1998).

[0186] 2) Deposition of chemically functionalized silica onto fabric (both natural and synthetic): Another approach to chemically functionalize fabrics directly is through in-situ synthesis of silica particles with amine groups at the surface of the fibers through Stober method (Stober, W.; Fink, A.; Bonn, E. J. *Colloid Interface Sci.* 1968, 26, 62). Through this method, the silica microparticles could covalently bond to the surface of natural and synthetic fabrics (See FIGS. 9A-9C). With the creation of the silica surface, one could further fluorosilanize the surface through the vapor/liquid phase silanization methods.

[0187] With chemically functionalized fabrics, one can apply the lubricating fluids by a broad range of deposition methods, such as dip/spray coatings. With these slippery coatings, it was shown that they can effectively repel a broad range of aqueous, hydrocarbons, and complex fluids. For example, FIGS. 10A-10C demonstrate SLIPS fabrics for

functional clothing against various complex fluids and high temperature fluids in accordance with certain embodiments.

Example 2

Self-Cleaning and Self-Replenishing SLIPS Optical Coating

[0188] Optical parts suffer from contamination by dust particle, grease, and other complex liquids. SLIPS coating can be applied to keep optics free from fouling. With combined mechanism of removing condensed water on SLIPS coating layer, tilt, air flow, or vibration, condensed water can also be removed effortlessly.

[0189] FIG. 11 demonstrates photographs of a fog test on a 60° C. water. The left half of the glass is uncoated; the right half of the glass is SLIPS coated. The left photo shows the result after 10 seconds of fog test. The right photo shows the result after 3 minutes. FIG. 12 shows a schematic illustration of a fog-free optical viewing cover for microscope.

[0190] An optical quality SLIPS coating can prevent fouling by foreign material and condensation while the lubricating liquid can be replenished from surrounding materials such as the O-rings, bearings, and housing holding the optics in place. For example, a silicone lubricant can be infiltrated in an O-ring made of silicone rubber from which the lubricant can be continuously supplied to replenish and coated surface automatically or manually by external control (e.g., by turning a screw to squeeze the lubricant from the reservoir). FIG. 13 contains a schematic illustration of a circular optics encased in a lubricant-containing O-ring serving as a reservoir in accordance with certain embodiments.

[0191] FIG. 14 demonstrates a photograph of camera lens protectors without coating (left) and with coating (right), in accordance with certain embodiments. When water is applied on the lens protector, the water spreads on the coated lens protector but beads up on the coated lens protector. When the coated lens protector is tilted, the water droplet slides and cleans dusts off the surface. FIG. 15 further demonstrates a photograph of camera lens protectors without coating (left) and with coating (right), in accordance with certain embodiments. After the lens protector is tilted, the water droplet spreads and mostly remains on the uncoated lens protector; while the water droplet slides to the bottom of the coated lens protector. The coating can also provide an anti-reflective feature due to the nanostructure on the surface of the coated lens.

Example 3

SLIPS Containers

[0192] A SLIPS layer can be coated onto the inner and/or outer surface of containers, such as bottles, bags, and tubes, that are made out of common plastics (i.e., high density polyethylene (HDPE); low density polyethylene (LDPE); polypropylene (PP); polystyrene (PS); polyethylene terephthalate (PET); polycarbonate (PC); polylactic acid (PLA); polyvinyl chloride (PVC)) plastic-lined metal containers, metal containers, glass containers, ceramic containers, or containers of composite materials. Lubricants can be chosen from food and cosmetics compatible liquids, including but not limiting to olive oil, canola oil, coconut oil, corn oil, rice bran oil, cottonseed oil, grape seed oil, hemp oil, mustard oil, palm oil, peanut oil, pumpkin seed oil, safflower oil, sesame oil, soybean oil, sunflower oil, tea seed oil, walnut oil, and a mixtures of any of the above oils. In another embodiment, the

lubricants can be chosen from biocompatible liquids, including but not limited to fatty acids, glycerolipids, glycerophospholipids, sphingolipids, sterol lipids, prenol lipids, saccharolipids, polyketides, and their solutions. The lubricating oils can be applied to the interior of the bottles or bags by spray-coating, dip-coating, and vapor deposition process etc.

[0193] In certain embodiments, for the complex fluid and paste-like mixtures (ketchup, mayonnaise, paints, shampoos, conditioners, tooth paste, the inner surface of the container or part thereof will be designed to have appropriate roughness and chemical functionalization so as to ensure its high affinity towards one or more major liquid components of the complex fluid/paste (like various food grade natural oils (olive, vegetable, sunflower, canola, etc. and their mixtures) for ketchup and mayonnaise; oil base (mixture of aliphatic and aromatic hydrocarbons and short chain ketones) of oil paints; essential fatty acids, fatty alcohols, silicone polymers and their mixtures for shampoos and conditioners) and thereby produce the needed overlaying liquid layer inherently within the container.

[0194] In certain embodiments a range of food and biocompatible, widely used in food/medical/healthcare applications oligomers, polymers, copolymers of various molecular weights and chemical structures and their blends can be used for making a roughened surface and for its functionalization by chemical and/or deposition means. The examples include, but are not limited to polylactic acid, polyglycolic acid, polylactide-co-glycolide, poly-ethyleneglycol, polyethyleneoxide, polypropyleneoxide and their copolymers, polysulfone, polytetrafluoroethylene, other fully and partially fluorinated polymers, copolymers and oligomers, as well as polyolefins, polyesters, polyacetals, polyvinylidene fluoride, polyacrylates, polyurethanes, silicones, polycarbonate. An additional non-exhaustive list of polymers used in food industry, their trade names and approval status by various regulatory bodies is given in FIG. 16A (adapted from Food Processing—Handling Brochure 2011 by Professional Plastics, Inc. which is incorporated here as a reference in its entirety).

[0195] After the slippery coatings are applied on the plastic bottles, it is shown that the bottles can be capable of repelling a broad range of complex food fluids and cosmetics, including but not limiting to ketchup, mayonnaise, honey mustard dressing, Caesar dressing, ranch dressing, thousand island dressing, blue cheese dressing, French dressing, ginger dressing, honey Dijon, Italian dressing, Louis dressing, vinaigrette, Russian dressing, and a mixture of the above components. The lubricating oils can be chosen from an oil component/mixture of the oil components that are present in the food fluids or cosmetics that one wants to repel (where the oil component is immiscible with the other contents that are present in the food fluids or cosmetics). The common oil component can allow for the self-replenishing and self-lubricating effects of the slippery coatings within the bottles. FIG. 16B illustrates SLIPS-treated bottles repelling complex food products, such as ketchup and mayonnaise. FIG. 16C similarly shows a SLIPS-treated plastic bag repelling warm oatmeal.

[0196] FIG. 16D shows a SLIPS-treated ice tray repelling ice.

[0197] In yet another example, after the slippery coatings are applied on the plastic bags, it is shown that the bags can be capable of repelling a broad range of 1) biological solids/fluids, including but not urine, blood, feces, whole blood, plasma, serum, sweat, feces, urine, saliva, tears, vaginal fluid,

prostatic fluid, gingival fluid, amniotic fluid, intraocular fluid, cerebrospinal fluid, seminal fluid, sputum, ascites fluid, pus, nasopharyngeal fluid, wound exudate fluid, aqueous humour, vitreous humour, bile, cerumen, endolymph, perilymph, gastric juice, mucus, peritoneal fluid, pleural fluid, sebum, vomit, and combinations thereof; 2) complex food fluids including but not limited to ketchup, mayonnaise, honey mustard dressing, Caesar dressing, ranch dressing, thousand island dressing, blue cheese dressing, French dressing, ginger dressing, honey Dijon, Italian dressing, Louis dressing, vinaigrette, Russian dressing, oatmeals, and a mixture of the above components; 3) cosmetics including but not limited to body/facial lotions. The lubricating oils can be chosen from an oil component/mixture of the oil components that are present in the food fluids or cosmetics that one wants to repel (where the oil component is immiscible with the other contents that are present in the food fluids or cosmetics). The common oil component can allow for the self-replenishing and self-lubricating effects of the slippery coatings within the containers.

Example 4

Fragrance/Flavor-Enhanced SLIPS

[0198] Slippery surfaces with fragrance or flavor enhancement, which can be applied onto polymeric, ceramic, metallic or composite surfaces for different industrial and medical applications where imparting of a pleasant odor, masking of an unpleasant odor, imparting or supporting of a particular flavor or taste or any combination of the above effects are required. The key novelty of the invention is the incorporation of tailor-made lubricants that in addition to their ability to be functional elements of the slippery, liquid/solid/complex fluid-repellant surfaces, possess the desired odor/taste/flavor characteristics.

[0199] In this embodiment, a slippery, repellent coating is that includes a chemically or physically modified/conditioned/functionalized structured solid surface having a desired degree of roughness that is infused with a lubricating fluid is described. Various modifications of the concept that are based on hybrid materials that are pre-swollen with said lubricating fluid are included and covered by this embodiment, as well.

[0200] The lubricating fluids can be chosen from a variety of natural and synthetic oils, a subset of which would include food or biologically-compatible liquids, including but not limited to olive oil, canola oil, coconut oil, corn oil, rice bran oil, cottonseed oil, grape seed oil, hemp oil, mustard oil, palm oil, peanut oil, pumpkin seed oil, safflower oil, sesame oil, soybean oil, sunflower oil, tea seed oil, walnut oil, and a mixtures of any of the above oils.

[0201] Another subset of lubricating liquids includes synthetic oligomeric and polymeric long-chain hydrocarbon-, silicone-, fully or partially fluorinated materials with carbon-carbon, carbon-nitrogen, carbon-oxygen, carbon-sulfur, carbon-phosphorus and other carbon-heteroatom linkages and combinations thereof, with varying molecular weights, linear or having varying degrees of branching and varying relative proportions of the different types of co-monomers or linkages present within their structures. These lubricating oils can be further modified by the addition of or functionalization with odor- or flavor-imparting components or modifiers to provide the desired multi-sensory functions, such as imparting of a

pleasant odor, masking of an unpleasant odor, imparting or supporting of a particular flavor or taste or any combination of the above effects.

