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(54) Title: SPILL RESISTANT SURFACES HAVING HYDROPHOBIC AND OLEOPHOBIC BORDERS

Figure 1

Figure 1 Panel A

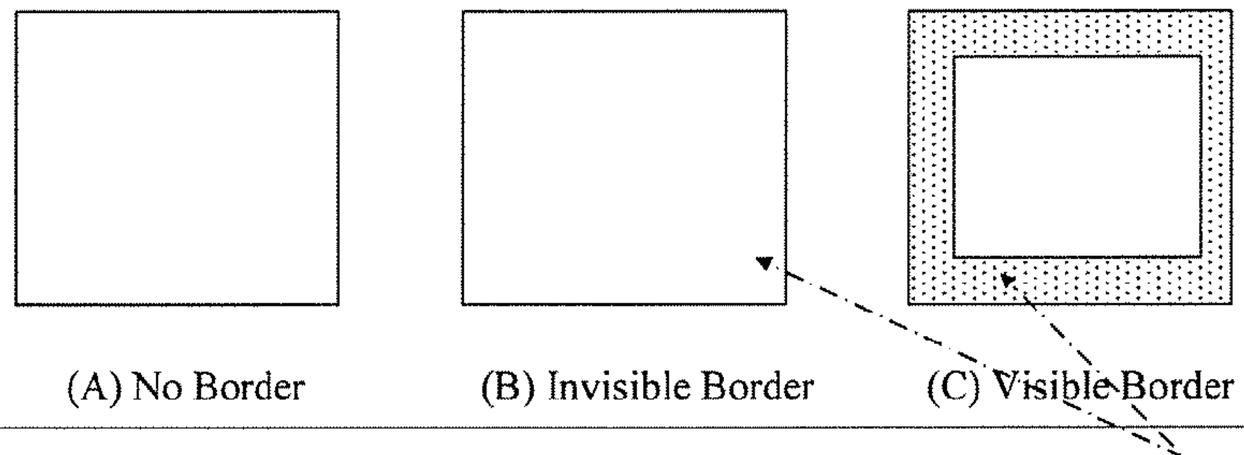
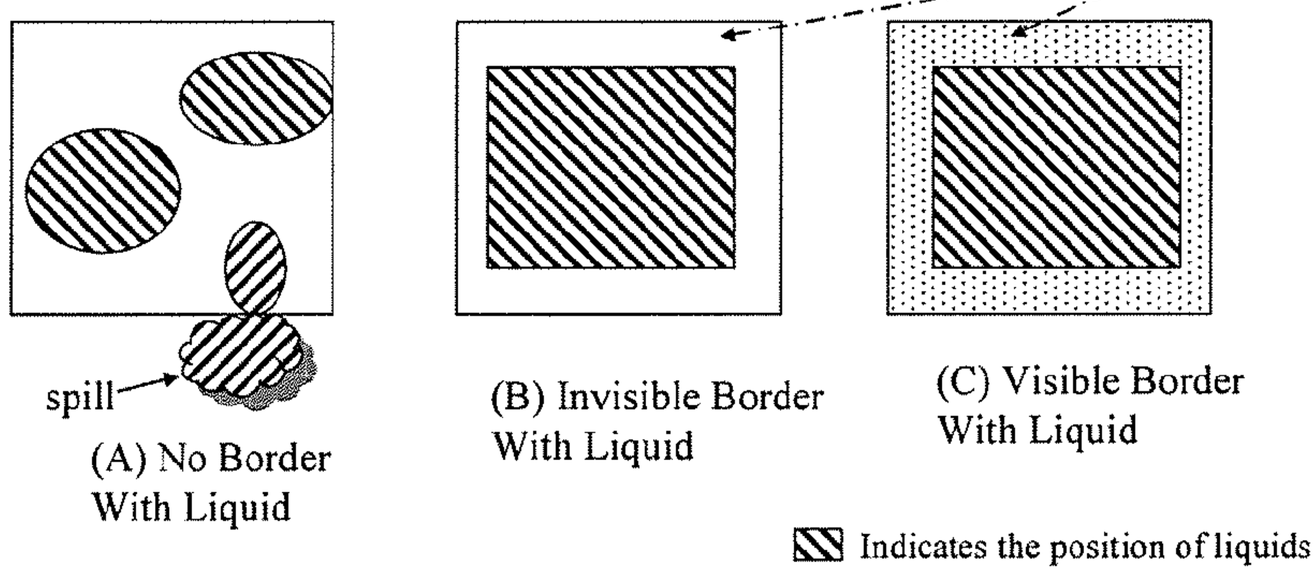


Figure 1 Panel B



(57) Abrégé/Abstract:
Described herein are methods for creating spill-proof or spill-resistant surfaces through the use of hydrophobic or oleophobic (H-SH) edges, borders or/and boundaries that contain the water and other liquids within inside the edges, borders and/or boundaries.

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(57) Abrégé(suite)/Abstract(continued):
Also described herein are spill-proof/spill-resistant surfaces. Liquid (e.g., water and other aqueous solutions/suspension) heights of 3-6 mm on a level planar surface can be sustained by such edges, borders and/of boundaries. The H-SH borders can be created on glass, metal, wood, plastic, and concrete surfaces.

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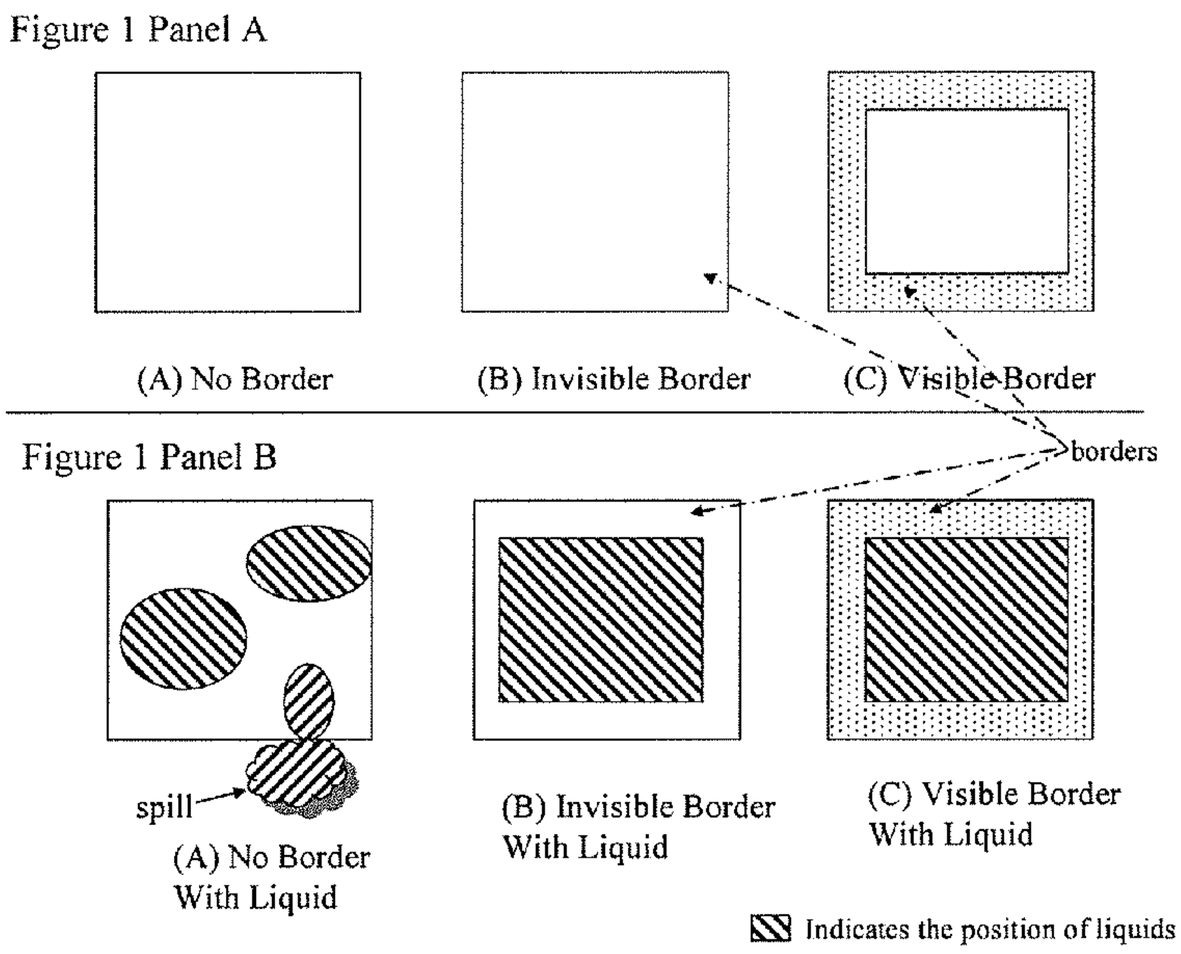
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[Continued on next page]

(54) Title: SPILL RESISTANT SURFACES HAVING HYDROPHOBIC AND OLEOPHOBIC BORDERS

(57) Abstract: Described herein are methods for creating spill-proof or spill-resistant surfaces through the use of hydrophobic or oleophobic (H-SH) edges, borders or/and boundaries that contain the water and other liquids within inside the edges, borders and/or boundaries. Also described herein are spill-proof/spill-resistant surfaces. Liquid (e.g., water and other aqueous solutions/ suspension) heights of 3-6 mm on a level planar surface can be sustained by such edges, borders and/of boundaries. The H-SH borders can be created on glass, metal, wood, plastic, and concrete surfaces.

Figure 1



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Spill-Resistant Surfaces Having Hydrophobic and Oleophobic Borders

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application 61/103,295, filed on October 7, 2008, which is hereby incorporated by reference in its entirety.

Background

[0002] Most liquids, when properly contained, do not give rise to damage, either to the containers in which they are stored or to physical structure or equipment that may be used to store the liquids or containers of liquids. If spilled, however, the same liquids can cause a variety of problems including contamination, corrosion, and/or damage to equipment or surface that may be used to store the liquids or that come in contact with the spilled liquids. For example, unwanted spills of water and other liquids include spills in refrigerators where unwanted microbial growth can occur (particularly where liquid runs from shelf to shelf requiring excessive cleaning) and spills on hardwood floors causing swelling and/or discoloration due to the joints in the wood becoming wet. Spills on, or in the vicinity of, computers and other electronics can cause damage and/or performance problems in the equipment receiving the spilled liquid or other electronic equipment in the vicinity of the spill. In addition, spills from a drink dispenser in residential or commercial settings, such as restaurants and fast food establishments can lead to hazardous situation including microbial contamination and situations where individuals may slip and become injured. Where spills of foods and beverages are capable of supporting microbial growth, there can be concern over microbial contamination if those spills are not properly cleaned, particularly in areas where the preparation and/or the storage of food occur. Spill may also occur in setting other than those where food is prepared, such as laboratories, lavatories, factory settings and the like.

Summary

[0003] Embodiments of this disclosure provide for spill-resistant borders and/or barriers that may be applied to surfaces. Such spill-resistant borders and barriers can prevent water and other liquids from spreading or flowing beyond the position of a border on a planer or substantially planar surface that is placed in a substantially level horizontal position. In embodiments disclosed herein, such borders can prevent the spread of an aqueous liquid until it exceeds a level that is about 4.5 mm higher than the surface. In

some instances the liquids can be aqueous solutions, suspensions or emulsions. In other instances, the liquids can be lipids or oils that are prevented from spreading beyond a border until the level of the oil or lipid exceeds, e.g., 2 mm above the surface on which the border is formed. In other instances liquid can be an alcohol (e.g., methanol, ethanol, a propanol, a butanol, or a pentanol) or a liquid comprising an alcohol (e.g., water and alcohol combination including alcoholic beverages such as beer, wine and distilled liquors).

[0004] Where the surface, or a portion of the surface, is substantially planar, the spill-resistant border may be placed at or near the edges of the planer surface or near the edge of the portion that is substantially planer, such that the spill-resistant border surrounds a region of the surface that has a lower hydrophobicity or lower oleophobicity than the spill-resistant border. Alternatively, the border may be placed so as to form a boundary encompassing one or more portions of the surface that have a lower hydrophobicity or oleophobicity than the border. Thus, borders may, in some cases, be placed at the edges of (e.g., at or near the edges of the treated surface) or form one or more barriers separating regions of a surface that have lower hydrophobicity than the borders or barriers.

[0005] The spill-resistant borders described herein can be made by treating the surface with a variety of compositions that comprise agents that cause water, alcohols, oils and/or other liquids to be retained within the area encompassed by the border. In some instances, the borders are formed by applying a composition to a surface that increases the hydrophobicity or oleophobicity of a portion of the surface that will server as a border (e.g., applying a reagent that converts a portion of the surface into a more hydrophobic or more oleophobic surface by covalently attaching one or more alkyl, fluoroalkyl, or prefluoroalkyl groups to the surface). In such embodiments, the border forms a perimeter around at least one area of the surface that has a lower hydrophobicity or oleophobicity than the border, (i.e., the resulting border is more hydrophobic and/or more oleophobic than the area immediately adjacent to it within its perimeter). Surfaces prepared by such methods are also provided.

