US 20140363579A1

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2014/0363579 A1

(43) Pub. Date: Dec. 11, 2014

Grunlan et al.

(54) THIN FILM DIFFUSION BARRIER

(71) Applicants: **Compagnie Generale Des Establissment Michelin**, Clermont-Ferrand (FR); **Michelin Recherche Et Technique S.A.**, Granges-Paccot (CH); **The Texas A&M University System**, College Station, TX (US)

(72) Inventors: **Jaime C. Grunlan**, College Station, TX (US); **Morgan A. Priolo**, College Station, TX (US); **Brian R. Bergman**, Simpsonville, SC (US); **John J. Mchugh**, Greenville, SC (US)

(21) Appl. No.: **14/369,957**

(22) PCT Filed: **Dec. 28, 2012**

(86) PCT No.: **PCT/US12/71905**

§ 371 (c)(1), (2), (4) Date: **Jun. 30, 2014**

Related U.S. Application Data

(60) Provisional application No. 61/581,743, filed on Dec. 30, 2011.

Publication Classification

(51) **Int. Cl.**

B05D 1/36 (2006.01)
B05D 5/00 (2006.01)
B05D 7/00 (2006.01)
B05D 1/02 (2006.01)

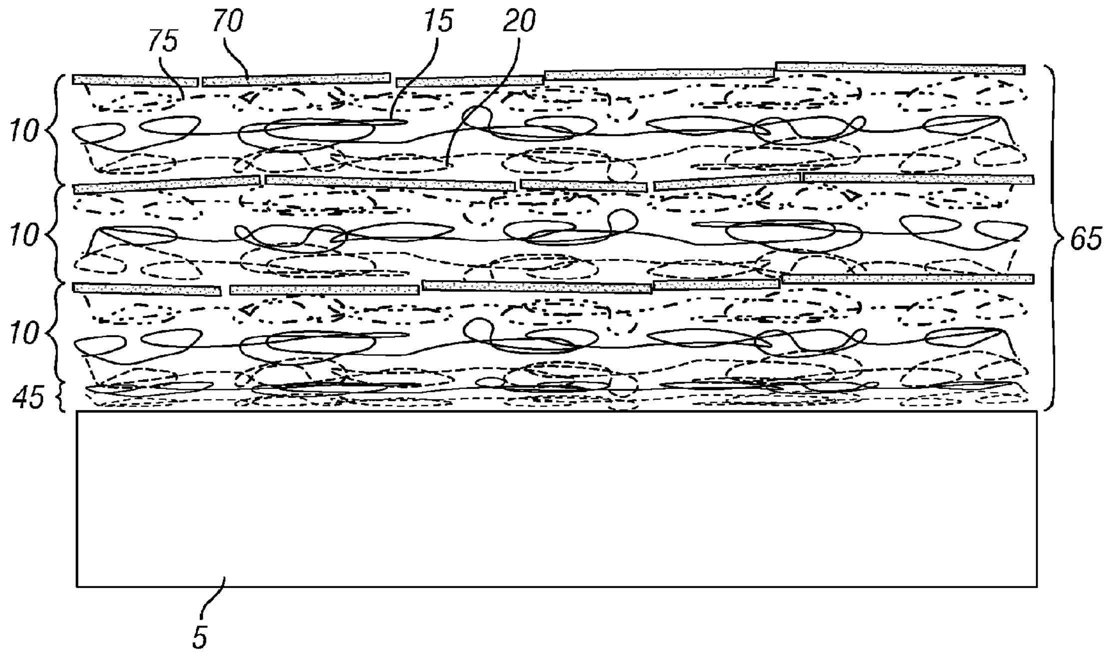
(52) **U.S. Cl.**

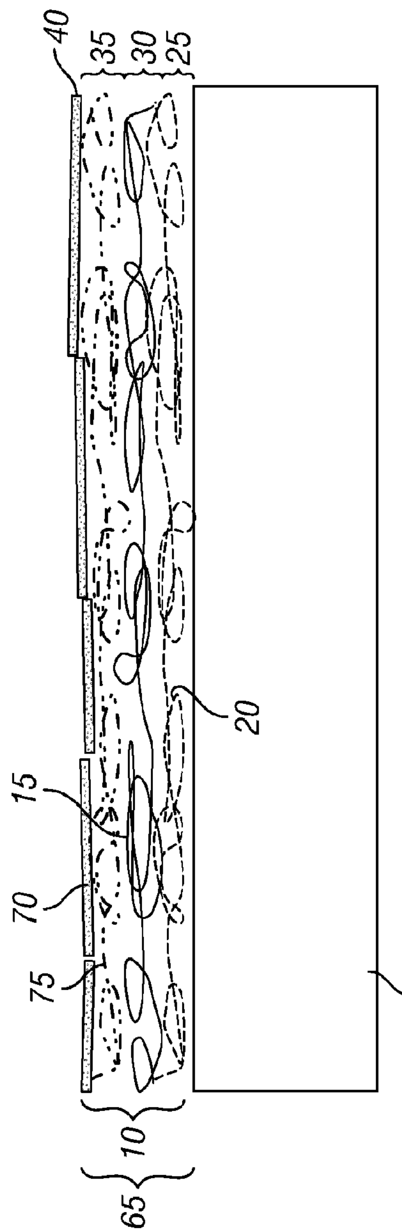
CPC .. ***B05D 1/36*** (2013.01); ***B05D 1/02*** (2013.01); ***B05D 5/00*** (2013.01); ***B05D 7/5483*** (2013.01); ***B05D 7/5883*** (2013.01)

USPC **427/412.1**; 427/402

(57) **ABSTRACT**

An elastomeric substrate has a material diffusion harrier, and a method produces the same. In an embodiment, a method for producing a material diffusion barrier on an elastomeric substrate includes exposing the elastomeric substrate to a cationic solution to produce a cationic layer on the elastomeric substrate. The method also includes exposing the cationic layer to an anionic solution to produce an anionic layer on the cationic layer. The layer includes the cationic layer and the anionic layer. The layer comprises the material diffusion barrier.




40
35
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70
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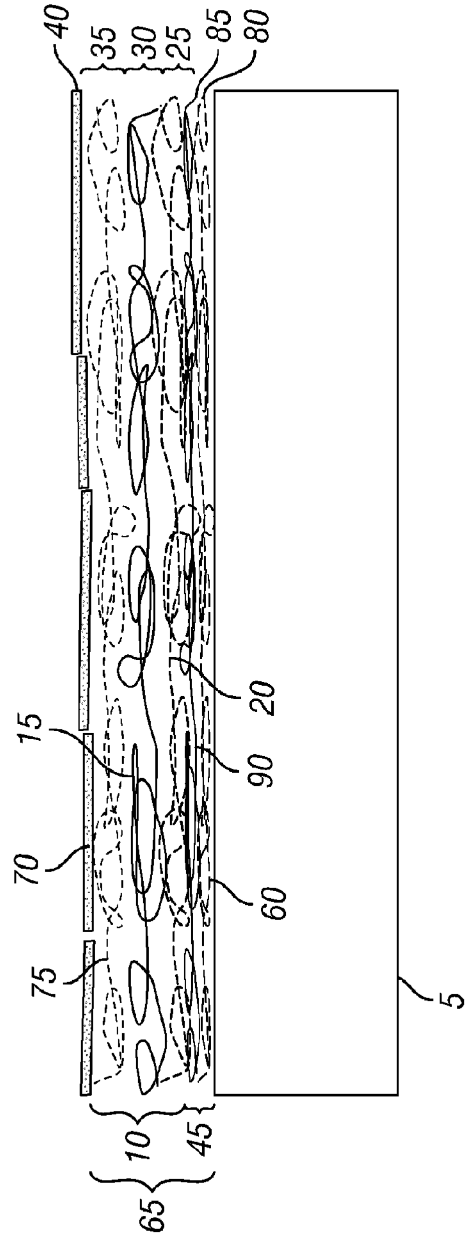
65

FIG. 1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60
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45
65