[0202] As shown in FIG. 17, these odor- or flavor-imparting components can be added to the base oil, as such, to be dissolved (Method 1), emulsified, or otherwise dispersed (Method 3); alternatively, they can be included together with specially-engineered carrier matrices that are formulated for slow release (Method 2); they can also be chemically attached to the molecules comprising the lubricating liquid. There is a wide variety of the fragrant and flavor materials to be chosen from natural, nature-identical and fully synthetic ones, including those produced by means of biotechnology.

[0203] Those skilled in art will recognize that the list of the chemicals used in flavor, fragrance, cosmetics and food industries is extremely broad, so by the way of reference, two following exemplary sources are included here:

[0204] 1. Rowe, D. J. (2005). *Chemistry and Technology of Flavour and Fragrance*, John Wiley & Sons

[0205] 2. Berger, R. G. (2007). *Flavours and Fragrances: Chemistry, Bioprocessing and Sustainability*, Springer.

[0206] A large proportion of fragrance chemicals are hydrophobic in nature and therefore compatible/soluble with hydrophobic lubricating fluids. Common classes of hydrophobic fragrant chemicals include olefins, esters, ketones, long chain alcohols and aldehydes and many more. An exemplary, not meant to be limiting list of the typical molecules that could be combined with the non-polar lubricants includes, e.g., S-limonene, R-limonene, dipentene, phenethyl isobutyrate, phenethyl isovalerate, octanol, nonanol, or their mixtures etc. The fragrance/favor enhanced lubricating oils can be applied by spray-coating, dip-coating, and even vapor deposition process etc. For certain embodiments, the fragrance or flavor enhancers are chosen such that they are biodegradable/with biological origins, and with smells or flavors viewed positively and considered pleasant by a big proportion of the general population; the other important considerations are the cost and IP: there is a big number of industrially produced, inexpensive fragrant chemicals that are either not patentable or are off patents, which can be used as art of the formulation of the fragrance-enhanced lubricants.

[0207] The fragrance/flavor-enhanced slippery surfaces described above are capable of repelling a broad variety of aqueous-based complex fluids including food and human excretes. The slippery surfaces can be coated onto surfaces that are made out of common plastics (e.g., high density polyethylene (HDPE); low density polyethylene (LDPE); polypropylene (PP); polystyrene (PS); polyethylene terephthalate (PET); polyvinyl chloride (PVC)), ceramics (e.g., glass), and metals (e.g., aluminum).

[0208] Such fragrance or flavor-enhanced SLIPS structures can be utilized as odor-neutralizer/fragrance enhancer for ostomy bags, sanitary and toiletry products, toilet bowls, as well as fragrance/flavor enhancer for food and cosmetic containers and other surfaces that come in contact with materials that need to be repelled or move freely on the surface and where the resulting odor and/or flavor characteristics, when added to the repellent behavior of the surfaces, add positively to the overall performance and/or perception of the performance.

Example 5

SLIPS Gas Pipelines

[0209] According to Energy Information Administration, natural gas pipelines consume an average of two to three percent of throughput to overcome frictional losses compared to electric transmission lines, which lose six to seven percent of the energy they carry due to electric resistance (Energy Information Administration, Frequently Asked Questions (national-level losses were 6.5 percent of total electricity disposition in 2007), available at http://tonto.eia.doe.gov/ask/electricity_faqs.asp#electric_rates2.) According to Interstate Natural Gas Association of America (Interstate Gas Pipe Efficiency, Interstate Natural Gas Association of America, Washington, D.C, release date Nov. 1, 2010, <http://www.ingaa.org/11885/Reports/10927.aspx>), one way to mitigate these losses is to use internally coated pipes, that provide some improvement at a cost of \$2-\$8 per foot depending on the pipe diameter and the coating used. In this example, internally coated pipe required less horsepower than uncoated pipe, reducing fuel from 1.627 to 1.452 MMcf/d. For example, FIG. 18 illustrates pressure drop on internally coated pipe as a function of flow in accordance with certain embodiments.

[0210] Drag and friction reducing SLIPS layers can be formed on a variety of substrates for the applications involving gas flows. For example, a slippery coating of tubes and pipes can be formed based on SLIPS. The gas is understood to include gas phase, liquefied, and supercritical fluids that are subject to high flow rates and associated energy losses due to friction and drag. The examples of gases include but are not limited to air, steam, liquefied natural gas (methane), liquefied petroleum gas, higher alkanes, ethylene, acetylene, higher alkenes and mixtures thereof, carbon monoxide, carbon dioxide, oxygen, hydrogen, inert gases (nitrogen, helium, and noble gases), reactive gases (halogens, hydrogen halides, ammonia, hydrazine, phosphine, arsine), pure and mixed halogenated hydrocarbons, pure and mixed hydrofluorocarbons, halogenated fluorocarbons, etc. In certain embodiments, mixtures of gases, both reactive and inert can be used (like synthesis gas—CO/H₂) as well as the gaseous reactant mixtures, product mixtures and Side/waste streams.

[0211] A non-exhausting list of combinations of roughened material surfaces and methods of their functionalization for retaining different lubricating liquids are presented below. The surfaces are proposed to possess the desired levels of roughness and when necessary further functionalized to ensure that the lubricating liquid is immobilized and retained within the roughened surface. For all the examples below, one can, in principle, design omniphobic slippery surfaces (those based on polyfluorinated oils retained within roughened surfaces functionalized to have a strong affinity to fluorinated molecules), hydrophobic slippery surfaces (those based on natural or synthetic/mineral oils retained within roughened surfaces having hydrophobic (not necessarily fluorine containing) functionalization), and oleophobic slippery surfaces (those based on aqueous lubricating liquids retained within the roughened surfaces having appropriately functionalized hydrophilic surface). The list below is not assumed to include only the most relevant materials for gas transporting pipes, but it rather includes several types of materials that may find application in the friction/drag-reducing applications involving gas flows. It is also worth noting that the combinations

included in this non-exhaustive list can be applicable for all other applications, in addition to gas/fluid drag and friction reduction.

[0212] 1. Stainless steel, other steels can be modified by several methods: with silica or related oxide materials using atomic layer deposition or by sol-gel method, or electrochemically with a range of thiol-terminated molecules, or wet etching with acids catalyzed with iron that selectively etches some portions with defined domain sizes present in the alloy. The resulting anchor coatings can be used as such (as in the case of thiol SAMs) or modified further using Si—OH (or related) functionalities of silica (or other ALD or sol-gel coating) or the head groups of thiol SAMs. Fully, partly, or non-fluorinated functionalities introduced this way can provide the stainless steel with the surface chemistry suitable for retention of appropriately chosen lubricating liquid. The lubricating liquid can then be selected, depending on the target application, from a variety of fluorinated oils or non-fluorinated natural (olive oil, vegetable oils and such) or synthetic liquids (higher hydrocarbons—aliphatic, aromatic, mixed, silicon oils and mixtures thereof).

[0213] 2. Titanium, Tantalum, Niobium and other early and middle transition metal surfaces (generally covered with oxide layer) can be functionalized with (polyfluoro)alkane phosphates/phosphonates/sulfonates/carboxylates that can form stable SAMs on their surface. The following modification with a lubricating liquid and its choice are the same as above.

[0214] 3. Aluminum surface modification can be done using a range of physical, chemical and electrochemical techniques. These can include controlled conductive polymer deposition and growth, ALD, sol-gel deposition, Boehmite formation, SAM formation similar to described above for titanium and other metals, as well as silanization/fluorosilanization from solution or gas phase. The following modification with a lubricating liquid and its choice are the same as above.

[0215] 4. Polymer surfaces, especially those that themselves are lacking pendant chemical functionalities, can use chemical (hydrolytic, high-temperature steam, strong acids, bases, oxidants) and/or plasma etching to provide sufficient number of chemical functional group (hydroxyls, carboxyls) to allow one to install the desired surface chemistry. However, in many cases, even the non-functionalized polymer surfaces are already compatible with a number of lubricating liquids. In other cases, the combination of plasma treatment and ALD of silica or related materials can provide sufficient number of functionalizable reactive groups needed to modify the polymer surface enough to retain the desired lubrication liquid. The functionalization can then be carried out using chlorosilane coupling, amide coupling, glycidyl chemistry, etc.

[0216] 5. Sapphire surface can use high-energy laser treatment to achieve installation of appreciable numbers of chemical functional groups.

[0217] 6. Glass and related mixed oxide materials can be etched with appropriate etchant (e.g., HF, acid piranha) or plasma treated, if necessary, and then the Si—OH (or other related —OH) functionalities can be used for further modifications using various chemical methods. For example, a range of commercially available fluorinated or non-fluorinated chloro- or alkoxy-silanes can be used to install the desired surface chemistry. Fully, partly, or non-fluorinated functionalities introduced this way will provide glass with the surface chemistry suitable for retention of the appropriately

chosen lubricating liquid. The lubricating liquid can then be selected, depending on the target application, from a variety of fluorinated oils or non-fluorinated natural or synthetic liquids and mixtures thereof.

[0218] Other potential applications of SLIPS can include inner surface of tubes and pipes used in gas transport systems, watch glasses within the gas transport systems, blades of wind turbines (the SLIPS-type coating may combine the gas friction reduction and ice repelling), gas turbines, and gas lines in chemical and petroleum industries and civilian objects.

Example 6

Anti-Corrosive and Anti-Scaling Coatings

[0219] Many metal surfaces have issues with corrosion that create pitting, decarburization leading to cracks and mechanical breakdown of structures caused by contact with acid, base, brine, oxidizing and reducing chemicals, and acid rain. In addition, metallic, plastic, ceramic, or composite pipelines and surfaces exposed to aqueous and non-aqueous systems are subject to the growth of oxide, hydroxide or oxoacid scale (precipitation fouling) and the deposition of solid fouling commonly found in boilers and heat exchangers reducing thermal conduction and in reservoirs and wells in oil field deteriorating their productivity. Common industrial fouling deposits include calcium carbonate, calcium sulfate, calcium oxalate, barium sulfate, magnesium hydroxide, magnesium oxide, silicates, aluminum oxide hydroxide, aluminosilicate, copper, phosphates, magnetite, or nickel ferrite. Solid deposits may also form on the surface of chemical reactors that decreases thermal conduction, induces undesirable chemical reactions such as oxidation, polymerization, carbonization, catalyzed by the metallic walls.