[0006] Other embodiments provide surfaces comprising a hydrophobic and/or oleophobic spill-resistant border, wherein the border forms a perimeter around at least one area of the surface that has a lower hydrophobicity and/or lower oleophobicity than the border. In another embodiment, the surface may comprise a hydrophobic and/or

oleophobic spill-resistant border, wherein said border forms a perimeter around at least two, or at least three, or at least four, areas of the surface that have a lower hydrophobicity and/or lower oleophobicity than the border.

[0007] Other embodiments will be apparent to skilled artisans from reading this disclosure, including the figures and appended claims.

Brief Description of the Drawings

[0008] Figure 1 illustrates multiple embodiments of this disclosure. Shown in Fig. 1 (perspective vertically down) are three glass plates. Panel A depicts the plates in the absence of liquid and Panel B depicts the plates in the presence of liquid. Plate "(A)" is a "control" glass plate without any spill-resistant barrier; plate "(B)" is a glass plate bearing a spill-resistant barrier that is not visible (i.e., it is invisible); and plate "(C)" is a glass plate bearing a spill-resistant border that is visible

[0009] Figure 2 is a schematic illustrating one embodiment of a method comprising transformation steps that may be employed to convert a flat glass sheet into a glass sheet having a spill-resistant border.

[0010] Figure 3 depicts five different surfaces with regions (stippled) that have a lower hydrophobicity and/or lower oleophobicity than the spill-resistant border and spill-resistant borders as unmarked (white) regions. In (A), a surface with a spill resistant border in the form of an edge (at its edge) is depicted. (B) shows a surface with a spill resistant border in the form of a spill-resistant edge along with two diagonal spill resistant barriers. The diagonal barriers may retain liquids at the same height as the spill-resistant edge or optionally may have a lesser ability to retain liquids than the border at the edge (i.e., the barrier lines optionally may retain liquids to lower heights than the border at the edge). (C) shows a surface with a spill resistant border in the form of a spill-resistant edge along with a series of spill resistant barriers in the form of a grid, where the barrier lines optionally may have a lesser ability to retain liquids than the edge. (D) depicts a surface with a spill resistant border in the form of a spill-resistant edge along with a series of partial spill resistant barriers, that optionally may have a lesser ability to retain liquids and which may be used to channel liquids toward a drain (or drains), or a site where one or more drain tube(s) are connected (black oval). The barrier lines in such an embodiment may extend to the drain. (E) shows a surface with a spill resistant border in the form of a spill-resistant edge along with two diagonal spill resistant barriers that terminate at a drain (black oval). The diagonal barriers lines

optionally may have a lesser ability to retain liquids than the edge and can be used to channel or direct liquids to the drain. Where drains are attached to a surface, the surface may be formed inclined or depressed so that the opening of the drain is lower than the edge of the surface so that liquids will be channeled to the drain.

[0011] Figure 4 is a plot of etchant pH and its effect on height of water retained by spill-resistant borders formed with Gelest Inc. silanizing agent SIT 8174 on glass plates.

[0012] Figure 5 shows a comparison of the height of water retained for three sets of glass plates prepared in three different trials using four different treatment methods in each trial.

[0013] Figure 6 shows the average height of water retained for each different treatment method employed in Figure 5

[0014] Figure 7 shows the height of water retained by glass plates prepared by four different treatment methods before and after repeated abrasion with a glass jar.

Detailed Description:

[0015] Embodiments disclosed herein provide spill-resistant borders that may be formed on a variety of surfaces and methods of their preparation. An example of a spill-resistant border is depicted in Figure 1, where the spill-resistance property of the surface is contrasted with an untreated, "control" surface.

[0016] Embodiments described herein provide, a spill-resistant border that is a portion of surface forming a perimeter around an area of a surface that has a lower hydrophobicity and/or lower oleophobicity than the border (e.g., the portion of the surface within the perimeter formed by the border is not treated with a composition that modifies the surface to be more hydrophobic and/or oleophobic). In other embodiments, a spill resistant border can be formed on a surface that has a contact angle with water at room temperature that is less than about 10, 15, 20, 30, 40, 50, 60, 70, 80, 90 100, 110, or 120 degrees, and where the border has a contact angle with water at room temperature that is greater than the contact angle of water with the surface on which it is formed by about 7, 8, 9, 10, 20, 30, 40, 50, or 60 degrees measured at room temperature (about 68°-72° F).

[0017] Steps that may be employed to prepare a spill-resistant border (e.g., at the edge of a substantially planar surface) can, in one embodiment, include masking areas that are not intended to be modified to be hydrophobic/oleophobic, activation of the unmasked areas, reaction with a hydrophobic/oleophobic agent, curing, and unmasking

(alternatively, surfaces may be unmasked prior to curing). These steps are outlined in Figure 2. As will be apparent from the description that follows, the steps outlined in that figure are not limiting to the method, and the method may be modified in numerous ways that will be apparent to the skilled artisan. For example, surfaces need not be masked where other means of controlling the either activation of the surface or reaction of the surface with compositions comprising agents that impart hydrophobicity or oleophobicity to a portion of the surface are employed. In addition, surfaces need not be activated where a border can be formed on the surface in the absence of activation. Moreover, curing may not be necessary for all compositions or agents that impart sufficient hydrophobicity or oleophobicity without curing. Thus, in one embodiment, a method of forming a spill-resistant border may include applying a composition to a surface that increases the hydrophobicity or oleophobicity of the portion of the surface that will server as a border, wherein said border forms a perimeter around at least one area that has a lower hydrophobicity or oleophobicity than the border once it is formed.

[0018] The present disclosure provides embodiments of methods for forming a spill-resistant border on a surface comprises applying a composition to the surface that increases the hydrophobicity or oleophobicity of a portion of the surface that will server as a border. Surfaces prepared by such methods are also provided.

[0019] In other embodiments, the present disclosure provides for a surface comprising a hydrophobic or oleophobic spill-resistant border, wherein the border forms a perimeter round at least one area that has a lower hydrophobicity and/or lower oleophobicity than the spill-resistant border.

1.0 Surfaces for Forming Spill-Resistant Borders

[0020] Spill-resistant borders can be formed on a variety of surfaces, provided the material that the surface is made from, or a portion thereof, can be made more hydrophobic and/or more oleophobic. In some embodiments the surface can be made from a material selected from glass, metal, metalloid, ceramic, wood, plastic, resin, rubber, stone, concrete or a combination thereof. In other embodiments the surface may be made from a material selected from the group consisting of glass, ceramic and a combination thereof. In other embodiments, the surfaces may be comprised of metalloids (e.g., B, Si, Sb, Te and Ge).

[0021] Any glass that can be made hydrophobic or oleophobic on a portion of its surface may be employed as a surface upon which to form a spill-resistant border.

Glasses that may be employed as a surface include, without limitation: soda lime glass, borosilicate glass, sodium borosilicate glass, aluminosilicate glass, aluminoborosilicate glass, optical glasses, lead crystal glass, fused silica glass, germania glasses, germanium selenide glasses, and combinations thereof.

[0022] Any metal that can be made more hydrophobic and/or more oleophobic on a portion of its surface may be employed as a surface upon which to form a spill-resistant border. Such metals include without limitation: iron, nickel, chrome, copper, tin, zinc, lead, magnesium, manganese, aluminum, titanium silver, gold, and platinum or combinations thereof, or alloys comprising those metals. In one embodiment the metal is forming the surface comprises steel or stainless steel. In another embodiment the metal used for the surface is chromium, is plated with chromium, or comprises chromium or a chromium containing coating.

[0023] Any ceramic that can be made more hydrophobic and/or more oleophobic on a portion of its surface may be employed as a surface upon which to form a spill-resistant border. Such ceramics include, without limitation: earthenware (typically quartz and feldspar), porcelain (e.g., made from kaolin), bone china, alumina, zirconia, and terracotta. For the purpose of this disclosure a glazing on a ceramic may be considered either as a ceramic or a glass.

[0024] Any wood that can be made more hydrophobic and/or more oleophobic on a portion of its surface may be employed as a surface upon which to form a spill-resistant border. Such woods include without limitation hard and soft woods. In some embodiments, woods may be selected from alder, poplar, oak, maple, cherry, apple, walnut, holly, boxwood, mahogany, ebony teak, luan, and elm. In other embodiments woods may be selected from ash, birch, pine, spruce, fir, cedar, and yew. In still other embodiments the a wood surface may be a composite such as woods products formed from bamboo, chipped woods, or saw dust and the like.

[0025] Any plastic or resin that can be made more hydrophobic and/or more oleophobic on a portion of its surface may be employed as a surface upon which to form a spill-resistant border. Such plastics/resins include, without limitation, polyolefins (such as a polypropylene and polyethylene), a polyvinylchloride plastics, a polyamides, a polyimides, a polyamideimides, a polyesters, aromatic polyesters, polycarbonates, polystyrenes, polysulfides, polysulfones, polyethersulfones, polyphenylenesulfides, a phenolic resins, polyurethanes, epoxy resins, a silicon resins, acrylonitrile butadiene

styrene resins/plastics , methacrylic resins/plastics, acrylate resins , polyacetals, polyphenylene oxides, polymethylpentenes, melamines, alkyd resins, polyesters or unsaturated polyesters, polybutylene terephthlates, combinations thereof, and the like.

[0026] Any rubber that can be made more hydrophobic and/or more oleophobic on a portion of its surface may be employed as a surface upon which to form a spill-resistant barrier. Such rubbers include, without limitation, styrene-butadiene rubber, butyl rubber, nitrile rubber, chloroprene rubber, polyurethane rubber, silicon rubber and the like.

[0027] Any type of stone, concrete, or combination thereof, that can be made more hydrophobic or more oleophobic on a portion of its surface, may be employed as a surface upon which to form a spill-resistant border. In some embodiments, the stone that may be employed as a surface, or a component of a surface, is selected from igneous, sedimentary and metamorphic stone (rock). In one embodiment the stone is selected from granite, marble, limestone, hydroxylapatite, quartz, quartzite, obsidian and combinations thereof. Stone may also be used in the form of a conglomerate with other components such as concrete and/or epoxy to form an aggregate that may be used as a surface upon which a spill-resistant border may be formed (e.g., terrazzo).

2.0 Spill-Resistant Borders

[0028] The spill-resistant borders described herein can be formed by causing a portion of a surface to become more hydrophobic and/or more oleophobic by treatment with composition comprising agents that impart those properties to the surface. The hydrophobic/oleophobic properties of the surface will be affected by both the nature of the surface and the type of agent that is applied to the surface to form the border.

[0029] A spill-resistant border may be placed on a surface so that the border forms a perimeter around one or more areas that have a lower hydrophobicity and/or lower oleophobicity than the border, thereby providing an area within the border that can retain liquids. In other embodiments, a spill resistant border can be formed on a surface that has a contact angle with water at room temperature that is less than about 10, 15, 20, 30, 40, 50, 60, 70, 80, 90 100, 110, or 120 degrees, and where the surface can be modified to form a border that has a contact angle with water at room temperature that is greater than the contact angle of water with the surface on which it is formed by about 7, 8, 9, 10, 20, 30, 40, 50, or 60 degrees measured at room temperature (about 70-72° F).

[0030] In some embodiments a border may be placed at the edge of a surface, in which case it may be referred to as an "edge." In other embodiments a border may be placed near an edge of a surface, such as in the form of a strip parallel or substantially parallel to one or more edges of a surface. In some embodiments a border may be placed on a surface at a position that is not the edge such that the border forms a perimeter around one or more areas that are have a lower hydrophobicity and/or lower oleophobicity than the border

[0031] Where a border is not placed at the edge it may be termed a "barrier." Barriers may divide a surface into several regions that have a lower hydrophobicity and/or lower oleophobicity than the border. Each area having a barrier as a perimeter will separately prevent the spreading of liquid between different areas of the surface. The regions separated by barriers may be in variety of forms. For example, the regions may be in the form of a series of concentric circles or a series of regular quadrilaterals (e.g., squares or rectangles, hexagons, or triangles). In some embodiments a border in the form of an edge, or a border located at or near the edge of the surface, may be employed with borders in the form of barriers. In such an embodiment the surface will not only prevent the spread of liquids between regions separated by barriers, but also prevent or stop liquids from flowing off the surface by blocking passage of the liquid over the border at the edge. Some examples of spill-resistant borders, including those with edges and barriers, and combinations thereof may be seen in Figure 3.