FIG. 2

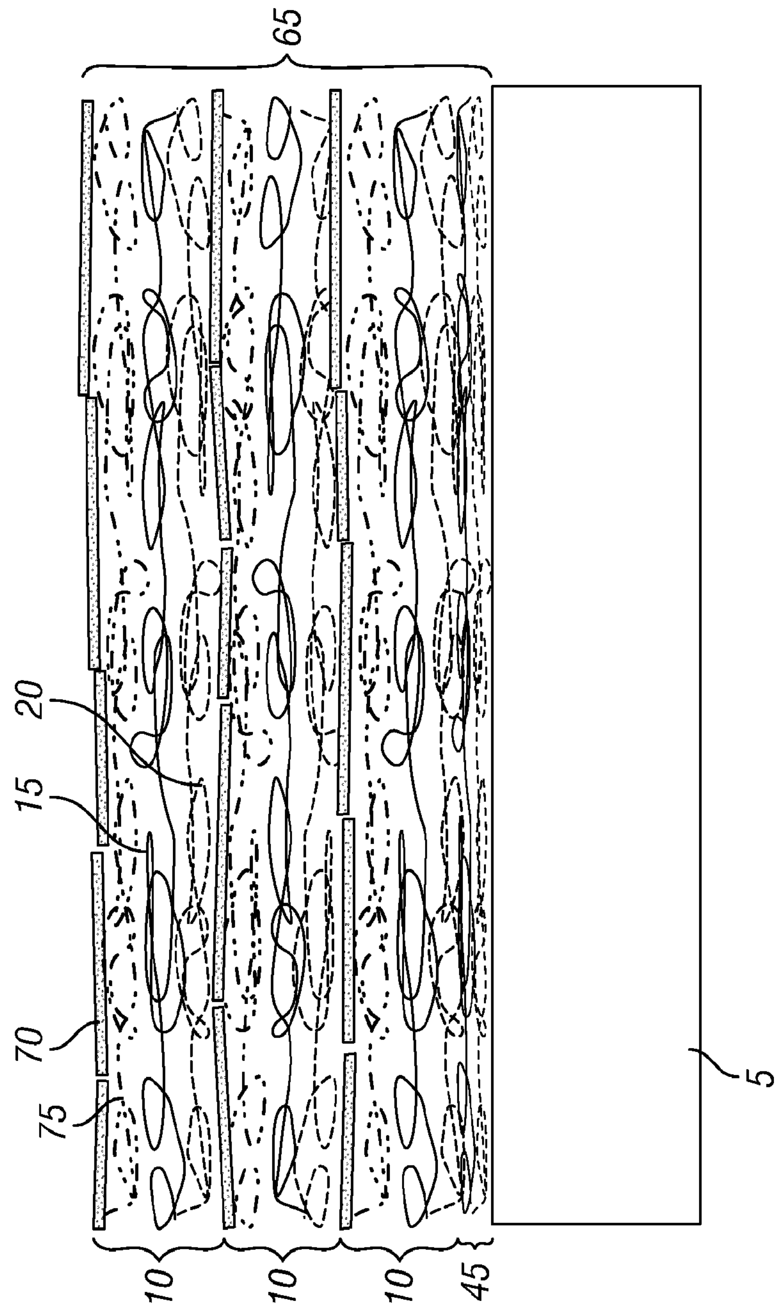

FIG. 3

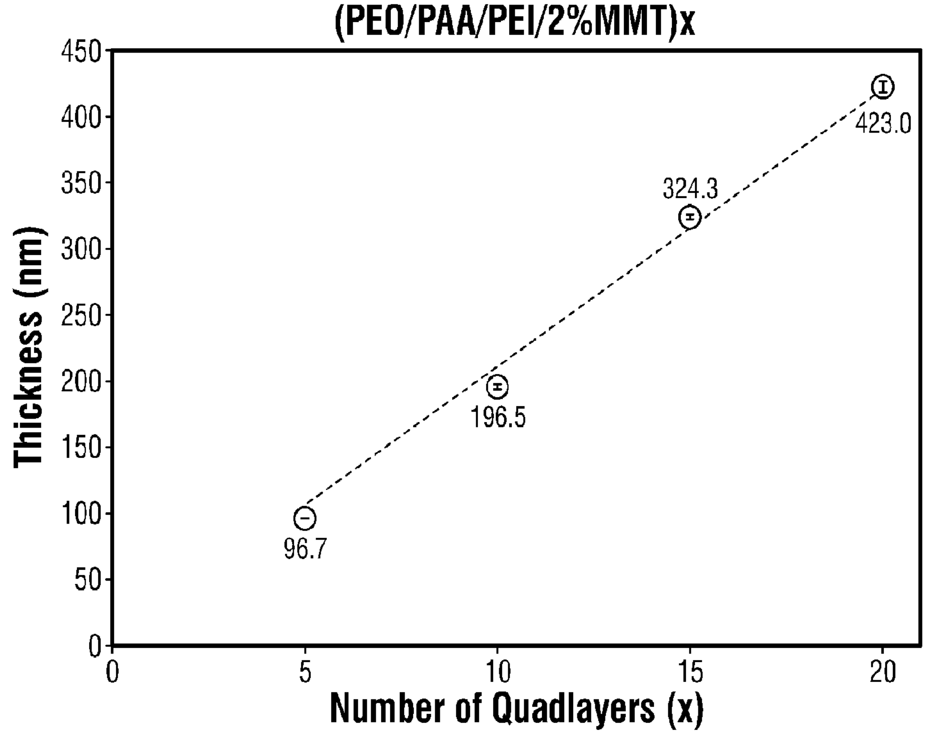
(PEO/PAA/PEI/2%MMT)x
Thickness (nm)
450
400
350
300
250
200
150
100
50
0
0
5
10
15
20
Number of Quadlayers (x)
96.7
196.5
324.3
423.0

FIG. 4

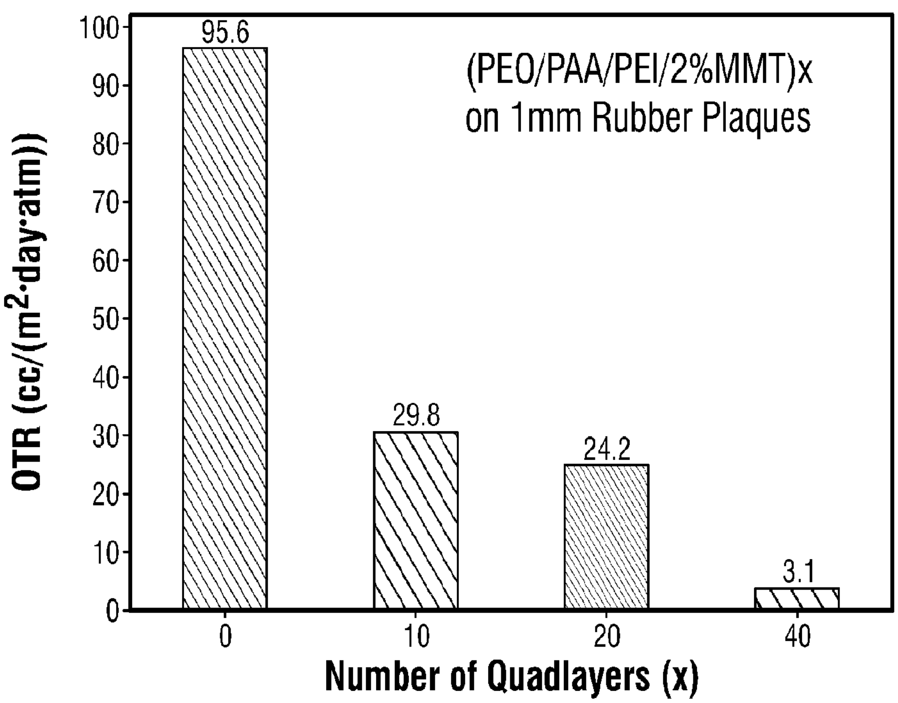
OTR (cc/(m2·day·atm))
100
90
80
70
60
50
40
30
20
10
0
95.6
29.8
24.2
3.1
(PEO/PAA/PEI/2%MMT)x
on 1mm Rubber Plaques
0
10
20
40
Number of Quadlayers (x)