[0220] A SLIPS coating can prevent corrosion, scaling, and unwanted solid deposition by creating repellent surfaces to various liquids and solids, in particular, liquids with high acidity or basicity, sea water, concentrated brine, and hard water. The coatings can be directly formed on some metals (e.g. aluminum) or by application of coating materials (e.g. sol-gel alumina based Boehmite) followed by appropriate chemical functionalization and addition of immiscible lubricant. In certain embodiments, the lubricating fluid/appropriately functionalized surface combinations can be used as anti-corrosive protecting coatings for metal and metalized surfaces designed to resist the corrosion-inducing environments, both liquid (fresh, salt and sea water, highly corrosive chemical and waste streams) and otherwise (exposure to aggressive vapors, aerosols and mist through evaporation or convection).

[0221] FIG. 19 illustrates the time lapse of untreated Al (left) and SLIPS-coated Al (right) immersed in 1 M KOH solution at room temperature showing rapid degradation of untreated aluminum while coated Al essentially remains unchanged.

Example 7

SLIPS Surfaces for Fluid Collection

[0222] Efficient collection of water condensate can be important for a number of industrial applications, such as heat transfer and dew collection. SLIPS surfaces have a very high mobility for even small water droplets, also cause a very rapid condensation of small water droplets from the vapor phase.

Water droplets on conventional, hydrophobic surfaces have a contact angle $>60^\circ$, and are not highly mobile. The edges of the droplet are pinned such that a reasonably high tilt angle of the substrate is required to move a droplet of some given size. Conversely, for a vertically-oriented surface, a droplet must achieve a critical volume before becoming mobile (V_{crit}). FIG. 20 (top) shows the steps involved in the nucleation, coalescence and sliding of water droplets on a conventional hydrophobic surface. The V_{crit} for SLIP surfaces is much lower than for conventional hydrophobic surfaces (FIG. 20B, bottom). Therefore, water droplets coalesce and slide much more readily than on a conventional surface, and the efficiency and rate of condensation collection is much higher. In addition, the condensed droplets on SLIPS tend to suddenly run quickly due to the large energy gain from coalescence events which would have been used by friction on other surfaces hence facilitating the growth of droplets very rapidly by picking up more droplets. This process promotes the collection of condensed moisture on SLIPS coated surfaces before they go back to atmosphere by evaporation.

[0223] The biggest disadvantage of spin coating is the lack of material efficiency. Only 2-5% of total dispensed materials are used while the rest goes to the surface of coating bowl and disposed. Not only the cost of the material itself (e.g. photoresist used in semiconductor industry) is gradually increasing but also the cost for properly disposing of these materials are increasing. The materials used as the body of spin coaters are generally metals or plastics that can be easily coated with SLIPS, such as boehmite coating. This specific application does not require optical clarity nor mechanical durability. A possible product is in the form of either SLIPS-coated spin coater or SLIPS-coated liners/sleeves that the users can attach and replace when needed. The collected materials should be able to be reused and to reduce the cost of production of semiconductor devices.

Example 8

SLIPS Surfaces for Anti-Graffiti

[0224] A surface was partly treated with SLIPS and adherence of paint and stickers were tested. As shown in FIG. 21, SLIPS treated surfaces were highly resistant to spray paint as whereas surfaces that were not treated with SLIPS were not able to repel the spray paint. As shown in FIG. 22, SLIPS treated surfaces were highly resistant to stickers where the stickers were extremely easy to remove and left no residue. In contrast, the stickers adhered strongly to surfaces that were not treated with SLIPS and left residue when removed. Hence, SLIPS surface can be utilized as anti-graffiti signs.

Example 9

SLIPS Assembled by Layer-by-Layer Deposition Process

[0225] In this example, a layer-by-layer process to alternately assemble positively charged polyelectrolytes and negatively charged silica nanoparticles onto a given substrate is utilized. Surface modification of the particles by silane chemistry and infusion of a lubricant with matching chemical composition creates a stable substrate/lubricant interface that repels any immiscible second liquid. The coating protocol uses adsorption from aqueous solutions and is thus environmentally benign and can be applied to arbitrary surfaces,

given that they can be brought in contact with water. The process is completely scalable and can be readily automated.

[0226] FIG. 23A schematically shows the fabrication of the surface coating. Negative charges are introduced to the substrate (i) and subsequent layers of positively charged polyelectrolyte (ii) and negative charged silica nanoparticles (iii) are adsorbed to form a hybrid thin film (iv) that can but not necessarily has to be calcined to produce a porous silica coating (v). After fluorosilanization (vi), a fluorinated lubricant is wicked into the coating (vii) and will not be displaced by a second, immiscible liquid that slides off the substrate with ease (viii).

[0227] In certain embodiments, negative charges are created on the substrate by plasma treatment, UV-ozone or immersion in base piranha. The substrate is subsequently immersed into a solution of positively charged polyelectrolyte (poly-diallyldimethyl ammonium chloride, PDAD-MAC), rinsed and immersed into a solution of negatively charged LudoxTM silica nanoparticles. Electrostatic attraction leads to the formation of a fuzzy, disordered film of polymer and nanoparticles. The assembled hybrid film is calcined or plasma treated to remove the polymer and leave a disordered, porous silica nanoparticle assembly on the substrate, the surface of which is subsequently silanized with 1H,1H,2H,2H-(tridecafluorooctyl)-trichlorosilane to introduce fluorinated surface functionalities. A fluorinated lubricant oil (DuPont KrytoxTM 100), matching the surface chemistry of the coating, is infiltrated into the porous structure. The matching surface chemistry between surface structures and lubricant creates a strong affinity and leads to a minimization of the total surface energy for a solid/lubricant/liquid system in which a second, immiscible liquid is not in contact with the solid substrate. If this criterion is fulfilled, the lubricant layer will not be displaced by other liquids and thus enable a highly efficient repellency of various, immiscible liquids by elimination of pinning points.

[0228] Any other combination of surface chemistry and lubrication can be used as well; including but not limited to alkyl-silanes with hydrocarbon oils, olive oil, sunflower oil, etc.; pegylated or hydrophilic silanes with water or ethylene glycol, and the like.

[0229] SEM images of the silica nanoparticle coating prepared with different deposition cycles taken after calcination are shown in FIG. 23B. An increase in particle number and film density with increasing deposition cycles is visible. Quartz Crystal Microbalance (QCM) measurements further show evidence of a constant addition of silica nanoparticles with each deposition cycle after the first two cycles (FIGS. 24A and 24B). This allows for a precise adjustment of the total roughness and thickness of the coating. UV-Vis-NIR transmittance measurements of the lubricated substrates show an increase in light transmittance throughout the visible spectrum compared to a reference glass slide for all coated substrates (FIG. 24C). A slight increase in transmittance with increasing number of layers is detected which is attributed to an increase in surface roughness leading to a more diffuse interface that reduces the reflection of light.

[0230] The repellent properties of the coatings with varying numbers of deposited layers were quantified by contact angle and sliding angle measurements using water and octane as test liquids. With increasing layer thickness, the static water contact angle after fluorosilanization steadily increased and leveled at 120° for 4 or more deposition cycles, indicating a complete coverage of the surface with silica nanoparticles.

Thus, the dry coating does not possess superhydrophobic properties due to the extremely small size of the silica nanoparticles and the absence of hierarchical superstructures. As a consequence, a droplet of water placed on a coated surface experiences strong pinning and slides only after tilting to very high substrate angles (FIG. 25A, light gray columns). Similarly, an octane droplet is pinned but, due to its lower surface tension it starts moving at approximately 350 (FIG. 25B). However, it leaves a stained surface behind. The addition of lubricant has strong effects on the repellency properties. The absence of pinning points for the liquid residing on top of the lubricant layer leads to highly efficient repellency with extremely low contact angle hysteresis and sliding angles of approximately 2° for both water and octane (FIGS. 25A-25B). FIGS. 25C and 25D exemplarily show the highly efficient removal of a droplet of water and octane on a lubricated substrate tilted at an angle of 2° coated with 5 layers of silica nanoparticles. Effective liquid repellency, characterized by a sliding angle dropping below 5° is achieved for coatings with at least 3 (octane) or 4 layers (water) (FIGS. 25A-25B). The low sliding angle, hinting at the absence of pinning points, indicates that the surface roughness in coatings from 3 or more deposition cycles is sufficient to enable stable repellency as the lubricant film is not displaced by the liquid to be repelled.

[0231] The solution-based assembly method allows for the coating of arbitrarily shaped surfaces. In FIGS. 26A-26D, time-lapsed images that demonstrate the efficient repellency of honey from the inside of a coated glass vial (FIG. 26A, lower row) and of crude oil from the inside of a glass tube (FIG. 26B, lower row) are shown, visualized by clear sliding of the fluid without getting stuck to the surface. Honey and crude oil were chosen as examples of extremely sticky complex fluids that cannot be removed from uncoated surfaces (FIGS. 26A-26B, upper row). Similarly, other complex fluids (PMMA solution in dimethylformamide, mustard) are easily repelled from arbitrarily-shaped glass objects such as chemical flasks and highly curved test-tube surfaces. The layer-by-layer deposition process can be applied to a large variety of substrate materials. The only requirement for the process is the possibility to create charges on the substrate surface, which can be achieved by a variety of methods, including treating the substrates with oxygen plasma, UV-ozone, acid or base piranha or a corona discharger. The treatment time can be chosen to be short enough not to degrade the substrate material since a very short exposure is sufficient to create a charged interface. FIGS. 26C and 26D exemplarily demonstrate the successful assembly of the omniphobic, highly repellent layer-by-layer silica nanoparticle coating on a metal (stainless steel) and a polymer substrate (poly methyl-methacrylate) by showing the sliding of a stained octane droplet under an angle of 15° without leaving traces on the surface. Untreated substrates were completely stained by the same treatment (FIGS. 26C and 26D, upper row). Further examples of successfully coated surfaces, include aluminum, poly propylene and polysulfone.