[0032] Spill-resistant borders (including borders in the form of edges and barriers), regardless of the pattern in which they are formed, are substantially 2-dimensional structures. The width of the hydrophobic/oleophobic regions of a surface forming spill-resistant borders can vary depending on the specific application in which the borders are intended to be used. In some embodiments, the borders may be from about 0.2 to about 2 inches in width, or alternatively, about 0.2, 0.25, 0.3, 0.4. 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.25, 1.3 1.4, 1.5, 1.75 or 2.0 inches (about 5 mm to 50 mm) in width. In one embodiment, where the borders are intended for use on food preparation or storage surfaces, (e.g., cutting boards, glass shelving for refrigerators, or countertops) the borders in the range of 0.2 to 2.0 inches. In other embodiments, such as where the spill-resistant borders are intended for use on food preparation or storage surfaces, the borders can be about 0.4 to 1 inch wide, or alternatively, about, 0.4, 0.5, 0.6 0.7 0.75, 0.8, 0.9, or 1.0 inches wide. Border width does not have to be uniform, and where

borders on a surface comprise an edge and barriers, the edge and barriers may be of different widths or even varying widths on the same surface.

[0033] Where a combination of a border, such as a border in the form of an edge, and a barrier are used, the hydrophobicity of the barrier and edge may be controlled such that liquids will be prevented from spreading between different areas of the surface, but the highest resistance to liquid spreading (the highest height of liquid retained) will be at the edge. Thus, in the case of a spill that overflows an area surrounded by a barrier, the spill would flow to an adjacent area, rather than over the edge.

[0034] Spill-resistant borders and barriers may be used to direct liquid toward one or more drains in a surface and can be arranged to channel spilled liquids toward a drain (see e.g., Figure 3 panels D and E). Borders in the forms of edges and/or barriers may be also combined with drains in a surface so as to direct liquids to a drain or collection site/container. Drains may be in the form of an opening, depression or trough (e.g., slot, hole, or groove) in the surface bearing the border. Openings, depressions, or troughs may be connected to tubing or pipes that will permit liquid to be collected or channeled to a desired location (e.g., a collection container or sewer waste line). Barrier lines that form incomplete perimeters around areas of a surface may also be used to channel liquids towards a drain (see Figure 3, Panel D); particularly where the barrier lines form a complete perimeter except at the point where they end at or near a drain (see Figure 3, Panel E). In one embodiment, one or more drains may be placed at the edge of surface so that the border forms a continuous perimeter around an area of the surface up to the point where the drain is located, with the drain completing the perimeter formed by the border.

[0035] For the purpose of this disclosure a border that is not visible is a border that cannot be readily seen with the unaided human on a clean dry surface using transmitted or reflected light in the spectrum visible to the human eye. Borders that are not visible may be prepared by treating a surface with an agent that makes the region forming the border hydrophobic or oleophobic. If the surface needs to be activated for the application of an agent that makes the surface hydrophobic and/or oleophobic, that may be accomplished by chemical etching with agents such as HF for brief periods or polishing of the surface with very fine powders such as cerium oxide powder or diamond powders.

[0036] For the purpose of this disclosure a border that is visible can be seen with the unaided human eye on a clean dry surface using transmitted or reflected light in the spectrum visible to the human eye. A border can be visible but clear, in which case it may, for example, be clear but colored. A border may also be visible due to surface treatments, such as etching or abrading (e.g., sand blasting or grinding).

[0037] A fine visible spill-resistant border, also referred to as a "fine border", is a visible border one having fine features on the order of 30 to 80 microns, or 40 to 70 microns, or 50 to 60 microns, or about 30, about 40, about 50 or about 60 microns. Fine borders can be prepared, for example, by sand blasting with materials in the range of about 200 to about 450 mesh, or 225 to 350 mesh, or 250 to 325 mesh, or materials about 200, 250, 300, 350, 400, or 450 mesh (generally metal oxides or carbide powders).

[0038] A coarse visible spill-resistant border, also referred to as a "coarse border", is one having features on the order of about 150 to about 250 microns, or 175 to about 225 microns, or about 200 microns. Coarse visible borders can be prepared, for example, by sand blasting with materials in the range of about 20 to 60 mesh, or 30 to 50 mesh, or 40 to 60 mesh, or materials about 20, 25, 30, 35, 40, 45, 50, 55, or 60 mesh.

[0039] A medium visible spill-resistant border, also referred to as a "medium border", is a visible border one having features on the order of about 80 to about150 microns, or about 85 to about 140 microns, or about 90 to about 120 microns, or about 80, 90, 100, 110, 120, 130, 140 or 150 microns. Medium borders can be prepared, for example, by sand blasting with a mixture of coarse and fine meshed materials (e.g., approximately equal amounts by weight, or in the range of a mixture from 1:4 to 4:1 of coarse : fine materials by weight). Alternatively, medium borders can be prepared by blasting with materials from about 80 to about 150 mesh, or 90 to 145 mesh, 100 to 140 mesh, or about 80, 90, 100, 110, 120, 130, 140, or 150 mesh.

[0040] Data for fine, medium, and coarse spill-resistant boarders produced by sand blasting glass surfaces appears in Example 17. Fine medium and coarse borders may also be prepared by etching the surface of glass, ceramics or plastics with chemical etching/activation agents.

2.1 Forming Hydrophobic and Oleophobic Borders on Regions of a Surface

[0041] Borders, whether they are visible or not visible, must be more hydrophobic and/or more oleophobic than the regions they surround. Modification of the properties

of a surface, or a portion thereof that serves as a boarder, to impart the desired hydrophobic and/or oleophobic nature can be accomplished by chemical modification. Such modifications can be accomplished by applying to a surface a composition comprising an agent that increases the hydrophobicity and/or oleophobicity of the surface upon which it is applied. The result of such chemical modification is covalent binding of one or more hydrophobic and/or oleophobic functionalities to the portion of the surface (i.e. modification of the surface) where the border is to be located.

[0042] For the purposes of this disclosure a hydrophobic border or surface is one that results in a water droplet forming a surface contact angle exceeding about 45° and less than about 150° at room temperature. Similarly, for the purposes this disclosure a superhydrophobic border or surface is one that results in a water droplet forming a surface contact angle exceeding about 150° but less than the theoretical maximum contact angle of about 180° at room temperature. Some authors further categorize hydrophobic behavior and employ the term "ultrahydrophobic." Since for the purposes of this disclosure, a superhydrophobic surface has contact angles of about 150° to about 180°, superhydrophobic behavior is considered to include ultrahydrophobic behavior. Throughout this disclosure where a surface (e.g., a border region of a surface) is recited as being hydrophobic and no specific contact angles are recited, a superhydrophobic surface may also be employed. For the purpose of this disclosure hydrophobic shall include superhydrophobic unless stated otherwise.

[0043] For the purposes of this disclosure an oleophobic material or surface is one that results in a droplet of light mineral oil forming a surface contact angle exceeding about 25° and less than the theoretical maximum contact angle of about 180° at room temperature.

[0044] A variety of methods to increase the hydrophobicity and/or oleophobicity of a surface can be employed. Such methods including the used of one or more agents, or compositions comprising such agents, that will chemically bind alkyl, fluoroalkyl, or perfluoroalkyl groups to the surface. Such agents include the use of alkyl, fluroalkyl, or perfluoroalkyl silanizing agents. Other agents that can be used to form hydrophobic or oleophobic borders will depend on the functionalities available for forming chemical (covalent) linkages to the surfaces. For example where surfaces have, or can be modified to have hydroxyl or amino groups, acid anhydrides and acid chlorides of alkyl, fluoroalkyl, or perfluoroalkyl compounds (e.g., the acid chlorides: Cl-C(O)(CH2)4-

18CH3; Cl-C(O)(CH2)4-10(CF2)2-14CF3 ; Cl-C(O)(CF2)4-18CF3 or the anhydrides of those acids) can be employed.

2.2 The Use of Silanizing Agents to Apply a Spill-Sesistant Border to a Surface

[0045] A variety of silanizing agents can be employed to convert a portion of the surface into a spill resistant border. Silanizing agents have both leaving groups and terminal functionalities. Terminal functionalities are groups that are not displaced by reaction with silicate containing glasses (e.g., R groups of compounds of the formula (I)). Leaving groups are those groups that are displaced from silanizing agents upon reaction with silicate containing glasses to form bonds with the glass surface. Such silanizing agents include, but are not limited to, compounds of the formula (I):

R4-nSi-Xn

(I)

where n is an integer from 1-3;

each R is an independently selected from

(i) alkyl or cycloalkyl group optionally substituted one or more fluorine atoms,

(ii) C1 to 20 alkyl optionally substituted with one or more independently selected substituents selected from fluorine atoms and C6-14 aryl groups, which aryl groups are optionally substituted with one or more independently selected halo, C1 to 10 alkyl, C1 to 10 haloalkyl, C1 to 10 alkoxy, or C1 to 10 haloalkoxy substituents,

(iii) C6 to 20 alkyl ether optionally substituted with one or more substituents independently selected from fluorine and C6-14 aryl groups, which aryl groups are optionally substituted with one or more independently selected halo, C1 to 10 alkyl, C1 to 10 haloalkyl, C1 to 10 alkoxy, or C1 to 10 haloalkoxy substituents,

(iv) C6-14 aryl, optionally substituted with one or more substituents independently selected from halo or alkoxy, and haloalkoxy substituents;

(v) C6 to 20 alkenyl or C6 to 20 alkynyl, optionally substituted with one or more substituents independently selected from halo, alkoxy, or haloalkoxy;

each X is independently selected from -H, -Cl, -I, -Br, -OH, -OR2, -NHR3, or -N(R3)2;

each R2 is an independently selected C1 to 4 alkyl or haloaklyl group; and

each R3 is independently an independently selected H, C1 to 4 alkyl or haloalkyl group.

[0046] In one embodiment, R is an alkyl or fluoroalkyl group having from 6 to 20 carbon atoms.

[0047] In another embodiment, R is an alkyl or fluoroalkyl group having from 8 to 20 carbon atoms.

[0048] In another embodiment, R is an alkyl or fluoroalkyl group having from 10 to 20 carbon atoms.

[0049] In another embodiment, R is an alkyl or fluoroalkyl group having from 6 to 20 carbon atoms and n is 3

[0050] In another embodiment, R is an alkyl or fluoroalkyl group having from 8 to 20 carbon atoms and n is 3

[0051] In another embodiment, R is an alkyl or fluoroalkyl group having from 10 to 20 carbon atoms and n is 3.

[0052] In another embodiment, R has the form –Z-((CF2)q(CF3))r, wherein Z is a C1-12 divalent radical derived from an alkane, alkene or alkyne, and q is an integer from 1 to 12, and r is an integer from 1-4.

[0053] In any of the previously mentioned embodiments of compounds of formula (I) the value of n may be varied such 1, 2 or 3 terminal functionalities are present in compounds of formula (I). In one embodiment, n is 3. In another embodiment, n is2, and in still another embodiment n is 1.

[0054] In any of the previously mentioned embodiments of compounds of formula (I), the all halogen atoms present in any one or more R groups are fluorine atoms in some embodiments.

[0055] In any of the previously mentioned embodiments of compounds of formula (I), X is independently selected from H, Cl, -OR2, -NHR3, -N(R3)2, or combinations thereof in some embodiments. In another, embodiment, X may be selected from Cl, -OR2, -NHR3, -N(R3)2, or combinations thereof. In still another embodiment, X may be selected from, Cl, -NHR3, -N(R3)2 or combinations thereof.

[0056] Any border described herein may be formed from one, two, three, four or more compounds of formula (I) employed alone or in combination to convert a surface into a hydrophobic or oleophobic surface.

[0057] Alkyl as used herein denotes a linear or branched alkyl radical. Alkyl groups may be independently selected from C1 to C20 alkyl, C2 to C20 alkyl, C4 to C20 alkyl, C6 to C18 alkyl, C6 to C16 alkyl, or C6 to C20 alkyl. Unless otherwise indicated, alkyl does not include cycloalkyl. Cycloalkyl groups may be independently selected from: C1 to C20 alkyl comprising one or two C4 to C8 cycloalkyl functionalities; C2 to C20

alkyl comprising one or two C4 to C8 cycloalkyl functionalities; C6 to 20 alkyl comprising one or two C4 to C8 cycloalkyl functionalities; C6 to C18 alkyl comprising one or two C4 to C8 cycloalkyl functionalities; C6 to C16 alkyl comprising one or two C4 to C8 cycloalkyl functionalities. One or more hydrogen atoms of the alkyl groups found in compounds of formula (I) may be replaced by fluorine atoms.

[0058] Fluoroalkyl as used herein denotes an alkyl group in which one or more fluorine atoms have been substituted for hydrogen atoms.

[0059] Perfluoroalkyl as used herein denotes an alkyl group in which fluorine atoms have been substituted for each hydrogen atom present in the alkyl group.

[0060] In another embodiment, specific compounds that can be employed to prepare spill-resistant borders include compounds that are commercially available (e.g., from Gelest, Inc., Morrisville, PA) including, but not limited to, those compounds found in the tables of the Examples that accompany this disclosure such as the compounds in Tables 1 to 9. Some compounds that may be employed to prepare spill-resistant borders include those that follow, which are identified by their chemical name followed by the commercial supplier reference number (e.g., their Gelest reference in parentheses): tridecafluoro-1,1,2,2-tetrahydrooctyl)silane (SIT8173.0); (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane (SIT8174.0); (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane (SIT8175.0); (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane (SIT8176.0); (heptadecafluoro-1,1,2,2-tetrahydrodecyl)dimethyl(dimethylamino)silane (SIH5840.5); (heptadecafluoro-1,1,2,2-tetrahydrodecyl)tris(dimethylamino)silane (SIH5841.7); n-octadecyltrimethoxysilane (SIO6645.0); n-octyltriethoxysilane (SIO6715.0); and nonafluorohexyldimethyl(dimethylamino)silane (SIN6597.4).

