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[Continued on next page]

(54) **Title:** IMPROVING ADHESION OF ORGANIC COATINGS ON GLASS

(57) **Abstract:** Methods of manufacturing and coating glass including depositing an inorganic oxide on an exterior surface of the glass, and then applying an organofunctional silane to the glass over the inorganic oxide. The methods also may include applying an organic coating to the glass over the organofunctional silane, and curing the organic coating.

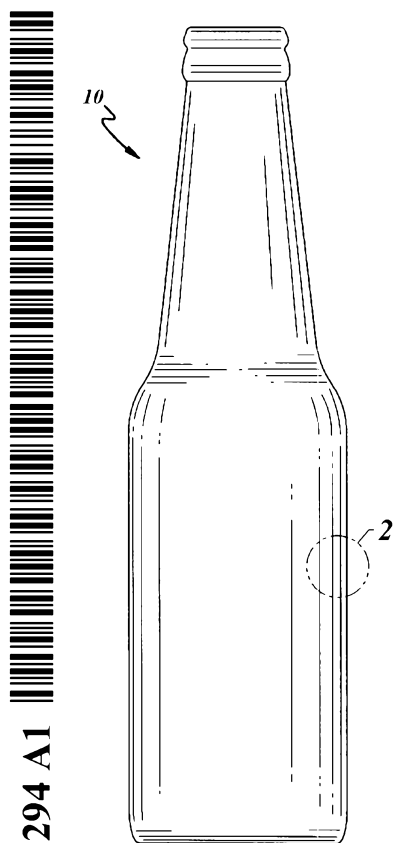


FIG. 1

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IMPROVING ADHESION OF ORGANIC COATINGS ON GLASS

FIELD OF THE INVENTION

[0001] The present disclosure is directed to coating processes, including methods and materials for coating glass, and to improving adhesion of organic coatings on the glass.

BACKGROUND TO THE INVENTION

[0002] Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

[0003] Various processes have been developed to apply coatings to glass substrates for different purposes, including decoration, adhesion and glass strengthening for damage prevention. For example, U.S. Patent 3,522,075 discloses a process for coating a glass container in which the container is formed, coated with a layer of metal oxide such as tin oxide, cooled through alehr, and then coated with an organopolysiloxane resin-based material over the metal oxide layer.

[0004] A general object of the present disclosure, in accordance with one aspect of the disclosure, is to increase bonding between glass coatings for better adhesion of organic coatings to a product thereby improving product appearance, ultraviolet protection, durability and/or the like.

SUMMARY OF THE INVENTION

[0005] The present disclosure embodies a number of aspects that can be implemented separately from or in combination with each other.

[0006] In a first aspect, the present invention provides a method of manufacturing a glass container, which includes the following steps in the sequence set forth:

- (a) forming a glass container substrate,
- (b) applying a hot end coating of SnO_2 to an exterior surface of the glass container substrate,
- (c) annealing the glass container,

- (d) applying a cold end coating of polyethylene to the exterior surface of the glass container during or after said step (c),
- (e) inspecting the glass container,
- (f) after completion of said step (e), depositing an inorganic oxide coating on the exterior surface of the glass container over the cold end coating,
- (g) applying an organofunctional silane coating to the glass container over the inorganic oxide coating.
- (h) applying an organic coating to the glass container after step (g), over the organofunctional silane coating, and then
- (i) curing said organic coating.

[0007] In a second aspect, the present invention provides a method of coating a glass container, which includes the following steps in the sequence set forth:

- (a) applying a cold end coating of polyethylene to an exterior surface of a glass container substrate,
- (b) depositing an inorganic oxide on the exterior surface of the glass container substrate over the cold end coating,
- (c) applying an organofunctional silane to the glass container over the inorganic oxide, and then
- (d) applying an organic coating to the glass container over the organofunctional silane.

[0008] In a third aspect the present invention provides a glass container made in accordance with the method according to any one of the first two aspects of the invention.

[0009] In another aspect the present invention provides a glass container produced by either one of the methods set forth above, wherein the glass container consists essentially of:

- a glass substrate,
- a protective cold end coating consisting essentially of polyethylene on an exterior surface of the glass substrate,
- a silicon-based inorganic oxide coating on the exterior surface of the glass substrate over the cold end coating,
- an organofunctional silane coating over the inorganic oxide coating, and an organic coating over the organofunctional silane coating.