FIG. 5

PEO/PAA/PEI/MMT - 10 on 2.5 mm Rubber

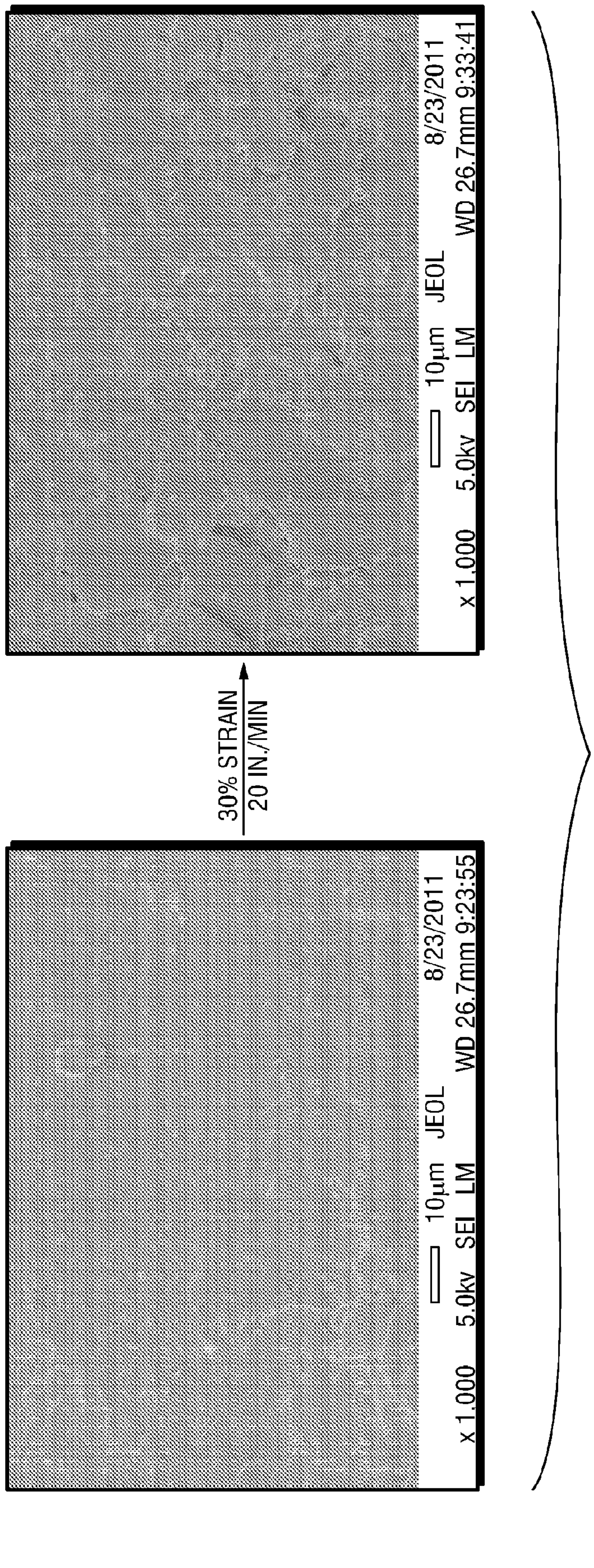

FIG. 6

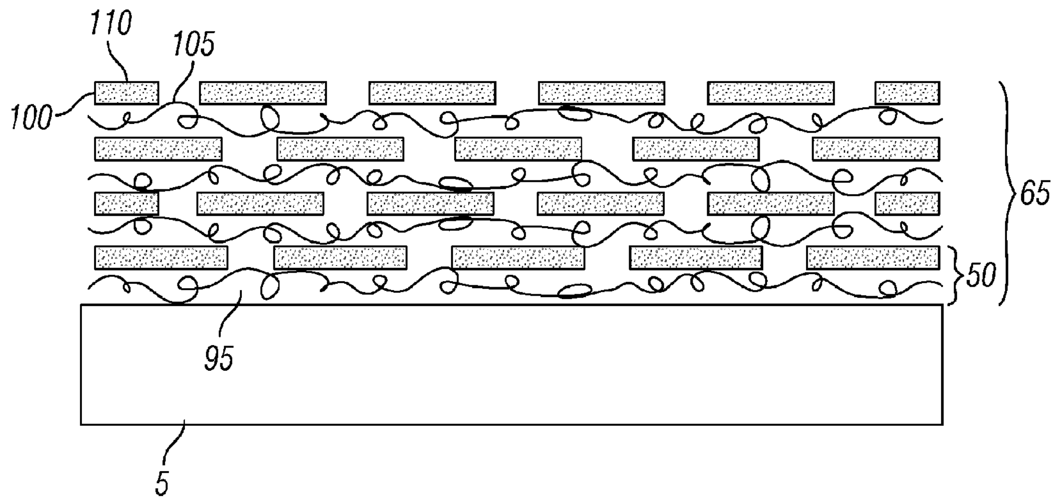

FIG. 7

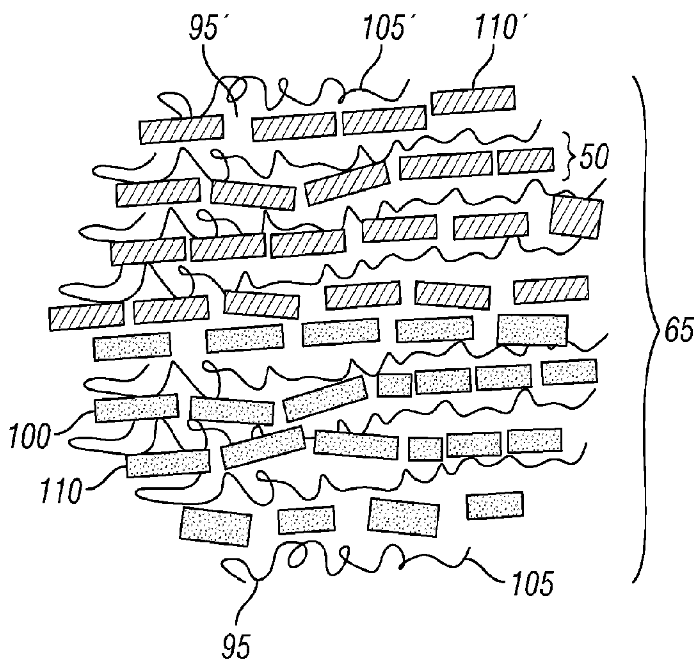

FIG. 8

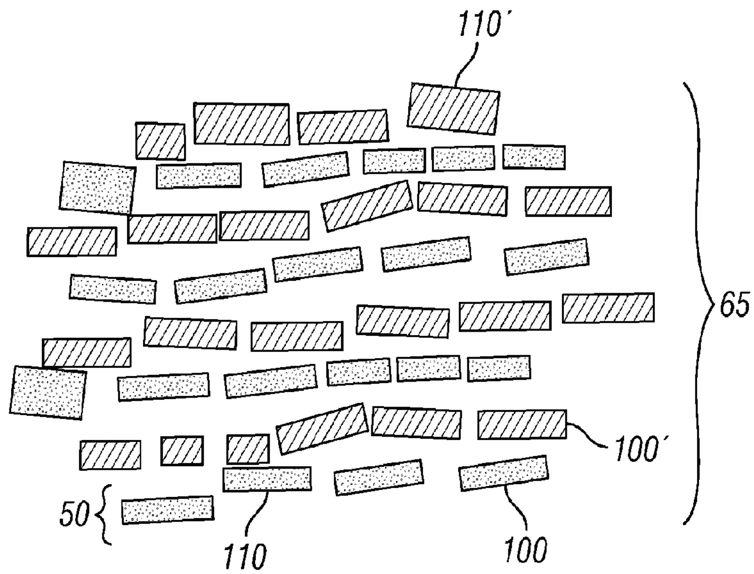

FIG. 9

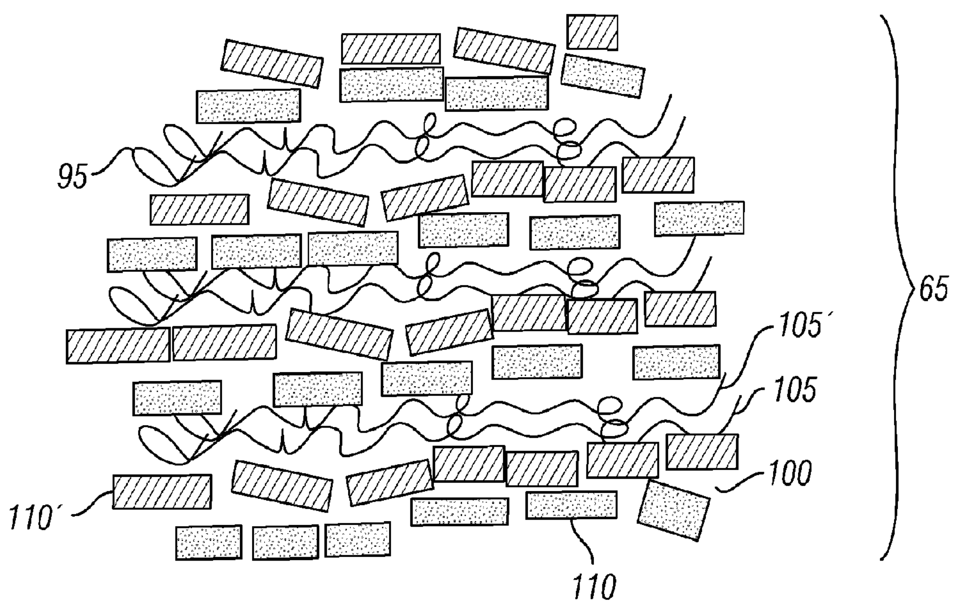

FIG. 10

THIN FILM DIFFUSION BARRIER

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates to the field of diffusion barriers and more specifically to the field of thin film barriers against diffusion of materials.

