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**Grunlan et al.**

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(54) **METHOD FOR APPLYING  
GAS-IMPERMEABLE COATINGS**

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(2013.01); *C08J 2479/02* (2013.01)

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CPC ..... B05D 1/00; B05D 1/18; B05D 1/40  
See application file for complete search history.

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(\*) Notice: Subject to any disclaimer, the term of this  
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application No. PCT/US2017/057121 on Oct. 18,  
2017, now Pat. No. 11,518,903.  
(Continued)

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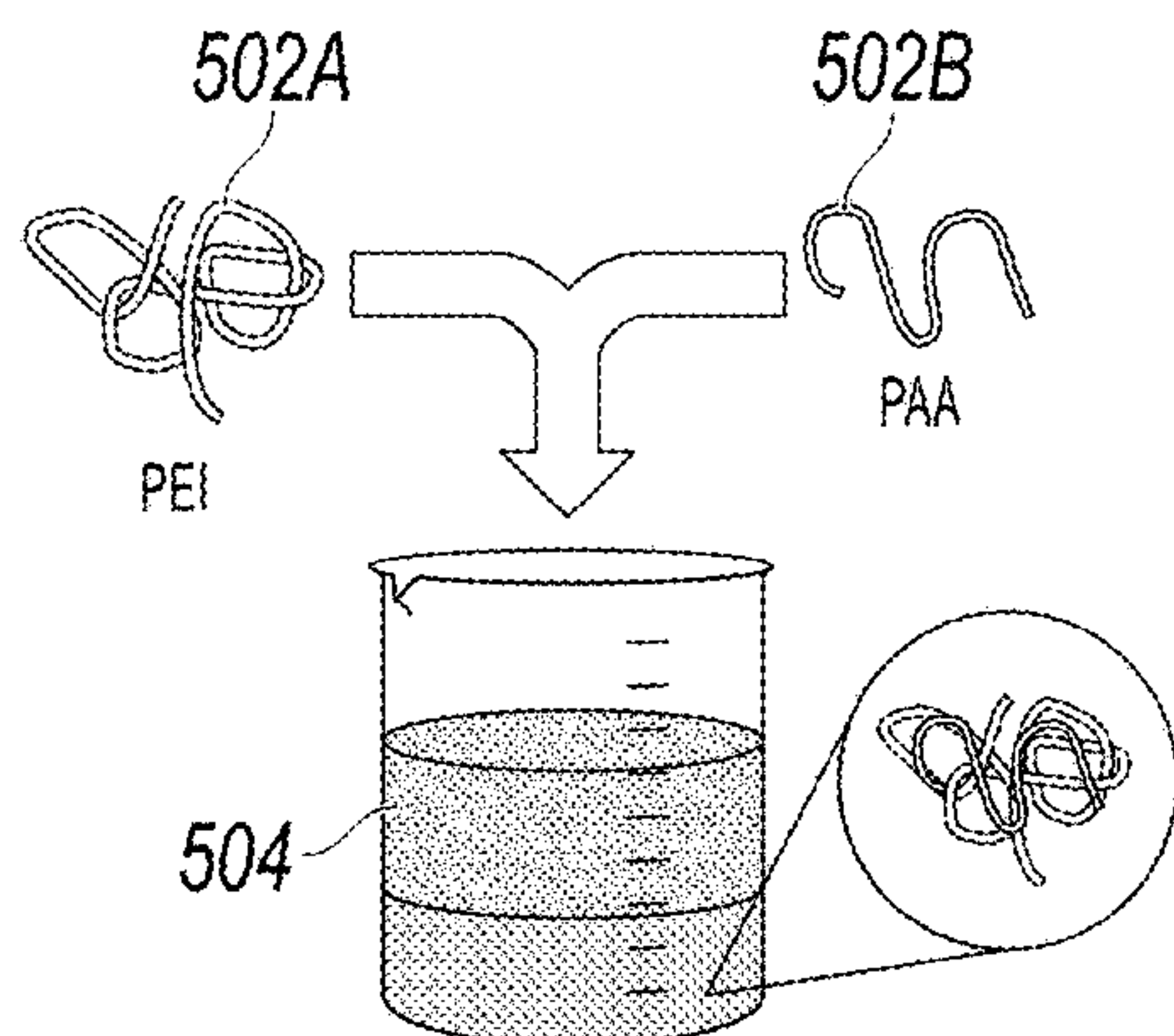
(51) **Int. Cl.**  
**B05D 1/00** (2006.01)  
**B05D 1/18** (2006.01)  
**B05D 1/40** (2006.01)  
**C09D 133/02** (2006.01)  
**C08J 7/04** (2020.01)  
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(57) **ABSTRACT**

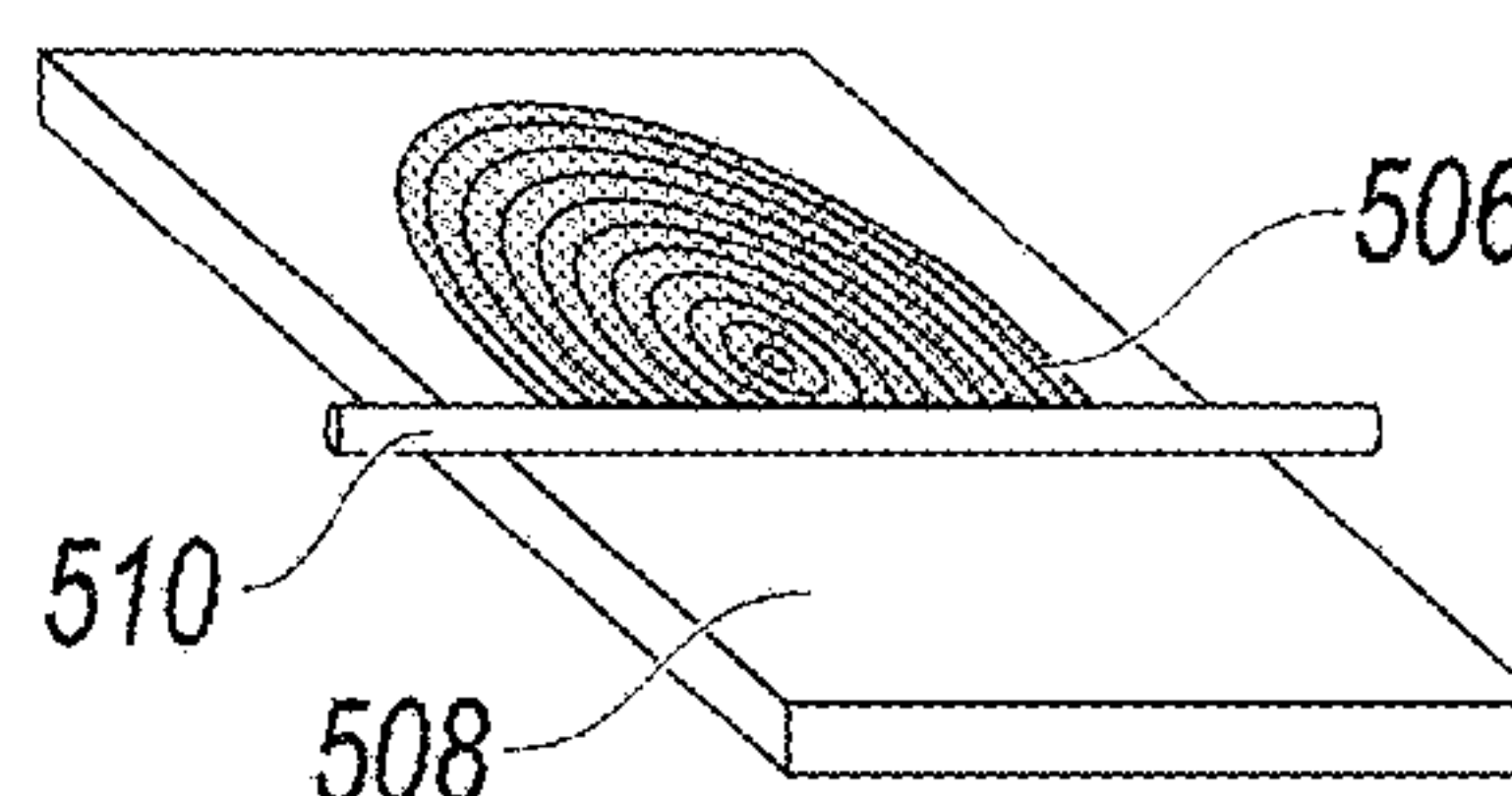
A method of applying a gas-impermeable coating includes  
forming a polyelectrolyte complex suspension. The poly-  
electrolyte complex suspension is applied to a substrate. The  
substrate having the polyelectrolyte complex applied  
thereon is treated. The treating reduces salt content of the  
polyelectrolyte complex. The treating results in a gas-im-  
permeable coating being formed on the substrate.

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(2013.01); **C08J 7/048** (2020.01); **C08J**  
**7/0427** (2020.01); **C09D 179/02** (2013.01);

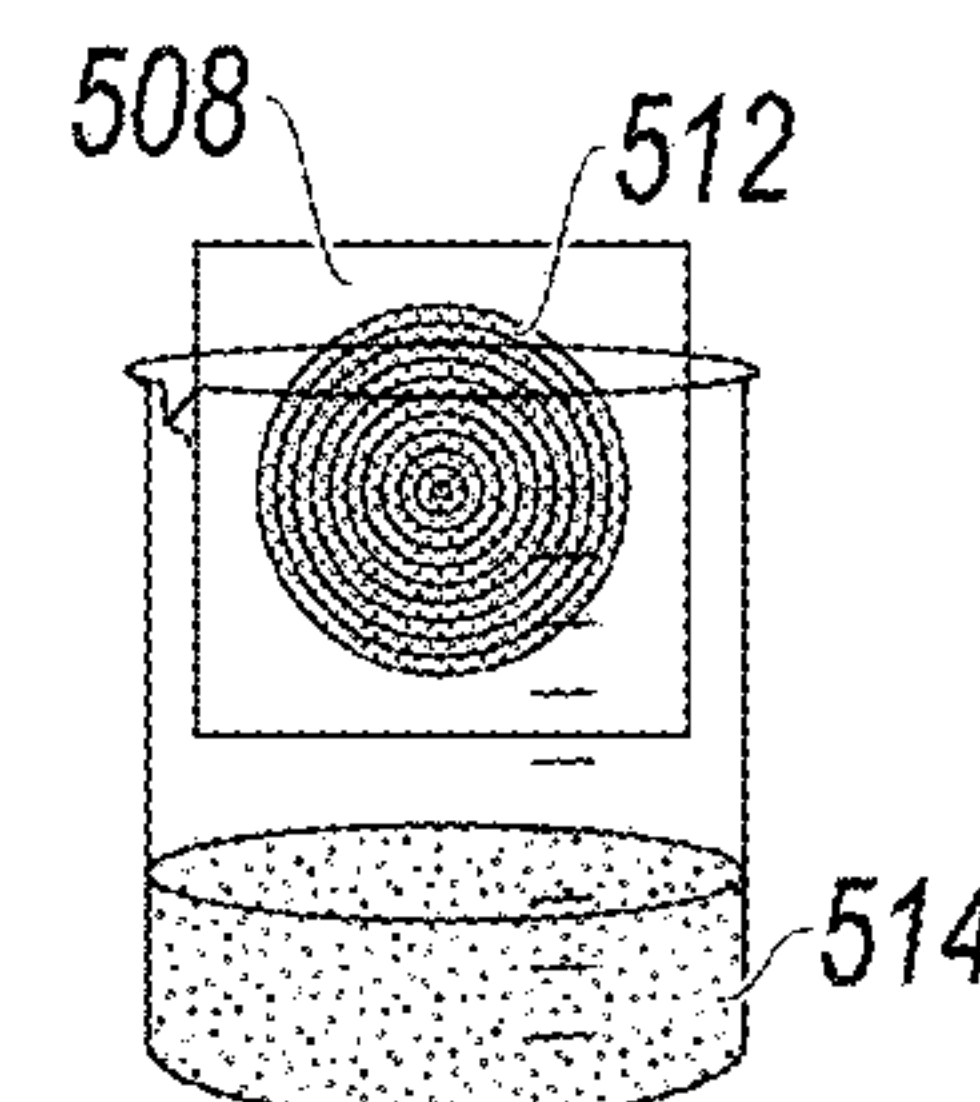
**19 Claims, 13 Drawing Sheets**



MAKING PEC SUSPENSION



COATING WITH SUSPENSION



TREATING THE FILM

Related U.S. Application Data

- (60) Provisional application No. 62/410,083, filed on Oct. 19, 2016.
- (51) **Int. Cl.**  
**C08J 7/048** (2020.01)  
**C09D 179/02** (2006.01)