[0232] Table 3 quantifies the wetting behavior of all tested substrates by comparing the sliding angles of water and octane for uncoated samples, fluorosilanized layer-by-layer silica nanoparticle coatings and the same coatings after addition of lubricant. All uncoated samples failed to remove water as the droplets remained pinned even after tilting the substrate to 90° and were wetted and stained by octane. The introduction of the surface coating changed the wetting properties

consistently for all samples but showed high contact angle hysteresis and sliding angles for both liquids. The presence of octane stains on the surfaces indicated the failure of the dry coating in repelling the liquid. All coated, lubricated samples showed extremely small sliding angles, contact angle hysteresis and absence of staining, thus demonstrating the highly efficient repellency of water and octane as an example of a low surface tension liquid.

TABLE 3

Sliding angles of octane and water on different substrates coated with a layer-by-layer silica nanoparticles coating (7 deposited layers).						
Substrate Material	Water sliding angle/°			Octane sliding angle/°		
	Un-coated	Dry coating	Lubricated coating	Un-coated	Dry coating*	Lubricated coating**
Glass	56 ± 8	66 ± 5	2 ± 1	16 ± 3	31 ± 3	2 ± 1
Aluminum	pinned	63 ± 4	2 ± 1	wetted	51 ± 13	2 ± 1
Stainless Steel	pinned	85 ± 5	1 ± 1	wetted	49 ± 7	1 ± 1
PMMA	pinned	pinned	2 ± 1	wetted	46 ± 5	2 ± 1
PP	pinned	pinned	1 ± 1	wetted	48 ± 6	2 ± 1
PSu	pinned	pinned	2 ± 1	wetted	44 ± 5	2 ± 1

*octane droplet left stains on the surface after sliding

**no contamination of the surface after sliding

[0233] In conclusion, a simple coating to introduce efficient liquid repellency has been demonstrated to a wide variety of materials with completely arbitrary shapes. The surface structure is prepared by a layer-by-layer deposition of positively charged polyelectrolytes and negatively charged silica nanoparticles. After fluorosilanization of the silica nanoparticles, a fluorinated lubricant is infiltrated into the porous coating and firmly held in place by matching surface chemistry. The strong affinity of the lubricant to the substrate prevents a second liquid from getting into contact with the substrate and resides on top of the lubricant layer, whose fluid nature gives rise to an extremely smooth interface without pinning points. Therefore, the liquid slides off the substrate with ease. The small size of the silica nanoparticles applied in the process does not interfere with light of visible wavelengths and, thus, gives rise to a completely transparent coating. Successful repellency of water, octane as a low surface tension liquid and various complex fluids on a variety of arbitrarily shaped ceramic, metal and polymer surfaces has been demonstrated. The deposition process is conceptually simple, of low cost, based on aqueous solvents and thus environmentally benign, completely scalable and readily automatable. The presented method thus combines all the remarkable properties of previously reported liquid infused coatings with an unprecedented degree of simplicity and versatility with respect to accessible substrate materials, shapes and sizes.

Example 10

SLIPS Assembled by Layer-by-Layer Deposition Process Over PDMS Substrate

[0234] PDMS is a material widely used in medical equipment, for example in catheters. Also, it is the material of choice for microfluidic technologies. Therefore, repellent coatings on PDMS are of relevance. A layer-by-layer adsorption process was applied on PDMS that was oxygen plasma treated for 1 minute to induce negative surface charges. The

layer-by-layer assembly technique shown in FIG. 23A was utilized to form SLIPS surfaces.

[0235] Contact angle hysteresis and sliding angle (20 μ l) measurements of water and hexadecane confirm the presence of a repellent coating, as shown in FIGS. 27A-27D.

[0236] In addition, the effect of strain (0% to 20%) on the retention of the slippery nature of layer-by-layer coated, lubricant infiltrated PDMS with 0 layers (reference, top) and 9 layers (bottom) are compared in FIG. 28. As shown, the slippery properties are retained with significant amounts of strain.

Example 11

SLIPS from Sol-Gel Derived Nanoporous Boehmite Nanofiber Paper

[0237] Another potential class of SLIPS substrate is based on free-standing nanoporous films/membranes using high-aspect-ratio boehmite nanofibers. High-aspect-ratio boehmite nanofibers can be prepared using a solvothermal synthesis.

[0238] FIGS. 29A-29D show SEM images of such a porous “paper” produced from boehmite nanofibers. As shown, the boehmite nanofibers tend to align.

Example 12

Free Standing Boehmite Films

[0239] In an experiment similar to Example 11, 6.8 g of aluminum isopropoxide (precursor) is added dropwise to 60 mL of water heated to 75° C. to maximize the hydrolysis of the precursor. If precursor is added too fast there is potential for premature self-condensation of the particles resulting in the formation of agglomerated chunks rather than fibers. Once the entire precursor is added, the solution is heated to 90° C. to allow the vaporization of isopropyl alcohol (byproduct of the reaction). The hot solution is then transferred to a Teflon-lined stainless steel pressure vessel and 0.61 g of glacial acetic acid is slowly added to the solution with stirring to lower the pH to ~3. The acetic acid increases the rate of hydrolysis of the precursor in addition to promoting unidirectional growth of boehmite along one plane of the particles. The autoclave is heated to 150° C. for 6-24 h. The time of the reaction directly correlates to the length of the nanofibers obtained, longer reaction time results in longer nanofibers. TEM characterization was performed on a drop cast sample of the resultant solution to determine the aspect ratio of nanofibers.

[0240] The resulting solution from the reaction is diluted to approximately 2.8 wt. % nanofibers and 1 wt. % polyvinyl alcohol (3000-4000 MW) is added. The mixture is sonicated for 30 min and the resulting solution is degassed under vacuum. The solution is cast in a Teflon-lined dish and slowly dried in an oven at 40° C. for 48-72 h. The resulting free-standing boehmite nanofiber film can be gently peeled off of the dish. FIG. 29E shows a TEM image of individual solvothermal boehmite nanofibers with some agglomerated particles. FIG. 29F shows SEM image of bundled boehmite nanofibers drop cast on a copper conductive tape.

[0241] The film thickness can be adjusted by modifying the concentration of boehmite nanofibers and polyvinyl alcohol.

[0242] Modification of the standard SLIPS procedure via alumina sol-gel route can be successfully altered to produce comparable surfaces with a greater range of application methods.

Example 13

Carbon Nanofiber—Epoxy Surfaces for SLIPS Applications

[0243] Epoxy EPON 862 and curing agent EPIKURE W were purchased from Miller-Stephenson, carbon nanofibers, graphitized (iron-free) were purchased from Sigma-Aldrich, and acetone was purchased from Sigma-Aldrich.

[0244] The epoxy-based carbon nanotube composites were fabricated by immersing the MW-CNT fibers into an acetone for 30 min in ultrasonic bath, then solution of Epon 862 epoxy was added to the mixture CNT/Acetone. Acetone reduces viscosity of the epoxy making it possible to better dispersion of CNTs. Solution of CNT-Acetone/Epon 862 was gradually heated to 70° C. under vigorous stirring to remove residue of acetone, then Epikure curing agent W was added in the ratio of 100:25 to the Epon 862 and stirred for additional 30 min. Degassing is performed under vacuum to remove the bubbles generated during mixing. Samples were cured in vacuum oven at 70° C. for 48 h. Plasma etching was used to etch epoxy matrix.

[0245] FIGS. 30A and 30B show a (A) top view and (B) cross section HR-SEM images of multi wall carbon nanotubes dispersed in epoxy resin matrix prior plasma etching. Scale bars are 200 nm. Samples were sputtered with 3 nm Pt/Pd alloy prior to image acquisition.

Example 14

Superhydrophobic Alumina Nanoparticles and their Nanocomposites

[0246] Nanoporous surfaces for fabricating SLIPS can be prepared using materials with inherently robust mechanical properties. FIG. 31A shows an exemplary method to generate surface functionalized alumina nanoparticles (AlNPs) for use as filler material in nanocomposites, so that hydrophobicity is achieved that is sufficient for forming robust SLIPS.

[0247] As shown in FIG. 31A, AlNPs naturally have a native oxide layer which is neutral. However, for surface modification using compounds such as organophosphonic acids and organophosphate esters, high density of surface hydroxyl groups is required. As shown in Step 1 of FIG. 31A, this is achieved by applying Fenton chemistry (Iron catalyzed mild piranha solution) with stirring in a 4:1 ratio of H₂SO₄ (0.1 M): H₂O₂ (30%) for extended periods of time.

[0248] FIG. 31B shows the normalized FTIR absorbance spectra of O—H stretching mode recorded from AlNPs taken at different treatment times with Fenton chemistry. The ‘X’ indicates no modification and ‘XOH’ indicates surface modification using O₂ plasma treatment.

[0249] Next, as shown in Step 2 of FIG. 31A, the hydroxylated AlNPs are charged into FS100 solution with zirconia grinding dispersion media and rotated on a ball mill. This maximizes de-agglomeration and surface modification of the particles. Post modification, the AlNPs are retrieved by centrifugation and are rinsed with ethanol at least three times to remove any excess surfactant. Excess solvent is evaporated from the particles at 70° C. and in the presence of vacuum.

[0250] Surface functionalized AINPs can now be re-dispersed in compatible solvents such as hydrofluoroether (HFE) or 2,2,2-trifluoroethanol (TFE). The resulting dispersions can be used to cast films onto oxygen plasma treated glass substrates and the solvent is evaporated at elevated temperatures. To permanently bind particles to substrates, 1) the particle can be modified with mixed ligands (e.g. fluorinated and acrylate), 2) epoxy, polyurethane or a similar binding agent is used. To decrease the viscosity of the epoxy resin, acetone is added in 5:1 w/w ratio and the resulting solution is sonicated until it forms a homogeneous mixture. The curing agent is then added in a 4:1 w/w ratio and is sonicated for 30 min. The functionalized AINPs are then uniformly coated over the epoxy and placed at 70° C. in an oven for 48 h to fully cure the epoxy resin. Initial qualitative observations showed resulting surface to be superhydrophobic to support SLIPS and much more mechanically robust than compared to conventional alumina sol-gel coating. On the other hand the AINPs can be used as a filler material in a curable nanocomposite with varying volume fractions and subsequently be applied to surfaces to form nanoporous films to support SLIPS.