[0003] 2. Background of the Invention

[0004] Diffusion barriers to gas and vapors are key components in a variety of applications, such as food packaging and flexible electronics. For instance, there is an increased need for improved barrier performance against diffusion of materials for food packaging. Drawbacks to conventional packaging include gas and liquid permeability of the packaging. Such drawbacks may lead to damage to trod contained within the packaging. Coatings and liners have been developed for conventional packaging to reduce gas and liquid permeability. Drawbacks to the developed coatings and liners include increased thickness and rigidity of the packaging. Increased thickness may cause an undesired weight increase of the packaging. In addition, such increased rigidity may cause unwanted damage to the packaging.

[0005] Consequently, there is as need for unproved diffusion barriers. There are also further needs for improved thin film barriers against fluid and solid diffusion.

BRIEF SUMMARY OF SOME OF THE PREFERRED EMBODIMENTS

[0006] These and other needs in the art are addressed in one embodiment by a method for producing a material diffusion barrier on an elastomeric substrate. The method includes exposing the elastomeric substrate to a cationic solution to produce a cationic layer on the elastomeric substrate. The method also includes exposing the canonic layer to an anionic solution to produce an anionic layer on the cationic layer. In addition, the method includes a layer having the cationic layer and the anionic layer. The layer includes the material diffusion barrier.

[0007] These and other needs in the art are addressed by another embodiment of as method fur producing a material diffusion barrier on an elastomeric substrate. The method includes exposing the elastomeric substrate to an anionic solution to produce an anionic layer on the elastomeric substrate. The method also includes exposing the anionic layer to a cationic solution to produce as cationic layer on the anionic layer. In addition, the method includes a layer having the anionic layer and the cationic layer. The layer includes the material diffusion barrier.

[0008] The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and the specific embodiments disclosed may be readily utilized as a basis for modifying or designing other embodiments for carrying out the same purposes of the present invention. It should also be realized, by those skilled in the art that such equivalent embodiments do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] For a detailed description of the preferred embodiments of the invention, reference will now be made to the accompanying drawings in which:

[0010] FIG. **1** illustrates an embodiment of a quadlayer on an elastomeric substrate;

[0011] FIG. **2** illustrates an embodiment of a quadlayer, an elastomeric substrate, and a primer layer;

[0012] FIG. **3** illustrates an embodiment of three quadlayers and an elastomeric substrate;

[0013] FIG. **4** illustrates thickness as a function of the number of quadlayers;

[0014] FIG. **5** illustrates oxygen transmission rate as a function of the number of quadlayers;

[0015] FIG. **6** illustrates images of elasticity of coating;

[0016] FIG. **7** illustrates an embodiment of a bilayer on an elastomeric substrate;

[0017] FIG. **8** illustrates an embodiment of bilayers of layerable materials and additives;

[0018] FIG. **9** illustrates an embodiment of bilayers with alternating layers of layerable materials and additives; and

[0019] FIG. **10** illustrates an embodiment with bilayers of layerable materials and additives.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0020] In an embodiment, as multilayer thin film coating method provides an elastomeric substrate with a diffusion retardant coating by alternately depositing positive and negative charged layers on the substrate. Each pair of positive and negative layers comprises a layer. In embodiments, the multilayer thin flint coating method produces any number of desired layers on substrates such as bilayers, trilayers, quadlayers, pentalayers, hexalayers, heptalayers, octalayers, and increasing layers. Without limitation, a layer or plurality of layers may provide a desired yield. Further, without limitation, a plurality of layers may provide a desired retardant to transmission of material through the elastomeric substrate. The material may be any diffusible material. Without limitation, the diffusible material may be a solid, a fluid, or any combinations thereof. The fluid may be any diffusible fluid such as a liquid, a gas, or any combinations thereof. In an embodiment, the diffusible fluid is a gas.

[0021] The positive and negative layers may have any desired thickness. In embodiments, each layer is between about 0.5 nanometers and about 100 nanometers thick, alternatively between about 1 nanometer and about 100 nanometers thick, and alternatively between about 0.5 nanometers and about 10 nanometers thick. In some embodiments of the multilayer thin film coating method, one or more of the positive layers are neutral rather than positively charged.

[0022] The elastomeric substrate comprises material having viscoelasticity. Any desirable elastomeric substrate may be coated with the multilayer thin film coating method. Without limitation, examples of suitable elastomeric substrates include polyisoprene, polychloroprene, butadiene-styrene copolymers, acrylonitrilebutadiene copolymers, ethylenepropylene-diene rubbers, polysulfide rubber, nitrile rubber, silicone, polyurethane, butyl rubber, or any combinations thereof.

[0023] The negative charged (anionic) layers comprise layerable materials. The layerable materials include anionic polymers, colloidal particles, or any combinations thereof.

Without limitation, examples of suitable anionic polymers include polystyrene sulfonate, polymethacrylic acid, polyacrylic acid, poly(acrylic acid, sodium salt), polyanetholesulfonic acid sodium salt, poly(vinylsulfonic acid, sodium salt), or any combinations thereof. In addition, without limitation, colloidal particles include organic and/or inorganic materials. Further, without limitation, examples of colloidal particles include clays, colloidal silica, inorganic hydroxides, silicon based polymers, polyoligomeric silsesquioxane, carbon nanotubes, graphene, or any combinations thereof. Any type of clay suitable for use in an anionic solution may be used. Without limitation, examples of suitable clays include sodium montmorillonite, hectorite, saponite, Wyoming bentonite, vermiculite, halloysite, or any combinations thereof. In an embodiment, the clay is sodium montmorillonite. Any inorganic hydroxide that may provide retardancy to gas or vapor transmission may be used. In an embodiment, the inorganic hydroxide includes aluminum hydroxide, magnesium hydroxide, or any combinations thereof.

[0024] The positive charge (cationic) layers comprise cationic materials. In some embodiments, one or more cationic layers are neutral. The cationic materials comprise polymers, colloidal particles, nanoparticles, or any combinations thereof. The polymers include cationic polymers, polymers with hydrogen bonding, or any combinations thereof. Without limitation, examples of suitable cationic polymers include branched polyethylenimine, linear polyethylenimine, cationic polyacrylamide, cationic poly diallyldimethylammonium chloride, poly(allyl amine), poly(allyl amine) hydrochloride, poly(vinyl amine), poly(acrylamide-co-diallyldimethylammonium chloride), or any combinations thereof. Without limitation, examples of suitable polymers with hydrogen bonding include polyethylene oxide, polyglycidol, polypropylene oxide, poly(vinyl methyl ether), polyvinyl alcohol, polyvinylpyrrolidone, polyallylamine, branched polyethylenimine, linear polyethylenimine, poly (acrylic acid), poly(methacrylic acid), copolymers thereof, or any combinations thereof. In embodiments, the polymers with hydrogen bonding are neutral polymers. In addition, without limitation, colloidal particles include organic and/or inorganic materials. Further, without limitation, examples of colloidal particles include clays, layered double hydroxides, inorganic hydroxides, silicon based polymers, polyoligomeric silsesquioxane, carbon nanotubes, graphene, or any combinations thereof. Without limitation, examples of suitable layered double hydroxides include hydrotalcite, magnesium LDH, aluminum LDH, or any combinations thereof.

[0025] In embodiments, the positive (or neutral) and negative layers are deposited on the elastomeric substrate by any suitable method. Embodiments include depositing the positive (or neutral) and negative layers on the elastomeric substrate by any suitable liquid deposition method. Without limitation, examples of suitable methods include bath coating, spray coating, slot coating, spin coating, curtain coating, gravure coating, reverse roll coating, knife over roll (i.e., gap) coaling, metering (Meyer) rod coating, air knife coating, or any combinations thereof. Bath coating includes immersion or dip. In an embodiment, the positive (or neutral) and negative layers are deposited by bath. In other embodiments, the positive and negative layers are deposited by spray.