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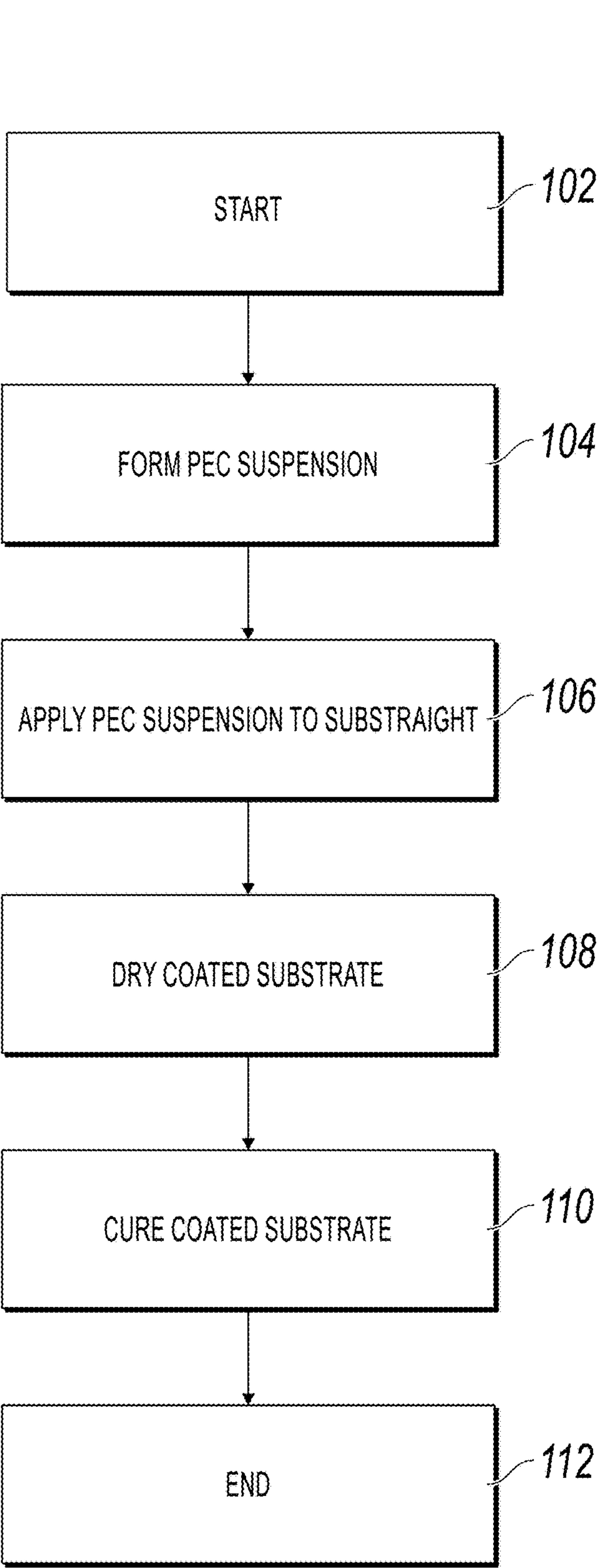