[0061] Two attributes of silanizing agents that may be considered when forming a spill-resistant border are the leaving group (e.g., X groups of compounds of the formula (I)) and the terminal functionality (e.g., R groups of compounds of the formula (I)). Silanizing agent leaving groups determine the reactivity of the agent with a substrate. Where, the substrate is a silicate glass or stone, the leaving group can be displaced to form the Si-O-Si bonds (see Schemes I-VII). The terminal functionality determines the level of hydrophobicity that results from application of the silane to the surface.

[0062] In addition to assessing the hydrophobicity of a border formed on a surface as a means of assessing its effectiveness for the preparation of spill-resistant borders, a

measurement of the height of water retained by the border can be employed. In some embodiments the height of water retained by the borders described herein will be at least 2, 3 4 or 5 mm above the surface on which the border is formed (measured at room temperature). Within such embodiments, the height of water retained by the borders described herein will be from 2-3.5, or from 2.5 to 4, or from 3 to 5, or from 3.25 to 5.25 mm above the surface on which the border is formed (measured at room temperature).

[0063] In order to test the effectiveness of leaving group and terminal functionalities of silanizing agents, nine different agents are used to prepare spill-resistant borders on glass plates (see Example 14). The contact angles of water with surfaces treated with the agents are summarized in Table 14. Data for silanizing agents SIT8173, SIT8174, SIT8175, and SIT8176, which have different leaving groups but the same terminal functional groups, should depend only depend on the effectiveness of the leaving group. Among those four silanizing agents, the leaving group effectiveness is ranked in the decreasing order as chloro > methoxy > hydro (H) > ethoxy (measured as trichloro > trimethoxy > trihydro > triethoxy). This ranking of the leaving groups is consistent with their bond dissociation energy.

Bond Dissociation Energies for Various Leaving Groupsa

Bond	Dissociation Energy Kcal/mole
Me3Si-NMe2 (dimethyamine)	98
Me3Si-N(SiMe3)2 tris(dimethylamino)	109
Me3Si-Cl (chloro)	117
Me3Si-OMe (methoxy)	123
Me3Si-OEt (ethoxy)	122

aData from Gelest, Inc.

[0064] Silanes SIH5840.5 and SIH5841.7 contain the (heptadecafluoro-1,1,2,2-tetrahydrodecyl) functional group, however, water-height data suggests the tris(dimethylamino) leaving group, has a lower bond dissociation energy than the dimethylamino leaving group. This is also consistent with the bond dissociation energies given above.

2.3 Effect of Terminal Groups on Liquid Retention by Spill-Resistant Borders

[0065] The choice of hydrophobic or oleophobic agents, particularly the terminal groups of silane reagents, influences a border's ability to retain various liquids. Alkyl functionalities, and particularly alky terminal functional functionalities of silanizing agents, while suitable for use in the preparation of borders, generally are not as effective as their fluorinated or perfluorinated counterparts at retaining aqueous liquids based on the height of water the borders can retain. Compare the data in Examples 5-7 with Examples 8 and 9.

[0066] In addition to the ability to retain aqueous based solutions, suspension, and emulsions, embodiments of the borders disclosed herein tend to have oleophobic behavior, permitting them to retain oils. This is particularly true where the borders have been prepared with silanizing agents having fluorinated or perfluorinated alkyl groups (e.g., where the terminal functionality of a silane of the formula R4-nSi-Xn is a fluorinated alkyl or perfluoroalkyl). See, for example, the contact angle data in Example 14 and Table 14, for mineral oil and borders comprising fluorinated alkenes. The height of mineral oil that can be retained by boarders comprising fluorinated alkyl groups is exemplified in Example 15, in which data for two fluoroalkyl silanizing agent treatments and mineral oil is presented.

2.4 Use of Compounds Other Than Silanizing Agents to Form Spill-Resistant Borders

[0067] Other agents that can be used to form hydrophobic or oleophobic borders will depend on the functionalities available for forming chemical (covalent) linkages between hydrophobic/oleophobic component and the surfaces. For example where surfaces have, or can be modified to have, hydroxyl or amino groups then acid anhydrides and acid chlorides of alkyl, fluoroalkyl, and perfluoroalkyl compounds may be employed (e.g., the acid chlorides: Cl-C(O)(CH2)4-18CH3; Cl-C(O)(CH2)4-10(CF2)2-14CF3 ; Cl-C(O)(CF2)4-18CF3 or the anhydrides of those acids) can be employed.

3.0 Surface Activation

[0068] Surfaces may benefit from, or even require, activation to effectively react with agents that will increase the hydrophobicity and/or oleophobicity of the surface. Where surfaces do not comprise a suitable type or suitable number of functionalities for reaction with compositions comprising agents that will increase the hydrophobicity

and/or oleophobicity of the surfaces, they may be activated to change the surface properties

[0069] Where a surface does not contain a suitable type of functional group, or sufficient numbers of those functional groups, to permit effective increases in hydrophobicity an/or oleophobicity, the surface can be reacted with reagents that will modify the surface so as to introduce a sufficient numbers of suitable functionalities. Alternatively, where desired functional groups on a surface are blocked or otherwise unavailable, the surface may be activated by various physical or chemical treatments.

3.1 Activation of Glass and Ceramic Surfaces

[0070] In one embodiment, where a surface is a silicate containing glass or ceramic having less than a desirable number of functional groups for reaction with silanizing agents (*e.g.*, alkylsilyl chlorides or perfluoroalkylsilyl chlorides, or more generally compounds of formula (I), that can covalently bind hydrophobic and/or oleophobic functionalities to the surface), the surface can be activated by chemical or physical means. Activation of SiO_2 containing glasses (silicate glasses or silicate containing glasses) is considered to require exposure of SiO_2 (*e.g.*, Si-OH groups) on the glass surface. Some glass compositions that contain SiO_2, along with glasses that do not, are recited in the table that follows. A skilled artisan will appreciate that ceramics and glasses that do not comprise SiO_2 may be activated for reaction with agents that result in converting the portion of a surface that is to serve as a border into a hydrophobic or oleophobic surface using the methods described for silicate glasses or similar methods.

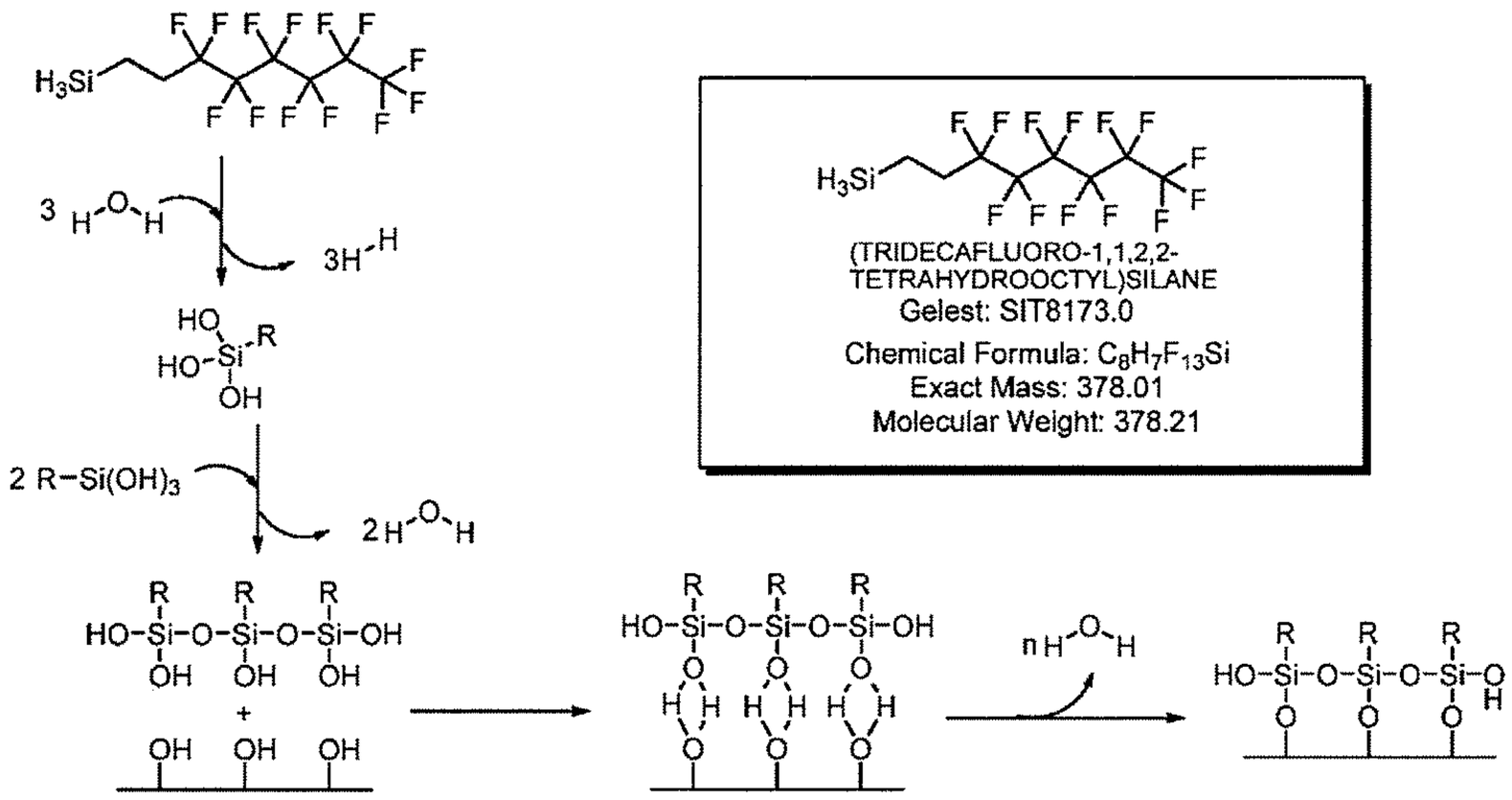
Chemical Composition and Physical Properties of Some Glasses

Properties	Soda-lime glass (for containers)	Borosilicate (low expansion, similar to Pyrex, Duran)	Glass Wool (for thermal insulation)	Special optical glass (similar to Lead crystal)	Fused silica	Germania glass	Germanium selenide glass
Chemical composition, wt%	74 SiO_2, 13 Na_2O, 10.5 CaO, 1.3 Al_2O_3, 0.3 K_2O, 0.2 SO_3, 0.2 MgO, 0.01 TiO_2, 0.04 Fe_2O_3	81 SiO_2, 12.5 B_2O_3, 4 Na_2O, 2.2 Al_2O_3, 0.02 CaO, 0.06 K_2O	63 SiO_2, 16 Na_2O, 8 CaO, 3.3 B_2O_3, 5 Al_2O_3, 3.5 MgO, 0.8 K_2O, 0.3 Fe_2O_3, 0.2 SO_3	41.2 SiO_2, 34.1 PbO, 12.4 BaO, 6.3 ZnO, 3.0 K_2O, 2.5 CaO, 0.35 Sb_2O_3, 0.2 As_2O_3	SiO_2	GeO_2	$GeSe_2$
Viscosity $\log(\eta, Pa{\cdot}s) = A + B / (T \text{ in } °C - T_o)$	550–1450°C: A = -2.309 B = 3922 T_o = 291	550–1450°C: A = -2.834 B = 6668 T_o = 108	550–1400°C: A = -2.323 B = 3232 T_o = 318	500–690°C: A = -35.59 B = 60930 T_o = −741	1140–2320°C: A = -7.766 B = 27913 T_o = −271.7	515–1540°C: A = -11.044 B = 30979 T_o = −837	

Glass transition temperature, T_g, °C	573	536	551	~540	1140	526 ± 27[27][28][29]	395 [30]
Coefficient of thermal expansion, ppm/K, ~100–300°C	9	3.5	10	7	0.55	7.3	
Density at 20°C, [g/cm^3], x1000 to get [kg/m^3]	2.52	2.235	2.550	3.86	2.203	3.65 [31]	4.16 [30]
Refractive index n_D] at 20°C	1.518	1.473	1.531	1.650	1.459	1.608	1.7
Dispersion at 20°C, $10^4\times(n_F - n_C)$	86.7	72.3	89.5	169	67.8	146	
Young's modulus at 20°C, GPa	72	65	75	67	72	43.3 [33]	
Shear modulus at 20°C, GPa	29.8	28.2		26.8	31.3		
Liquidus temperature, °C	1040	1070[34]			1715	1115	
Heat capacity at 20°C, J/(mol·K)	49	50	50	51	44	52	
Surface tension, at ~1300°C, mJ/m^2	315	370	290				