[0026] In embodiments, the multilayer thin film coating method provides two pairs of positive and negative layers, which two pairs comprise a quadlayer. Embodiments include the multilayer thin film coating method producing a plurality of quadlayers on an elastomeric substrate. FIG. **1** illustrates an embodiment of elastomeric substrate **5** with coating **65** of quadlayer **10**. In an embodiment to produce the coated elastomeric substrate **5** shown in FIG. **1**, the multilayer thin film coating method includes exposing elastomeric substrate **5** to cationic molecules in a cationic mixture to produce first cationic layer **25** on elastomeric substrate **5**. The cationic mixture contains first layer cationic materials **20**. In an embodiment, first layer cationic materials **20** are positively charged or neutral. In embodiments, first layer cationic materials **20** are neutral. In some embodiments, first layer cationic materials **20** are polymers with hydrogen bonding having a neutral charge. Embodiments include first layer cationic materials **20** comprising polyethylene oxide. Without limitation, first layer cationic materials **20** comprising neutral materials (i.e., polyethylene oxide) may provide a desired yield. In such an embodiment, elastomeric substrate **5** is negatively charged or neutral. Embodiments include elastomeric substrate **5** having a negative charge. Without limitation, a negatively charged elastomeric substrate **5** provides a desired adhesion. The cationic mixture includes an aqueous solution of first layer cationic materials **20**. The aqueous solution may be prepared by any suitable method. In embodiments, the aqueous solution includes first layer cationic materials **20** and water. In other embodiments, first layer cationic materials **20** may be dissolved in a mixed solvent, in which one of the solvents is water and the other solvent is miscible with water (e.g., water, methanol, and the like). The solution may also contain colloidal particles in combination with polymers or alone, if positively charged. Any suitable water may be used. In embodiments, the water is deionized water. In some embodiments, the aqueous solution may include from about 0.05 wt. % first layer cationic materials **20** to about 1.50 wt. % first layer cationic materials **20**, alternatively from about 0.01 wt. % first layer cationic materials **20** to about 2.00 wt. % first layer cationic materials **20**, and further alternatively from about 0.001 wt. % first layer cationic materials **20** to about 20.0 wt. % first layer cationic. materials **20**. In embodiments, elastomeric substrate **5** may be exposed to the cationic mixture for any suitable period of time to produce first cationic layer **25**. In embodiments, elastomeric substrate **5** is exposed to the cationic mixture from about 1 second to about 20 minutes, alternatively from about 1 second to about 200 seconds, and alternatively from about 10 seconds to about 200 seconds, and further alternatively from about instantaneous to about 1,200 seconds. Without limitation, the exposure time of elastomeric substrate **5** to the cationic mixture and the concentration of first layer cationic materials **20** in the cationic mixture affect the thickness of first cationic layer **25**. For instance, the higher the concentration of first layer cationic materials **20** and the longer the exposure time, the thicker the first cationic layer **25** produced by the multilayer thin film coating method.

[0027] In embodiments, after formation of first cationic layer **25**, multilayer thin film coating method includes removing elastomeric substrate **5** with the produced first cationic layer **25** from the cationic mixture and then exposing elastomeric substrate **5** with first cationic layer **25** to anionic molecules in an anionic mixture to produce first anionic layer **30** on first cationic layer **25**. The anionic mixture contains first layer layerable materials **15**. Without limitation, the positive or neutral first cationic layer **25** attracts the anionic molecules to form the cationic (or neutral)-anionic pair of first cationic layer **25** and first anionic layer **30**. The anionic mixture includes an aqueous solution of first layer layerable materials **15**. In an embodiment, first layer layerable materials **15** comprise polyacrylic acid. The aqueous solution may be prepared by any suitable method. In embodiments, the aqueous solution includes first layer layerable materials **15** and water. First layer layerable materials **15** may also be dissolved in a mixed solvent, in which one of the solvents is water and the other solvent is miscible with water (e.g., ethanol, methanol, and the like). Combinations of anionic polymers and colloidal particles may be present in the aqueous solution. Any suitable water may be used. In embodiments, the water is deionized water. In some embodiments, the aqueous solution may include from about 0.05 wt. % first layer layerable materials **15** to about 1.50 wt. % first layer layerable materials **15**, alternatively from about 0.01 wt. % first layer layerable materials **15** to about 2.00 wt. % first layer layerable materials **15**, and further alternatively from about 0.001 wt. % first layer layerable materials **15** to about 20.0 wt. % first layer layerable materials **15**. In embodiments, elastomeric substrate **5** with first cationic layer **25** may be exposed to the anionic mixture for any suitable period of time to produce first anionic layer **30**. In embodiments, elastomeric substrate **5** with first cationic layer **25** is exposed to the anionic mixture from about 1 second to about 20 minutes, alternatively from about 1 second to about 200 seconds, and alternatively from about 10 seconds to about 200 seconds, and further alternatively from about instantaneous to about 1,200 seconds. Without limitation, the exposure time of elastomeric substrate **5** with first cationic layer **25** to the anionic mixture and the concentration of first layer layerable materials **15** in the anionic mixture affect the thickness of the first anionic layer **30**. For instance, the higher the concentration of first layer lay materials **15** and the longer the exposure time, the thicker the first anionic layer **30** produced by the multilayer thin film coating method.

[0028] In embodiments as further shown in FIG. **1**, after formation of first anionic layer **30**, the multilayer thin film coating method includes removing elastomeric substrate **5** with the produced first cationic layer **25** and first anionic layer **30** from the anionic mixture and then exposing elastomeric substrate **5** with first cationic layer **25** and first anionic layer **30** to cationic molecules in a cationic mixture to produce second cationic layer **35** on first anionic layer **30**.

[0029] The cationic mixture contains second layer cationic materials **75**. In an embodiment, second layer cationic materials **75** are positively charged or neutral. In embodiments, second layer cationic materials **75** are positive. In some embodiments, second layer cationic materials **75** comprise polyethylenimine. The cationic mixture includes an aqueous solution of second layer cationic materials **75**. The aqueous solution may be prepared by any suitable method. In embodiments, the aqueous solution includes second layer cationic materials **75** and water. In other embodiments, second layer cationic materials **75** may be dissolved in a mixed solvent, in which one of the solvents is water and the other solvent is miscible with water (e.g., water, methanol, and the like). The solution may also contain colloidal particles in combination with polymers or alone, if positively charged. Any suitable water may be used. In embodiments, the water is deionized water. In some embodiments, the aqueous solution may include from about 0.05 wt. % second layer cationic. materials **75** to about 1.50 wt. % second layer cationic materials **75**, alternatively from about 0.01 wt. % second layer cationic materials **75** to about 2.00 wt. % second layer cationic materials **75**, and further alternatively from about 0.001 wt. % second layer cationic materials **75** to about 20.0 wt. % second layer cationic materials **75**. In embodiments, elastomeric substrate **5** may be exposed to the cationic mixture for any suitable period of time to produce second cationic layer **35**. In embodiments, elastomeric substrate **5** is exposed to the cationic mixture from about 1 second to about 20 minutes, alternatively from about 1 second to about 200 seconds, and alternatively from about 10 seconds to about 200 seconds, and further alternatively from about instantaneous to about 1,200 seconds.

[0030] In embodiments, after formation of the second cationic layer **35**, multilayer thin film coating method includes removing elastomeric substrate **5** with the produced first cationic layer **25**, first anionic layer **30**, and second cationic layer **35** from the cationic mixture and then exposing elastomeric substrate **5** with first cationic layer **25**, first anionic layer **30**, and second cationic layer **35** to anionic molecules in an anionic mixture to produce second anionic layer **40** on second cationic layer **35**. The anionic mixture contains second layer layerable materials **70**. Without limitation, the positive or neutral second cationic layer **35** attracts the anionic molecules to form the cationic (or neutral)-anionic pair of second cationic layer **35** and second anionic layer **40**. The anionic mixture includes an aqueous solution of second layer layerable materials **70**. In an embodiment, second layer layerable materials **70** comprise clay. Embodiments include the clay comprising sodium montmorillonite. The aqueous solution may be prepared by any suitable method. In embodiments, the aqueous solution includes second layer layerable materials **70** and water. Second layer layerable materials **70** may also be dissolved in a mixed solvent, in which one of the solvents is water and the other solvent is miscible with water (e.g., ethanol, methanol, and the like). Combinations of anionic polymers and colloidal particles may be present in the aqueous solution. Any suitable water may be used. In embodiments, the water is deionized water. In some embodiments, the aqueous solution may include from about 0.05 wt. % second layer layerable materials **70** to about 1.50 wt. % second layer layerable materials **70**, alternatively from about 0.01 wt. % second layer layerable materials **70** to about 2.00 wt. % second layer layerable materials **70**, and further alternatively from about 0.001 wt. % second layer layerable materials **70** to about 20.0 wt. % second layer layerable materials **70**. In embodiments, elastomeric substrate **5** with first cationic layer **25**, first anionic layer **30**, and second cationic layer **35** may be exposed to the anionic mixture for any suitable period of time to produce second anionic layer **40**. In embodiments, elastomeric substrate **5** with first cationic layer **25**, first anionic layer **30**, and second cationic layer **35** is exposed to the anionic mixture from about 1 second to about 20 minutes, alternatively from about 1 second to about 200 seconds, and alternatively from about 10 seconds to about 200 seconds, and further alternatively from about instantaneous to about 1,200 seconds. Quadlayer **10** is therefore produced on elastomeric substrate **5**. In embodiments as shown in FIG. **1** in which elastomeric substrate **5** has one quadlayer **10**, coating **65** comprises quadlayer **10**. In embodiments, quadlayer **10** comprises first cationic layer **25**, first anionic layer **30**, second cationic layer **35**, and second anionic layer **40**.