[0010] In accordance with another preferred aspect of the disclosure, there is provided a method of manufacturing a glass container including the steps of forming the glass container, applying a hot end coating to an exterior surface of the glass container, annealing the glass container, applying a cold end coating to the exterior surface of the glass container, inspecting the glass container, and then depositing an inorganic oxide on the exterior surface of the glass container and applying an organofunctional silane to the glass container over the inorganic oxide. According to a preferred aspect, this method also may include applying an organic coating to the glass container over the organofunctional silane.

[0011] Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The disclosure, together with additional features, advantages and aspects thereof, will be best understood from the following description, the appended claims and the accompanying drawings, in which:

[0013] FIG. 1 is an elevational view of a glass container in accordance with an exemplary embodiment of the present disclosure; and

[0014] FIG. 2 is an enlarged sectional view of the glass container, taken from circle 2 of FIG. 1.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0015] In general, products and processes will be described using one or more examples of exemplary embodiments of materials and steps to improve adhesion of organic coatings on glass. The example embodiments will be described with reference to use for glass containers. However, it will be appreciated as the description proceeds that the invention is useful in many different applications and may be implemented in many other embodiments including, but not limited to glass dishware, and other glass products.

[0016] Referring now to the drawings, FIG. 1 illustrates an exemplary embodiment of a glass container 10 (e.g., glass bottle, jar, or the like) that may be produced in accordance with

exemplary embodiments of a manufacturing process presently disclosed hereinbelow. FIG. 2 illustrates that the glass container 10 preferably includes a glass substrate 12, a hot end coating 14 on the substrate, a cold end coating 16 over the hot end coating 14, an inorganic oxide coating 18 over the cold end coating 16, an organofunctional silane coating 19 over the inorganic oxide coating 18, and an organic coating 20 over the organofunctional silane coating 19.

[0017] Although the various coatings 14-20 are shown as adjacent layers overlying one another sequentially, one or more of the coatings may penetrate into or even through one or more of the other coatings. Accordingly, the various coatings 14-20 may be fairly described as being applied generally to the glass container 10, regardless of how or to what extent any given coating contacts any of the other coatings and/or the substrate 12. Similarly, when a material is described as being applied to an exterior surface of the glass container 10, the material may contact one or more of the coatings 14-20 and/or the glass substrate 12 itself.

[0018] Glass containers can be produced in any suitable manner. This typically would involve a "hot end" including one or more melting furnaces, forming machines, and annealing lehrs, and a "cold end" after the annealing lehr(s) and including inspection equipment and packaging machines. Accordingly, a "hot end coating" is a coating applied at the hot end of a glass container manufacturing process before passage through the annealing lehr, and a "cold end coating" is a coating applied at the cold end of the glass container manufacturing process during or after passage through the annealing lehr.

[0019] After forming glass containers, but prior to annealing, the glass containers may be hot-end coated in any suitable manner. For example, the glass containers may be coated with one or more metal oxides, for instance, under a hood between the forming machines and an annealing lehr. The hot-end coating 14 may include oxides of tin, titanium, vanadium, zirconium, and/or the like.

[0020] The glass containers then may be annealed in any suitable manner, such as in an annealing lehr.

[0021] At or downstream of the annealing operation, the glass containers may be cold-end coated in any suitable manner. For example, the glass containers may be coated with the cold end coating 16, which may be a protective organic coating applied downstream or at an end of

the annealing Lehr. The cold end coating may include polyethylene, stearate, oleic acid, or any other suitable material(s).

[0022] After the cold end coating is or coatings are applied, the glass containers may be inspected for any suitable characteristics and in any suitable manner. For example, the glass containers may be manually or automatically inspected for cracks, inclusions, surface irregularities, hot end and/or cold end coating properties, and/or the like.