FIG. 1

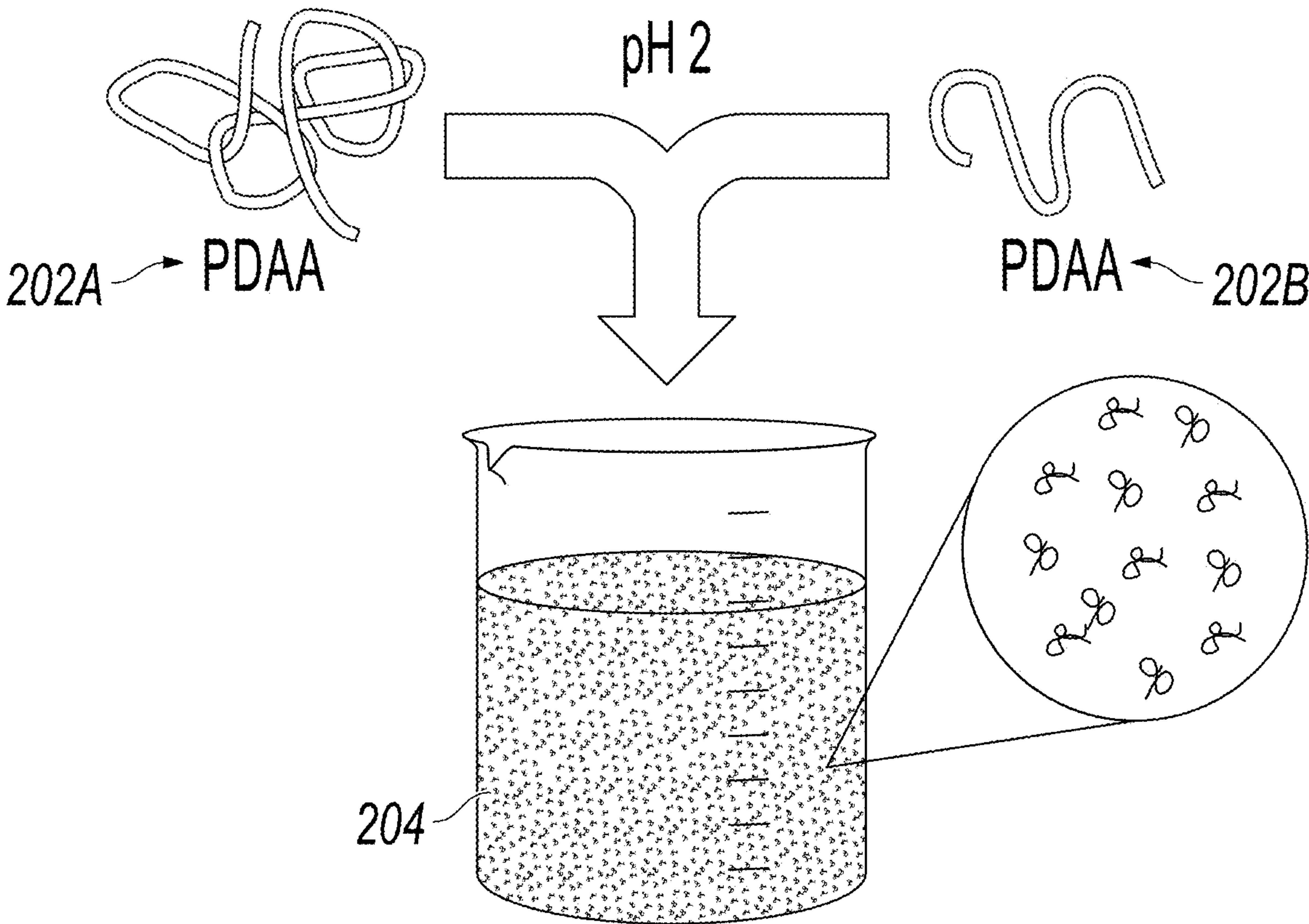


FIG. 2A



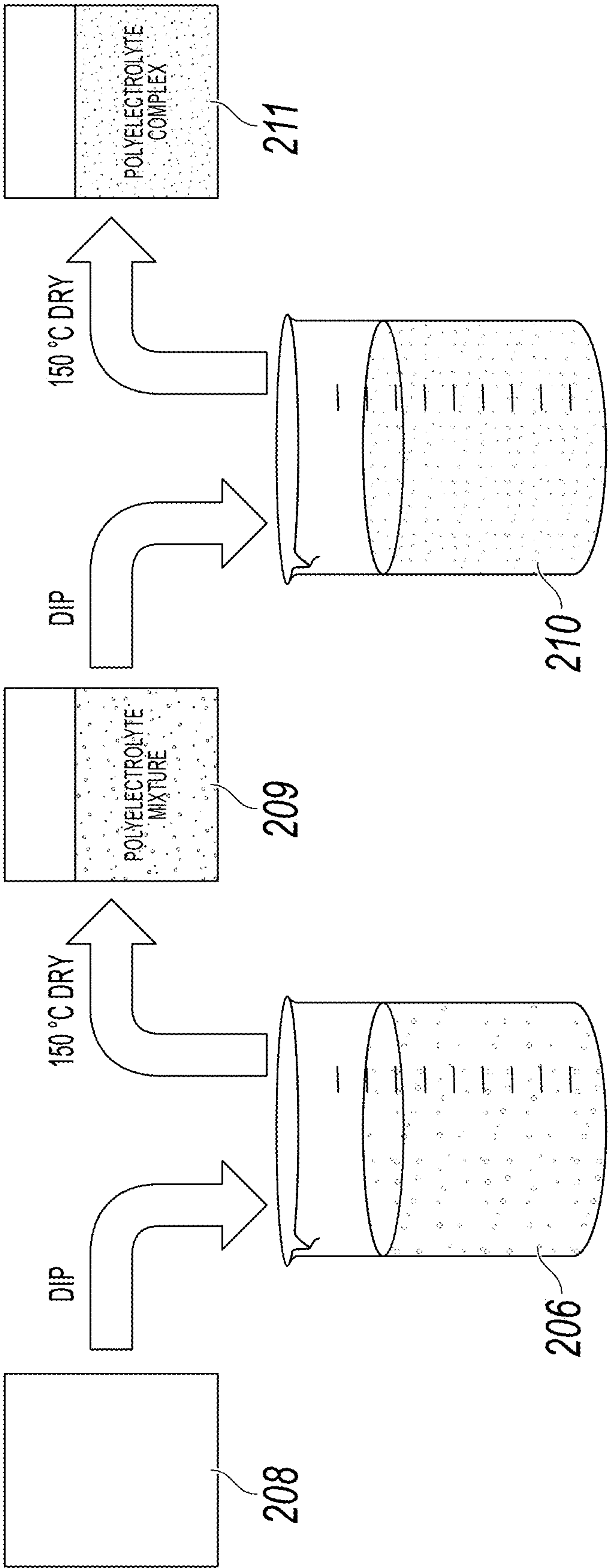


FIG. 2B

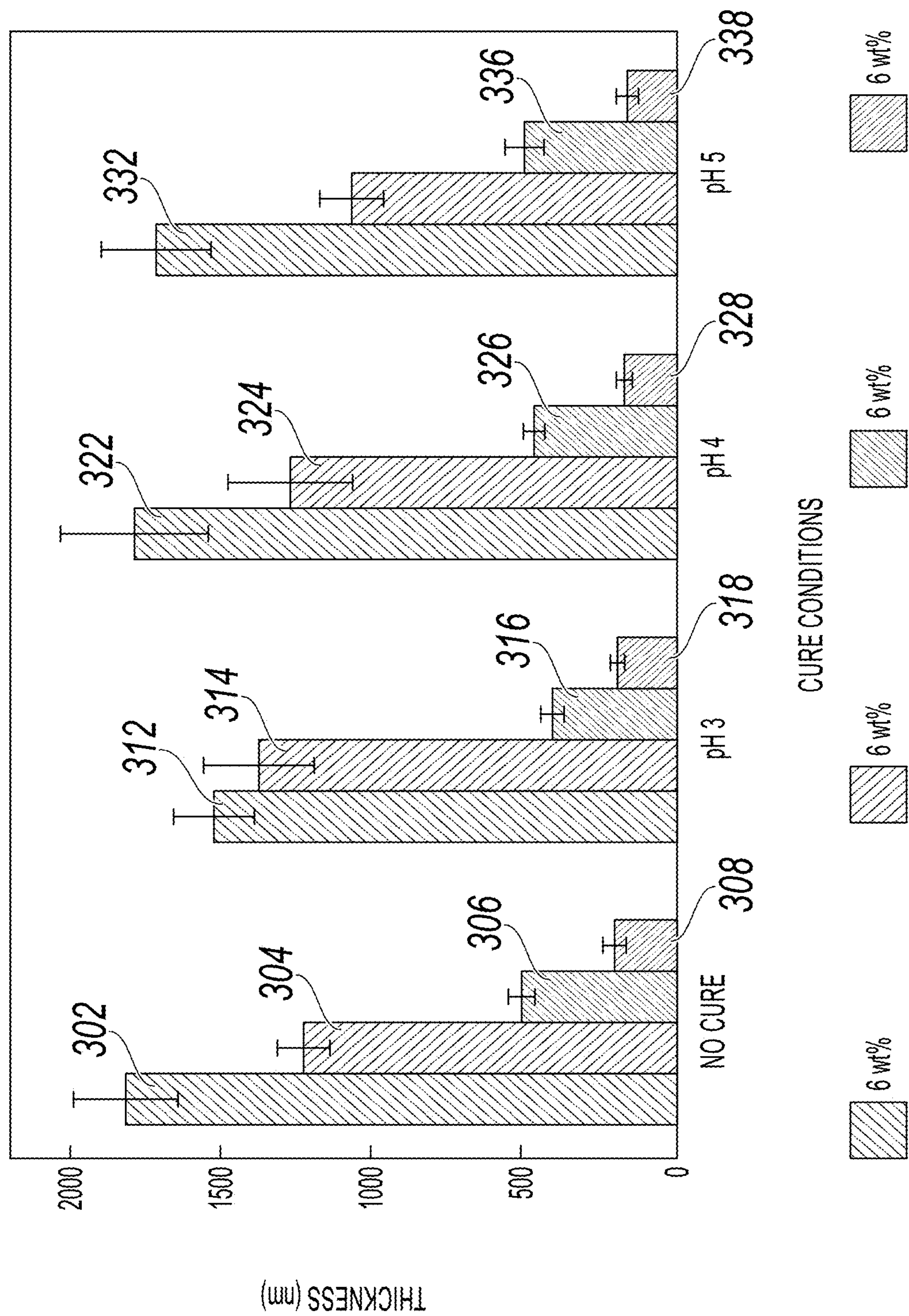
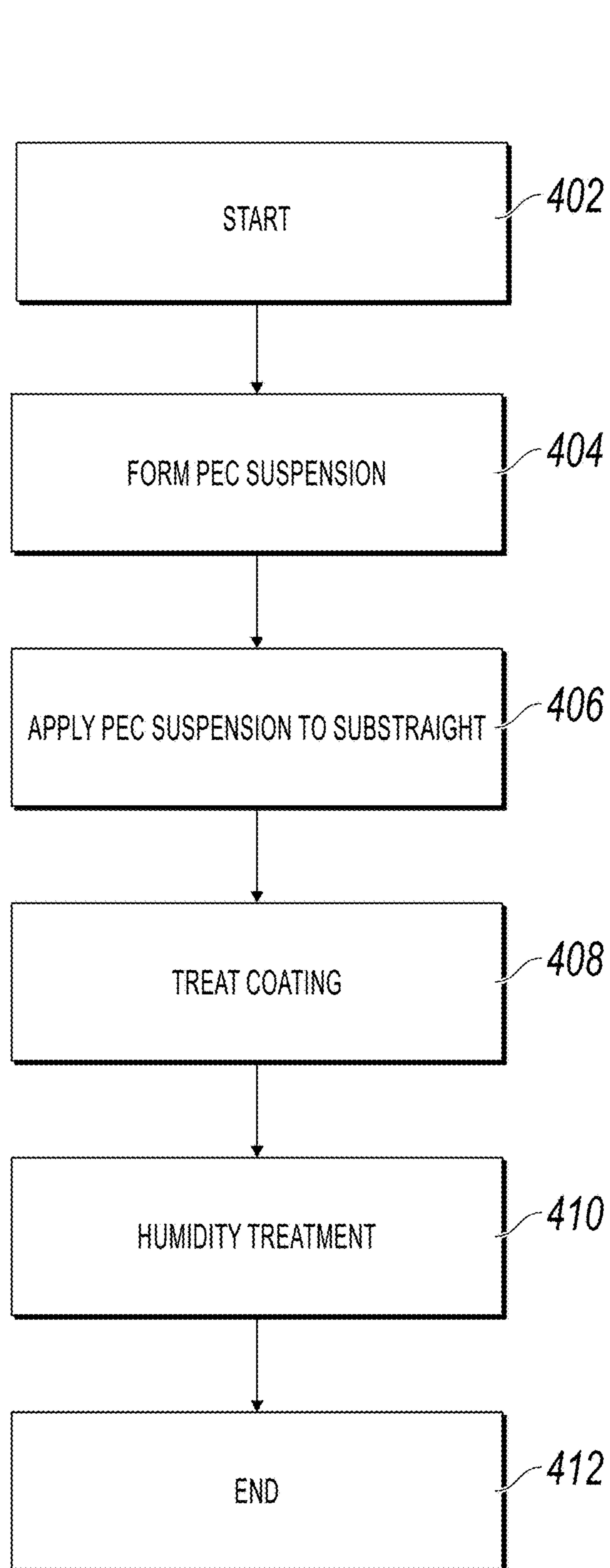