[0031] In an embodiment as shown in FIG. **2**, coating **65** also comprises primer layer **45**. Primer layer **45** is disposed between elastomeric substrate **5** and first cationic layer **25** of quadlayer **10**. Primer layer **45** may have any number of layers. The layer of primer layer **45** proximate to elastomeric substrate **5** has a charge with an attraction to elastomeric substrate **5**, and the layer of primer layer **45** proximate to first cationic layer **25** has a charge with an attraction to first cationic layer **25**. In embodiments as shown in FIG. **2**, primer layer **45** is a bilayer having a first primer layer **80** and a second primer layer **85**. In such embodiments, first primer layer **80** is a cationic layer (or alternatively neutral) comprising first primer layer materials **60**, and second primer layer **85** is an anionic layer comprising second primer layer materials **90**. First primer layer materials **60** comprise cationic materials. In an embodiment, first primer layer materials **60** comprise polyethylenimine. Second primer layer materials **90** comprise layerable materials. In an embodiment, second primer layer materials **90** comprise polyacrylic acid. In other embodiments (not shown), primer layer **45** has more than one bilayer.

[0032] In further embodiments as shown in FIG. **2**, the multilayer thin film coating method includes exposing elastomeric substrate **5** to cationic molecules in a cationic mixture to produce first primer layer **80** on elastomeric substrate **5**. The cationic mixture contains first primer layer materials **60**. In an embodiment, first primer layer materials **60** are positively charged or neutral. In embodiments, the cationic mixture includes an aqueous solution of first primer layer materials **60**. The aqueous solution may be prepared by any suitable method. In embodiments, the aqueous solution includes first primer layer materials **60** and water. In other embodiments, first primer layer materials **60** may be dissolved in a mixed solvent, in which one of the solvents is water and the other solvent is miscible with water (e.g., water, methanol, and the like). The solution may also contain colloidal particles in combination with polymers or alone, if positively charged. Any suitable water may be used. In embodiments, the water is deionized water. In some embodiments, the aqueous solution may include from about 0.05 wt. % first primer layer materials **60** to about 1.50 wt. % first primer layer materials **60**, alternatively from about 0.01 wt. % first primer layer materials **60** to about 2.00 wt. % first primer layer materials **60**, and further alternatively from about 0.001 wt. % first primer layer materials **60** to about 20.0 wt. % first primer layer materials **60**. In embodiments, elastomeric substrate **5** may be exposed to the cationic mixture for any suitable period of time to produce first primer layer **80**. In embodiments, elastomeric substrate **5** is exposed to the cationic mixture from about 1 second to about 20 minutes, alternatively from about 1 second to about 200 seconds, and alternatively from about 10 seconds to about 200 seconds, and further alternatively from about instantaneous to about 1,200 seconds.

[0033] In embodiments as shown in FIG. **2**, after formation of first primer layer **80**, multilayer thin film coating method includes removing elastomeric substrate **5** with the produced first primer layer **80** from the cationic mixture and then exposing elastomeric substrate **5** with first primer layer **80** to anionic molecules in an anionic mixture to produce second primer layer **85** on first primer layer **80**. The anionic mixture contains second primer layer materials **90**. The anionic mixture includes an aqueous solution of second primer layer materials **90**. The aqueous solution may be prepared by any suitable method. In embodiments, the aqueous solution includes second primer layer materials **90** and water. Second primer layer materials **90** may also be dissolved in a mixed solvent, in which one of the solvents is water and the other solvent is miscible with water (e.g., ethanol, methanol, and the like). Combinations of anionic polymers and colloidal particles may be present in the aqueous solution. Any suitable water may be used. In embodiments, the water is deionized water. In some embodiments, the aqueous solution may include from about 0.05 wt. % second primer layer materials **90** to about 1.50 wt. % second primer layer materials **90**, alternatively from about 0.01 wt.% second primer layer materials **90** to about 2.00 wt. %. second primer layer materials **90**, and further alternatively from about 0.001 wt. % second primer layer materials **90** to about 20.0 wt. % second primer layer materials **90**. In embodiments, the elastomeric substrate **5** with first primer layer **80** may be exposed to the anionic mixture fur any suitable period of time to produce second primer layer **85**. In embodiments, elastomeric substrate **5** with first primer layer **80** is exposed to the anionic mixture from about 1 second to about 20 minutes, alternatively from about 1 second to about 200 seconds, and alternatively from about 10 seconds to about 200 seconds, and further alternatively from about instantaneous to about 1,200 seconds. Elastomeric substrate **5** with primer layer **45** is then removed from the anionic mixture and then the multilayer thin film coating method proceeds to produce quadlayer **10**.

[0034] In embodiments as shown in FIG. **3**, the exposure steps are repeated with substrate **5** having quadlayer **10** continuously exposed to the cationic mixture and then the anionic mixture to produce a coating **65** having multiple quadlayers **10**. The repeated exposure to the cationic mixture and then the anionic mixture may continue until the desired number of quadlayers **10** is produced. Coating **65** may have any sufficient number of quadlayers **10** to provide elastomeric substrate **5** with a desired retardant to gas or vapor transmission. In an embodiment, coating **65** has between about 1 quadlayer **10** and about 40 quadlayers **10**, alternatively between about 1 quadlayer **10** and about 1,000 quadlayers **10**.

[0035] In an embodiment, the multilayer thin film coating method provides a coated elastomeric substrate **5** (e.g., comprising coating **65**) with a yield between about 0.1%, and about 100% alternatively between about 1% and about 10%. In addition, embodiments include the multilayer thin film coating method providing a coated elastomeric substrate **5** having a gas transmission rate between about 0.03 cc/(m^2*day*atm) and about 100 cc/(m^2day*atm), alternatively between about 0.3 cc/(m^2day*atm) and about 100 cc/(m^2*day*atm), and alternatively between about 3 cc/(m^2*day*atm) and about 30 cc/(m^2*day*atm).

[0036] It is to be understood that the multilayer thin film coating method is not limited to exposure to a cationic mixture followed by an anionic mixture. In embodiments in which elastomeric substrate **5** is positively charged, the multilayer thin film coating method includes exposing elastomeric substrate **5** to the anionic mixture followed by exposure to the cationic mixture. In such embodiment (not illustrated), first anionic layer **30** is deposited on elastomeric substrate **5** with first cationic layer **25** deposited on first anionic layer **30**, and second anionic layer **40** is deposited on first cationic layer **25** followed by second cationic layer **35** deposited on second anionic layer **40** to produce quadlayer **10** with the steps repeated until coating **65** has the desired thickness. In embodiments in which elastomeric substrate **5** has a neutral charge, the multilayer thin film coating method may include beginning with exposure to the cationic mixture followed by exposure to the anionic mixture or may include beginning with exposure to the anionic mixture followed by exposure to the cationic mixture.

[0037] In embodiments (not shown), quadlayers **10** may have one or more than one cationic layer (i.e., first cationic layer **25**, second cationic layer cationic layers in primer layer **45**) comprised of more than one type of cationic materials. In an embodiment (not shown), quadlayers **10** may have one more than one anionic layer (i.e., first anionic layer **30**, second anionic layer **40**, anionic layers in primer layer **45**) comprised of more than one type of anionic material. In some embodiments. one or more cationic layers are comprised of the same materials, and/or one or more of the anionic layers are comprised of the same anionic, materials. It is to be understood that coating **65** is not limited to one layerable material but may include more than one layerable material and/or more than one cationic material.

[0038] FIG. **7** illustrates an embodiment of elastomeric substrate **5** with coating **65** of multiple bilayers **50**. It is to be understood that the multilayer thin film coating method produces the coated elastomeric substrate **5** by the embodiments set forth above and shown in FIGS. **1-3**. As shown in FIG. **7**, each bilayer **50** has cationic layer **95** and anionic layer **100**. In embodiments as shown, cationic layer **95** has cationic materials **105**, and anionic layer **100** has layerable materials **110**. In the embodiment as shown, the multilayer thin film coating method produces coating **65** by exposure to a cationic mixture followed by an anionic mixture according to the embodiments above. In an embodiment, bilayer **50** has cationic materials **105** comprising polyethylene oxide or polyglycidol, and layerable materials **110** comprising clay. In some embodiments, bilayer **50** has cationic materials **105** comprising polyethylene oxide or polyglycidol, and layerable materials **110** comprising polyacrylic acid or polymethacrylic acid.

[0039] It is to be understood that the multilayer thin film coating method for preparing an elastomeric substrate **5** with coating **65** having bilayers **50** is not limited to exposure to a cationic mixture followed by an anionic mixture. In embodiments in which elastomeric substrate **5** is positively charged, the multilayer thin film coating method includes exposing elastomeric substrate **5** to the anionic mixture followed by exposure to the cationic mixture. In such embodiment (not illustrated), anionic layer **100** is deposited on elastomeric substrate **5** with cationic layer **95** deposited on anionic layer **100** to produce bilayer **50** with the steps repeated until coating **65** has the desired thickness. In embodiments in which elastomeric substrate **5** has a neutral charge, the multilayer thin film coating method may include beginning with exposure to the cationic mixture followed by exposure to the anionic mixture or may include beginning with exposure to the anionic mixture followed by exposure to the cationic mixture.