[0251] Functionalized AINPs in epoxy composite provide an alternative to alumina sol-gel coated substrates with increased mechanical properties.

Example 15

Fabrics Coated with Lubricated Nanostructures Displaying Robust Omniphobicity

[0252] The development of a stain-resistant and pressure-stable textile is desirable for consumer and industrial applications alike, yet it remains a challenge that current technologies have been unable to fully address. Herein the rational design and optimization of nanostructured lubricant-infused fabrics are presented. The improved fabrics demonstrate markedly improved performance over traditional superhydrophobic (TSH) textile treatments: SLIPS-functionalized cotton and polyester fabrics exhibit decreased contact angle hysteresis and sliding angles, omnirepellent properties against various fluids including polar and nonpolar liquids, pressure tolerance and mechanical robustness, all of which are not readily achievable with the state-of-the-art superhydrophobic coatings.

[0253] As shown in FIG. 32, two methods were developed to create nanoscale surface roughness: I) coating the textile fibers with silica micro-particles (SiM), and II) boehmite nanostructure formation on the textile fibers from sol-gel alumina treatment (SgB). As shown, a single, bare fiber being functionalized with SLIPS is depicted in a schematic (A-D). A bare fiber (A) is roughened with the silica micro-particle (SiM) or sol-gel boehmite (SgB) approach (B) and fluorinated to achieve chemical similarity to (perfluoroether) polymer Krytox (C) before the lubricating film is applied (D). This confers pressure-tolerant, self-healing repellency against a broad range of fluids. The flow chart (E) contains more specific information regarding the SiM and SgB functionalization protocols applied to cotton and polyester fabrics. Upon fluorination and subsequent infiltration with the lubricant, SLIPS-fabric can be produced from either approach.

[0254] The two surface modification methods were applied to seven different types of fabric samples—two cotton and five polyester (PE)—and the nonwetting performance was evaluated by quantifying static contact angle, contact angle

hysteresis, liquid repellency after mechanical stress, pressure tolerance, and breathability. The characterization herein provides strong evidence that SLIPS-fabrics exhibit unique combination of liquid repellency, durability, and pressure-tolerance that are difficult to achieve based on state-of-the-art traditional superhydrophobic materials.

[0255] The Dense polyester was purchased from Sew-Lew Fabrics, Cambridge, Mass., the microfiber polyester was purchased from MicroFibres, Inc. and the Nike polyester was cut from Nike Dri-Fit 100% polyester running shorts purchased from City Sports, Cambridge, Mass. The rest of the fabrics were purchased from nearby fabric stores, including Sew-Lew in Cambridge, Mass. and Winmill Fabrics in Boston, Mass. With regard to terminology, “fibers” are twisted together to make “threads”, which are in turn woven to make the fabric. The polyester fabrics were treated before silica micro-bead deposition. Amines readily react with polyester by nucleophilic acyl cleavage of the ester linkages for surface activation. Five to eight 2×2 cm squares of polyester were first cleaned with DI water, ethanol, and then hexane. Fabrics were dried for at least 1 h at 70° C. and further dried with a heat gun before adding to a 1% solution of aminopropyltriethoxysilane (APTES, Sigma Aldrich) in anhydrous toluene (Sigma Aldrich) and stirring for 24 h at 65° C. under dry nitrogen. Samples were then removed, rinsed with toluene several times, and dried under vacuum. Dried samples were submerged in deionized water overnight, removed, rinsed with water, and dried for at least 3 h under vacuum before immersing in a 1% tetraethyl orthosilicate (TEOS) solution in water for 4-8 h. Samples were rinsed with water and dried overnight before silica particle deposition.

[0256] In-situ polymerization of silica-microparticles onto cotton or activated polyester was performed to obtain a roughened substrate for SLIPS. Jersey cotton and Muslin were cleaned with water, ethanol, and isopropyl alcohol prior to reaction. The prepared samples were submerged into a 1:3 mixture of methanol and isopropanol, 20 mL ammonium hydroxide (Sigma Aldrich, St. Louis Mo.), and 12 mL TEOS (Sigma Aldrich, St. Louis Mo.). All solvents and chemicals were used without further modification. The mixture was stirred for 6 h at room temperature, and the samples were isolated and rinsed extensively with toluene several times. Dried fabrics were blown with compressed air to remove any residual detached particles that were not firmly attached to the fabric fibers. Subsequent fluorosilanization renders the fabric surface superhydrophobic.

[0257] The roughened silica-bead surface was fluorosilanized either with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (Sigma-Aldrich) or perfluorododecyl-1H,1H,2H,2H-triethoxysilane (Gelest). A solution of 4.8% silane stock and >99.7% acetic acid were mixed in equal parts in 200 proof ethanol (i.e., in a 1:1:19 ratio of the above ingredients). After this, mixture was stirred for 60 min (to allow sufficient oligomerization), the fabrics were dipped into the mixture for 2-4 min and allowed to hang dry. The silane chains attach to the surface of the silica coating of the fabric and render the rough surface superhydrophobic. Silica-microparticle (SiM) deposition is an effective method used to confer microscale surface roughness on cotton fabrics. FIG. 33 summarizes the steps for this scalable process. Fewer steps may be needed to achieve the desired surface treatment for chemically reactive, hydroxyl-rich cotton fabrics. To induce covalent adherence of silica particles to more inert polyesters, a two-step surface activation process was utilized whereby polyester cleavage

using (3-aminopropyl)triethoxysilane (APTES) and subsequent reaction with TEOS created silica-like surface functionalities. Chemical composition of each fabric surface was confirmed using FTIR. Once silica-like surface chemistry was achieved, uniform particles were synthesized within all fabric samples to ultimately form a rough, nanostructured surface. Lastly, fabrics were dipped into an perfluoroalkylsilane/ethanol solution to render the rough surface superhydrophobic, thus completing the SiM functionalization.

[0258] All cotton and polyester samples were oxygen plasma cleaned for 300 s (250 watts, oxygen flow of 15 cm³/min). Cleaned samples were dipped in alumina sol-gel pre-cursor. After 10 min, the fabric was removed and dried overnight at 70° C. Dried samples were immersed in a 95° C. water bath for 15 min to create boehmite nanostructures, removed, dried, and then submerged in a 1% solution of FS-100, a perfluoroalkyl phosphate surfactant (Mason Chemical Company), in ethanol (Chemguard Inc., Mansfield, Tex., USA) for 1 h at 70° C. Samples were rinsed with ethanol and dried overnight before performing the contact angle and SEM analyses. Boehmite, formed in a reaction between aluminum and 80-100° C. water, is a dense network of nano-scale AlO(OH) crossed leaflets that can be fluorinated to become an effective superhydrophobic surface. The sol-gel approach schematically shown in FIG. 33 was utilized to coat fabrics with boehmite nanostructures.

[0259] The surface of SgB or SiM functionalized samples has a strong affinity to fluorinated oils. To avoid excessive lubrication, perfluoropolyether lubricant Krytox™ (Dupont Inc.) was applied to wick through the sample and the excess was removed by contacting the surface of the sample with a Kimwipe. About 30-100 μL of oil infused 4 cm² of the material, depending on the fabric thickness.

[0260] SEM characterization was performed with a Zeiss Supra field emission microscope. Samples were coated by Pt—Pd sputtering for 60-150 s prior to SEM characterization.

[0261] Contact angles were recoded using a contact angle goniometer (CAM 101, KSV Instruments, resolution=0.01°) at room temperature. 10 μL droplets of DI water were used for all static contact angle measurements. Contact angle hysteresis (CAH) values were obtained by slowly increasing and decreasing droplet volume using a syringe needle while imaging the droplet movement, measuring advancing and receding contact angles, respectively, from these images, and subtracting the averages of these values. At least seven independent measurements were taken for static, advancing, and receding contact angles.

[0262] For a twisting test, a 2×3 cm SiM or SgB fabric sample was secured between two medium sized clamp-type paper clips, and the assembly was hung by affixing one of the clips to a hook. By rotating the unbound lower clip, the fabrics were twisted ±360°; the first twist was defined as a 360° rotation clockwise followed by a return to rest position, the second twist was 360° counterclockwise followed by a return to rest position, and so on. After the specified number of twists (0, 5, or 50), the sliding angle of a 20 μL droplet of DI water was measured at least 3 times. The sliding angle is the tilting angle at which the droplet begins to slide along the surface without pinning. The sliding angle data and the SEM characterization provide a complete picture of the performance deterioration resulting from the twisting test.

[0263] A SgB or SiM fabric sample was secured to a surface with tape and vigorously rubbed with a rolled up Kimwipe for approximately 10 s. This is a preliminary abrasion

test that simulates a contact with other fabrics or the surrounding environment. Damage was qualitatively observed by testing the repellency of water before and after rubbing, and SEM characterization showed the physical damage occurring to the nanostructure.

[0264] The American Association of Textile Chemists and Colorists (AATCC) test #193 was used to analyze the repellency of non-lubricated (TSH) and lubricated (SLIPS) fabric samples to low surface-tension aqueous test liquids. Eight test liquids, composed of different volume fractions of IPA in de-ionized water, were prepared. Beginning with the highest surface tension liquid, a test droplet was applied to the surface of the fabric sample and allowed to sit for 30 s. The droplet was then observed to assess the wetting of the fabric: if the fabric is not wetted, then the process is repeated for the next test liquid, and if the surface is wetted then the fabric receives a score corresponding to the previously applied test liquid (i.e., the lowest surface tension liquid repelled by the fabric). If the test liquid only slightly wets the surface, the fabric is assigned a non-integer score halfway between the previous and current test liquid. A maximum score of 8 may be achieved, if the sample is not wetted by any of the test liquids.