FIG. 3

**FIG. 4**

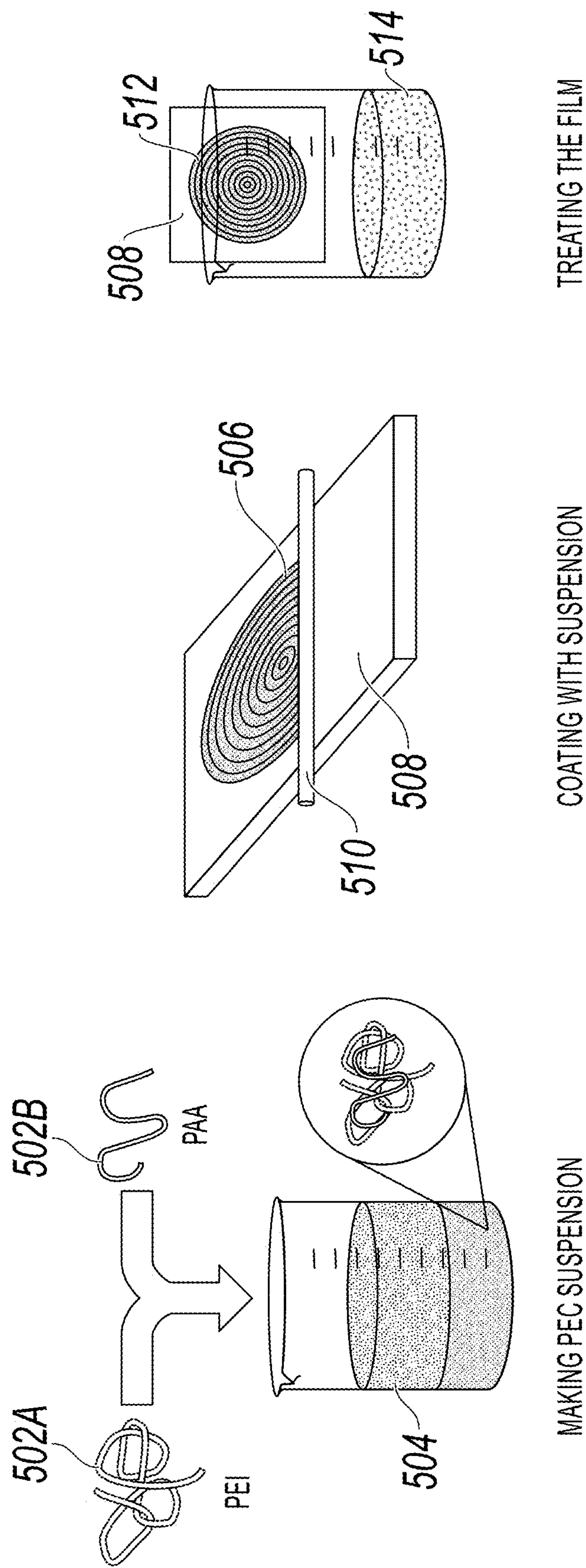


FIG. 5



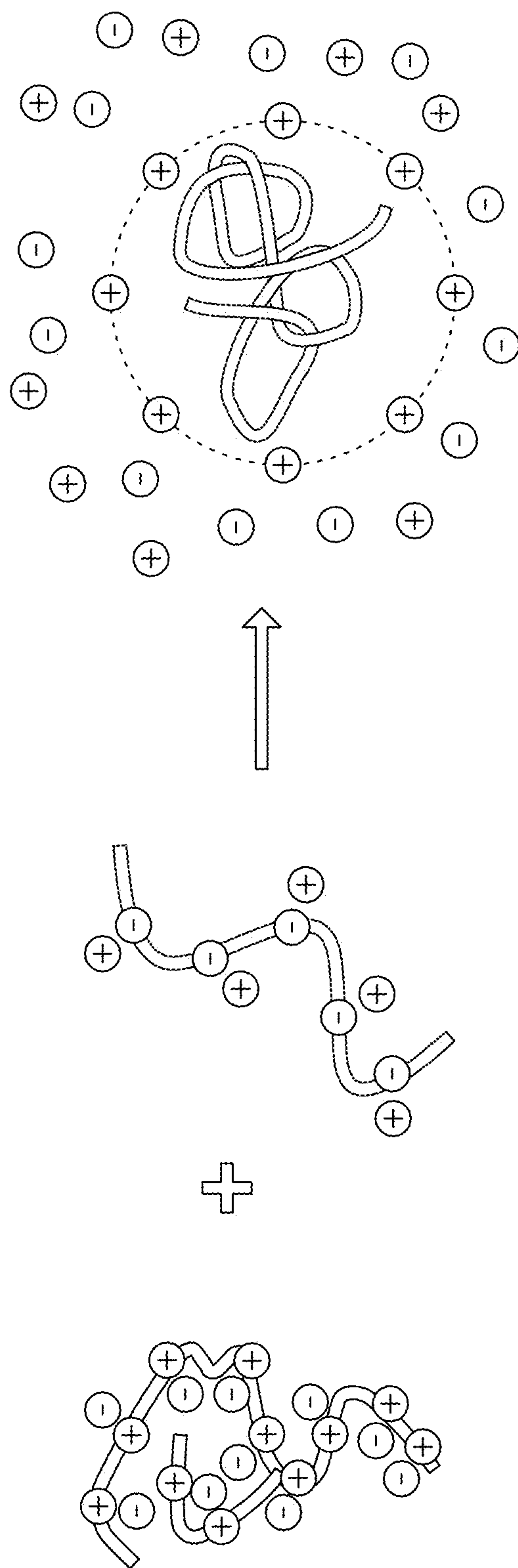


FIG. 6A

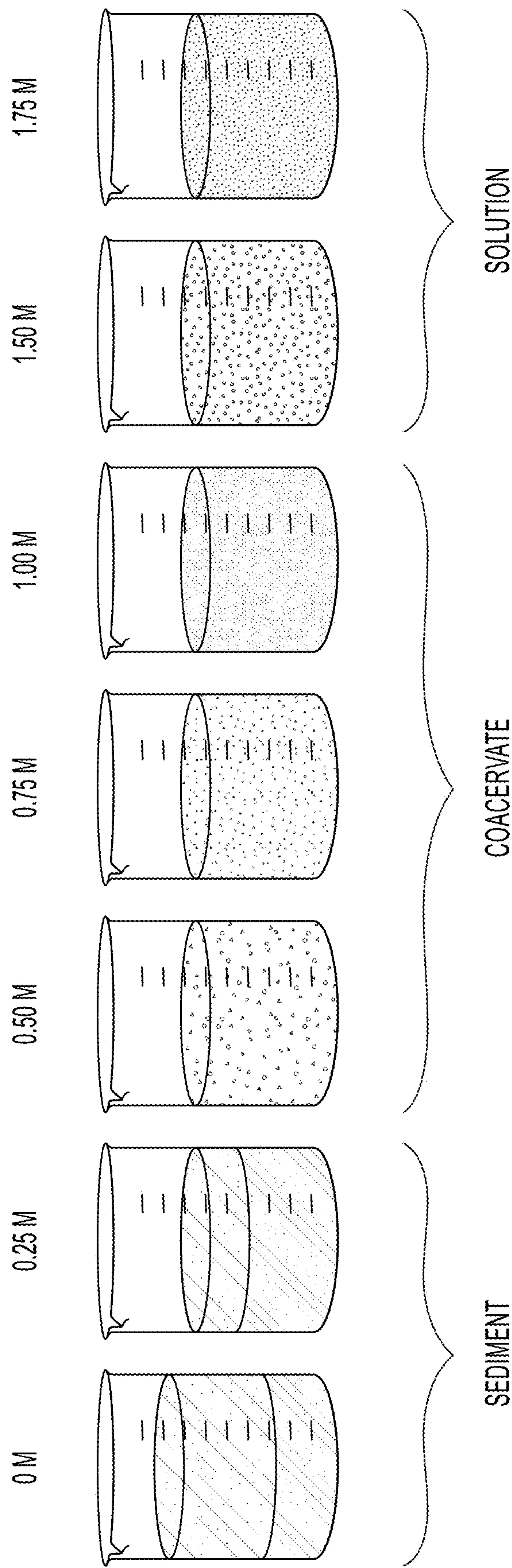


FIG. 6B

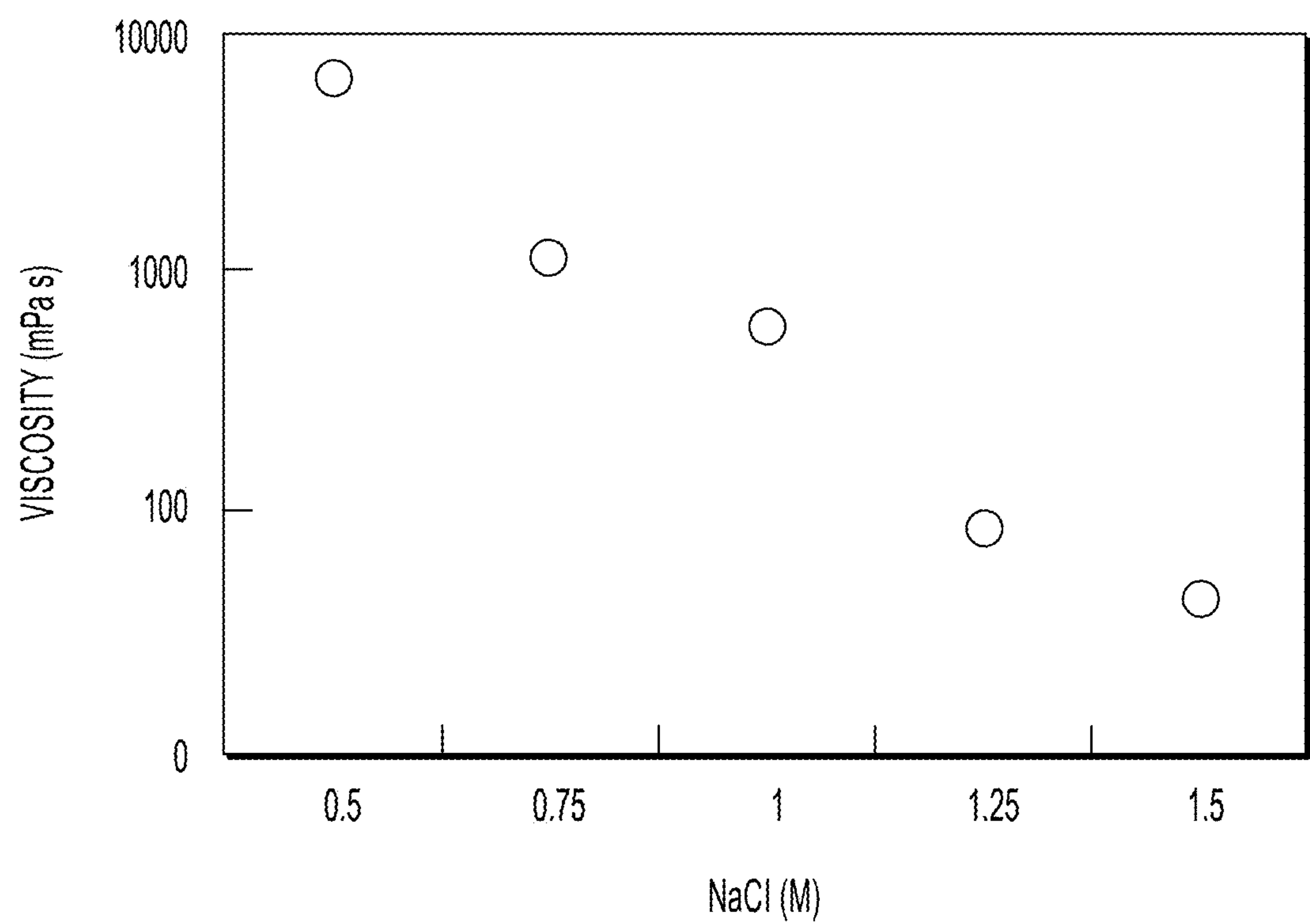


FIG. 7



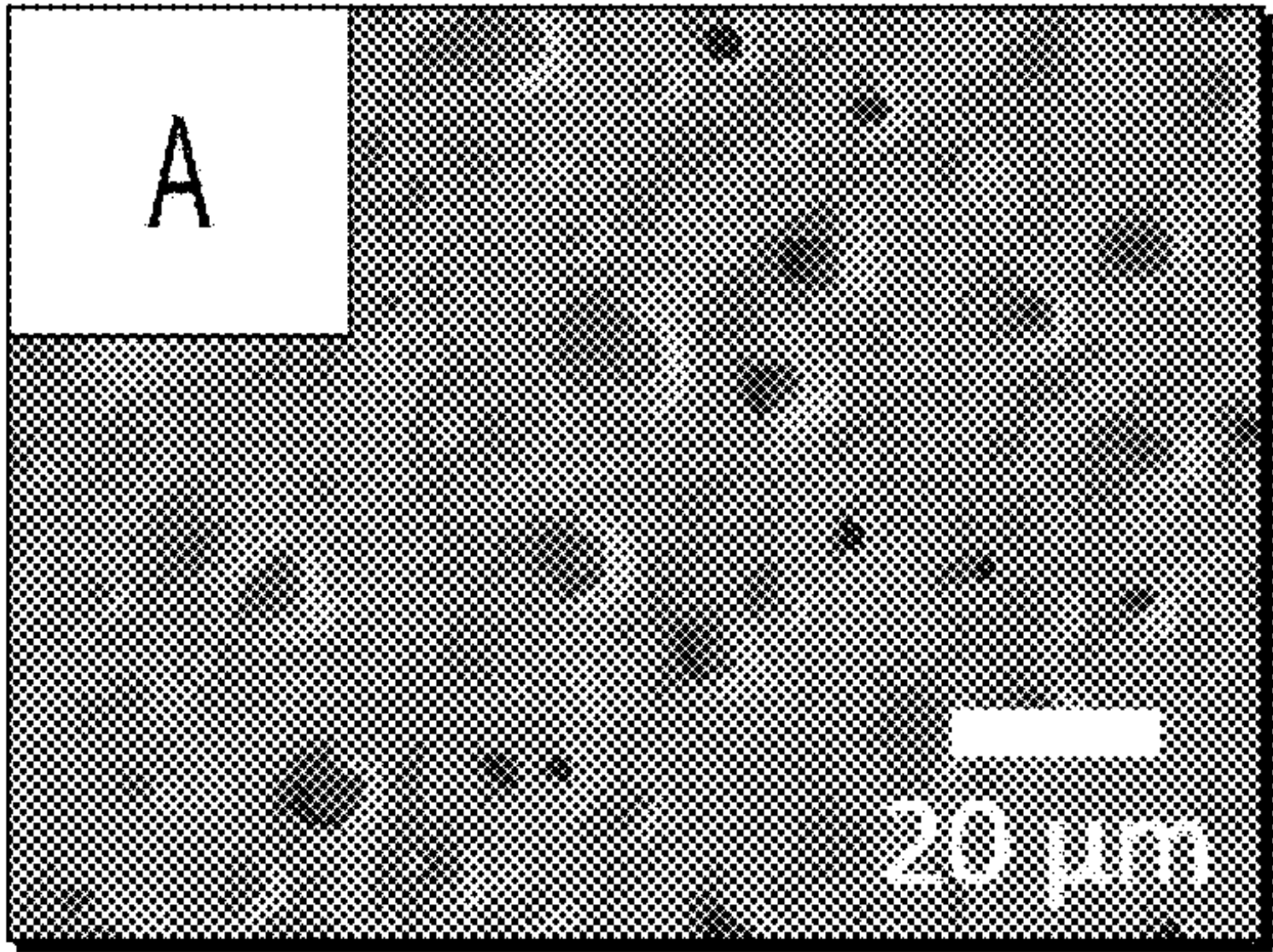


FIG. 8A

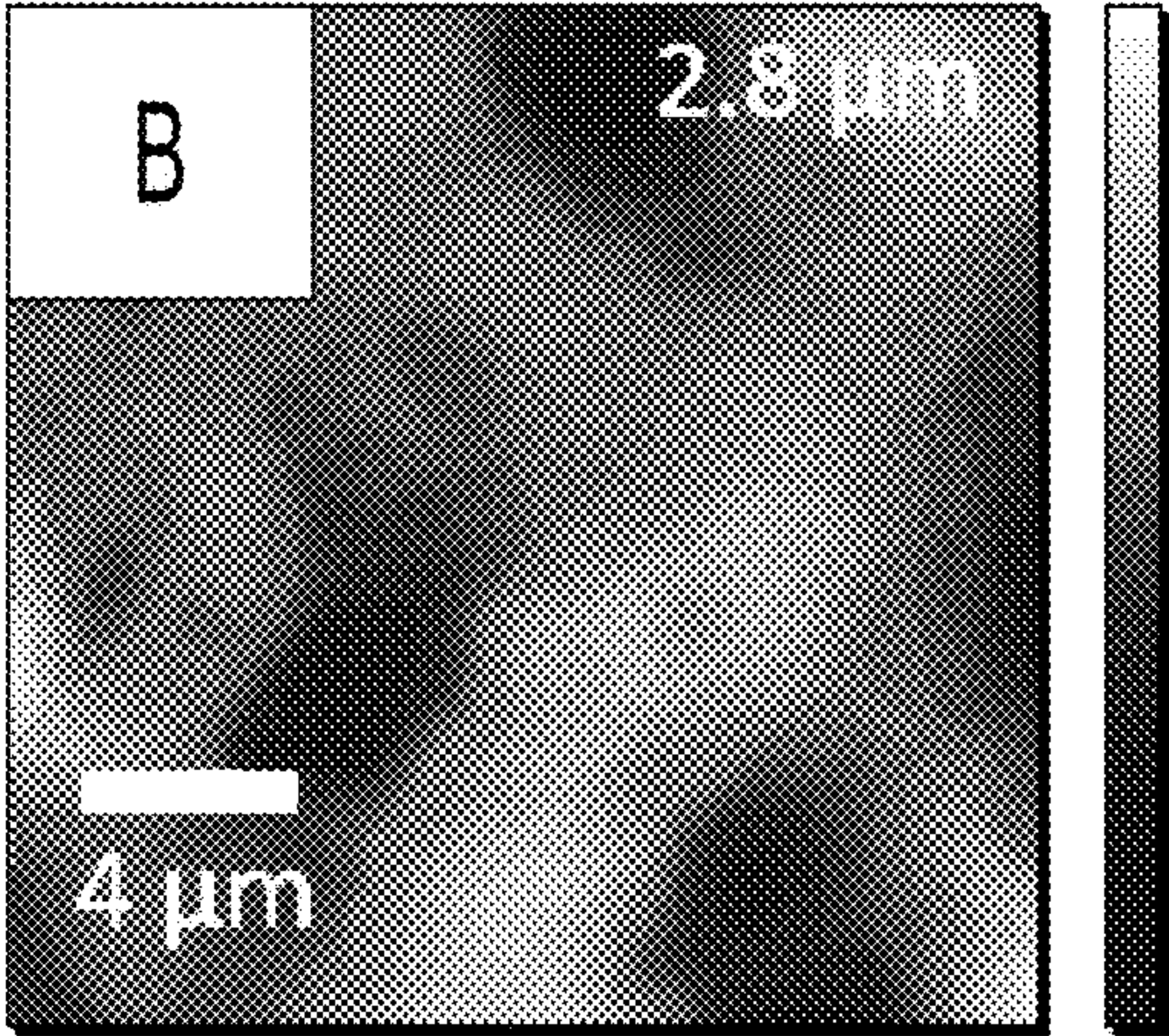


FIG. 8B

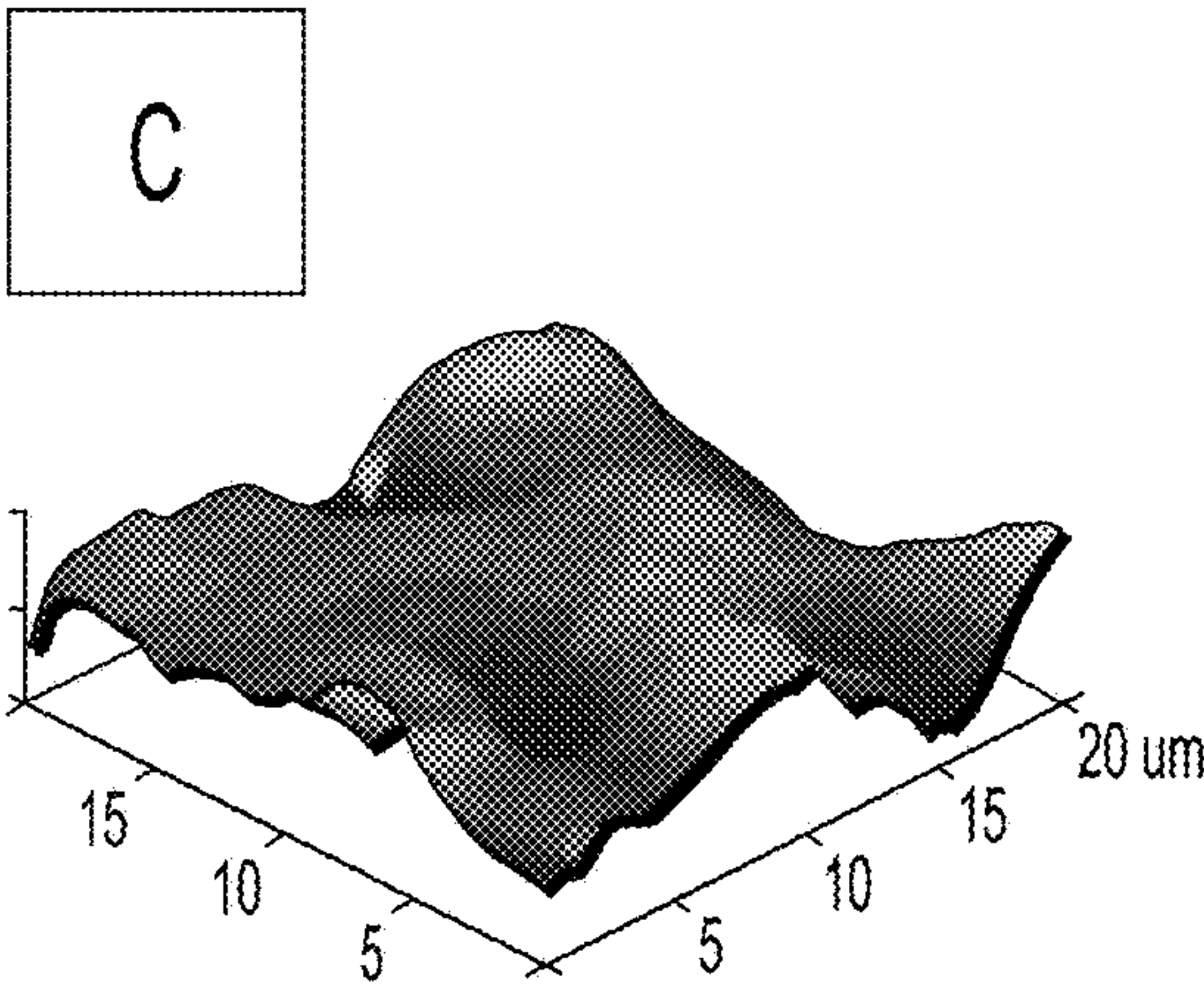


FIG. 8C

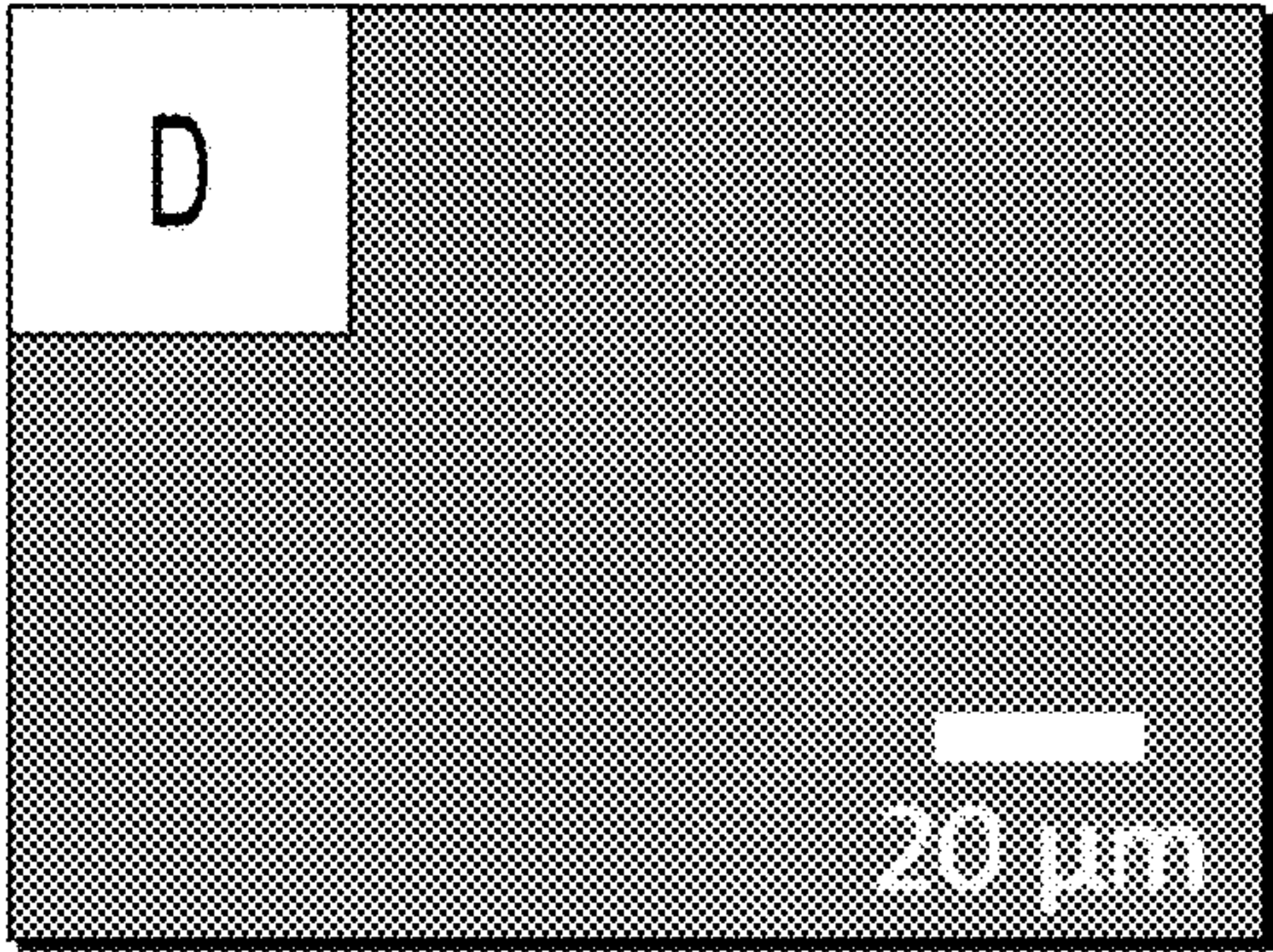


FIG. 8D



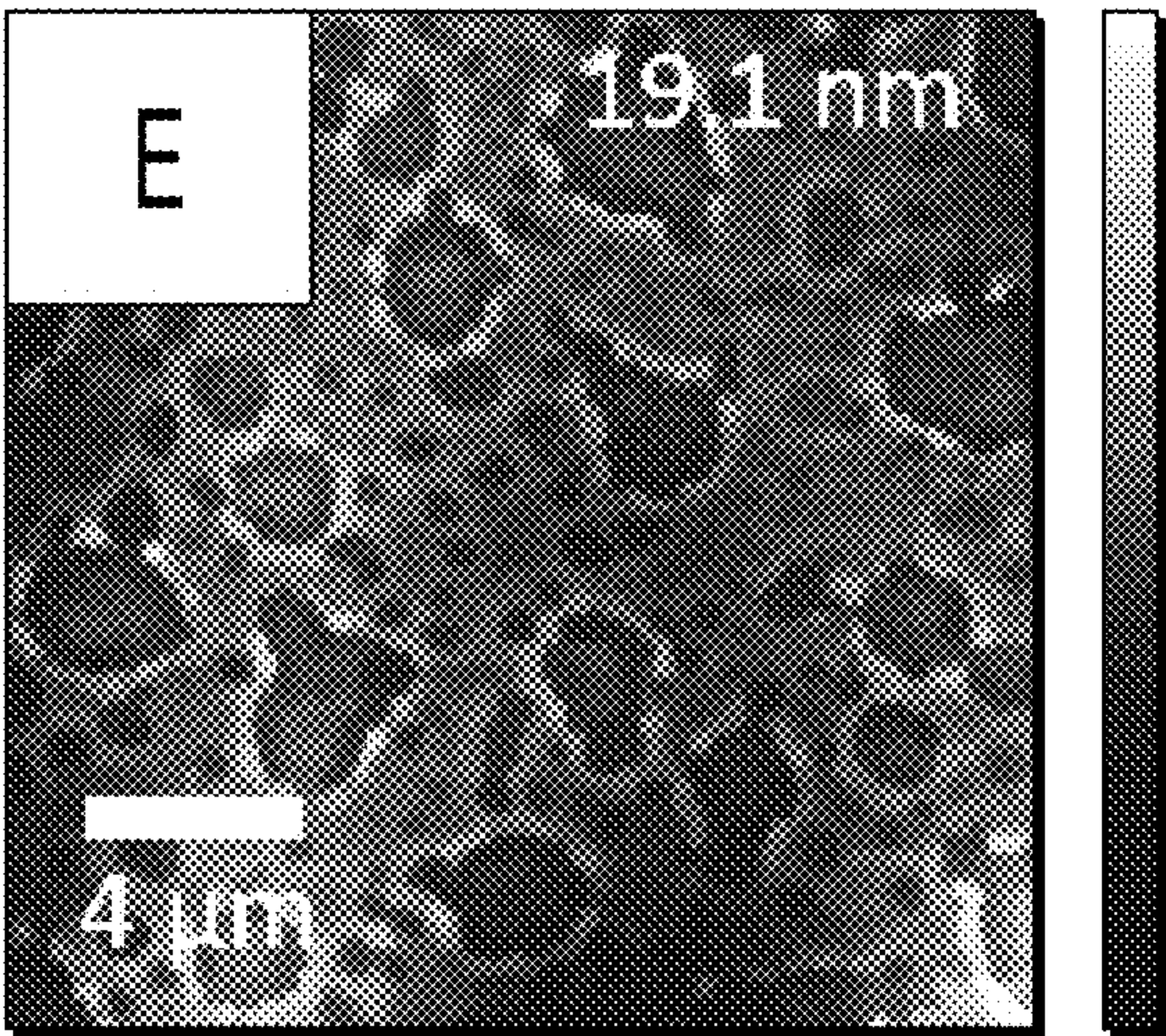


FIG. 8E

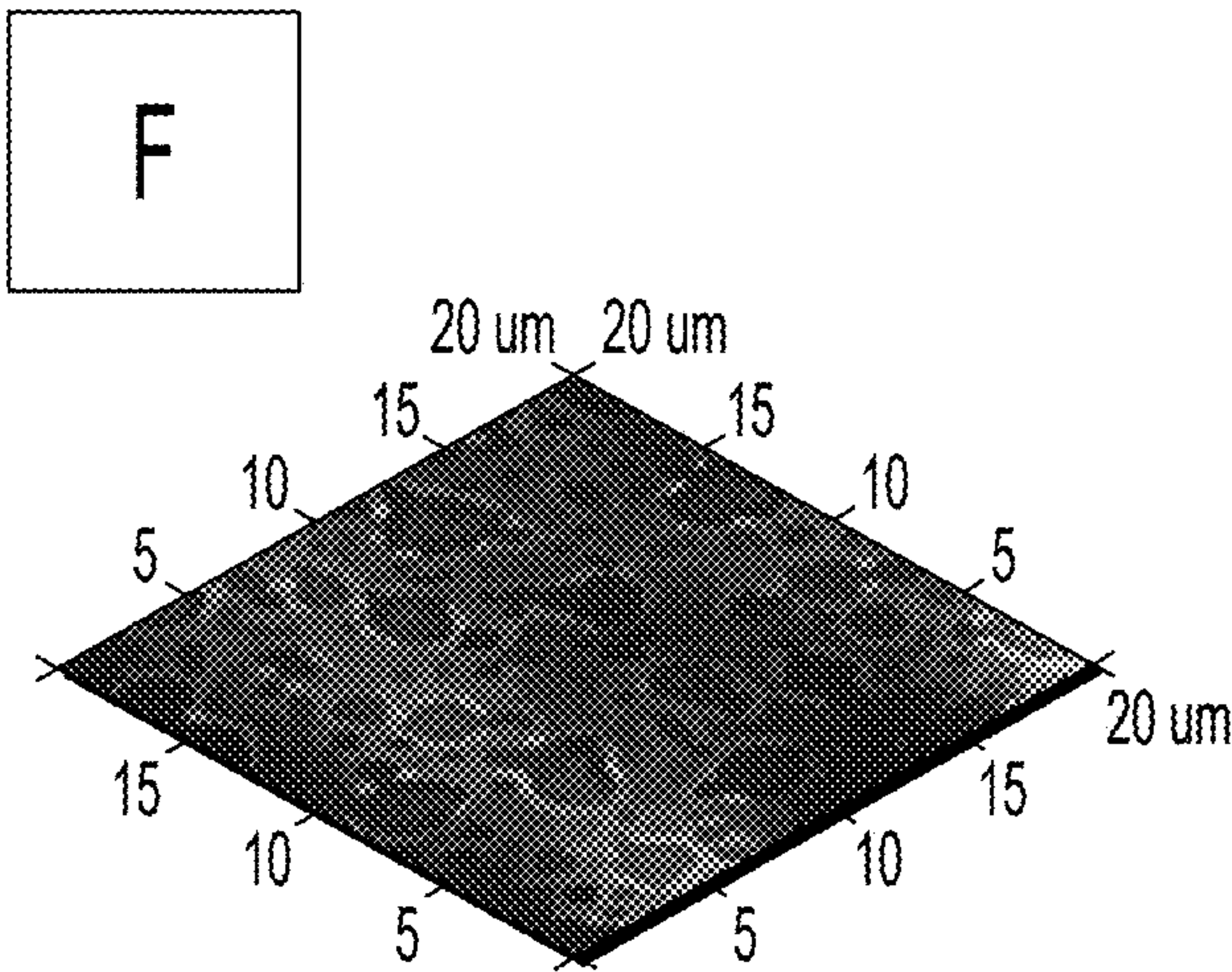


FIG. 8F

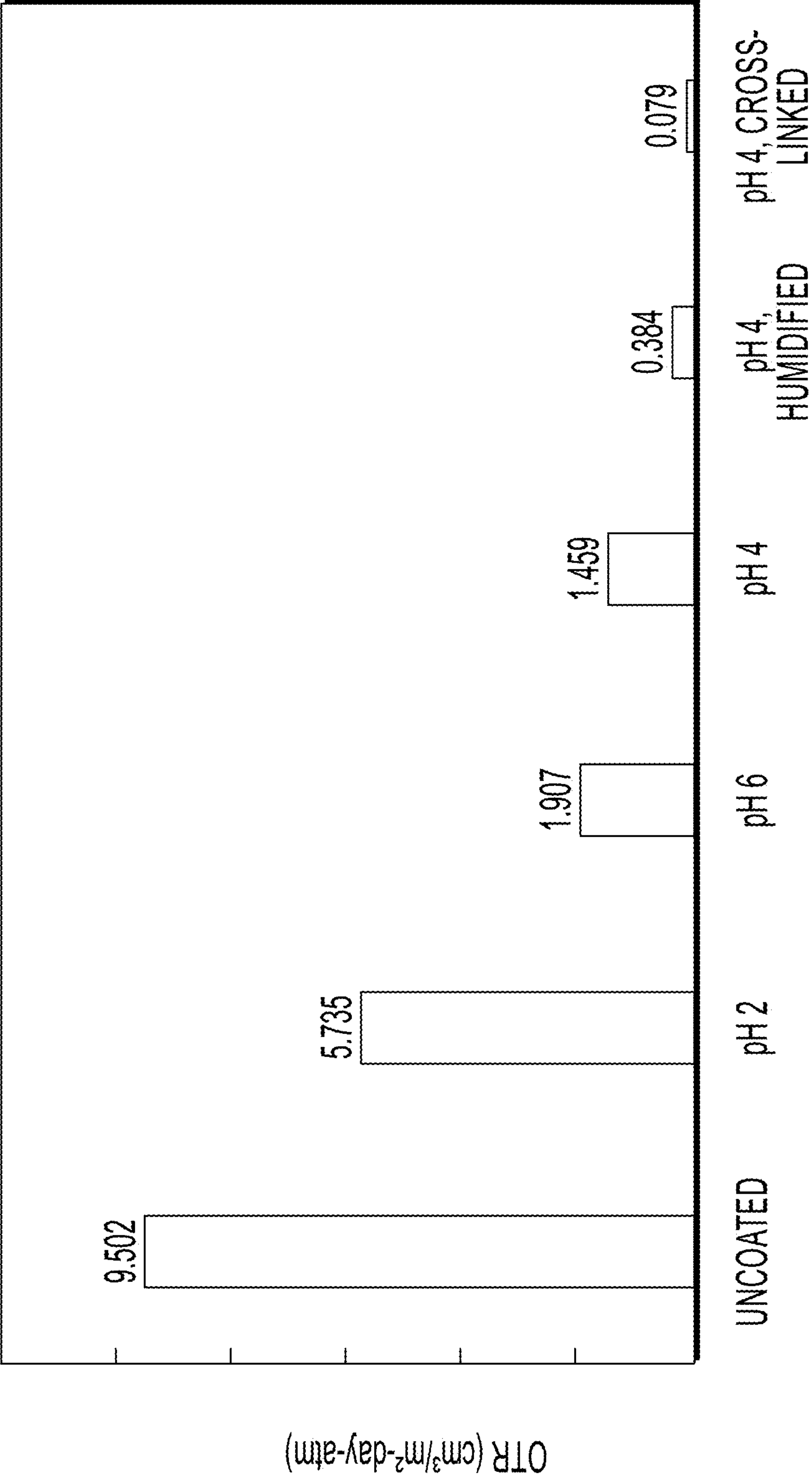


FIG. 9

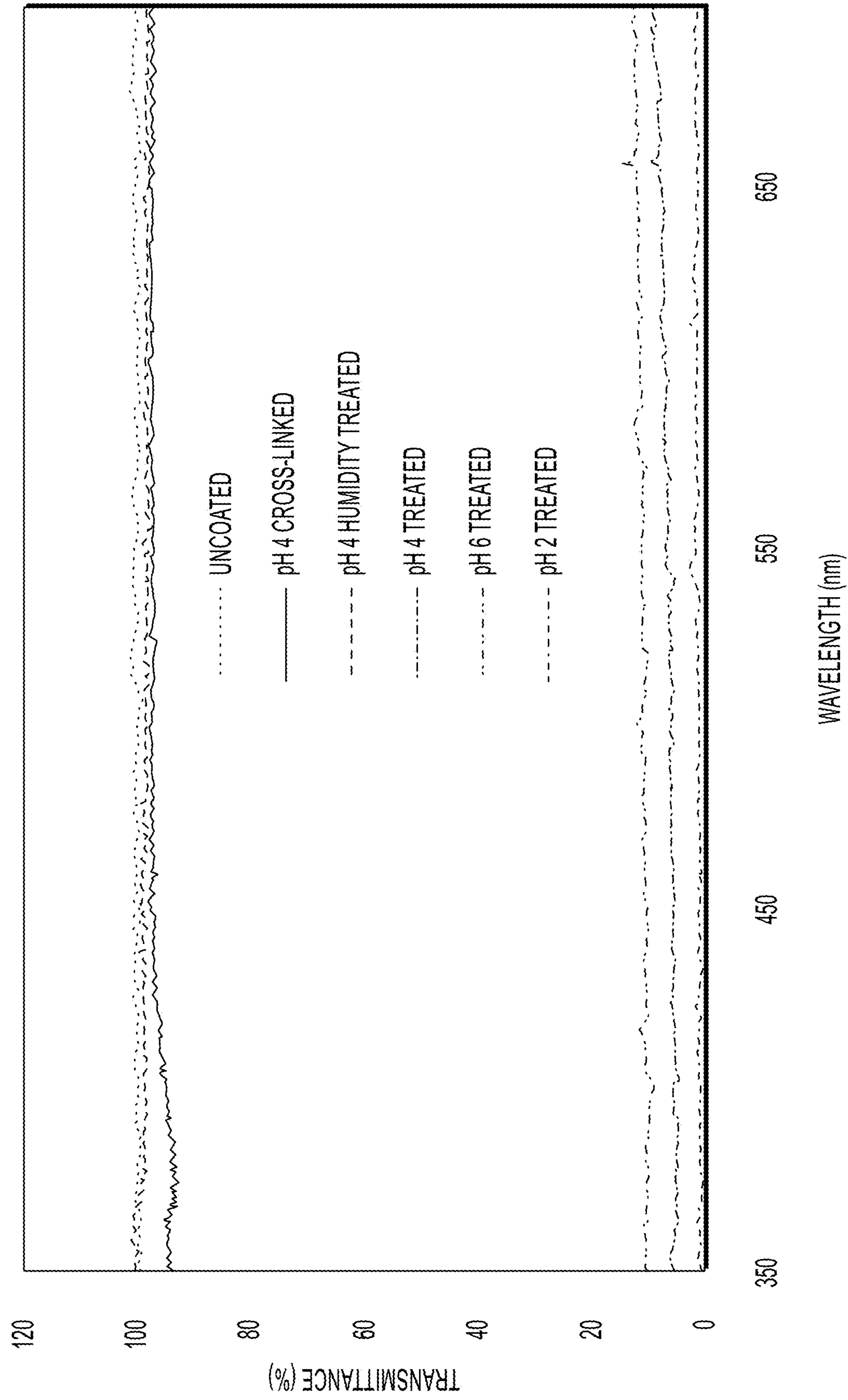


FIG. 10



## 1

METHOD FOR APPLYING  
GAS-IMPERMEABLE COATINGSCROSS-REFERENCE TO RELATED  
APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 16/338,958, having a 371(c) date of Apr. 2, 2019, which is a national stage entry of PCT/US2017/057121, filed on Oct. 18, 2017. PCT/US2017/057121 claims priority to U.S. Provisional Patent Application No. 62/410,083, filed on Oct. 19, 2016. Each of the aforementioned applications are incorporated herein by reference in their entirety.

## TECHNICAL FIELD

The present application relates generally to coatings and more particularly, but not by way of limitation, to thin gas-impermeable coatings.

## BACKGROUND

This section provides background information to facilitate a better understanding of the various aspects of the disclosure. It should be understood that the statements in this section of this document are to be read in this light, and not as admissions of prior art.

Optically transparent, flexible thin films that provide a high oxygen barrier are desirable for applications such as pressurized systems, food packaging, and protection of flexible electronics. Prevailing technologies, such as silicon oxide ("SiOx") and aluminum oxide ("AlxOy") thin films, provide a relatively impermeable layer to oxygen, but tend to have poor