[0040] It is to be further understood that coating **65** is not limited to one layerable material **110** and/or one cationic material **105** but may include more than one layerable material **110** and/or more than one cationic material **105**. The different layerable materials **110** may be disposed on the same anionic layer **100**, alternating anionic layers **100**, or in layers of bilayers **50** (i.e., or in layers of trilayers or increasing layers). The different cationic materials **105** may be dispersed on the same cationic layer **95**, alternating cationic layers **95**, or in layers of bilayers **50** (i.e., or in layers of trilayers or increasing layers). For instance, in embodiments as illustrated in FIGS. **8-10**, coating **65** includes two types of layerable materials **110**, **110'** (i.e., sodium montmorillonite is layerable material **110** and aluminum hydroxide is layerable material **110'**). It is to be understood that elastomeric substrate **5** is not shown for illustrative purposes only in FIGS. **8-10**. FIG. **8** illustrates an embodiment in which layerable materials **110**, **110'** are in different layers of bilayers **50**. For instance, as shown in FIG. **8**, layerable materials **110'** are deposited in the top bilayers **50** after layerable materials **110** are deposited on elastomeric substrate **5** (not illustrated). FIG. **9** illustrates an embodiment in which coating **65** has layerable materials **110**, **110'** in alternating bilayers **50**. It is to be understood that cationic materials **105** are not shown for illustrative purposes only in FIG. **9**. FIG. **10** illustrates an embodiment in which there are two types of bilayers **50**, comprised of particles (layerable materials **110**, **110'**) and cationic materials **105**, **105'** polymers).

[0041] FIGS. **7-10** do not show coating **65** having primer layer **45**. It is to be understood that embodiments of coating **65** having bilayers **50** also may have primer layer **45**. Embodiments (not illustrated) of coating **65** having trilayers, pentalayers, and the like may also have primer layer **45**.

[0042] It is to be understood that the multilayer thin film coating method produces coatings **65** of trilayers, pentalayers, and increasing layers by the embodiments disclosed above for bilayers **50** and quadlayers **10**. It is to be understood that coating **65** is not limited to only as plurality of bilayers **50**, trilayers, quadlayers **10**, pentalayers, hexalayers, heptalayers, octalayers, or increasing layers. In embodiments, coating **65** may have any combination of such layers.

[0043] In some embodiments in which coating **65** comprises trilayers, the trilayers comprise a first cationic layer comprising polyethylenimine, a second cationic layer comprising polyethylene oxide or polyglycidol, and an anionic layer comprising clay. In such an embodiment, the second cationic layer is disposed between the first cationic layer and the anionic layer. In another embodiment in which coating **65** comprises trilayers, the trilayers comprise a first cationic layer comprising polyethylenimine, an anionic layer comprising clay, and a second cationic layer comprising polyethylene oxide or polyglycidol. In such an embodiment, the anionic layer is disposed between the first cationic layer and the second cationic layer. In some embodiments in which coating **65** comprises trilayers, the trilayers comprise a cationic layer comprising polyethylene oxide or polyglycidol, a first anionic layer comprising polyacrylic acid or polymethacrylic acid, and a second anionic layer comprising sodium montmorillonite. In such an embodiment, the first anionic layer is disposed between the cationic layer and the second anionic layer.

[0044] In some embodiments, the multilayer thin film coating method includes rinsing elastomeric substrate **5** between each (or alternatively more than one) exposure step (i.e., step of exposing to cationic mixture or step of exposing to anionic mixture). For instance, after elastomeric substrate **5** is removed from exposure to the cationic mixture, elastomeric substrate **5** with first cationic layer **25** is rinsed and then exposed to an anionic mixture. In some embodiments, quadlayer **10** is rinsed before exposure to the same or another cationic and/or anionic mixture. In an embodiment, coating **65** is rinsed. The rinsing is accomplished by any rinsing liquid suitable for removing all or a portion of ionic liquid from elastomeric substrate **5** and any layer. In embodiments, the rinsing liquid includes deionized water, methanol, or any combinations thereof. In an embodiment, the rinsing liquid is deionized water. A layer may be rinsed for any suitable period of time to remove all or a portion of the ionic liquid. In an embodiment, a layer is rinsed for a period of time from about

5 seconds to about 5 minutes. In some embodiments, a layer is rinsed after a portion of the exposure steps.

[0045] In embodiments, the multilayer thin film coating method includes drying elastomeric substrate **5** between each (or alternatively more than one) exposure step (i.e., step of exposing to cationic mixture or step of exposing to anionic mixture), For instance, after elastomeric substrate **5** is removed from exposure to the cationic mixture, elastomeric substrate **5** with first cationic layer **25** is dried and then exposed to an anionic mixture. In some embodiments, quadlayer **10** is dried before exposure to the same or another cationic and/or anionic mixture. In an embodiment, coating **65** is dried. The drying is accomplished by applying a drying gas to elastomeric substrate **5**. The drying gas may include any gas suitable for removing all or a portion of liquid from elastomeric substrate **5**. In embodiments, the drying gas includes air, nitrogen, or any combinations thereof. In an embodiment, the drying gas is air. In some embodiments, the air is filtered air. The drying may be accomplished for any suitable period of time to remove all or as portion of the liquid from a layer (i.e., quadlayer **10**) and/or coating **65**. In an embodiment, the drying is for a period of time from about 5 seconds to about 500 seconds. In an embodiment in which the multi layer thin film coating method includes rinsing after an exposure step, the layer is dried after rinsing and before exposure to the next exposure step. In alternative embodiments, drying includes applying a heat source to the layer (i.e., quadlayer **10**) and/or coating **65**. For instance, in an embodiment, elastomeric substrate **5** is disposed in an oven for a time sufficient to remove all or a portion of the liquid from a layer. In some embodiments, drying is not performed until all layers have been deposited, as a final step before use.

[0046] In some embodiments (not illustrated), additives may be added to elastomeric substrate **5** in coating **65**. In embodiments, the additives may be mixed in anionic mixtures with layerable materials. In other embodiments, the additives are disposed in anionic mixtures that do not include layerable materials. In some embodiments, coating **65** has a layer or layers of additives. In embodiments, the additives are anionic materials. The additives may be used for any desirable purpose. For instance, additives may be used for protection of elastomeric substrate **5** against ultraviolet light or for abrasion resistance. For ultraviolet light protection, any negatively charged material suitable for protection against ultraviolet light and for use in coating **65** may be used. In an embodiment, examples of suitable additives for ultraviolet protection include titanium dioxide, or any combinations thereof. In embodiments, the additive is titanium dioxide. For abrasion resistance, any additive suitable for abrasion resistance and for use in coating **65** may be used. In embodiments, examples of suitable additives for abrasion resistance include crosslinkers. Any crosslinker suitable for use with an elastomer may be used. In an embodiment, crosslinkers comprise a di-aldehyde. Examples of crosslinkers include glutaraldehyde, bromoalkanes, or any combinations thereof. The crosslinkers may be used to crosslink the anionic layers and/or cationic layers (i.e., first cationic layer **25** and first anionic layer **30**). In an embodiment, elastomeric substrate **5** with coating **65** is exposed to additives in an anionic mixture.

[0047] In some embodiments, the pH of the anionic and/or cationic solution is adjusted. Without being limited by theory, reducing the pH of the cationic solution reduces growth of coating **65**. Further, without being limited by theory, the coating **65** growth may be reduced because the cationic solution may have a high charge density at lowered pH values, which may cause the polymer backbone to repel itself into a flattened state. In some embodiments, the pH is increased to increase the coating **65** growth and produce a thicker coating **65**. Without being limited by theory, a lower charge density in the cationic mixture provides an increased coiled polymer. The pH may be adjusted by any suitable means such as by adding an acid or base. In an embodiment, the pH of an anionic solution is between about 0 and about 14, alternatively between about 1 and about 7. Embodiments include the pH of a cationic solution that is between about 0 and about 14, alternatively between about 3 and about 12.

[0048] The exposure steps in the anionic and cationic mixtures may occur at any suitable temperature. In an embodiment, the exposure steps occur at ambient temperatures. In some embodiments, coating **65** is optically transparent.

[0049] To further illustrate various illustrative embodiments of the present invention, the following examples are provided.

