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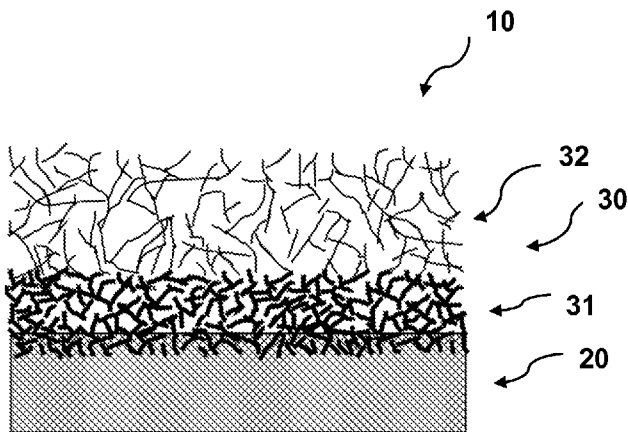
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(54) Title: DURABLE HYDROPHILIC COATING PRODUCED BY MULTIPLE STAGE PLASMA POLYMERIZATION



(57) Abstract: The present invention discloses methods for producing a durable hydrophilic coating for hydrophobic substrates such as silicone elastomer using multiple stage plasma polymerization of compounds containing hydrophilic functional groups. The first stage plasma polymerization creates a highly cross-linked hydrophilic polymer barrier to prevent hydrophobic moieties from migrating from the bulk to the surface; the final stage creates a hydrogel-like layer on the top of the coating to render the surface more hydrophilic and lubricious. Advantageously, such methods produce a durable hydrophilic surface that resists hydrophobic recovery of highly hydrophobic substrates such as silicone elastomer.

FIG. 1



DURABLE HYDROPHILIC COATING PRODUCED BY MULTIPLE STAGE
PLASMA POLYMERIZATION

Cross-Reference to Related Application

[0001] This application claims priority of U.S. Provisional Patent Application No. 62/062,150, filed October 10, 2014, the entire contents of which are incorporated by reference herein.

Field of the Invention

[0002] The present invention discloses methods for producing a durable hydrophilic coating for hydrophobic substrates such as silicone elastomer using multiple stage plasma polymerization of compounds containing hydrophilic functional groups. The first stage plasma polymerization creates a highly cross-linked hydrophilic polymer barrier to prevent hydrophobic moieties from migrating from the bulk to the surface; the final stage creates a hydrogel-like layer on the top of the coating to render the surface more hydrophilic and lubricious. Advantageously, such methods produce a durable hydrophilic surface that resists hydrophobic recovery of highly hydrophobic substrates such as silicone elastomer.

Background of the Invention

[0003] Silicone elastomer is widely used in industry due to its inert properties and its ease of manufacturing and shaping. It is generally non-reactive, stable, and resistant to extreme environments and temperatures from -55 °C to +300 °C while still maintaining its useful properties. Silicone elastomer has a hydrophobic surface with water contact angle

higher than 90°C. However, in many applications, such as contact lens, it is desirable to modify the surface to make it more hydrophilic and lubricious to avoid tear breaking due to the hydrophobic surface and discomfort due to high friction.

[0004] Prior arts of imparting hydrophilic property to silicone surface include oxygen plasma treatment. Although the method can render the silicone surface hydrophilic, the surface will undergo hydrophobic recovery with time (Kim et al. “The Mechanisms of Hydrophobic Recovery of Polydimethylsiloxane Elastomers Exposed to Partial Electrical Discharges”, *Journal of Colloid and Interface Science* 244, 200–207 (2001)). This is thought to be due to the migration of low molecular weight species from the bulk to the surface of the silicone elastomer.