adhesion, flexibility, and require costly vacuum-based processing. Multilayer films deposited from water using layer-by-layer (LbL) assembly have shown extraordinarily low oxygen permeability and are of high interest due to their robustness, tailorability and ease of fabrication. Despite all the advantages associated with LbL assembly, the large number of processing steps remains a considerable challenge for commercial use.

## SUMMARY

A method of applying a gas-impermeable coating according to aspects of the disclosure includes forming a polyelectrolyte complex suspension and applying the polyelectrolyte complex suspension to a substrate. In some embodiments, the method may include drying the polyelectrolyte complex suspension after application to the substrate. In some embodiments, the method may include curing the polyelectrolyte complex suspension after application to the substrate.

A method of applying a gas-impermeable coating according to aspects of the disclosure includes forming a polyelectrolyte complex suspension, applying the polyelectrolyte complex suspension to a substrate, and treating the substrate having the polyelectrolyte complex applied thereon. The treating reduces salt content of the polyelectrolyte complex and causes solid film formation on the substrate. The treating results in a gas-impermeable coating being formed on the substrate.

This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or

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essential features of the claimed subject matter, nor is it to be used as an aid in limiting the scope of the claimed subject matter.

## BRIEF DESCRIPTION OF THE DRAWINGS

A more complete understanding of the method and system of the present disclosure may be obtained by reference to the following Detailed Description when taken in conjunction with the accompanying drawings wherein:

FIG. 1 is a flow diagram illustrating a process for applying a gas impermeable coating according to an exemplary embodiment;