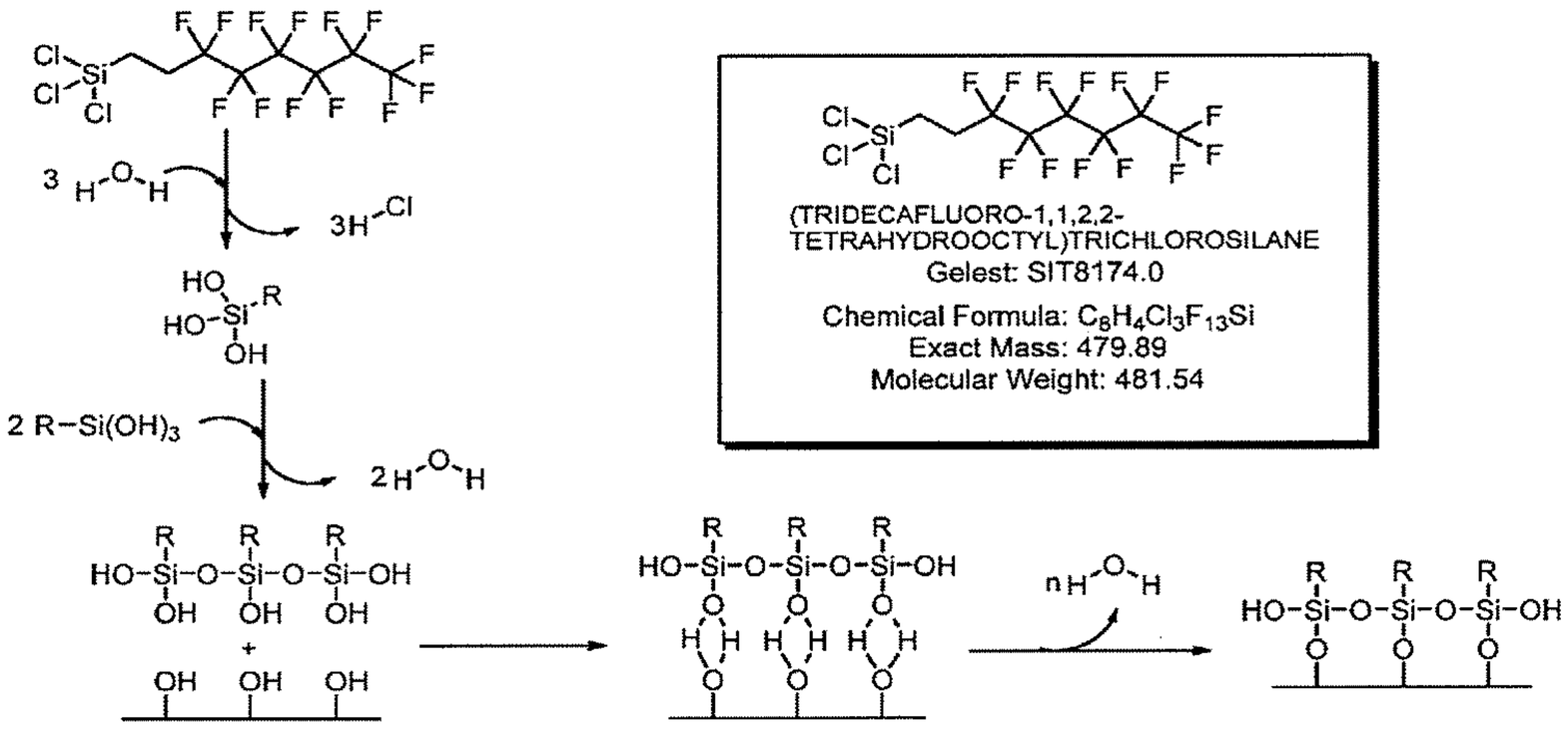
[0071] Some of the potential interactions of silicate containing substrates (*e.g.*, many glasses) with compounds of formula (I) having hydrogen, halogens (illustrated by chlorine), -O-alkyl, or –N(alkyl)$_2$ substituents as leaving groups are illustrated in Schemes I-VII.

Scheme I



Reaction Mechanism: Hydrolytic deposition of silane. The reaction of water with the corresponding silane results in the loss of three equivalents H_2 gas producing a triol-silane, followed by polymerization and reactivity with the substate producing hydrogen bonding that results in net silica-oxygen bond formation.

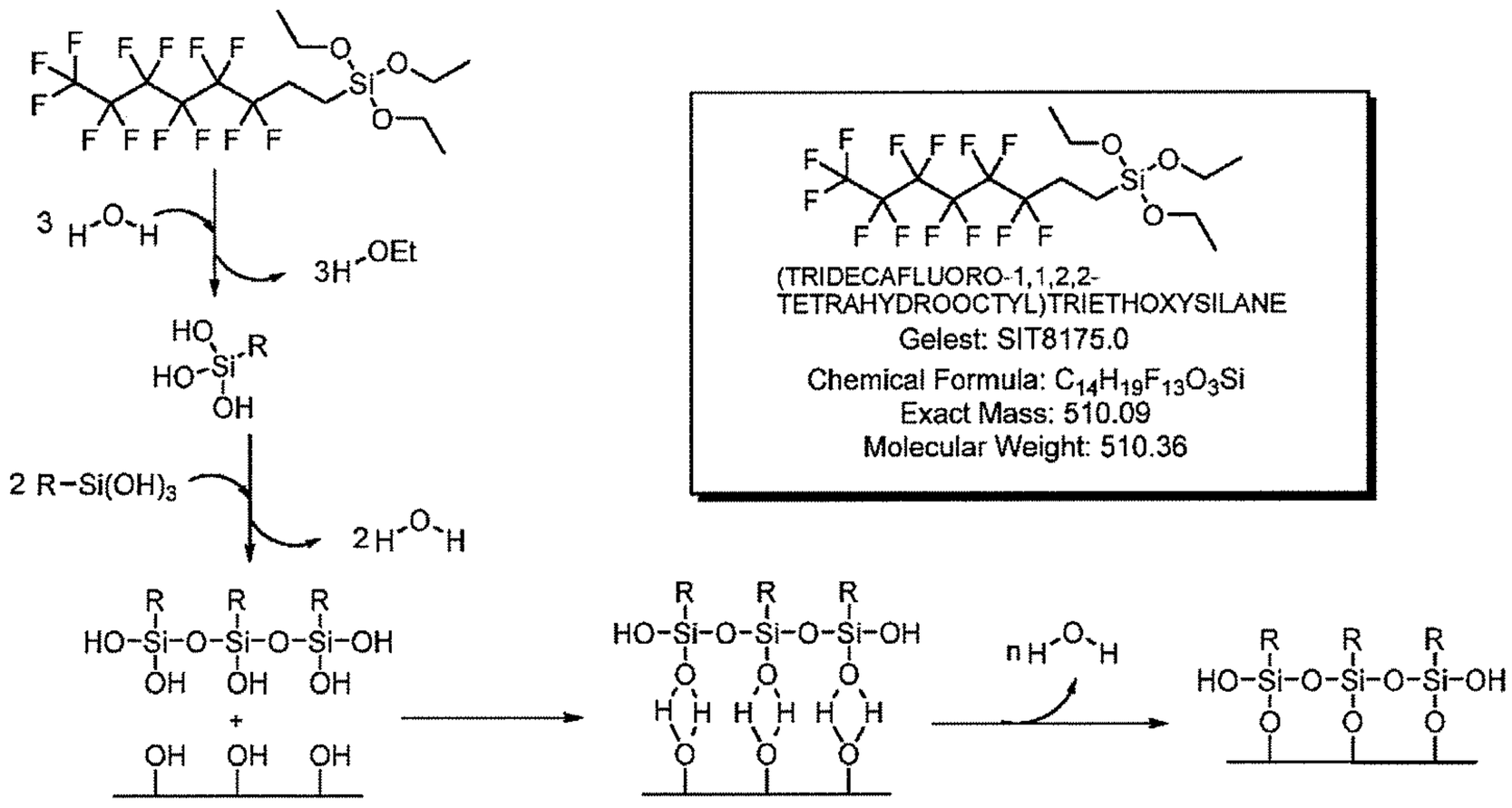
Scheme II



(TRIDECAFLUORO-1,1,2,2-TETRAHYDROOCTYL)TRICHLOROSILANE
Gelest: SIT8174.0
Chemical Formula: $C_8H_4Cl_3F_{13}Si$
Exact Mass: 479.89
Molecular Weight: 481.54

Reaction Mechanism: Hydrolytic deposition of silane. The reaction of water with the corresponding trichloro-silane results in the loss of three equivalents of hydrogen chloride producing a triol-silane, followed by polymerization and reactivity with the substate producing hydrogen bonding that results in net silica-oxygen bond formation.

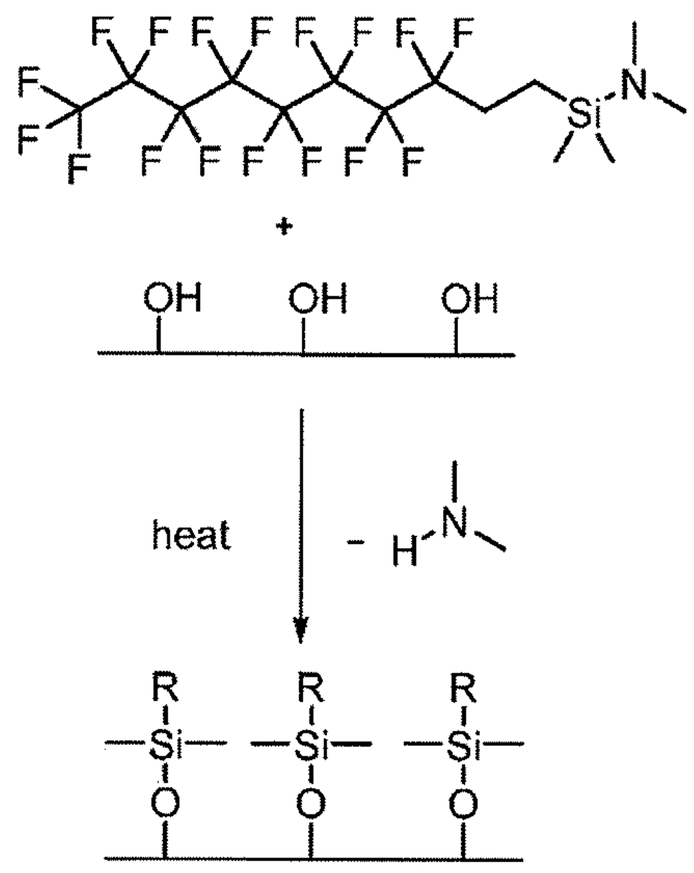
Scheme III

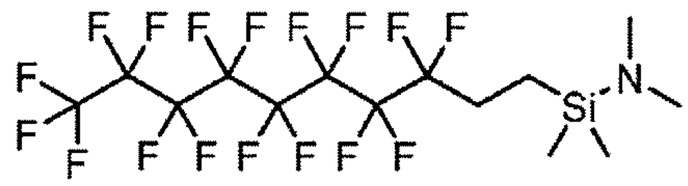


(TRIDECAFLUORO-1,1,2,2-TETRAHYDROOCTYL)TRIETHOXYSILANE
Gelest: SIT8175.0
Chemical Formula: $C_{14}H_{19}F_{13}O_3Si$
Exact Mass: 510.09
Molecular Weight: 510.36

Reaction Mechanism: Hydrolytic deposition of silane. The reaction of water with the corresponding triethoxy-silane results in the loss of three equivalents of ethanol producing a triol-silane, followed by polymerization and reactivity with the substate producing hydrogen bonding that results in net silica-oxygen bond formation.