[0005] Other prior arts methods of rendering the silicone surface hydrophilic involve solution coating processes where the silicone substrate is immersed in a hydrophilic polymer solution to allow for the coating of the hydrophilic polymer. For example, in US patent 8,944,592, a method is disclosed where the silicone substrate (contact lens) is heated in an aqueous solution in the presence of the hydrophilic polymeric material to and at a temperature from about 40°C to about 140°C. There are a few disadvantage of these prior art methods that involves a solution coating step. One disadvantage is that the silicone substrate needs to be pre-activated either by oxygen plasma, UV/ozone, corona discharges, plasma polymerization, or other methods, which increases the complexity of the surface coating process. For example, in US patent 8,944,592, the disclosed method requires that the silicone substrate contains pre-incorporated amino or carboxyl groups before performing the solution coating step. Another disadvantage is that these methods cannot be used for substrates that contain components (such as biosensor components) that can be damaged by water or other solvents due to the requirement of the solution coating step.

[0006] Plasma polymerization has the ability to produce a polymer coating on the substrates in a dry state. However, prior art plasma polymerization methods have not been able to provide a durable hydrophilic coating for silicone substrate. Therefore in prior art methods plasma polymerization is often used as an intermediate step before a solution coating step, which results in a complicated coating process and incompatibility with substrates that contain water-sensitive components. Therefore it is desirable to provide a

plasma polymerization method that is able to produce a durable hydrophilic coating without the use of solution coating steps.

Summary of the Invention

[0007] A method is disclosed herein for applying a durable, hydrophilic coating using multiple stage plasma polymerization of compounds containing hydrophilic functional groups.

[0008] In the first stage of plasma polymerization, a high plasma excitation power is used to generate plasma glow discharge with high intensity. The high intensity plasma glow discharge, in the presence of the vapor of compounds containing hydrophilic functional groups, is used to create a polymer layer with high degree of cross-linking. This highly cross-linked polymer functions as a durable hydrophilic layer and a barrier to prevent hydrophobic moieties from migrating from the bulk of the substrate to the surface.

[0009] In the final stage of plasma polymerization, a low plasma excitation power is used to generate plasma glow discharge with low intensity. The low intensity plasma glow discharge, in the presence of chemical vapor of compounds containing hydrophilic functional groups, is used to create a polymer layer with low degree of cross-linking. This polymer layer increases hydrophilicity and lubricity for the surface.

[0010] More stages of plasma polymerization, in between the first and final stages, can be used to create more layers with different degree of cross-linking and thickness.

[0011] One advantage of the disclosed method is that the hydrophilicity of the coated surface can be preserved for a very long time with minimum hydrophobic recovery due the barrier created in the first stage of high power plasma polymerization.

[0012] A further advantage of the disclosed method is that the hydrophilic coating is formed in a dry state without the use of any solvent. This is advantageous for coating devices with electronic and/or biosensing components.

[0013] These and other features of the invention will be better understood through a study of the following detailed description and accompanying drawings.

Brief Description of the Figures

[0014] FIG. 1 is a drawing representing a substrate coated using subject invention multiple stage plasma polymerization of compounds containing hydrophilic functional groups. The bottom or innermost layer of polymer coating is created by the first stage high plasma excitation power driven plasma polymerization, the top or outermost layer of polymer coating is created by the final stage low plasma excitation power driven plasma polymerization.

[0015] FIG. 2 is a chart showing the radiofrequency power level and plasma polymerization deposition rate during a 2-stage plasma polymerization process.

[0016] FIG. 3 is a chart comparing the stability of the hydrophilicity of the silicone surface after various hydrophilic modifications. The hydrophilicity of the surface is characterized by water contact angle measurement using a 5 microliter water droplet. The stability of the hydrophilic surface was monitored over 100 days during which the silicone substrates were stored in air. The hydrophilic surface modification methods compared include (1) oxygen plasma treatment method, (2) single stage plasma polymerization with low power, (3) single stage plasma polymerization with high power, and (4) 2-stage plasma polymerization method (subject invention method).

[0017] FIG. 4 is a chart comparing the lubricity of an uncoated silicone substrate and a silicone substrate coated with subject invention method.