FIG. 2(a) is a diagrammatic illustration of a polyelectrolyte complex suspension according to an exemplary embodiment;

FIG. 2(b) is a diagrammatic illustration of the process illustrated in FIG. 1;

FIG. 3 is a table illustrating coating thickness at various cure conditions according to an exemplary embodiment;

FIG. 4 is a flow diagram illustrating a process for applying a gas impermeable coating according to an exemplary embodiment;

FIG. 5 is a diagrammatic illustration of the process illustrated in FIG. 1;

FIG. 6(a) is an illustration of a polycation and polyanion associating to form a polyelectrolyte complex according to an exemplary embodiment;

FIG. 6(b) is a photographic illustration of polyethylenimine and polyacrylic acid suspensions one hour after mixing at various concentrations of sodium chloride;

FIG. 7 is a graphical illustration of the viscosity of polyelectrolyte complex suspensions as a function of sodium chloride concentration, measured at a shear rate of  $1 \text{ s}^{-1}$ .

FIG. 8(a) is a scanning electron micrograph of a high oxygen barrier film before humidity treatment according to an exemplary embodiment;

FIG. 8(d) is a scanning electron micrograph of a high oxygen barrier film after humidity treatment according to an exemplary embodiment;

FIGS. 8(b) and 8(e) are both atomic force micrographs.

FIGS. 8(c) and 8(f) illustrate 3-dimensional topography maps for pH 4 treated polyethylenimine/polyacrylic acid coacervate deposited films before and after humidity post-treatment;

FIG. 9 is a graphical illustration of oxygen transmission rate versus pH; and

FIG. 10 is a graphical illustration of wavelength versus transmittance of film.

## DETAILED DESCRIPTION

Various embodiments will now be described more fully with reference to the accompanying drawings. The disclosure may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein.