[0265] The AATCC test #188 was used to test repellency against alkanes of decreasing surface tension to characterize the repellency of oils and other nonpolar liquids. This test is very similar to the aqueous liquid repellency test: the droplets were placed on TSH and SLIPS samples for 10 s before the wetting behavior was observed. Again, the lowest surface tension liquid that does not wet the surface of the liquid determines the score. Non-integer scores may be assigned, if only partial wetting occurs, and a maximum score of 8 is achieved when even test liquid 8, the lowest surface tension liquid in the test, does not wet the surface of the fabric.

[0266] The tolerance of fabric samples to pressurized liquids of high and low surface tension was measured with the droplet impact test. A pipette was fixed 20.3±0.5 cm above a fabric sample immobilized on a tilting stage with double-sided tape. A 10 μL test droplet was carefully ejected from the pipette and impacted the surface of the fabric at a controlled velocity, and the sliding angle of the droplet was measured immediately after impact. The dynamic pressure was estimated by $P_{dynamic} = \frac{1}{2}\rho V^2$, where ρ is the density of the liquid and V is the impacting velocity. The impact velocity was estimated using kinematic equations, and thus the tetradecane droplet exerts a dynamic pressure of ~1520 Pa and the water droplet exerts a dynamic pressure of ~1990 Pa. Irreversible pinning occurs for the superhydrophobic samples and cannot be recorded; the most important information comes from whether the droplet slides or does not slide.

[0267] The breathability test was adapted from the standard ASTM E96-E upright cup water vapor transmission test. Each fabric sample was tested by a single 3D printed capsule; the inside of the capsule was dried by 20 g of Drierite desiccant (Drierite, Inc., Xenia Ohio) and separated from the moist air outside of the capsule by the fabric sample that was sealed onto the capsule by a ring-shaped cap clamped in place. In between repeated experiments, the desiccant was regenerated by placing into a vacuum oven at ~150° C. overnight. The external environment of the chambers was carefully controlled in a custom made environmental chamber maintained at 50% relative humidity and 23±1° C. Minimal airflow in the chamber prevented temperature gradients and inconsistencies. The water vapor was pulled into the chamber through the sample by the humidity gradient. After initial weighing, the

test capsules were removed from the environmental chamber and weighed after 1, 2, 3, 4, 5, 6, 8, 22, 24 h, and the mass increase of each chamber was plotted (FIGS. 6 and 7). To confirm the omniphobicity, sliding angles of hexadecane and/or de-ionized water droplets on lubricated samples were recorded. The mass of the lubricated membranes (and thus the mass of the lubricant) before and after 24 h was also recorded. A typical experiment included up to 9 capsules running simultaneously. In each experiment, two controls were always present to ensure consistency in conditions between experiments: an open chamber without a membrane and a chamber sealed by Parafilm, which is impermeable to water vapor (Pechiney Plastic Company, Chicago, Ill.). Lubricated and untreated samples were tested against each other to observe the effect of SLIPS on the breathability of the fabric. Each sample was tested a minimum of three times, either with three separate samples in a single experiment or with one sample across three separate experiments.

[0268] Fabrics introduce unique physical features (hierarchical feature sizes coming from fiber-thread-weave length scales), logistical considerations (cost, complexity of procedure), and demanding applications (requiring durability, breathability, etc.) into the design space of the final material. Cotton and polyester (PE) are inexpensive, readily available, widely used, and environmentally friendly. The weave of the fabric is an important parameter since it inherently has a much more complex topography than a simple, flat surface. There are textiles available of myriad thread sizes, weave densities, and weave patterns; the effect of these parameters on the quality of the SLIPS coating is unknown and needs to be investigated.

[0269] A very common weave pattern is a basic, square-type weave. Since this is a relatively simple system, a number of different square-weave fabrics were selected—Dense PE, Nike PE, Crepe PE, and Muslin Cotton (M. Cotton)—with weave densities ranging from very high (tightly woven) to very low (loosely woven with larger spaces present) to investigate the role of this parameter in developing effective omniphobic SLIPS-fabrics. Three fabrics of different weave patterns were also tested, including the randomly oriented microfiber (μ fiber) threads, the V-shaped weave of Gavadeen PE (Gay), and the column-based weave of the Jersey Cotton (J. Cotton) (see FIG. 33). As shown in FIG. 33, the square-weave fabrics are arranged along the top row (A-D) in order of decreasing weave density, and the fabrics of other weaves are arranged along the bottom row (E-G). The two cotton fabrics are on the right edge of the figure (D, G). Dense Polyester (PE) (A) showcases a tight, squaretype weave with threads $\sim 150\ \mu\text{m}$ across, resulting in a virtually flat surface free of loose fibers. Nike PE (B) exhibits a looser square-type weave and is comprised of threads $\sim 200\ \mu\text{m}$ across. Crepe PE (C) is the most loosely woven square-type PE fabric, with fibers $\sim 300\ \mu\text{m}$ across. Muslin Cotton (D) is the least densely woven square-type fabric, with vertically oriented threads $\sim 350\ \mu\text{m}$ in diameter, horizontally oriented threads $\sim 250\ \mu\text{m}$ in diameter, and large gaps in between thread intersections. Note the presence of loose threads on this sample. Gavadeen PE (E) displays a V-type weave comprised of threads $\sim 300\ \mu\text{m}$ across; the vertically aligned fibers in the image are comprised of smaller fibers while the horizontally aligned threads are comprised of larger fibers, resulting in a diagonally ridged structure. μ fiber (F) has small fibers $\sim 5\ \mu\text{m}$ in diameter that create a disordered, “hairy” structure. Jersey Cotton (G) con-

sists of an entangled weave of sparsely woven threads $\sim 200\ \mu\text{m}$ across; many loose threads are present.

[0270] SiM and SgB treatment and surface fluorination according to the procedure outlined in FIG. 32, resulted in fabrics uniformly covered with silica micro-particles (~ 150 - $500\ \text{nm}$ in diameter) or boehmite nanoflakes, respectively. As shown in FIG. 34, a scanning electron microscope was used to evaluate the surface roughness and durability of the sol-gel boehmite (SgB) (A-D) and silica microparticle (SiM) (E-H) treatments on Nike polyester fabric. All scale bars are $2\ \mu\text{m}$. Freshly treated SgB fibers (A) show full coverage of the fiber with SgB; dramatic microbead coverage is apparent on freshly treated SiM fibers (E). High magnification of the microstructures (B, F) reveals the surface roughness that facilitates good SLIPS performance. When twisted 50 times, smoother boehmite is still present (C) in crevices between fibers, while the outside of the fibers have become smooth. Also after 50 twists, the SiM threads (G) exhibit some cracking while maintaining good microparticle coverage. After vigorous rubbing with a Kimwipe, SgB fabric (D) exhibits cracking and smoothness on the outer fibers, while under the same conditions the SiM coating remains intact (H).

[0271] Droplets bounce off the surface of these fabrics and static contact angles characteristic of superhydrophobic surfaces ($>150^\circ$) were observed (see FIG. 35A). SiM- and SgB-treated fabrics were then infused with a perfluoropolyether lubricant (KrytoxTM, DuPont) that remains stably anchored in the textured substrate. These SLIPS-fabrics show an unprecedented ability to repel a wide range of fluids and to be resistant to staining. To determine the optimal SLIPS fabric parameters, the static contact angle, contact angle hysteresis, pressure resistance, durability, and breathability were investigated. Three phases of testing on a successively smaller set of samples were investigated as shown in the Table 4 below.

TABLE 4

Fabric Name	Abbre- viation	Phase I		Phase II		Phase III	
		SgB	SiM	SgB	SiM	SgB	SiM
Muslin Cotton	M. Cotton	*	*	*	*		*
Jersey Cotton	J. Cotton	*	*	*			
Dense Polyester	Dense PE	*	*		*		*
Nike Polyester	Nike PE	*	*	*	*		*
Microfiber	μ fiber	*	*		*		*
Polyester							
Gavadeen	Gav.	*	*	*			
Polyester							
Crepe Polyester	Crepe	*	*	*			

[0272] To begin Phase I characterization, the static contact angle were measured on all fabrics to quantify the hydrophobicity of non-lubricated (TSH) and lubricated (SLIPS) samples. Fabric samples, both un-lubricated and lubricated with Krytox 102 (K102), were functionalized with either silica microbeads (SiM) or sol-gel boehmite (SgB). Contact angles were measured using a contact angle goniometer. As shown in FIG. 35A, a $10\ \mu\text{L}$ water droplet was placed onto the surface of the fabric sample for measurement. FIG. 35B shows the advancing and receding contact angles that were recorded and these values were subtracted to determine the hysteresis. $N=7$; error bars are $\pm$ SD. Asterisks denote statistically significant results (Student's two-tailed t-test, $P<0.05$); comparisons are only made between SiM+K102 and SgB+K102 for each fabric sample. As shown, each non-lubricated sample has a static contact angle in the range of

150-160°, and when the Krytox lubricating film is applied this angle decreases to approximately 110-120°. To quantify the repellency of the fabrics, the contact angle hysteresis (CAH), which is the difference between advancing and receding contact angles as a droplet slides on a surface and directly relates to droplet mobility on a surface, was measured. Low CAH was observed on almost all SLIPS fabric samples. FIG. 35B shows all CAH data for the 14 fabric samples. In the case of non-lubricated fabrics, there are multiple sources of pinning, including fibrillar protrusions, structural defects, and perhaps incomplete fluorination leaving hydrophilic areas on the surface. CAH values increase with increasing density of defects, or pinning points, on the surface of the material. Application of a lubricant dramatically reduces hysteresis for every fabric sample except for J. Cotton and Crepe PE—droplets easily slide over the smooth surface created by the lubricating film. In the case of Gavadeen PE treated with SiM-SLIPS, which has a static contact angle of $156.6^\circ \pm 3.1$ and a hysteresis value of $5.35^\circ \pm 0.31$, a combination of superhydrophobic and SLIPS-type performance was observed. It appears that the lubricant entrapped within and around each nanostructured thread prevents pinning even if the test liquid is partially exposed to the non-lubricated, superhydrophobic surface, a scenario suggested by a relatively high static contact angle and a relatively low hysteresis value. Thus, fabrics that combine slippery performance with both SLIPS and TSH attributes have been produced for excellent overall water repellency.