Detailed Description of the Invention

[0018] With reference to FIG. 1, a device **10** is depicted of comprising a substrate **20** and a coating composition **30**. The coating composition **30** is composed of a bottom or innermost polymer layer **31** produced by a high plasma excitation power driven plasma polymerization of compounds containing hydrophilic functional groups, and a top or outermost polymer layer **32** produced by a low plasma excitation power driven plasma polymerization of compounds containing hydrophilic functional groups. As a result of high plasma excitation power, the polymer formed in the innermost layer is composed of a polymer with high cross-linking degrees; this layer functions as a durable hydrophilic layer and a barrier to prevent hydrophobic moieties from migrating from the bulk of the substrate to the surface. As the result of low plasma excitation power, the polymer formed in the

outermost layer is composed of a polymer with low cross-linking degrees; this layer increases hydrophilicity and lubricity for the polymer surface.

[0016] Any known technique can be used to generate plasma. The plasma may be generated using AC or DC power, radio-frequency (RF) power or micro-wave frequency power. Preferably, the plasma system uses a single radio-frequency (RF) power supply; typically at 13.56 MHz. The plasma system can either be capacitively coupled plasma, or inductively coupled plasma.

[0017] The substrate may be made of any materials, including polymers, glass, metal and silicon. Examples of polymers include polydimethylsiloxane, polystyrene, polypropylene, polyethylene, polyester, polyurethane, ABS, PVC, polytetrafluoroethylene, polyvinylidene, and mixtures thereof. In a preferred embodiment, the substrates are made of silicone or polydimethylsiloxane elastomer. In one example, the substrates are silicone contact lenses.

[0018] The hydrophilic functional groups used can be charged or uncharged polar group. Charged functional groups include amino and carboxyl groups. Polar groups include hydroxyl and ethylene glycol groups. In a preferred embodiment, the compounds used for plasma polymerization contain hydrophilic ethylene glycol groups such as Tri(ethylene glycol) monoethyl ether ($\text{CH}_3\text{CH}_2(\text{OCH}_2\text{CH}_2)_3\text{OH}$) or Tri(ethylene glycol) monomethyl ether ($\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OH}$).

EXAMPLES

Example A

[0019] A silicone substrate (polydimethylsiloxane elastomer) is coated with subject invention multiple stage plasma polymerization method in a radiofrequency plasma glow discharge chamber in the presence of the vapor of hydrophilic carboxyl group containing compound acrylic acid. In the first stage of plasma polymerization process, the radiofrequency power is set at approximately 200 W and the plasma polymerization is proceeded for 5 minutes. In the second stage of plasma polymerization process, the

radiofrequency power is adjusted to approximately 20 W and the plasma polymerization is proceeded for 20 minutes.

Example B

[0020] A silicone substrate (polydimethylsiloxane elastomer) is coated with subject invention multiple stage plasma polymerization method in a radiofrequency plasma glow discharge chamber in the presence of the vapor of hydrophilic hydroxyethyl group containing compound 2-hydroxyethyl methacrylate. In the first stage of plasma polymerization process, the radiofrequency power is set at approximately 200 W and the plasma polymerization is proceeded for 5 minutes. In the second stage of plasma polymerization process, the radiofrequency power is adjusted to approximately 20 W and the plasma polymerization is proceeded for 20 minutes.

Example C

[0021] A silicone substrate (polydimethylsiloxane elastomer) is coated with subject invention multiple stage plasma polymerization method in a radiofrequency plasma glow discharge chamber in the presence of the vapor of hydrophilic ethylene glycol containing compound Tri(ethylene glycol) monomethyl ether ($\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OH}$). In the first stage of plasma polymerization process, the radiofrequency power is set at approximately 200 W and the plasma polymerization is proceeded for 5 minutes. In the second stage of plasma polymerization process, the radiofrequency power is adjusted to approximately 20 W and the plasma polymerization is proceeded for 20 minutes.