FIG. 1 is a flow diagram of a process 100 for applying a gas impermeable coating. FIG. 2(a) is a diagrammatic illustration of a polyelectrolyte complex. FIG. 2(b) is a diagrammatic illustration of the process 100. Referring to FIGS. 1-2(b) collectively, the process 100 begins at block 102. At block 104, a polyelectrolyte complex (PEC) suspension is formed. PECs are formed by the entropy-driven association of oppositely-charged polyelectrolytes in water and can exist as stable colloids, flocculants, or metastable coacervates. Governed by conditions such as, for example,



pH and ionic strength, PEC coacervation is marked by a liquid-liquid phase separation, where a polymer-rich coacervate phase is in equilibrium with a polymer-poor solution phase. PEC coacervates are comprised of weakly bound polyelectrolytes, and have viscous liquid-like behavior that can be exploited to quickly apply them as thin films.

As illustrated in FIG. 2(a), the PEC coacervate complex is comprised of at least two oppositely charged polyelectrolytes (**202a** and **202b**) in water **204**. In various embodiments, cationic polydiallyldimethylammonium chloride (PDDA) and anionic polyacrylic acid (PAA), for example, may be used to form the coacervate. Other embodiments may make use of strong polyelectrolytes. Other further embodiments may make use of, for example, Polyethylenimine, Poly(allyl amine), polyethylenimine (PEI), Chitosan, Functionalized starch, Poly(vinyl amine), Poly(vinylbenzyltrimethylammonium) bromide, and Poly(4-vinyl-N-butyl-pyridinium) chloride as a polycation, and Poly(acrylic acid) and sodium polyacrylate, Poly(styrene sulfonic acid) and sodium poly(styrene sulfonate), Carboxymethylcellulose, Alginic acid, Hyaluronic acid, Heparin, and Polyphosphoric acid and Polyphosphate salts as a polyanion. The ionic strengths of the polycation and polyanion are controlled in order to make the polyanion and the polycation suitable for a coating process. The ionic strength is normally manipulated by the addition of salt such as, for example, NaCl. The pH of the PEC is controlled such that the polyelectrolytes dissolve and there is no hydrogen bonding or electrostatic interaction between the polyelectrolytes. In embodiments utilizing a strong polyanion and a weak polycation, the PEC is formed at a pH of, for example, 2. In embodiments utilizing a strong polycation and a weak polyanion, the pH of the PEC is controlled to have a basic (i.e. greater than 7) pH to dissolve the polyelectrolytes. As used herein, the term “strong” (e.g. strong polyelectrolyte, strong polycation, or strong polyanion) refers to a polyelectrolyte that dissolves completely in solution for most pH values. The term “weak” (e.g. weak polyelectrolyte, weak polycation, or weak polyanion) refers to a polyelectrolyte that are not fully charged in solution and are partially dissociated at intermediate pH. The fractional charge of a weak polyelectrolyte can be modified by changing the solution pH, counter-ion concentration, or ionic strength. As used herein, the term “ionic strength” refers to a measure of the concentration of ions in a solution. In various embodiments, regulation of ionic-strength via, for example, addition of salt, could be utilized in lieu of, or in addition to, pH regulation in order to control interaction of the polyelectrolytes. Other embodiments may utilize two weak polyelectrolytes. In embodiments utilizing two weak polyelectrolytes, the polyelectrolytes are controlled utilizing at least one of a low-pH solution, a high-pH solution, and ionic-strength control.

At block **106**, the PEC suspension is applied to a substrate such as, for example, polyethylene terephthalate (PET), poly(lactic acid) (PLA), polyurethane (PU), polyethylene (PE), polystyrene (PS). The substrate **208** may be of any thickness as dictated by the particular application. As illustrated in FIG. 2(b), in a typical embodiment, the PEC suspension **206** is applied to the substrate **208** using, for example, a dip process. In other embodiments, however, the PEC suspension could be applied to the substrate using, for example, gravure application, slot-die application, roll-to-roll application, or by use of an instrument such as, for example, a Mayer rod. During application of the PEC suspension **206** to the substrate **208**, the thickness of the applied PEC suspension **206** is controlled by viscosity and the presence of dissolved solids.

At block **108**, the coated substrate **209** is dried. In a typical embodiment, the coated substrate **208** is dried, for example, for approximately 20 minutes at, for example, approximately 150° C.; however, in other embodiments, other temperatures and drying times could be utilized. Such drying evaporates excess water from the PEC **206** and has been demonstrated to improve optical clarity of the gas-impermeable coating when compared to processes where the drying block **108** is omitted.

At block **110**, the coated substrate **209** is immersed in a buffering solution **210**. In a typical embodiment, the buffering solution **210** has a pH of a weak acid such as, for example, in the range of 3-5. In various embodiments, the buffering solution **210** may be, for example, acetic acid, citric acid, a phosphate buffer, or a trizma buffer as dictated by the polyelectrolytes used in the PEC **206**. In embodiments utilizing a strong polyanion and a weak polycation, a buffering solution **210** having a basic pH is desirable. During block **110**, the pH of the buffering solution **210** causes pH-induced ionic bonding in the PEC **206**, which results in curing of the PEC **206**. In a typical embodiment, utilization of the buffering solution **210** to result in a cured PEC coating **211** results in approximately a 10-fold improvement in gas-impermeability than if the buffering solution **210** were not utilized. In various embodiments, one or both of blocks **108** and **110** may be omitted from the process **100** depending on the needs of the particular application. The process **100** ends at block **112**.

FIG. 3 is a table illustrating thickness of the gas-impermeable coating at various cure conditions. By way of example, the data shown in FIG. 3 utilizes a PEC having a 1:3 molar ratio of cation to anion; however, in various embodiments, other molar ratios could be utilized as dictated by design requirements. As shown in FIG. 3, the presence of a higher weight percentage of solid content in the PEC **206** gives rise to thicker gas impermeable coatings. Group **302** illustrates 6 wt % solid PEC with no cure. Group **304** illustrates 4.5 wt % solid PEC with no cure. Group **306** illustrates 3 wt % solid PEC with no cure. Group **308** illustrates 1.5 wt % solid PEC with no cure. Group **312** illustrates 6 wt % solid PEC utilizing a buffering solution with a pH of 3 for curing. Group **314** illustrates 4.5 wt % solid PEC utilizing a buffering solution with a pH of 3 for curing. Group **316** illustrates 3 wt % solid PEC utilizing a buffering solution with a pH of 3 for curing. Group **318** illustrates 1.5 wt % solid PEC utilizing a buffering solution with a pH of 3 for curing. Group **322** illustrates 6 wt % solid PEC utilizing a buffering solution with a pH of 4 for curing. Group **324** illustrates 4.5 wt % solid PEC utilizing a buffering solution with a pH of 4 for curing. Group **326** illustrates 3 wt % solid PEC utilizing a buffering solution with a pH of 4 for curing. Group **328** illustrates 1.5 wt % solid PEC utilizing a buffering solution with a pH of 4 for curing. Group **332** illustrates 6 wt % solid PEC utilizing a buffering solution with a pH of 5 for curing. Group **334** illustrates 4.5 wt % solid PEC utilizing a buffering solution with a pH of 5 for curing. Group **336** illustrates 3 wt % solid PEC utilizing a buffering solution with a pH of 5 for curing. Group **338** illustrates 1.5 wt % solid PEC utilizing a buffering solution with a pH of 5 for curing.

FIG. 4 is a flow diagram illustrating a process **400** for applying a gas impermeable coating. FIG. 5 is a diagrammatic illustration of the process **400**. Referring to FIGS. 4-5 in combination, the process **400** begins at block **402**. At block **404**, a polyelectrolyte complex (PEC) suspension is formed.



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As illustrated in FIG. 5, the PEC coacervate complex is comprised of at least two oppositely charged polyelectrolytes (**502a** and **502b**) in water **504**. In various embodiments, cationic polyethylenimine (PEI) and anionic polyacrylic acid (PAA), for example, may be used to form the coacervate. Other embodiments may make use of strong polyelectrolytes. Other further embodiments may make use of Polyethylenimine, Poly(allyl amine), Poly(diallyldimethyl ammonium chloride), Chitosan, Functionalized starch, Poly(vinyl amine), Poly(vinylbenzyltrimethyl-ammonium) bromide, and Poly(4-vinyl-N-butyl-pyridinium) chloride as a polycation, and Poly(acrylic acid) and sodium polyacrylate, Poly(styrene sulfonic acid) and sodium poly(styrene sulfonate), Carboxymethylcellulose, Alginic acid, Hyaluronic acid, Heparin, and Polyphosphoric acid and Polyphosphate salts as a polyanion. The ionic strengths of the polycation and polyanion are controlled in order to make it suitable for a Meyer rod coating process. The ionic strength is normally manipulated by the addition of salt such as, for example, NaCl.

At block **406**, the PEC suspension **506** is applied to a substrate. As illustrated in FIG. 5, in a typical embodiment, the PEC suspension **506** is applied to the substrate **508** using, for example, a Meyer rod **510**. The Meyer rod **510** is drawn across the substrate, doctoring off coating fluid, using formed or wired grooves to deposit a specific wet-film thickness onto the substrate **508**. The PEC suspension **506** used for this process must have sufficient viscosity to resist dewetting and contain enough weight polymer to deposit a uniform layer. In a typical embodiment, NaCl concentration heavily influences the viscosity and maintaining a proper concentration is vital to the coating process. In certain embodiments, the substrate **508** may be corona-treated or plasma treated to increase surface energy. In certain embodiments, a wetting agent, such as, for example, a surfactant, may be added to the PEC suspension **506** to decrease surface tension and achieve more complete wetting of the substrate **508** by the PEC suspension **506**.

At block **408**, the coating is treated. As illustrated in FIG. 5, once the substrate **508** is coated the film **512** must be treated to allow the applied film to become solid. In a typical embodiment, salt must be driven out from the film **512** to allow the film **512** to solidify. Thus, any solution containing a lower salt concentration should be able to facilitate this process. In certain embodiments, a buffer **514** may also be used such as, for example, a citric acid/citrate buffer aqueous solution, where the buffer improves the film's **512** durability to rinsing and produces higher cohesive energy density, thereby preventing gas molecules from moving aside polymer chains. In some embodiments, and as illustrated in FIG. 5, the treatment may be performed by immersion of the film **512**. Various other embodiments may make use of spraying the film or a combination of the immersion and spraying. Additionally, various embodiments may utilize various forms of drying such as air drying, oven drying, or suspension. Various other embodiments, however, may not dry the solid film **512**. In a typical embodiment, the resulting film thickness is less than 10 microns. In a typical embodiment, the oxygen transmission rate through the film is less than approximately  $10 \text{ cm}^3/(\text{m}^2 \text{ day atm})$ . FIG. 6 provides a graphical illustration of oxygen transmission rate versus pH.

After treatment in block **408**, the film **512** is subjected to a high humidity treatment in block **410** in order to remove porosity and uncover fissures. Pores likely arise from fast evaporation of water from the film during air drying and are not present in layer-by-layer assembled films. Water acts as a plasticizer, allowing polymer to fill the coating's pores. In

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various embodiments, exposure to high humidity such as, for example, greater than approximately 95% relative humidity for approximately 12 hours helps to close pores present in the film **512**. In other embodiments, thermal crosslinking chemically bonds the PEI to the PAA to create amide bonds. Thermal crosslinking may be performed by high heat at, for example, approximately  $150^\circ \text{C}$ . for approximately 2 hours. Various other embodiments may make use of other types of crosslinking. Some crosslinking may occur, for example, via chemical reaction. In certain embodiments, a crosslinking agent is added to the original PEC suspension and later activated. The final film **512** would be exposed to a crosslinking agent to finish the process. The process **400** ends at block **412**.

## EXAMPLES

Cationic branched polyethylenimine ( $M_w=25,000 \text{ g mol}^{-1}$ ), anionic polyacrylic acid solution ( $M_w=100,000 \text{ g mol}^{-1}$ , 35 wt % in water), anhydrous sodium hydroxide pellets (reagent grade,  $\geq 98\%$ ), sodium chloride, citric acid monohydrate, and sodium citrate dihydrate were purchased from Sigma-Aldrich (Milwaukee, Wisconsin). P-doped, single side polished (1 0 0) silicon wafers (University Wafer, South Boston, Massachusetts), with a thickness of  $500 \mu\text{m}$ , were used as substrates **408** for profilometer thickness measurements and microscopy. Films for oxygen transmission testing were deposited on a  $127 \mu\text{m}$  thick poly(ethylene terephthalate) (PET) film (ST505, Dupont-Teijin) purchased from Tekra (New Berlin, Wisconsin).