[0023] The inorganic oxide coating 18 is applied to exterior surfaces of the glass containers in any suitable manner and, preferably, after inspection. In one embodiment, one or more inorganic oxides may be deposited on the glass containers, for example, by flame pyrolysis. The inorganic oxide may include a reactive silica, for example, SiO_2 . Precursors to the inorganic oxide may be delivered as a vapor, an atomized liquid, an atomized solution, and/or the like. Suitable precursors may include one or more of the following compounds: tetraethoxy silane (TEOS), hexamethyldisiloxane (HMDSO), hexamethyldisilazane (HMDSA), R_4Si (where R is an alkyl or aryl group containing seven or less carbon atoms), R_3SiX (where R is an alkyl or aryl group containing seven or less carbon atoms and X is a halide, alkoxide, aryloxy, or amide group), and/or SiX_4 (where X is a halide, alkoxide, aryloxy, or amide group). Those of ordinary skill in the art will recognize that the thickness of the inorganic oxide coating 18 may be application specific and may be determined by trial and error. In an exemplary glass container embodiment, the thickness may be between 100 and 1000 Angstroms. The manufacturing speed for the inorganic coating step may be about 50 containers per minute (cpm) to about 600 cpm. In any case, the deposition of the inorganic oxide results in the inorganic oxide coating 18, which presents a highly reactive surface with increased bonding sites for an organofunctional silane, which may be applied, for example, as described below.

[0024] After the inorganic oxide is applied, the organofunctional silane coating 19 is applied to the glass containers in any suitable manner to facilitate adhesion of the subsequent organic coating 20. Because the inorganic oxide coating 18 provides increased bonding sites for the organofunctional silane coating 19, more organofunctional silane per unit area can be retained on the glass containers than otherwise would in the absence of the deposited inorganic oxide coating 18. In turn, and as will be described below, the more organofunctional silane that is retained on the glass containers, the more the organic coating 20 will adhere to the glass containers than otherwise would in the absence of the inorganic oxide and organofunctional silane coatings 18, 19.

[0025] The organofunctional silane coating 19 may be applied as a liquid or aqueous solution, for example, by spraying, rolling-on, brushing, dipping, and/or any other suitable application techniques. The chemistry of the organofunctional silane coating 19 may be chosen based on the chemistry of the organic coating 20 applied over the organofunctional silane coating 19. For example, if the organic coating 20 is a radiation curable material based on acrylate chemistry, then an appropriate organofunctional silane may contain an acrylate or methacrylate functionality. Those of ordinary skill in the art will recognize that the thickness of the organofunctional silane coating 19 may be application specific and may be determined by trial and error. In an exemplary glass container embodiment, the coating 19 may include one or two applications or layers. The manufacturing speed for the organofunctional silane coating step may be about 50 containers per minute (cpm) to about 600 cpm.

[0026] After the organofunctional silane is applied, the organic coating 20 is applied to the glass containers in any suitable manner, for example, for decoration, ultraviolet protection, durability, and/or the like. The organic coating 20 may be applied by spraying, dipping, powder coating, or the like. The organic coating 20 may be solvent-borne, water-borne, 100% solids, or the like. The organic coating 20 may be based on one or more of a variety of polymers including acrylates, epoxies, urethanes, and/or the like.

[0027] After applying the organic coating 20, the coating 20 may be cured in any suitable manner. The organic coating 20 may be a curable coating, for example, a radiation-curable organic coating cured by any suitable type of radiation like, for instance, ultraviolet, electron beam, or the like. In another embodiment, the organic coating 20 may be a thermally-curable coating cured by convection oven, infrared lamps, or the like. The curing step may be used to facilitate good bonding between the organic coating 20 and the organofunctional silane.

[0028] After curing, the glass containers may be packaged in any suitable manner.

[0029] The manufacturing process may or may not include all of the disclosed steps or be sequentially processed or processed in the particular sequence discussed, and the presently disclosed manufacturing process and coating methods encompass any sequencing, overlap, or parallel processing of such steps.

[0030] Contrary to conventional wisdom, it is possible to produce glass containers with effective bonding of organic coatings thereto without having to resort to undesirable process steps. Conventionally, it has been understood that organic coatings do not adhere well to glass

containers having been treated with hot and/or cold end coatings, and that flame, corona or plasma energy must be applied to the glass containers to achieve possible adhesion of the organic coating thereto.

[0031] In contrast, the application of the inorganic oxide coating of the presently disclosed method produces a highly reactive silica surface that allows increased organofunctional silane bonding per unit area, which in turn leads to increased adhesion of the organic coating to the glass containers. It is supposed that the organofunctional silane may facilitate adhesion of the organic coating 20 to the glass containers via strong bonding, perhaps via covalent bonds, of the organofunctional silane with both of the inorganic oxide coating 18 and the organic coating 20. In any event, a concomitant increase in durability of the organic coating can be achieved, thereby improving one or more of product appearance, adhesion, ultraviolet protection, durability, and/or the like.