Example D

[0022] A silicone substrate (polydimethylsiloxane elastomer) is coated with subject invention multiple stage plasma polymerization method in a radiofrequency plasma glow discharge chamber in the presence of the vapor

of a hydrophilic compound Tri(ethylene glycol) monoethyl ether ($\text{CH}_3\text{CH}_2(\text{OCH}_2\text{CH}_2)_3\text{OH}$). In the first stage of plasma polymerization process, the radiofrequency power is set at approximately 200 W and the plasma polymerization is proceeded for 5 minutes. In the second stage of plasma polymerization process, the radiofrequency power is adjusted to approximately 20 W and the plasma polymerization is proceeded for 20 minutes. A quartz crystal microbalance is placed in the chamber to monitor the deposition rate of the plasma polymerization coating on the surface. As shown in FIG. 2, the plasma polymerization coating deposition rate corresponds with the radiofrequency power input: high power results in higher deposition rate while low power results in lower deposition rate.

Example E

[0023] Four coating methods for silicone substrate (polydimethylsiloxane elastomer) are compared for hydrophobic recovery when stored in air for a prolonged period of time: (1) oxygen plasma treatment method, (2) single stage plasma polymerization with low power (the coating process described in Example D without the first stage high power plasma polymerization step), (3) single stage plasma polymerization with high power (the coating process described in Example D without the second stage low power plasma polymerization step), and (4) 2-stage plasma polymerization (subject invention method) as detailed in Example D. As can be seen in FIG. 3, the silicone substrate coated with prior art oxygen plasma treatment method demonstrated hydrophilicity with small water contact angle on the first day, but the water contact angle increased to about 90 degree after 10 days of storage, demonstrating the well-known hydrophobic recovery phenomenon. The silicone substrate coated with single stage plasma polymerization with low power improves the stability of the hydrophilic surface, however hydrophobic recovery still occurred and the water contact angle increases to over 80 degree after 20 days of storage. The silicone substrate coated with single stage plasma polymerization with high power further improves the

stability of the hydrophilic surface, although the starting water contact angle is not as low as desired, no significant increase in water contact angle is observed over 100 days. Finally, the silicone substrate coated with subject invention multiple stage plasma polymerization method has a desired low water contact angle, and no significant increase in water contact angle is observed over 100 days, demonstrating a durable hydrophilic surface created by the subject invention.

Example F

[0024] A silicone substrate (polydimethylsiloxane elastomer) coated with subject invention multiple stage plasma polymerization method was compared with an uncoated silicone substrate for lubricity. As can be seen in FIG. 4, both the static and kinetic frictions decrease significantly with the subject invention hydrophilic coating.

[0025] As will be appreciated by those skilled in the art, the subject invention can be used to produce a durable hydrophilic coating. By way of non-limiting example, the subject invention can be used to prepare surfaces of contact lenses made of silicone material, including contact lenses that contain electronic components and/or biosensing components such as glucose sensing enzymes.

What is Claimed is:

1. A device comprising a substrate and a coating composition produced by plasma polymerization, said coating composition comprises of at least two layers: the innermost layer being a polymer coating produced by plasma polymerization of compounds containing hydrophilic functional groups under the condition of high plasma excitation power; the outermost layer being a polymer coating produced by plasma polymerization of compounds containing hydrophilic functional groups under the condition of low plasma excitation power; wherein the coating composition impart highly durable hydrophilic property to the substrate.
2. A device of Claim 1, wherein said substrate contains silicone.
3. A device of Claim 1, wherein said substrate is a contact lens.
4. A device of Claim 1, wherein said substrate is a biosensor.
5. A device of Claim 1, wherein said substrate is a glucose monitoring device.
6. A device of Claim 1, wherein said substrate is a contact lens containing electronic components.
7. A device of Claim 1, wherein said substrate is a contact lens containing biosensing components.
8. A device of Claim 1, wherein said hydrophilic groups include ethylene glycol, hydroxyethyl, hydroxyl, carboxyl or amino groups.
9. A device of Claim 1, wherein said hydrophilic groups contains poly(ethylene glycol).