[0273] Reducing the sample pool with the selection criteria discussed earlier (Table 5), tests were carried to determine which treatment method—SgB or SiM—is more robust when subjected to rubbing and twisting, as observed by the effect of twisting on sliding angle and coating integrity as studied by SEM. These experiments simulate the expected wear that fabrics may experience in most functional applications.

[0274] The twist testing data are shown in FIG. 36. The fabric samples were twisted $\pm 360^\circ$ with a custom-made setup, and the sliding angle of water (20 μ L droplet volume) on a fabric sample lubricated with Krytox 102 was measured after 0, 5, and 50 twists. Sliding angles that exceeded 35° are indicated on FIG. 36 as being 35° with arrows (→) because of experimental constraints and the large variability associated with strong pinning behaviors. Notably, the test water droplet did not wet any of the fabric samples after twisting 50 times. Remarkably, even when pinning was observed, the colored test water droplets could be rinsed away without leaving a stain.

[0275] SgB Gav. and SgB M. Cotton were the worst performers in the twisting test: both fabrics failed to slide at 35° even before twisting, and it was qualitatively observed that droplet pinning worsens with further twisting. For those samples whose sliding angles remain less than 35° , a clear difference emerged between the SgB samples and the SiM samples: for the SgB-treated samples, there is a significant increase in the sliding angle for 0, 5, and 50 twists, while on the SiM treated samples there is either no significant increase, or an initial increase that stabilizes with additional twisting. The most telling result comes from comparing SgB Nike PE with the SiM variant: the SgB sample shows a clear, almost linear increase in the sliding angle with increased number of twists, while the SiM sample shows no significant change.

[0276] An increase in sliding angle indicates that damaged nanostructures give rise to a decreased affinity of the lubricant to the fiber surface either due to the loss of nanostructure or due to cracks exposing surfaces that are not fluorinated. SiM fabrics exhibit more durable nanostructures than SgB fabrics. SEM images of the Nike PE fabric treated with both SgB and SiM, before and after twisting, confirm this (see FIG. 34). The SiM layer on the Nike PE fabric showed only minimal damage after 50 twists, whereas the boehmite shows smoothening and flattening of its nanostructures. Self-healing behavior arises in SLIPS from a redistribution of the lubricant to cover moderate damage and to continue to provide omniphobicity. In this way, the liquid-repellent performance of SLIPS-fabrics is less susceptible to damage than that of TSH fabrics. The extensive damage of the SgB fabrics diminishes capillarity and therefore the lubricant's ability to redistribute. This effect is not seen on the more durable SiM treatment. SiM Nike PE maintained the same sliding angle throughout twisting and SgB Nike PE experienced a continuous increase in sliding angle as the nanostructures became critically damaged. Therefore, with respect to robustness, lubricated SiM-treated fabrics show best performance.

[0277] For additional durability characterization, non-lubricated fabric samples were vigorously rubbed with a Kimwipe, qualitatively observed the repellency, and characterized the surface with SEM (see FIG. 34). Though the ability to repel water appears to remain unaffected, SEM characterization reveals cracking damage on the SgB-treated fabrics and no damage to the SiM-treated fabric (see FIG. 34). Specifically, rubbing causes the alumina shell to crack and detach from the fiber surface, in a fashion similar to the twisting test. The adhesion of the sol-gel alumina to the fibers was not fully optimized yet to provide sufficiently strong damage tolerance against rubbing. In contrast, the silica microparticles that are covalently attached to the fabric surface show strong adherence between the silica shell and the fiber. Therefore SiM-treated SLIPS-fabrics maintain omniphobic performance even when subjected to abrasion. It was also observed that washing machine cycles have little effect on the integrity of the nanostructures. This further demonstrates that damage to the nanostructures can lead to premature loss of the lubricant and creation of new pinning points, reducing the functional lifetime of the fabric.

[0278] Given the results of the twisting and rubbing tests described above, SiM-treated fabrics were selected for Phase III testing. Specifically, M. Cotton, Dense PE, Nike PE, and μ fiber were selected to complete the characterization of the SLIPS fabrics and show the best overall performance. Water and hydrocarbon resistance testing was performed to observe the repellency of low-surface-tension fluids, and drop impact testing was performed to determine the pressure tolerance of the fabrics, and water vapor transmission testing was performed to characterize the fabric's breathability.

[0279] For each of the Phase III fabrics, a SLIPS (lubricated) sample was tested against a nonlubricated sample that serves as a representative TSH control. Liquid droplets of progressively lower surface tension (ranging from 72 mN/m for pure water to 24.0 mN/m for 60% isopropyl alcohol) were applied to fabric samples until the test droplet wets the surface. The scores for the four samples are shown in Table 5.

TABLE 5

Sample	AATCC 193 Aqueous Liquid Repellency Score*	
	SiM Treatment - dry	SiM Treatment - lubricated
M. Cotton	5	5.5
Dense PE	5.5	8
Nike PE	4	6.5
μ fiber	5	7

[0280] Clearly, the lubricated, SLIPS-fabric samples exhibit a higher score than their non-lubricated, superhydrophobic counterparts. In other words, the presence of the thin lubricating film around the threads prevents penetration of low-surface-tension liquids that would have otherwise wet the non-lubricated fabric. The Dense PE achieved the maximum score of 8: 60% IPA in water did not wet the sample and could slide off without pinning. M. cotton, Nike PE, and μ fiber PE were capable of repelling aqueous liquids down to surface tensions of 26.5, 25.0, and 24.5 mN/m, respectively. A particularly interesting trend emerges from these results: the scores for the SLIPS-fabric samples correlate with increasingly tight weaves. M. Cotton has the loosest weave and experiences the most pinning; Dense PE has the tightest weave and thus performs the best. This trend may be attributable to the overall smoothness of the SLIPS-fabric surface where even sub-millimeter scale roughness can still slightly compromise the ultrasmooth nature of lubricant-infused interface.

[0281] To extend the testing to organic liquids, the repellency of the Phase III fabrics Were tested against mineral oils and alkanes of progressively shorter chain length and lower surface tension. Table 6 summarizes the hydrocarbon repellency scores for the Phase III fabric samples.

TABLE 6

Sample	AATCC 118 Hydrocarbon Resistance Score*	
	SiM Treatment - dry	SiM Treatment - lubricated
M. Cotton	2	5.5
Dense PE	3.5	8
Nike PE	5	7
μ fiber	4.5	6

[0282] All test organic droplets pinned to the TSH fabrics and easily slid off of the lubricated, SLIPS-fabric samples. The TSH samples, particularly the M. Cotton and Dense PE, generally received lower scores than in the aqueous repellency test, indicating that organic liquids with even lower surface tensions are more prone to infiltrating the spaces within a fabric. Despite this, the scores of the lubricated samples in both the hydrocarbon and aqueous tests were within ± 1 from each other and follow the same trend of larger weave patterns causing reduced repellency of low-surface-tension liquids. Again, the dense polyester sample showed repellency to all of the test liquids and achieved the highest possible score of 8. SLIPS-fabric of a sufficiently dense weave can support a lubricating film that repels liquid compounds of broad compositions, polarities and surface tensions, which is a remarkable advancement to stain-resistant, fabric-based materials.

[0283] In certain embodiments, fabrics having a weave density that exceeds 100, 200, 300 and 400 threads/cm³ can be utilized. As used herein, the weave density can be calculated by obtaining an SEM image of a fabric, counting the number of threads horizontally across the fabric, within an imaged area.

[0284] Another important advantage of a lubricated fabric is that it maintains its slippery, omniphobic performance under pressure. To assess the pressure stability of the Phase III fabric samples, the drop impact test was carried out using water (surface tension=72.4 mN/m) and tetradecane (surface tension=26.55 mN/m) dropped from a height of 20.4 cm to achieve a dynamic pressure shown by the circle markers shown in FIG. 38. The results for the drop impact test are shown in FIG. 38: for a liquid of a given surface tension, the sliding angle is determined immediately after the droplet impacts the surface with the shown dynamic pressure. The SiM-SLIPS Nike PE and Dense PE fabrics retain their liquid repellency at high pressures (>1500 Pa) while typical lotus-type TSH surfaces fail at 400 Pa. The sliding angle of the test liquids on SiM-SLIPS treated μ fiber fabric increases after high impact, however sliding is still observed. This indicates that there is a SLIPS layer penetrated by the many protruding fibers on its disordered surface. Sliding angles for non-lubricated samples are not included because this pressure is above the threshold at which the Cassie-to-Wenzel transition occurs; water droplets are strongly pinned to the surface and will not slide even from the vertical surfaces, while tetradecane droplets simply wet the fabric as expected. SiM-SLIPS Nike PE shows sliding angles below 10° (10 μ L droplet) after a collisional pressure applied by the falling test liquid, while un-lubricated SiM Nike PE shows irreversible pinning in the same conditions. FIG. 38 shows that liquids of different surface tensions and dynamic impact pressures do not cause prominent increases in sliding angle of the SLIPS fabrics. As could be expected based on tightness of fabric weave and surface flatness, the Dense PE and Nike PE both show the best performance in this test with post-impact sliding angles of $8.8 \pm 1.0^\circ$ and $20.9 \pm 2.0^\circ$. The fiber showed an increase of $\sim 10^\circ$ in sliding angle after impact pressure due to the presence of loose fibers oriented approximately normal to the surface of the fabric. It is worth noting that despite droplet pinning the lubricated fabric was neither wet nor stained by the test liquid and the pinned droplets could be easily washed off the surface leaving no residue.