[0032] Laboratory testing was undertaken to illustrate the improvement provided by the present disclosure. A description of the test and results follow.

[0033] Glass bottles with SnO_2 /polyethylene coatings were prepared with various exterior surface conditions, and then compared in terms of average adhesion strength. Below, preparation of each of the example bottles is described, followed by a table comparing adhesion results.

[0034] A first set of glass bottles included only a SnO_2 /polyethylene coating and was otherwise non-treated before application of the organic coating.

[0035] A second set of glass bottles included a SnO_2 /polyethylene coating and was further subjected to flame treatment with a gas composed of 35% propane and 65% butane by weight. Distance between the flame jet and the exterior surfaces of the bottles was about 15 mm, bottle rotation speed was about 100 rpm, and treatment time was about 60 seconds including two trips (forth and back) across the bottle. The bottle surface temperature after the flame pretreatment was about 220-240°F, and the flame temperature at the bottle surface was about 1,800°F.

[0036] A third set of glass bottles included a SnO_2 /polyethylene coating and was further subjected to corona treatment using a corona surface treater model BD-80 from Electro-Technic Products, of Chicago, IL. The output voltage was set to maximum scale of

about 250 kV, with a distance between the treater electrode and the bottle surfaces of about 3 to 5 mm. Bottle rotation speed was about 100 rpm, and the treatment duration was about 3 minutes.

[0037] A fourth set of glass bottles included a SnO_2 /polyethylene coating and was further subjected to plasma treatment using argon. The treatment included an argon flow rate of about ten 1/min, arc voltage of about 20 V DC, arc current of about 100 A, and the distance between the plasma jet and the bottle surface was set to about 15 mm. Bottle rotation speed was about 100 rpm, with a treatment time of about 80 seconds, including two trips (forth and back) across the bottle.

[0038] A fifth set of glass bottles included a SnO_2 /polyethylene coating, with an organofunctional silane coating applied thereto.

[0039] A sixth set of glass bottles included a SnO_2 /polyethylene coating and was further subjected to the flame treatment described above, with an organofunctional silane coating applied thereto.

[0040] A seventh set of glass bottles was prepared in accordance with the present disclosure, including a SnO_2 /polyethylene coating, an inorganic oxide coating, an organofunctional silane coating, and an organic coating. The inorganic oxide coating was applied using a PYROSIL brand professional kit available from Bohle America, Inc. of Charlotte, NC. The distance between the pyrolytic flame and the bottle surfaces was about 15 mm, bottle rotation speed was about 100 rpm, with a treatment time of about 80 seconds. The bottle temperature after treatment was about 220°F (about 104°C). The bottle temperature during silane deposition was about 90 to 120°F (about 32 to 49°C), and the silane was deposited with a brush using about one ml of silane and took about thirty seconds to complete. The silane was aged after deposition for about ten minutes.

[0041] For all sets of glass bottles, the organic coating was applied by spraying, using a RECORD 2200 brand spray gun with a gravity flow cup available from La Ditta GAV of Italy. The spray gun included a nozzle diameter of about 1.5 mm, with an air pressure of about 4 bar. The coating application time was about 5 to 25 seconds, and bottle rotation speed was about 60 to 65 rpm. The distance between the bottles and the spray gun was about 30 cm, and the application rate was about 0.4 to 1.3 g per bottle (on average 0.8 g per bottle).

[0042] All sets of glass bottles were allowed to dry at room temperature of about 15.5 to 21°C (about 60 to 70°F) and humidity of about 30 to 50% for about 30 to 35 seconds.

[0043] Then all sets of glass bottles were exposed to infrared drying for about 120 to 150 seconds. An infrared dryer used 1 kW of reflector power, and the distances between the reflector tube and the bottle surfaces ranged from about 9 cm to about 14 cm. Bottle temperature at the end of the infrared drying was about 76.7 to 82.2°C (about 170 to 180°F).

[0044] Thereafter, the organic coatings of the glass bottles were ultraviolet radiation cured for about 15 seconds. Bottle rotation speed was about 60 to 65 rpm, a distance between an ultraviolet lamp and the bottle surfaces was about 6 cm, irradiance was set to about 1200 mW/cm², and ultraviolet dosage was about 9000 mJ/cm² (UV-A and UV-B). Two 3000 Watt UV lamps were used: model DRTI-3000A, available from Razryad Ltd, of Zelenograd, Russia.