10. A device of Claim 1, wherein a single compound or a same mixture of compounds are used for plasma polymerization coating of all the layers.
11. A device of Claim 1, wherein said high plasma excitation power is a radiofrequency power of more than 50 W per cubic foot of plasma zone volume and said low plasma excitation power is a radiofrequency power of less than 50 W per cubic foot of plasma zone volume.
12. A device of Claim 1, wherein the plasma excitation power is varied from the highest level to the lowest level continuously during the plasma polymerization process.

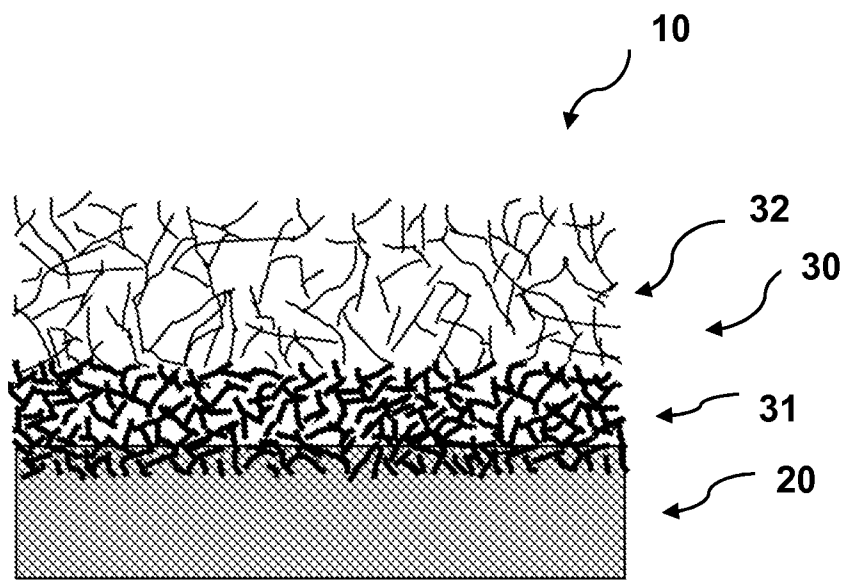


FIG. 1

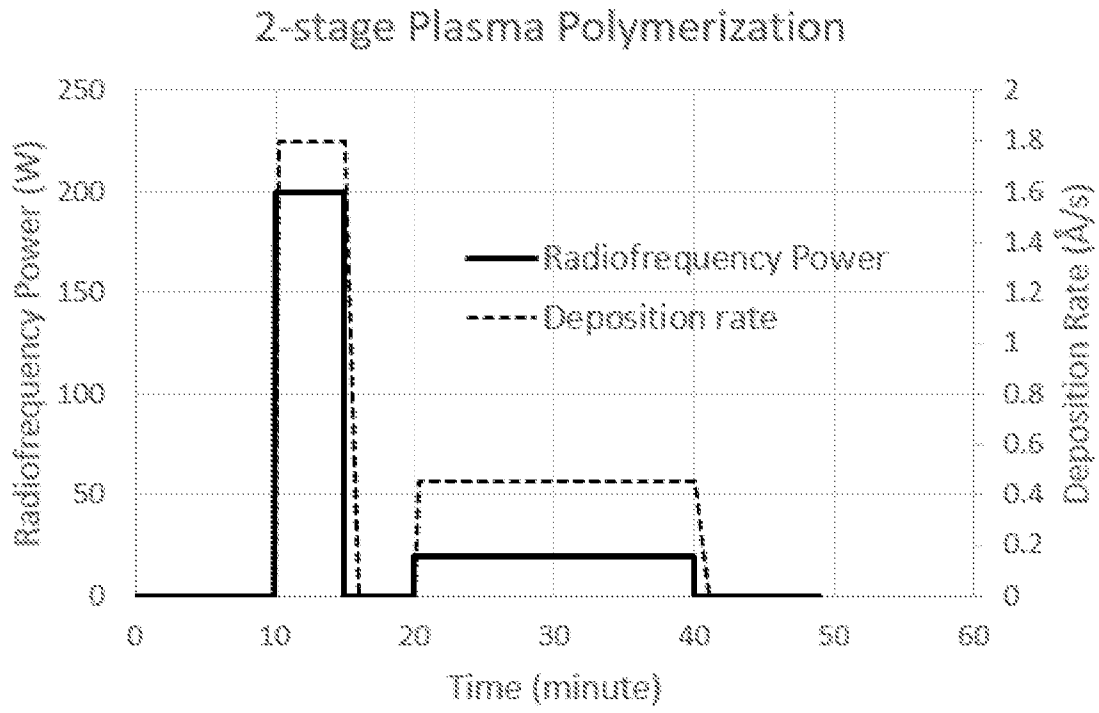


FIG. 2