[0285] Breathability, or more specifically, water vapor transmission rate (WVTR), is an important factor in determining suitable applications for SLIPS fabrics. For each experiment, a non-lubricated and a lubricated sample were tested alongside two controls: a capsule sealed by (impermeable) Parafilm and an open capsule. In all cases, the lubricated fabric showed a large decrease in breathability relative to the non-lubricated samples. Table 7 summarizes the WVTR mass change after 24 h for the fabrics and PTFE controls.

TABLE 7

Material	Lubrication	WVTR (g/24 h/m ²)	Fold Change
No Membrane*	Control	947.5 $\pm$ 38.7	25.5
Parafilm*	Control	37.2 $\pm$ 18.4	
μ fiber*	None	497.5 $\pm$ 61.4	11.1
μ fiber*	K102	44.6 $\pm$ 6.8	
Nike PE*	None	507.5 $\pm$ 70.9	11.5

TABLE 7-continued

Material	Lubrication	WVTR (g/24 h/m ²)	Fold Change
Nike PE*	K102	44.2 ± 15.6	
Dense PE*	None	270.5 ± 36.6	6.1
Dense PE*	K102	44.0 ± 22.4	
M. Cotton*	None	493.3 ± 17.1	3.5
M. Cotton*	K102	139.4 ± 17.9	
200 nm PTFE*	None	473.9 ± 35.8	11.3
200 nm PTFE*	K102	42.0 ± 8.0	
1 μm PTFE*	None	470.9 ± 41.1	14.9
1 μm PTFE*	K102	31.6 ± 18.7	
20 μm PTFE*	None	483.4 ± 49.0	14.1
20 μm PTFE*	K102	34.2 ± 19.6	
Punc. 200 nm PTFE*	None	460.5 ± 39.6	3.7
Punc. 200 nm PTFE*	K102	131.1 ± 76.0	

[0286] All of the SLIPS samples (lubricated with Krytox 102) except for M. Cotton did not show a statistically significant difference in breathability from that of the Parafilm control. Non-lubricated μfiber, Nike PE, and Cotton samples exhibit similar breathability despite large differences in their relative weave pattern and weave density. Also, the μfiber, Nike PE, and Dense PE all show no breathability (i.e., no difference from the Parafilm control) while Cotton, the least densely woven fabric, shows significant (but still low) breathability. This intimates the presence of a certain macro-scale pore size threshold above which the Krytox does not wick across, leaving a space through which air and water vapor can flow.

[0287] While lotus-effect superhydrophobic surfaces have been thoroughly investigated for years and continue to show improvement, their design has some fundamental shortcomings that will always limit omniphobicity, stain resistance, durability and pressure tolerance. SLIPS overcome these problems, and nanostructured coatings that achieve the promising benefits using readily available fabrics as a substrate have been engineered. The lubricated structured surfaces display superior pressure-stable and damage-tolerant repellency to polar and non-polar liquids as compared to TSH surfaces. These lubricated nanostructure-coated fabrics can repel water, oil, dirt and mud; therefore, tents, boots, and other outerwear would be significantly improved. In demanding applications in extreme, contaminated environments, where breathability is not the most critical factor, SLIPS fabrics may already provide a unique solution as a stable, anti-fouling material for tactical suits for military, medical gowns and lab coats, specialty garments for construction and manufacturing. SLIPS-fabric confers pressure-tolerant and damage-tolerant omniphobicity on fabric-based substrates.

[0288] Those skilled in the art would readily appreciate that all parameters and configurations described herein are meant to be exemplary and that actual parameters and configurations will depend upon the specific application for which the systems and methods of the present invention are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that the invention may be practiced otherwise than as specifically described. Accordingly, those skilled in the art would recognize that the examples should not be limited as such. The present invention is directed to each individual feature, system, or method described herein. In addition, any combina-

tion of two or more such features, systems or methods, if such features, systems or methods are not mutually inconsistent, is included within the scope of the present invention.

What is claimed is:

1. An article having a repellant surface, the article comprising:

a substrate comprising fabric material having a weave density that is greater than 100 threads/cm²; and

a lubricant wetting and adhering to the fabric material to form a stabilized liquid overlayer,

wherein the stabilized liquid overlayer covers the fabric material at a thickness sufficient to form a liquid upper surface above the fabric material,

wherein the fabric material is functionalized to enhance chemical affinity with the lubricant such that the lubricant is substantially immobilized over the fabric material to form a repellant surface.

2. An article having a repellant inner surface, the article comprising:

a container comprising an inner surface to contain a complex fluid;

a complex fluid having a liquid and one or more other components within said container; and

wherein said liquid wets and adheres to the inner surface to form a stabilized liquid overlayer,

wherein the stabilized liquid overlayer covers the inner surface at a thickness sufficient to form a liquid surface on the inner surface,

wherein the inner surface and the liquid have an affinity such that the liquid is substantially immobilized on the inner substrate to form a repellant surface, the repellant surface repelling other components within said complex fluid.

3. An optical article having a repellant surface, the optical article comprising:

a substrate comprising transparent or translucent material with a surface;

a housing that holds the substrate; and

a lubricant wetting and adhering to the surface to form a stabilized liquid overlayer,

wherein the stabilized liquid overlayer covers the surface at a thickness sufficient to form a liquid upper surface above the surface,

wherein the surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, wherein the housing is infiltrated with the lubricant to replenish the lubricant onto the substrate.

4. A membrane-like article, the article comprising:

a membrane substrate comprising a top surface, a bottom surface, and a plurality of through-holes;

a low-surface tension fluid wetting and adhering the top surface, the bottom surface, and inner walls surrounding the plurality of through-holes, forming a pre-conditioning layer; and

a fluid deposited over the pre-conditioning layer to form a protective layer, the protective layer providing a repellant surface to the membrane substrate;

wherein the membrane substrate, the pre-conditioning layer, and the protective layer have an affinity to each other such that the protective layer is substantially immobilized on the membrane substrate to form the repellant surface.

5. An article for carrying fluid flow, the article comprising: a substrate comprising a roughened surface; and a lubricant wetting and adhering to the roughened surface to form a stabilized liquid overlayer, wherein the stabilized liquid overlayer covers the roughened surface at a thickness sufficient to form a liquid upper surface on top of the roughened surface, wherein the roughened surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a slippery surface, the slippery surface reducing drag and friction of the fluid flow.
6. A method for protecting metal or metalized surfaces from corrosion, the method comprising: providing a metal or metalized surface; introducing roughness; and chemically functionalizing the metal or metalized surface to enhance affinity of the metal surface with a lubricant; and introducing the lubricant to wet and adhere to the metal or metalized surface to form an overlayer; wherein the metal or metalized surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, providing anti-corrosion to the metal or metalized surface.
7. A method for protecting surfaces from scaling, the method comprising: providing a surface; introducing roughness; and chemically functionalizing the surface to enhance affinity of the surface with a lubricant; and introducing the lubricant to wet and adhere to the surface to form an overlayer; wherein the surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, providing anti-scaling to the metal surface.
8. An article having a repellant surface, the article comprising: a substrate comprising a roughened surface; a lubricant wetting and adhering to the roughened surface to form a stabilized liquid overlayer, wherein the liquid covers the roughened surface at a thickness sufficient to form a liquid upper surface above the roughened surface; and a fragrance enhancer located within said substrate and/or said lubricant; wherein the roughened surface and the lubricating liquid have an affinity for each other such that the lubricating liquid is substantially immobilized on the substrate to form a repellant surface.
9. An article having a repellant surface, the article comprising: a substrate comprising a plurality of nanostructures embedded in a medium and having a roughened surface; and a lubricant wetting and adhering to the roughened surface to form a stabilized liquid overlayer, wherein the liquid covers the roughened surface at a thickness sufficient to form a liquid upper surface above the roughened surface, wherein the roughened surface and the lubricating liquid have an affinity for each other such that the lubricating liquid is substantially immobilized on the substrate to form a repellant surface, wherein the roughened surface includes a microscale or nanoscale structure.
10. A method for protecting plastic, glass, ceramic, and composite surfaces from graffiti, the method comprising: providing a said solid surface; introducing roughness, chemically functionalizing the said surface to enhance affinity of the said surface with a lubricant; and introducing the lubricant to wet and adhere to the said surface to form an overlayer, wherein the said surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, providing anti-graffiti properties to the said surface.
11. A method for fluid collection, the method comprising: providing a solid surface; introducing roughness; chemically functionalizing the solid surface to enhance affinity of the surface with a lubricant; introducing the lubricant to wet and adhere to the solid surface to form an overlayer, wherein the solid surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface; condensing condensate droplets on the repellant surface for liquid collection; and receiving and recovering fluids dispensed in excess in a coating or processing equipment.
12. An article having a repellant surface, the article comprising: a substrate comprising a roughened surface; and a lubricant wetting and adhering to the roughened surface to form a stabilized liquid overlayer, wherein the liquid covers the roughened surface at a thickness sufficient to form a liquid upper surface above the roughened surface, wherein the roughened surface and the lubricating liquid have an affinity for each other such that the lubricating liquid is substantially immobilized on the substrate to form a repellant surface, wherein the substrate is a component of a ski, a luge, a surf board, a hovercraft, a winter sports item, or a water sports item, wherein the repellent surface is capable of repelling solid materials, fluid materials, or combinations thereof.
13. A method for protecting plastic, glass, ceramic, and composite surfaces from scaling, the method comprising: providing a said solid surface; introducing roughness; chemically functionalizing the said surface to enhance affinity of the said surface with a lubricant; and introducing the lubricant to wet and adhere to the said surface to form an overlayer, wherein the surface and the lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellant surface, providing anti-scaling to the said surface.
14. A method for forming a repellent surface, the method comprising: providing a substrate having a surface; depositing a first material having a charge to said surface;

depositing a second material having a charge that is opposite to the charge of the first material;
sequentially repeating said depositing a first material and said depositing a second material to provide a roughened surface;
introducing a lubricant to wet and adhere to said roughened surface to form an overlayer,
wherein said roughened surface and said lubricant have an affinity for each other such that the lubricant is substantially immobilized on the substrate to form a repellent surface.

15. The method of claim **14**, further comprising removing said first material or said second material after said sequentially repeating said depositing a first material and said depositing a second material.

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