Scheme IV





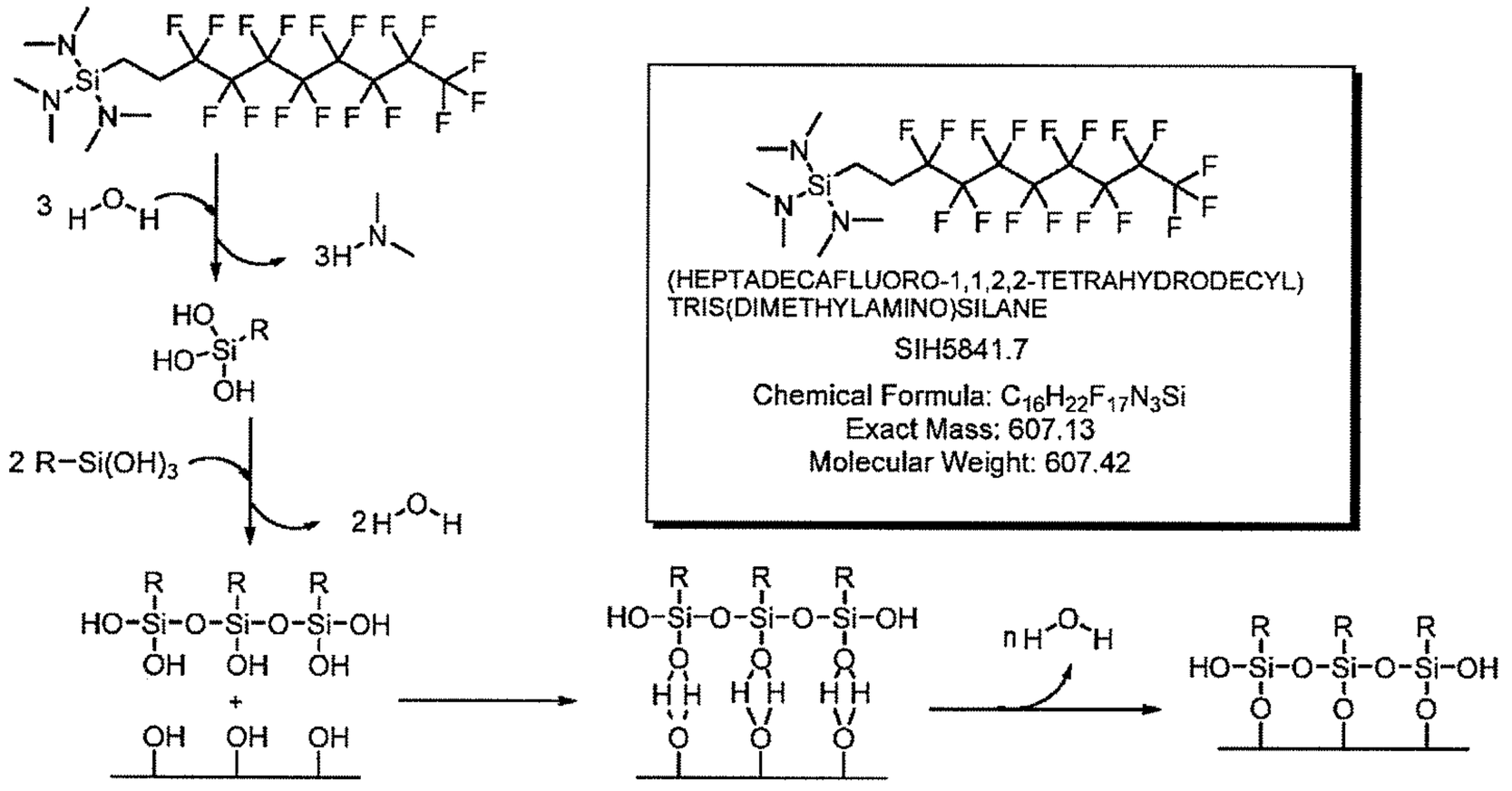
(HEPTADECAFLUORO-1,1,2,2-TETRAHYDRODECYL) DIMETHYL(DIMETHYLAMINO)SILANE

Gelest: SIH5840.5

Chemical Formula: $C_{14}H_{16}F_{17}NSi$
Exact Mass: 549.08
Molecular Weight: 549.34

Reaction Mechanism: Anhydrous Deposition of Silane. Higher temperatures and extended reaction times must occur for the reaction to occur at high yield. The reaction of alcohol substrate with the corresponding amino-silane results in the loss of dimethylamine and silica-oxygen bonding.

Scheme V



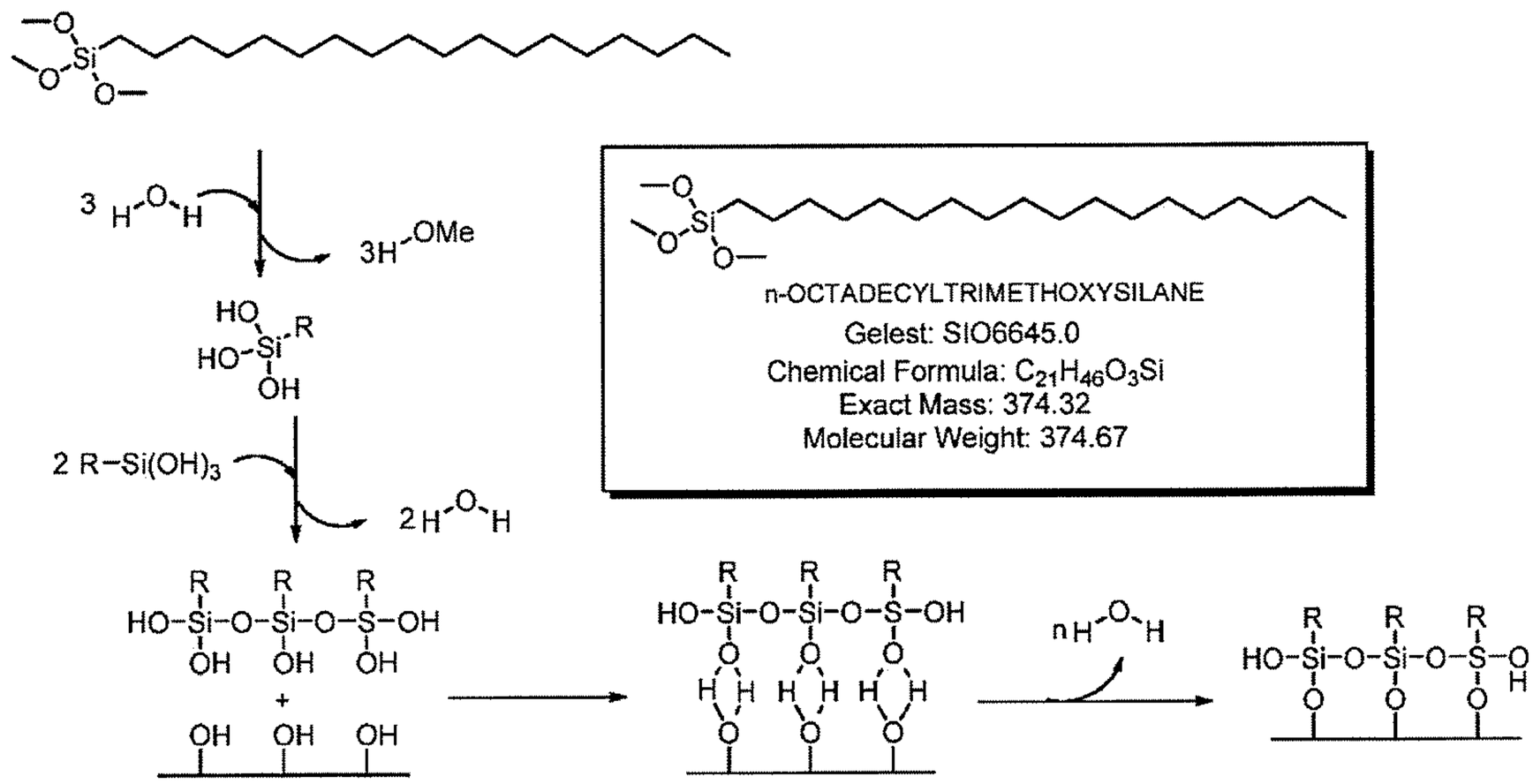
(HEPTADECAFLUORO-1,1,2,2-TETRAHYDRODECYL) TRIS(DIMETHYLAMINO)SILANE

SIH5841.7

Chemical Formula: $C_{16}H_{22}F_{17}N_3Si$
Exact Mass: 607.13
Molecular Weight: 607.42

Reaction Mechanism: Hydrolytic deposition of silane. The reaction of water with the corresponding triamino-silane results in the loss of three equivalents of dimethylamine producing a triol-silane, followed by polymerization and reactivity with the substrate producing hydrogen bonding that result in net silica-oxygen bond formation producing hydrophobicity.

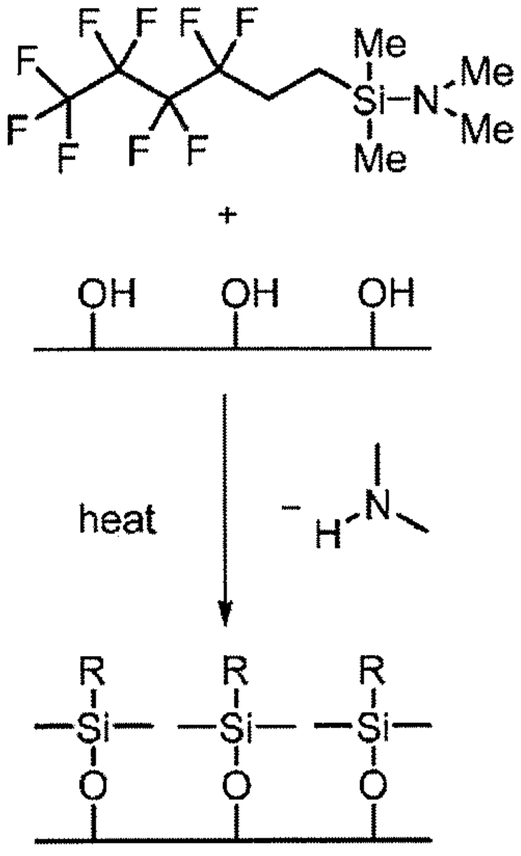
Scheme VI



n-OCTADECYLTRIMETHOXYSILANE
Gelest: SIO6645.0
Chemical Formula: $C_{21}H_{46}O_3Si$
Exact Mass: 374.32
Molecular Weight: 374.67

Reaction Mechanism: Hydrolytic deposition of silane. The reaction of water with the corresponding trimethoxy-silane results in the loss of three equivalents of methanol producing a triol-silane, followed by polymerization and reactivity with the substate producing hydrogen bonding that results in net silica-oxygen bond formation.

Scheme VII



NONAFLUOROHEXYLDIMETHYL (DIMETHYLAMINO)SILANE
Gelest: SIN6597.4
Chemical Formula: $C_{10}H_{16}F_9NSi$
Exact Mass: 349.09
Molecular Weight: 349.31

Reaction Mechanism: Anhydrous Deposition of Silane. Higher temperatures and extended reaction times must occur for the reaction to occur at high yield. The reaction of alcohol substrate with the corresponding amino-silane results in the loss of dimethylamine and silica-oxygen bonding.

[0072] Chemical means that can be used to activate and/or etch a surface and particularly glass or ceramic surfaces, include without limitation, reaction with: acids (*e.g.*, hydrofluoric acid); base (*e.g.*, 1 to 10 N NaOH or KOH with or without added

sodium or potassium silicate); sodium or potassium silicate; or fluorine containing salts (*e.g.*, a composition comprising ammonium fluoride). A variety of commercial etching agents that can be used to activate glass and/or ceramic surfaces are also available, including, but not limited to, "New Improved Armour Etch" (Armour Products, Hawthorn, NJ), with GALLERY GLASS® etching medium (Plaid Enterprises, Inc., Norcross, GA), Professional 30second Glass Etching Cream (Martronic Corp, Salkum, WA), ETCHALL® Etching Cream (B & B Products, Inc., Peoria, AZ), and VTX catalyst (Advanced Oxidation Technology, Inc.) in the presence of hydrogen peroxide.

[0073] The pH of activating agents/etchants used to treat glass/ceramic surfaces can vary widely. The activating agents/etchants listed in Example 5 and Table 5 varied in their pH from 1 to 14. As noted in Examples 1-5, and Tables 1-5, many of the compositions employed for glass etching are acidic with a pH of ~ 3, one is basic with a pH of 9, and sodium silicate and sodium hydroxide solutions are significantly more basic. The height of water retained on glass plates bearing spill-resistant borders formed with Gelest silane SIT8174 is plotted as a function of pH of the activating agent/etchant employed in Figure 4., which indicates that the height of water retained on the plates is basically independent of pH.

[0074] In one embodiment activation of glass by exposure of SiO_2, (Si-OH groups),l which can react with silanizing agents and the like, is carried out by chemical treatment with 5% HF, 1 or 10 N NaOH, sodium silicate, or VTX in the presence of peroxide.

[0075] In one embodiment, activation and/or etching of glass or ceramic is conducted with HF. In another embodiment, activation of glass and or ceramic surfaces is conducted by treatment of the surface with commercial etching compositions comprising a fluoride salt.

[0076] Some of the reactions that SiO_2 containing glasses undergo with HF are listed below.

SiO_2 (S) + 4 HF(aqueous (aq)) → SiF_4 (g) + 2 H_2O (l) (Equation (1a))

SiO_2 (S) + 6 HF(aq) → H_2SiF_6 (aq) + 2 H_2O (l) (Equation (1b))

The SiO_2 in the glass can be dissolved by both reactions (1a) and (1b).

[0077] In another embodiment, activation and/or etching of SiO2 containing glasses is conducted with ammonium bifluoride, such as in some acidic etching creams. Some of SiO2 containing glass undergoes with ammonium bifluoride, potassium fluoride, and sodium fluoride, are listed below.