[0045] All sets of bottles were measured for adhesion. Adhesion measurements were taken on roughly 2.5 cm x 2.5 cm samples with a custom built system consisting of a load cell (Honeywell SENSOTEC brand model 102) and a pneumatic cylinder. A 4.8 mm diameter dolly shaped to the curvature of the bottles was glued to the surfaces thereof using a universal cyanoacrylate adhesive (UCA), for example, TRAMEL UCA. A pull strength load was incrementally applied until destruction occurred. A table of results follows.

Bottle Set	Average Adhesion Strength (MPa)
First – non treated	6.1
Second – flame treated	4.6
Third – corona treated	1.4
Fourth – plasma treated	3.3
Fifth – organofunctional silane treated	8.4
Sixth – flame and silane treated	10.6
Seventh – inorganic oxide + silane	17.2

TABLE 1

[0046] Therefore, one example of the presently disclosed method results in an adhesion strength that is about two to three times greater than other surface treatments on a SnO₂/polyethylene surface of a glass container.

[0047] There thus has been disclosed methods of coating glass containers and methods of manufacturing glass containers that at least partially satisfy one or more of the objects and aims previously set forth. The disclosure has been presented in conjunction with several exemplary embodiments, and additional modifications and variations have been discussed. Other modifications and variations readily will suggest themselves to persons of ordinary skill in the art in view of the foregoing discussion.

CLAIMS

1. A method of manufacturing a glass container, which includes the following steps in the sequence set forth:
 - (a) forming a glass container substrate,
 - (b) applying a hot end coating of SnO_2 to an exterior surface of the glass container substrate,
 - (c) annealing the glass container,
 - (d) applying a cold end coating of polyethylene to the exterior surface of the glass container during or after said step (c),
 - (e) inspecting the glass container,
 - (f) after completion of said step (e), depositing an inorganic oxide coating on the exterior surface of the glass container over the cold end coating,
 - (g) applying an organofunctional silane coating to the glass container over the inorganic oxide coating.
 - (h) applying an organic coating to the glass container after step (g), over the organofunctional silane coating, and then
 - (i) curing said organic coating.
2. The method set forth in claim 1 wherein said step (f) is carried out by flame pyrolysis.
3. The method set forth in claim 1 wherein the inorganic oxide of said step (f) is SiO_2 .
4. A method of coating a glass container, which includes the following steps in the sequence set forth:
 - (a) applying a cold end coating of polyethylene to an exterior surface of a glass container substrate,
 - (b) depositing an inorganic oxide on the exterior surface of the glass container substrate over the cold end coating,
 - (c) applying an organofunctional silane to the glass container over the inorganic oxide, and then
 - (d) applying an organic coating to the glass container over the organofunctional silane.
5. The method set forth in claim 4 wherein said step (a) is carried out by flame pyrolysis.

6. The method set forth in claim 5 further including the step of: (d) curing said organic coating.
7. The method set forth in claim 6 including, prior to said step (a), applying a hot-end coating to the glass container substrate.
8. The method set forth in claim 7 wherein said hot-end coating is SnO_2 .
9. The method set forth in claim 4 wherein said inorganic oxide is a silicon-based inorganic oxide.
10. The method set forth in claim 9 wherein said silicon-based inorganic oxide is SiO_2 .
11. A glass container made in accordance with the method set forth in claim 1 or 4.
12. A glass container produced by the method set forth in claim 1 or 4, wherein the glass container consists essentially of:
 - a glass substrate,
 - a protective cold end coating consisting essentially of polyethylene on an exterior surface of the glass substrate,
 - a silicon-based inorganic oxide coating on the exterior surface of the glass substrate over the cold end coating,
 - an organofunctional silane coating over the inorganic oxide coating, and an organic coating over the organofunctional silane coating.
13. The container set forth in claim 12 wherein said inorganic oxide coating is silica (SiO_2).
14. A method of manufacturing a glass container substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.
15. A method of coating a glass container substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