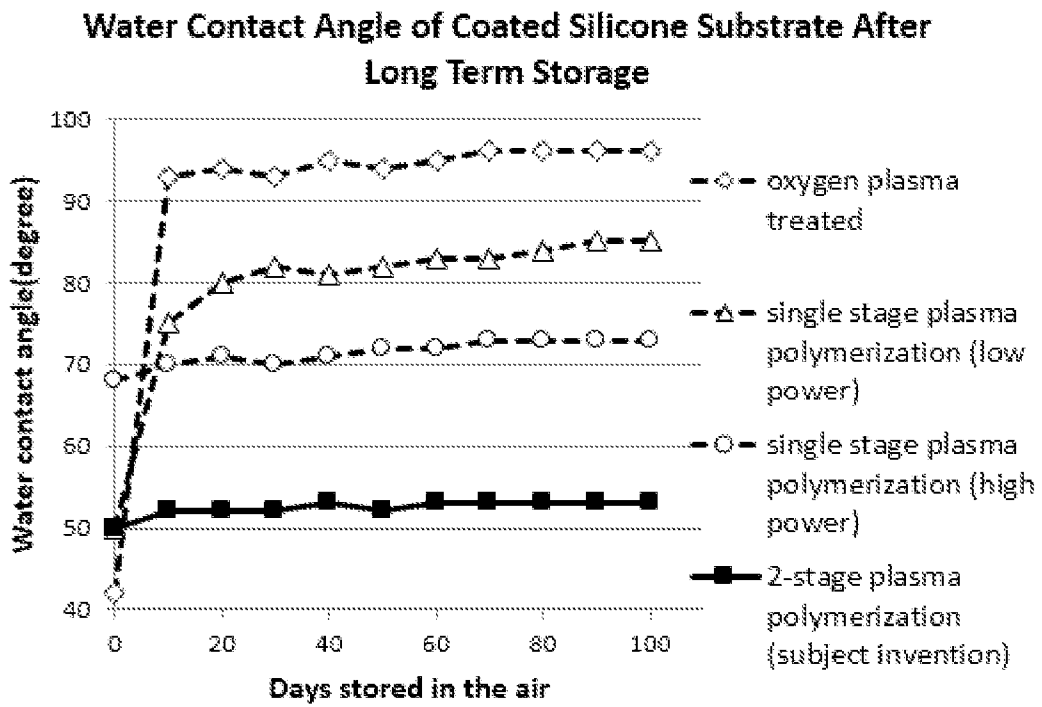


FIG. 3

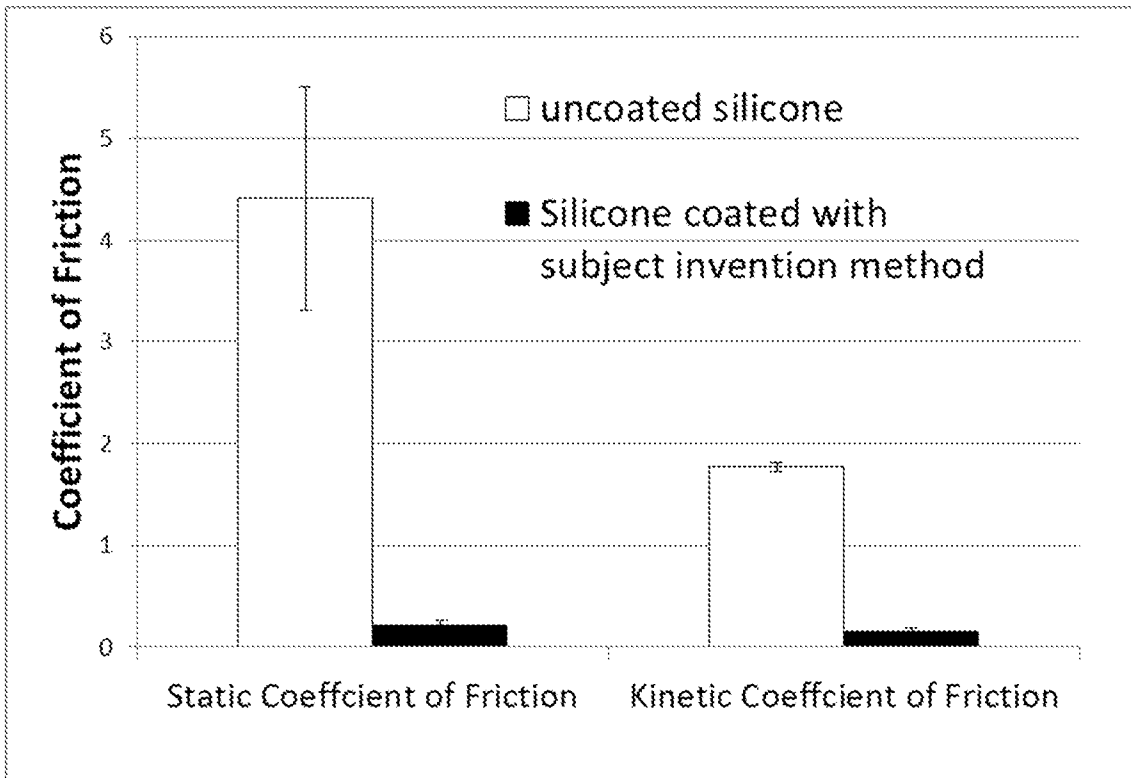


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2015/054834

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08J 7/18 (2015.01)

CPC - B05D 1/62 (2015.10)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - C08J 7/18; G02B 1/04; G02C 7/04 (2015.01)

CPC - B05D 1/62; C08J 7/18; G02B 1/043; G02C 7/049 (2015.11)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC - 351/159.33, 159.73; 427/2.1, 2.24; 523/106, 107; IPC(8) - C08J 7/18; G02B 1/04; G02C 7/04 (2015.01)

CPC - B05D 1/62; C08J 7/18; G02B 1/043; G02C 7/049 (2015.11) (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Orbit, Google Patents, Google Scholar

Search terms used: plasma polymer#+ glow discharge ophthalmic contact lens biosensor glucose

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/0113477 A1 (TIMMONS et al) 19 June 2003 (19.06.2003) entire document	1-4, 8-12
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Y		5-7
Y	US 7,087,149 B1 (MUGURUMA et al) 08 August 2006 (08.08.2006) entire document	5
Y	US 2012/0235277 A1 (PUGH et al) 20 September 2012 (20.09.2012) entire document	6
Y	US 2008/0063898 A1 (LALLY et al) 13 March 2008 (13.03.2008) entire document	7

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

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