EXAMPLE 1

[0050] Materials. Natural sodium montmorillonite (MMT) (CLOISITE® NA+, which is a registered trademark of Southern Clay Products, Inc.) clay was used as received. Individual MMT platelets had a negative surface charge in deionized water, reported density of 2.86 g/cm^3, thickness of 1 nm, and a nominal aspect ratio (l/d)≥200. Branched polyethylenimine (PEI) (M_w=25,000 g/mol and M_n=10,000 g/mol), polyethylene oxide (PEO) (M_w=4,000,000 g/mol) and polyacrylic acid (PAA) (35 wt.% in water, M_w=100,000 g/mol) were purchased from Sigma-Aldrich (Milwaukee, Wis.) and used as received. 500 μm thick, single-side-polished, silicon wafers were purchased from University Water (South Boston, Mass.) and used as reflective substrates for film growth characterization via ellipsometry.

[0051] Film Preparation. All film deposition mixtures were prepared using 18.2 MΩ deionized water, from a DIRECT-Q® Ultrapure Water System, and rolled for one day (24 h) to achieve homogeneity. DIRECT-Q® is a registered trademark of Millipore Corporation. Prior to deposition, the pH of 0.1 wt. % aqueous solutions of PEI were altered to 10 or 3 using 1.0 M HCl, the pH of 0.1 wt. % aqueous solutions of PF0 were altered to 3 using 1.0 M HCl, the pH of 0.2 wt. % aqueous solutions of PAA were altered to 3 using 1.0 M HCl, and the pH of 2.0 wt. % aqueous suspensions of MMT were altered to 3 using 1.0 M HCl. Silicon wafers were piranha treated for 30 minutes prior to rinsing with water, acetone, water again and finally dried with filtered air prior to deposition. Elastomeric substrates were rinsed with deionized water, immersed in a 40 wt. % propanol in water bath at 40° C. for 5 minutes, rinsed with RT 40 wt. % propanol in water, rinsed with deionized water, dried with filtered air, and plasma cleaned for 5 minutes on each side. Each appropriately treated substrate was then dipped into the PEI solution at pH 10 for 5 minutes, rinsed with deionized water, and dried with filtered air. The same procedure was followed when the substrate was next dipped into the PAA solution. Once this initial bilayer was deposited, the above procedure was repeated when the substrate was dipped into the PEO solution, then the PAA solution, then the PEI solution at pH 3, and finally the MMT suspension, using 5 second dip times for polymer solutions and using one minute dip times for the MMT suspension, until the desired number of quadlayers of PEO/PAA/PEI/MMT were achieved. All films were prepared using a home-built robotic dipping system.

[0052] Film Characterization. Film thickness was measured every one to five quadlayers (on silicon wafers) using an ALPHA-SE® ellipsometer. ALPHA-SE® is a registered trademark of J. A. Woollam Co., Inc. OTR testing was performed by Mocon, Inc, in accordance with ASTM D-3985, using an Oxtran 2/21 ML instrument at 0% RH.

[0053] From the results, FIG. **4** illustrates thickness as a function of the number of quadlayers PEO/PAA/PEI/MMT when deposited on a silicon wafer and measured via ellipsometry. FIG. **5** illustrates results of oxygen transmission rate (OTR) as a function of the number of quadlayers of PEO/PAA/PEI/MMT when deposited on a 1 mm thick rubber plaque. FIG. **6** illustrates the elasticity of a coating of which the image on the left is 10 QLs on rubber, and the image on the right is the same coating stretched at 20 inches per minute to 30% strain. This right image showed no sign of mud-cracking and revealed the conformality of the coating to the stretched rubber surface.

[0054] Although the present invention and its advantages have been described in detail, it should be understood that various changes, substitutions and alterations may be made herein without departing from the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

1. A method for producing a material diffusion barrier on an elastomeric substrate, comprising:

(A) exposing the elastomeric substrate to a cationic solution to produce a cationic layer on the elastomeric substrate;

(B) exposing the cationic layer to an anionic solution to produce an anionic layer on the cationic layer, wherein a layer comprises the cationic layer and the anionic layer, and wherein the layer comprises the material diffusion barrier.

2. The method of claim **1**, further comprising:

(C) exposing the anionic layer to a second cationic solution to produce a second cationic layer on the anionic layer, and wherein the layer comprises a trilayer comprising the cationic layer, the anionic layer, and the second cationic layer.

3. The method of claim **1**, further comprising:

(C) exposing the anionic layer to a second cationic solution to produce a second cationic layer on the anionic layer; and

(D) exposing the second cationic layer to a second anionic solution to produce a second anionic layer on the second cationic layer, wherein the layer comprises a quadlayer comprising the cationic layer, the anionic layer, the second cationic layer, and the second anionic layer.

4. The method of claim **1**, wherein the cationic solution comprises cationic materials, and wherein the cationic materials comprise a polymer, a colloidal particle, a nanoparticle, or any combinations thereof.

5. The method of claim **4**, wherein the polymer comprises a polymer with hydrogen bonding, wherein the polymer with hydrogen bonding comprises polyethylene oxide, polyglycidol, polypropylene oxide, poly(vinyl methyl ether), polyvinyl alcohol, polyvinylpyrrolidone, polyallylamine, branched polyethylenimine, linear polyethylenimine, poly(acrylic acid), poly(methacrylic acid), copolymers thereof, or any combinations thereof.

6. The method of claim **1**, wherein the anionic solution comprises layerable materials, and wherein the layerable materials comprise an anionic polymer, a colloidal particle, or any combinations thereof.

7. The method of claim **6**, wherein the anionic polymer comprises a polystyrene sulfonate, a polymethacrylic acid, a polyacrylic acid, a poly(acrylic acid, sodium salt), a polyanetholesulfonic acid sodium salt, poly(vinylsulfonic acid, sodium salt), or any combinations thereof.

8. The method of claim **6**, wherein the colloidal particle comprises a clay, a colloidal silica, an inorganic hydroxide, a silicon based polymer, a polyoligomeric silsesquioxane, a carbon nanotube, a graphene, or any combinations thereof.

9. The method of claim **1**, wherein the elastomeric substrate further comprises a primer layer disposed between the elastomeric substrate and the cationic layer.

10. The method of claim **1**, further comprising repeating steps (A) and (B) to produce a plurality of layers, wherein the material diffusion barrier comprises the plurality of layers.

11. A method for producing a material diffusion barrier on an elastomeric substrate, comprising:

(A) exposing the elastomeric substrate to an anionic solution to produce an anionic layer on the elastomeric substrate;

(B) exposing the anionic layer to a cationic solution to produce a cationic layer on the anionic layer, wherein a layer comprises the anionic layer and the cationic layer, and wherein the layer comprises the material diffusion barrier.

12. The method of claim **11**, further comprising:

(C) exposing the cationic layer to a second anionic solution to produce a second anionic layer on the cationic layer, and wherein the layer comprises as trilayer comprising the anionic layer, the cationic layer, and the second anionic layer.

13. The method of claim **11**, further comprising:

(C) exposing the cationic layer to a second anionic solution to produce a second anionic layer on the cationic layer; and

(D) exposing the second anionic layer to a second cationic solution to produce a second cationic layer on the second anionic layer, wherein the layer comprises a quadlayer comprising the anionic layer, the cationic layer, the second anionic layer, and the second cationic layer.

14. The method of claim **11**, wherein the cationic solution comprises cationic materials, and wherein the cationic materials comprise a polymer, a colloidal particle, a nanoparticle, or any combinations thereof.

15. The method of claim **14**, wherein the polymer comprises a polymer with hydrogen bonding, wherein the polymer comprises polyethylene oxide, polyglycidol, polypropylene oxide, poly(vinyl methyl ether), polyvinyl alcohol, polyvinylpyrrolidone, polyallylamine, branched polyethylenimine linear polyethylenimine, poly(acrylic acid), poly (methacrylic acid), copolymers thereof, or any combination thereof.

16. The method of claim **11**, wherein the anionic solution comprises layerable materials, and wherein the layerable materials comprise an anionic polymer, a colloidal particle, or any combinations thereof.

17. The method of claim **16**, wherein the anionic polymer comprises a polystyrene sulfonate, a polymethacrylic acid, a polyacrylic acid, a poly(acrylic acid, sodium salt), a polyanetholsulfonic acid sodium salt, poly(vinylsulfonic acid, sodium salt), or any combinations thereof.

18. The method of claim **16**, wherein the colloidal particle comprises a clay, a colloidal silica, an inorganic hydroxide, a silicon based polymer, a polyoligomeric silsesquioxane, a carbon nanotube, a graphene, or any combinations thereof.

19. The method of claim **11**, wherein the elastomeric substrate further comprises a primer layer disposed between the elastomeric substrate and the anionic layer.

20. The method of claim **11**, further comprising repeating steps (A) and (B) to produce a plurality of layers, wherein the material diffusion barrier comprises the plurality of layers.

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