$SiO_2 + 4\ [NH_4][HF_2] \rightarrow SiF_4 + 4\ [NH_4]F + 2\ H_2O$ (Equation (2a))

$SiO_2 + 4\ [K][HF_2] \rightarrow SiF_4 + 4\ [K]F + 2\ H_2O$ (Equation (2b))

$SiO_2 + 4\ [Na][HF_2] \rightarrow SiF_4 + 4\ [Na]F + 2\ H_2O$ (Equation (2c))

[0078] In yet other embodiments, activation and/or etching of SiO_2 containing glasses is conducted with sodium hydroxide or sodium silicate, which also attack SiO_2 and possible reactions with the glass include:

(X) SiO_2 glass + $2NaOH \rightarrow Na_2SiO_3 + H_2O$ + Etched glass (Equation (3))

(X) SiO_2 (glass) + Na_2SiO_3 (water glass) $\rightarrow$ Na_2SiO_3 (water glass with higher SiO_2 content) (Equation (4))

where X in Equations (3) and (4) represents a non-SiO_2 part of the glass.

[0079] In general, the aqueous etchants such as HF, NaOH, Na_2SiO_3, and VTX produced clear borders that are not visible. Etching creams that contained ammonium bifluoride with large quantities of inactive ingredients generally produce translucent or visible borders. Only one of the etching creams with a pH of 9 (Gallery Glass Window Etch) produces a clear border. That etching cream is liquid with minimum amounts of inactive ingredients. Without wishing to be bound by theory, it appears that translucent or visible borders produced by etching creams are caused by the presence of inert ingredients masking the surface which causes the etching reaction to take a longer time and also makes it irregular and translucent. The absence of inactive ingredients in pure aqueous solution causes them to produce a more uniform etching, which leaves the etched surface transparent or clear Attempts to employ inactive materials, such as 512 polymer particles, with 5% HF to produce a patterned border due to masking of the glass by the polymer particles is, however, ineffective as the 512 powder does not produce any significant masking effect.

[0080] Glasses and ceramics may also be abraded to improve their reaction with agents such as the silanizing agents of formula (I). Mechanical abrasion may be conducted using a variety of techniques known in the art, including but not limited to abrading or blasting (sand blasting) with hard particles such as SiC, SiO_2, or Al_2O_3. The particle sizes can be coarse (*e.g.*, 30-50 mesh) to cause a coarse appearance, or fine (*e.g.* 300 mesh) to obtain a fine appearance, or medium (*e.g.*, a blend of 30-50 and 300-400 mesh) to obtain a surfaces with an appearance that is intermediate between fine and coarse. Abrasion may also be conducted using immobilized particles of hard materials

in the form of sheets (*e.g.*, sand paper or emery cloth) or aggregated hard particles in the form of grinding equipment (*e.g.*, grinding stones an the like).

[0081] Without wishing to be bound by any theory, abrading processes are thought to activate SiO_2 containing glasses and ceramics by removing relatively more of softer non-SiO_2 components than the hard SiO_2 components of glass and ceramic compositions. Thus, SiO_2 sites (*e.g.*, existing as groups comprising Si-OH functionalities), which can react with silanizing agents, are preferentially exposed. Because of significant roughness, a boarder produced by abrasion is generally translucent or visible.

[0082] In contrast to abrasion with moderately large particles, where the particles of abrading agent are very fine (*e.g.*, 1,200 grit or 15 microns to 200,000 grit 0.125 microns) they may serve as a polishing agent, and still produce activation of a glass or ceramic surface. Thus, in one embodiment, polishing agents such as cerium oxide, tin oxide, iron oxide, silicon dioxide, chromium oxide, aluminum oxide, or diamond powders, having a size from about 1,200 mesh to about 200,000 mesh, or more typically from 50,000 to 200,000 mesh can be used to polish and activate ceramic and glass surfaces for the preparation of spill-resistant borders that are not visible. In some embodiments, the polishing powders can have a mesh (grit) size of about, 1,000, 2,000, 3,000, 4,000, 8,000, 12,000, 16,000, 20,000, 40,000, 50,000, 100,000 or 200,000 grit.

[0083] Polishing with fine particles, such as cerium oxide particles, is often conducted in slurry form using a motorized wheel. Data for the effect of cerium oxide polishing and its effect on the height of water retained by spill-resistant borders on glass surfaces is found Example 10.

[0084] In some embodiments, a combination of chemical treatments or a combination of mechanical (physical treatments such as abrasion or polishing) and chemical treatments may be employed to activate surfaces (*e.g.*, glasses and ceramics) on which spill-resistant borders are to be formed. Combining of treatments for surface activation do not necessarily produce the highest water retention on glass or ceramic plates. Treatment of plates with sodium silicate after sandblasting with coarse particles or fine particles resulted in spill-resistant borders having lower water height retention as can be noted from Table 5. This suggests that sodium silicate treatment can inactivate some of the sites to which silanizing agents might otherwise have attached. In addition, the data

in Table 5 indicates that NaOH etching of borders prepared by sandblasting produced even a larger reduction of the water height capacity than sodium silicate treatment.

[0085] While many chemical treatments are suitable for the activation of surfaces and have the ability to markedly increase the ability of spill-resistant borders formed on those surfaces to retain liquids, the use of chemical treatments often entails the use of materials that are toxic, caustic or corrosive, particularly where glass, stone, or ceramics are treated. In contrast, physical treatments, such as abrasion by sand blasting or polishing, tend to utilize or produce fewer noxious, toxic, caustic or corrosive chemicals; hence, the materials used and by-products produced are less likely to have the same degree of environmental impact as caustic etchants.

3.23 Activation of non-Glass and Non-Ceramic Surfaces

[0086] Activation of Metals: Metals and alloys can be activated by many different methods.

1. Blasting the surface with hard particles. The hard particles include oxides (SiO_2, Al_2O_3, ZrO_2, etc.), carbides (SiC, WC, etc.), steel shot, glass shot, etc.
2. Etching of surfaces with chemical reagents. All metals can be etched to reveal the grain boundaries and the grain interiors. By controlling the chemical concentration and exposure time, the grain interiors can be etched to create active sites for binding with silanes. The chemicals used include acids, alkalis, and salts.
3. Anodizing is another process used to activate metal surfaces. In this process, the metal or alloy to be activated is made an anode in an electrolytic bath containing acid. When a current is applied, the anode surface is oxidized with micron to nano size features. The anodizing process is most commonly used for aluminum but can also be applied to other metals and alloys. Titanium is another common material that is anodized.
4. Combined blasting and etching is another method for activating metals. Blasting creates the regions of high and low stresses and etching preferentially etches the high stress areas to create the desired micron/nano size features. The final size is controlled by the particle size and hardness of the blast media used, choice of an etchant, and etching time. Sometimes temperature is used to enhance the etching process.
5. Wood is porous and generally does not require activation, where binding if agents such as silanes will be to groups such as hydroxyl, that are already present in the cellulose. Its porous surface and body can also be impregnate with chemicals such as $SiCl_4$,

$Si(OEt)_4$, or $Si(OMe)_4$, or $Si(OR)_3Cl$ for creating Si-OH sites to which silanes attach to create covalent Si-O-Si bonds.

6. Plastics can also be chemically bonded to silanes. In some cases, plastics may be inert to bonding with agents that will impart a hydrophobic or oleophobic characteristic to a portion of the surface. Surface activation to bond to silanes requires creating active sites in the plastic molecules, which can generally be done by exposure to thermal plasma generated using electrical discharge methods. In certain circumstances, chemical treatments may also be used for plastic activation. In one instance, PVC can be activated by treating its surface with a solvent use as a PVC cleaner such as MEK.

4.0 Control of Spill-Resistant Border Dimensions, Placement and Shape – Masked and non-Masked Border Formation.

[0087] The shape, dimensions and placement of spill-resistant border on surfaces can be controlled by a variety of means that broadly fall into two categories, control of the activation process and control of portion of a surface exposed to compositions comprising agents that will increase the hydrophobicity and/or oleophobicity of the portion of the surface that will form the border (*e.g.*, silanizing agents such as compounds of formula I). Control of the activation process and the local placement of compositions comprising agents can be used alone or in combination.

[0088] Masks can control chemical, physical (*e.g.*, abrasion, sandblasting, polishing) or photochemical activation of surfaces. The choice of masking agents will depend on the treatments that the mask is expected to control. For example, where activation of a surface and/or the application of silanizing agent will not involve mechanical treatments such as abrasion or sand blasting, waxes can be used as a masking agent. Alternatively, where sand blasting is used activate and/or etch a surface, a more durable masking agent, such as a rigid or flexible plastic, resin, or rubber/rubberized material may be more desirable. Masking agents may be attached to the surface through the use of adhesives, which may be applied to the masking agent, the surface, or both. In one embodiment, the mask may formed from a photo sensitive agent such as a photo resist that upon exposure to light can be removed to expose the glass surface (see *e.g.*, U.S. Patent 4,415,405). Where masks are to be subject to chemical treatments in an etching and/or activation process, or chemical treatments involved in the application of

compositions that modify hydrophobic/oleophobic properties of a surface, the mask should be resistant to the reagents employed in those processes.

[0089] More than one type of mask can be used in the process of preparing items with spill-resistant borders. For example, one type of mask may be employed for control of activation/etching and another type of mask to control the application of composition comprising agents that increase the hydrophobic or oleophobic properties of a surface.

[0090] Masks need not be in direct contact with a surface for all types of treatments. For example, where glass is subject to photochemical etching with ultraviolet light or ultraviolet light and heat, the mask need only control the regions where light falls on the surfaces (*i.e.*, the mask is a photomask, see *e.g.*, U.S. Patents 5,840,201 or 6,136,210) Alternatively, a combination of a photoresistive coating as a mask to create pattern, and a chemical etchant can be employed to activate/etch glasses, ceramics, and other materials in specific regions where borders are to be formed.

[0091] As an alternative to the use of masks, it is possible control the location of border formation by limiting the portion of a surface to which activation/etching agents, and/or compositions comprising agents that will increase the hydrophobicity or oleophobicity of a surface will be applied. In one embodiment, activation or etching is carried out with a chemical composition that does not flow significantly from the area to which it is applied under the conditions employed (*e.g.*, the etchant is a cream or paste), thereby permitting activation of portion of a surface that will form a border without the use of a mask. In another embodiment, sandblasting can be conducted using equipment which produces a narrowed stream of particles permitting local abrasion of a surface without a mask (using such techniques the borders may have more diffuse edges). In still another embodiment, compositions comprising agents that will increase the hydrophobicity and/or oleophobicity of a surface may be applied to limited regions (*e.g.*, by the painting, printing, or stamping of silanizing agents on a portion of a surface). In one embodiment, or the use of applicators such as foams or spongy material formed in the shape of the border desired are employed. Thus, it is possible to prepare spill-resistant borders on surfaces omitting steps where masks are used.

5.0 Retention of Liquids by Spill-Resistant Borders

[0092] The spill-resistant borders described herein can prevent a large variety of liquids from moving beyond the borders edge until the height of the liquid exceeds a critical level. Included in the liquids that can be retained by the spill-resistant borders

described herein are water, and aqueous liquids, aqueous suspension, and aqueous emulsions. In addition, alcohols, and aqueous alcohol mixtures (*e.g.* wines and distilled alcohol containing liquids such as vodka) can be retained by the spill-resistant borders described herein. Non-aqueous materials including many oils and lipids can be retained by spill-resistant borders, particularly where the border is comprised of one or more types of fluorinated or perfluorinated alkane, alkene, or aryl groups (an alkyl group where all hydrogen atoms are replaced by fluorine atoms), or formed from one or more highly fluorinated alkanes, alkenes, alkynes or aryl group where greater than about 65%, 75%, 80%, 85% 90%, 95%, or 98% of the hydrogen atoms are replaced by fluorine atoms. In one embodiment, spill-resistant borders formed with agents (e.g., silanizing agents) comprising one or more perfluorinated alkane groups or highly fluorinated alkane groups are useful not only for preventing the spilling of aqueous materials, but also for non-aqueous materials, including alcohols, aqueous alcohol combinations, and many oils and lipids.

[0093] In some embodiments, the height of water retained by the borders described herein is about 2 to about 3.5, or about 2.5 to about 4, or about 3 to about 5, or about 3.5 to about 5.25 millimeters (mm). Alternatively, the height of water retained by spill-resistant borders above the surface on which the border is formed (measured at room temperature) is be about 2.0, 2.25, 2.5, 2.75, 3.0, 3.25, 3.5, 3.75, 4.0, 4.25, 4.5, 4.75, 5.0, 5.25 or 5.5 millimeters. In some embodiments the spill-resistant borders provide a contact angle of: about 45° to about 125°; about 50° to about 110°; about 50° to about 90°; about 90° to about 125°; or about 75° to about 115° with water on a glass surface that has a fine, medium or coarse visible border. In other embodiments the spill-resistant borders provide a contact angle of: about 60° to about 116°; about 65° to about 90°; about 90° to about 116°; or about 70° to about 115° with water on a glass surface that has a border that is not visible.