16. A glass container substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

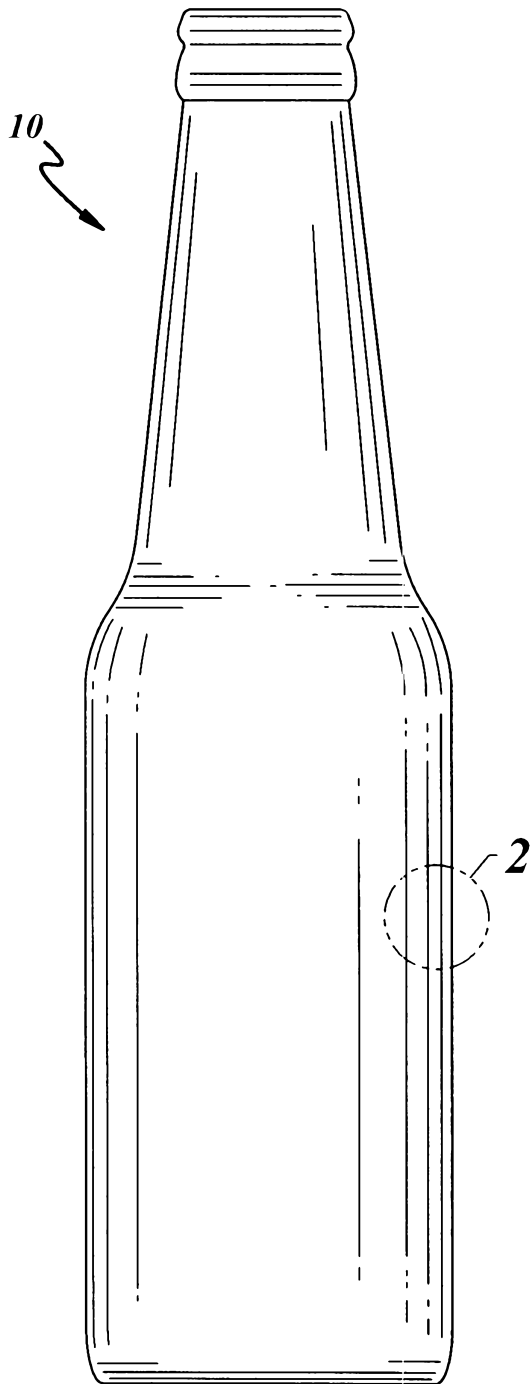


FIG. 1

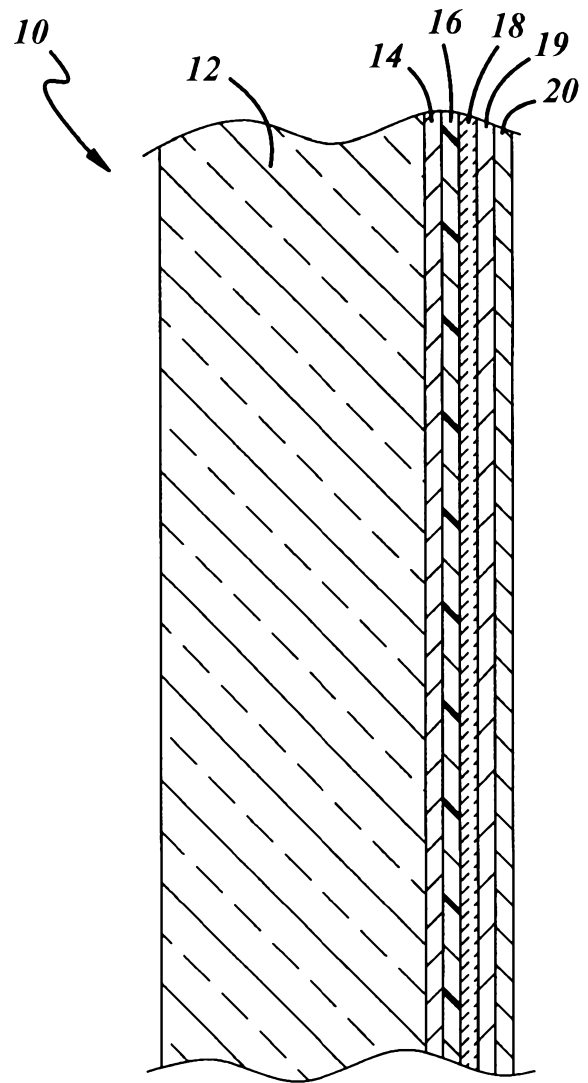


FIG. 2