All aqueous solutions were prepared with  $18.2 \text{ M}\Omega\cdot\text{cm}$  deionized water. The pH of individual 20 wt % solutions of PEI and PAA were adjusted to 8.0 using 5 M HCl and NaOH, respectively. After achieving pH 8.0, the solutions were diluted to 10 wt % polymer and the pH was adjusted to 8.0 again. The PEC suspensions **506** were prepared by taking equal volumes of the two solutions and adding sodium chloride to achieve the desired concentration NaCl. PEI was added dropwise to the PAA while stirring vigorously. A solution pH of 8 was used because it reduced localized flocculation during mixing relative to lower pH processing. The suspensions were stirred for 10 min and then allowed to sit for approximately 1 hour. Coacervates and solutions were "annealed" in an oven for approximately 2 hours at approximately  $70^\circ \text{C}$ . prior to characterization.

A PEI/PAA coacervate, prepared using 1.0 M NaCl, was separated from the dilute phase by pipet. PET substrates **508** were corona treated immediately before coating. Silicon and PET substrates **508** were mounted on glass and coacervate fluid **506** was deposited using the Meyer rod **510**. The Meyer rod **510** was approximately 0.5 inches in diameter, approximately 16 inches long and had an "equivalent wire diameter" of approximately 0.05 mm. The substrate **508** was then dipped in 100 mM citric acid/citrate buffer for 1 minute, followed by spraying with water to rinse and drying with a stream of filtered air. Humidity post-treatment involved placing the coated substrate **508** in a chamber with humidity varying from 93-97% relative humidity for approximately 12 hour. Thermal crosslinking was accomplished by placing the coated substrate **508** in an oven at approximately  $150^\circ \text{C}$ . for approximately 2 hour. All films were stored in a drybox for approximately 24 hours or more prior to characterization.

Film **512** thickness was measured on silicon wafers with, for example, a profilometer. Surface morphology was imaged using, for example, a JSM-7500F FESEM (JEOL, Tokyo, Japan). Prior to imaging, each film was sputter coated with approximately 5 nm of, for example, platinum/



palladium to reduce surface charging of the film. Atomic force microscopy was done using a Bruker Dimension Icon atomic force microscope ("AFM"). All mapping measurements were conducted using the tapping mode imaging of the AFM, under ambient conditions such as, for example, approximately 24° C. and approximately 45% relative humidity. Oxygen transmission rate measurements were performed by using, for example, an Oxtran 2/21 ML oxygen permeability instrument, in accordance with ASTM Standard D-3985, at approximately 23° C. and at approximately 50% relative humidity. Viscosity (TO) was measured using, for example, an AR G2 Rheometer (TA Instruments, New Castle, Delaware) using a 40 mm, 2° steel cone. Shear-stress experiments were performed at approximately 25° C. over a frequency range of approximately 1-100 Hz. Transmittance of PEC films **512** was measured using a USB2000 UV-Vis spectrometer (Ocean Optics, Dunedin, Florida). As illustrated in FIG. 7, viscosity decreases with higher salt concentration. FIG. 10 is a graphical illustration of transmittance versus wavelength for various pH films.

The effect of salt concentration on the complexation of the polyelectrolytes was studied by varying the concentration of sodium chloride in PEI and PAA solutions at, for example, 10 wt % polymer at pH 8.0, before mixing. In a range of 0 to approximately 0.25 M NaCl, PEI and PAA strongly associate into larger networks and form a macroscopic precipitate that is unsuitable for the Meyer rod **510** coating process. At concentrations of approximately 1.50 M and above, the ionic strength is high enough for PEI and PAA to be dissolved as individual chains, creating a true solution of polyelectrolytes. Coacervation is achieved at intermediate NaCl concentrations of, for example, approximately, 0.50-1.00 M, where phase separation of the polymer-rich coacervate layer and a polymer-poor dilute layer is observed. Samples of varying salt concentration 1 hour after mixing are shown in FIG. 6b. To further coalesce microphase droplets and better identify which suspensions phase separate, both the solutions and coacervates were "annealed" for approximately 2 hours at approximately 70° C., resulting in optically transparent phases. All coacervate phases were decanted for further characterization. All solutions have pH of approximately 8.0 and contain approximately 10% weight polymer with a 1:1 weight ratio of PEI to PAA.

Rheology was performed on the PEI/PAA solutions as well as the lower concentration salt coacervate phases to determine which PEC sample was suitable as the coating fluid for coating with the Meyer rod **510**. FIG. 7 is a graphical illustration of the viscosity of coacervate phases at varying NaCl concentration. The free chain polyelectrolyte solutions (1.25-1.50 M) have viscosities much lower than those of the coacervates (0.50 M-1.0 M), where there is stronger interaction between polymer chains. The viscosities of the free chain polyelectrolyte solutions were considerably higher than water such as, for example, 1 mPa·s, indicating critical overlap concentration was achieved. To utilize the Meyer rod **510** for coating with minimal defects, the viscosity of the fluid should be high enough to resist secondary flows induced by dewetting and surface tension. The coacervate suspensions are suitable candidates for these coatings as they remain within the range of viscosity suitable for the Meyer rod **510** technique such as, for example, in the range of approximately 300-800 mPa·s. The complex coacervate with 1.0 M NaCl was used for the gas barrier film because its viscosity remained suitable over a wide range of shear rates such as, for example, 0.2-100.0 s<sup>-1</sup>.

After separating from the top dilute phase of the polyelectrolyte complex, the coacervate prepared with 1.0 M

NaCl was applied to substrates using the Meyer rod **510** illustrated in FIG. 5. The PEC film **512** was then dipped in water to extract sodium chloride, allowing the polyelectrolyte chains to more strongly associate and solidify the complex. Because the polyelectrolyte coacervate is above critical overlap concentration, the complex solidifies into a coherent film rather than individual colloidal particles. Subsequent spray rinsing appeared to erode the film **512** and there was noticeable undesirable stickiness, likely due to the incomplete ionization of PEI at pH 8 in the film. When PEI is not completely protonated, there are less ammonium groups to ionically bond with the carboxylate ions of PAA.

After rod coating, the films were immersed into citric acid/citrate buffer solutions at pH 6, 4, and 2 to fully protonate PEI, which improved its association with PAA. In addition to improving the film's durability to rinsing, acid buffer treatment produces higher cohesive energy density, which prevents gas molecules from moving aside polymer chains. Spray rinsing removed buffer, persistent salt and excess polymer and the films were finally dried by a stream of dry air. PEC films on silicon treated by pH 6 buffer were depleted in some areas and coatings treated at pH 2 could not remain adhered after spray rinsing. Using pH 4 buffer proved to be the most effective treatment and produced highly conformal films, with average thickness of approximately 1.63±0.09 μm.

As illustrated in FIG. 8a, scanning electron micrographs of pH 4 treated PEC films revealed a considerable amount of porosity (FIG. 8a). Atomic force microscopy (AFM) revealed pores spanning the thickness of the film, inhibiting the film's ability to reduce gas permeability. Pores likely arise from the fast evaporation of water from the film during air drying and are not present in films assembled layer-by-layer. To remove these pores, films were post-treated for approximately 12 hours in a 95% relative humidity chamber. Water acts as a plasticizer, allowing polymer to fill the coating's pores. As shown in FIGS. 8d-8f, both SEM and AFM of humidity-treated films **512** reveal very smooth coatings. Roughness of treated films **512** was reduced two orders of magnitude (from approximately 395 nm to approximately 2.60 nm and thickness increased to 1.91±0.08 μm).

Although unsuccessful on silicon, PEC films treated by a pH 2 and 6 buffer were successfully deposited on PET substrates **508** along with pH 4 treated films. pH 4 and pH 6 treatment resulted in hazy films, with visible light transmittance of approximately 14 and approximately 11%, respectively. Films **512** treated with pH 2 buffer were completely opaque having approximately 3% visible light transmittance. FIG. 10 shows that pH 4 treatment results in the best oxygen barrier on PET, reducing the oxygen transmission rate (OTR) of 0.127 mm thick PET from 9.51 to 1.46 cm<sup>3</sup>/(m<sup>2</sup>·day·atm). Humidity treatment of the PEC coating reduced the porosity of the film **512**, marked by the substantial reduction of coating haziness (98% transparent), resulting in further reduction of OTR to 0.384 cm<sup>3</sup>/(m<sup>2</sup>·day·atm). An even further reduction in OTR resulted with thermal cross-linking of the humidified film **512**, achieving an OTR of 0.08 cm<sup>3</sup>/(m<sup>2</sup>·day·atm). Thermal cross-linking chemically bonds the PEI to PAA to create amide bonds. Unlike an earlier study incorporating thermal cross-linking, no contraction was observed here, with the film maintaining a thickness of 1.99±0.06 μm.

The rod coating of polyelectrolyte coacervate suspensions provides a framework in which multi-polyelectrolyte films can be deposited in a single step. With this technique, it is likely that many multilayer gas barrier coatings can be more



quickly and simply deposited. By affecting salt concentration, coacervates of sufficient viscosity can be formed to resist fluid flow and the film can be cured by using an appropriate pH buffer. Post-treatments of the film improved the oxygen barrier enormously and by combining humidity and cross-linking treatments, these PEC-based films provided PET with a two order of magnitude reduction in oxygen transmission rate, while also achieving optical transparency. This environmentally benign process offers the opportunity for scalable, less-costly barrier films.

Although various embodiments of the method and system of the present disclosure have been illustrated in the accompanying Drawings and described in the foregoing Specification, it will be understood that the disclosure is not limited to the embodiments disclosed, but is capable of numerous rearrangements, modifications, and substitutions without departing from the spirit and scope of the disclosure as set forth herein. For example, although the area 102 has been described herein as being an agricultural field, one skilled in the art will recognize that the area 102 could be any geographic area on which remote sensing could be performed. It is intended that the Specification and examples be considered as illustrative only.

What is claimed is:

1. A method of applying a gas-impermeable coating, the method comprising:

forming a polyelectrolyte complex suspension;

applying the polyelectrolyte complex suspension to a substrate, the polyelectrolyte complex suspension comprising a molar ratio of 1:3 of polycation to polyanion; treating the substrate having the polyelectrolyte complex applied thereon, wherein the treating reduces salt content of the polyelectrolyte complex and causes solid film formation on the substrate; and

wherein, the treating results in a gas-impermeable coating being formed on the substrate.

2. The method of claim 1, wherein the polyelectrolyte complex comprises at least two oppositely charged polyelectrolytes.

3. The method of claim 2, wherein the polyelectrolyte complex comprises a cationic polyethylenimine (PEI) and anionic polyacrylic acid (PAA).

4. The method of claim 1, further comprising controlling pH of the polyelectrolyte complex such that polyelectrolytes dissolve or there is a reduction of at least one of hydrogen bonding or electrostatic interaction between the polyelectrolytes.

5. The method of claim 1, wherein the polyelectrolyte complex comprises at least one of a polycation, a polyanion, polyethylenimine, Poly(allyl amine), poly(diallyldimethyl ammonium chloride), chitosan, functionalized starch, poly(vinyl amine), poly(vinylbenzyltrimethyl-ammonium) bromide, poly(4-vinyl-N-butyl-pyridinium) chloride, poly(acrylic acid), sodium polyacrylate, poly(styrene sulfonic acid), sodium poly(styrene sulfonate), carboxymethylcellulose, alginic acid, hyaluronic acid, heparin, polyphosphoric acid, or polyphosphate salts.

6. The method of claim 1, further comprising controlling ionic strength to thereby make the polycation and the polyanion suitable for a Meyer rod coating process.

7. The method of claim 6, wherein the ionic strength is manipulated by addition of a salt.

8. The method of claim 1, wherein the applying comprises dip coating.

9. The method of claim 1, wherein the applying comprises utilizing a Meyer rod to apply the polyelectrolyte complex suspension to the substrate.

10. The method of claim 1, wherein the treating comprises a humidity treatment.

11. The method of claim 10, wherein the humidity treatment removes porosity and uncovers fissures.

12. The method of claim 10, wherein the humidity treatment is conducted at greater than 95% relative humidity.

13. The method of claim 1, wherein the treating comprises addition of a cross-linking agent.

14. The method of claim 13, wherein method further comprises crosslinking chemical bonds of polyethylenimine and polyacrylic acid to create amide bonds.

15. The method of claim 14, wherein the crosslinking comprises thermal crosslinking performed by high heat at 150° C. for 2 hours.

16. The method of claim 1, wherein the treating comprises utilizing a buffer to improve durability to rinsing of the solid film formation and produce higher cohesive energy density.

17. The method of claim 16, wherein the buffer comprises a citric acid or a citrate buffer aqueous solution.

18. The method of claim 1, wherein the solid film formation is less than 10 microns.

19. The method of claim 1, wherein the solid film formation has an oxygen transmission rate of less than 10 cm<sup>3</sup>/(m<sup>2</sup>·day·atm).

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