[0094] Reduced temperatures do not prevent the spill-resistant borders described in this disclosure from retaining liquids. The performance of several, spill-resistant borders formed on glass at surface at temperatures typically employed in food refrigeration is depicted in Example 12. The height of ice cold water (about 0°-4° C or about 32° to 39°F) retained by the spill-resistant borders described herein is generally about 5% less than that observed with room temperature water.

[0095] Non-aqueous liquids that can be retained by the spill-resistant borders described in this disclosure include alcohols, liquid comprising an alcohol, a liquid comprising alcohol and water, oils such as mineral oil, lipids (*e.g.,* triglycerides, fatty acids or their esters). Combinations of aqueous and non-aqueous liquids, even where immiscible, can also be retained by the spill-resistant-borders described herein.

[0096] As depicted in Example 11, the spill-resistant borders described herein can retain alcohol containing liquids, (*e.g.*, a liquid comprising an alcohol, or a liquid comprising alcohol and water). In some embodiments, the height of those liquids retained by the spill-resistant borders described herein is about 1 to about 4.25 mm, or about 1.5 to about 4.2 mm, or about 2.0 to about 4.1, or about 2.5 to about 4.1 mm, above the surface of on which the border is formed. Alternatively, the height of those liquids (*e.g.*, wine or distilled liquors such as vodka) retained by spill-resistant borders above the surface on which the border is formed (measured at room temperature) can be about 0.8, 0.9, 1.0, 1.2, 1.3, `1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.75, 3.0, 3.25, 3.5, 3.75, 4.0, or 4.25 millimeters.

[0097] As can be observed from the data in Example 14, the contact angle of water with a hydrophobic and/or oleophobic surface is generally higher than the contact angle of mineral oil with that surface. The contact angle for water and silane treated surfaces/borders is typically 3 to 6 time higher than for control, untreated sample surfaces. In contrast, the contact angle for mineral oil and silane treated borders is typically 2 to 9 times higher than control, untreated sample surfaces. The data in Examples 14 and 15 indicate that silanizing agents that produce the highest contact angles for water also produce the highest contact angles for mineral oil, indicating that the higher the hydrophobicity of the border formed by the silane treatment, the better its performance will be in retaining water and oils. The data in those examples also indicate that trichlorinated silanizing agents (trichlorosilanes, e.g., compounds of formula (I) where n is 3 and X is Cl) produce the highest contact angles for both water and mineral oil.

[0098] Examples 14 and 15, indicate that the borders formed with fluorinated alkyl silanes SIT8174 and SIT5841.7 each produce mineral oil heights exceeding 1.9 mm, regardless of the treatment used to activate the surface prior to their deposition. This contrasts with the non-fluorinated alkyl silane SIO6715.0, which produces mineral oil heights of about 1 mm. This suggest that the higher contact angles observed for

SIT8174 and SIT5841.7 correlate with higher mineral oil heights and spill-resistance observed for borders formed with those agents. The data further indicate a correlation between the terminal functionalities' fluorine content (*e.g.*, the R groups of a compound of formula (I)) and their ability to serve as oleophobic spill-resistant borders that retain lipid/oils.

[0099] In some embodiments, the height of oils (*e.g.*, light mineral oil) retained by the borders described herein is about 0.8 to about 2.5mm, or about 0.9 to about 2.4mm, or about 1.0 to about 2.4, or about 1.5 to about 2.5 mm, or about 1.9 to 2.4 mm. Alternatively, the height of oils (*e.g.*, mineral oil) retained by spill-resistant borders above the surface on which the border is formed (measured at room temperature) can be about 0.8, 0.9, 1.0, 1.2, 1.3, `1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, or 2.5 millimeters. In some embodiments the spill-resistant borders provide a contact angle of: about 36° to about 91° with; about 40° to about 70°; about 70° to about 90°; about 45° to about 85°; or about 50° to about 80°; with oil (*e.g.*, light mineral oil) on a glass surface that has a fine, medium or coarse visible border. In other embodiments the spill-resistant borders provide a contact angle of: about 27° to about 109° with; about 30° to about 105°; about 40° to about 105°; about 40° to about 75°; about 75 to about 109°; or about 80° to about 100° with oil (*e.g.*, light mineral oil) on a glass surface that has a border that is not visible.

6.0 Effects of Surface Cleaning and Use on the Ability to Retain Liquids

[00100] Spill-resistant borders by their nature are exposed not only to the liquids spilled, but also to agents used to clear the surface after a spill. In addition, surfaces bearing spill-resistant borders are subject to wear from contact between items and the surface. Exposure to a diversity of liquids and wear can be exemplified by the use of spill-resistant borders on shelving for refrigerated enclosures for food storage. Refrigeration unit shelves in both commercial and home settings are subject to both frequent use and cleaning after exposure to a variety of spilled foods and food preparation materials. The spill-resistant borders described herein are durable and retain their ability to prevent the spread of spilled materials even after cleaning with detergent solutions and after significant contact with items that can cause ware on the surface.

[00101] Example 15 demonstrates the ability of spill-resistant borders on glass surfaces to retain a variety of food items after exposure to a variety of food items

followed by cleaning after each exposure. In addition, that example demonstrates the ability of the spill-resistant borders to retain water (cooled) even after repeated cleaning.

[00102] The type of ware/abrasion that would result from the typical use of spill-resistant borders on shelving in home or commercial refrigerated enclosures can be simulated. A test of spill-resistant borders subject to repeated abrasion by a glass jar to simulate ware shows the borders, and particularly coarse visible boarders, can withstand repeated abrasion. See Example 13 and Tables 13A and13B. The high abrasion resistance of these borders is likely the result of covalently bonded net works of Si-O-Si bonds formed in the interaction of the glass surface and silanizing agents. Overall, the spill-proof borders described herein are highly durable for expected use in refrigerators and in other applications.

EXAMPLES

Example 1: A spill-resistant border formed at the edge of glass plates employing hydrofluoric acid activation:

[00103] Glass plates (4-inch by 4-inch squares) are used to demonstrate border formation and to measure the border's water-holding capacity (height of water retained). Borders are a 0.5-inches wide hydrophobic and/or oleophobic regions applied to the outside edge of the glass plates. The center part of the glass that is not to be treated is masked with an adhesive plastic film (*e.g.*, vinyl electrical tape). After masking, glass plates are activated by etching with a 5% solution of HF, typically for 30 seconds. After etching plates are washed thoroughly with water, excess water blown away with a stream of air, and the plates are dried in a 200°F oven for 5 min. After cooling, a solution of the indicated silanizing agent in hexanes (1 % silane by weight) is applied to the border area. After the hexanes have evaporate, plates are cured at 200°F for 15 minutes, the plates are cooled, and the mask is removed. The appearance of the border region remained the same as the original plate after HF etching, silane application, and curing.

[00104] Plates prepared as described above are placed on a level surface, and the water-retention level of each plate is measured by filling the area within the border (the previously masked area) with water. Water is added to center of each plate until border breakage (water overflowing the border) is noted. The volume of water added to the center of a plate is divided by the area within the border of that plate to derive the height of the water retained by the plate. The appearance of the border, the name and molecular formula of the silane used to treat the plate, and the height of the retained water are summarized in Table 1 and plotted in the graph shown in Fig. 1. Although the pH of the etching solution is listed in Table 1 as "1", the value of the pH can be less than 1 depending on a number of factors including the temperature.

Table 1: 5% HF and Five Different Silanes*

Etchant	pH	Border Appearance	Silane	Molecular Formula	Water Height (mm)
5% HF	1	Clear	SIT 8174 (Tridecafluoro-1,1,2,2 Tetrahydrooctyl) Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.69
	1	Clear	SIN 6597.4 Nonafluorohexyldimethyl (dimethylamino)silane	$C_{10}H_{16}F_9NSi$	3.50
	1	Clear	SIH 5840.5 Heptadecafluorotetrahydrodecyidimethyl (dimethylamino)silane	$C_{14}H_{16}F_{17}NSi$	4.30
	1	Clear	SIH 5841.7 Heptadecafluoro-1,1,2,2 Tetrahydrodecyltris (dimethylamino) silane	$C_{16}H_{22}F_{17}N_3Si$	4.65
	1	Clear	SIT 8173 Tridecafluoro-1,1,2,2 Tetrahydrooctylsilane	$C_8H_7F_{13}Si$	3.91

*The silanes employed are procured from Gelest, Inc., whose product numbers are also given as an additional reference.

[00105] The brief etching with 5% HF and treatment with the indicted silanes produce a clear border that is not visible. While each of the silanizing agents listed produce a spill-resistant border, tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (SIT8174), and heptadecafluoro-1,1,2,2-tetrahydrodecyltris(dimethylamino)silane (SIH5841.7) retain water approximately equally well, and heptadecafluorotetrahydrodecylimethyl (dimethylamino)silane (SIH5840.5) retains water a level that is nearly as high.

Example 2 Spill-resistant border formation employing sodium silicate acid activation

[00106] Seven 4 inch x 4-inch glass plates are prepared as in Example 1, except that the plates are etched with an aqueous sodium silicate solution (SiO_2/Na_2O ratio3.22, with 8.9% Na_2O and 28.7% SiO_2 by weight) for 2 minutes and 30 seconds in place of HF etching. The etched borders are treated with one of the seven different silanes listed in Table 2, and the plates are cured at 200°F for 15-30 min. The tape mask is removed from the plates and height of water retained by the silanized borders is measured. Data from the plates is summarized in Table 2. Sodium silicate, like the 5% HF etch employed in Example 1, produces a clear border. Again, tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (SIT8174), and heptadecafluoro-1,1,2,2-

tetrahydrodecyltris(dimethylamino)silane (SIH5841.7) retain greater than 4.5 mm of water.

Table 2: Sodium Silicate Etch and Seven Different Silanes

Etchant	pH	Border Appearance	Silane	Molecular Formula	Water Height (mm)
Sodium Silicate	12.5	Clear	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.50
	12.5	Clear	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	3.96
	12.5	Clear	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.48
	12.5	Clear	Sin 6597.4 Nonafluorohexyldimethyl (dimethylamino) silane	$C_{10}H_{16}F_9NSi$	3.34
	12.5	Clear	SIH 5840.5 Heptadecafluorotetrahydrodecyldimethyl (dimethylamino) silane	$C_{14}H_{16}F_{17}NSi$	3.74
	12.5	Clear	SIH 5841.7 Heptadecafluoro-1,1,2,2,-Tetrahydrodecyltris (dimethylamino) silane	$C_{16}H_{22}F_{17}N_3Si$	4.50
	12.5	Clear	SIT 8173 Tridecafluoro-1,1,2,2-Tetrahydrooctyl silane	$C_8H_7F_{13}Si$	3.65

Example 3 A coarse visible spill-resistant border formed at the edge of glass plates employing sand blasting as a means to activate the glass surface

[00107] Nine 4 inch by 4-inch glass plates with the center masked with electrical tape as in Example 1 are sandblasted using coarse grit sand (43 mesh) to form a coarse visible border. The blasted surface is washed with water, dried, and silanated by applying one of nine different silanizing agents to the etched border of each plate. The silanated plates are cured at 200°F for 15-30 min. After cooling, the mask is removed and the plates are tested for their ability to retain water as described in Example 1. The height of water retained by plates with coarse visible borders are given in Table 3.

[00108] The use of coarse materials to etch and activate the surface of glass plates produces a visible border without the use of chemicals that require special handling and disposal. Sandblasting with coarse material to produce a visible edge also provides a means by which to form spill-resistant borders or barriers on glass with the

ability to retain greater than 4.5 mm of water for a number of silanizing agents. See Table 3.

Table 3: Coarse-Blasted and Nine Different Silanes

Etchant	pH	Border Appearance	Silane	Molecular Formula	Water Height (mm)
Coarse Grit Sandblast	N/A	Nice Visible	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.78
	N/A	Nice Visible	SIT 8175 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trimethoxysilane	$C_{14}H_{19}F_{13}O_3Si$	3.83
	N/A	Nice Visible	SIT 8176 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Triethoxysilane	$C_{11}H_{13}F_{13}O_3Si$	3.77
	N/A	Nice Visible	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	4.09
	N/A	Nice Visible	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.28
	N/A	Nice Visible	SIN 6597.4 Nonafluorohexyldimethyl (dimethylamino) silane	$C_{10}H_{16}F_9NSi$	4.25
	N/A	Nice Visible	SIH 5840.5 Heptadecafluorotetrahydrodecyldimethyl (dimethylamino) silane	$C_{14}H_{16}F_{17}NSi$	4.56
	N/A	Nice Visible	SIH 5841.7 Heptadecafluoro-1,1,2,2,-Tetrahydrodecyltris (dimethylamino) silane	$C_{16}H_{22}F_{17}N_3Si$	4.78
	N/A	Nice Visible	SIT 8173 Tridecafluoro-1,1,2,2-Tetrahydrooctyl silane	$C_8H_7F_{13}Si$	4.66

Example 4: A fine visible spill-resistant border formed at the edge of glass plates employing sand blasting as a means to activate the glass surface

[00109] Eight plates are prepared for silanization as in Example 3 substituting fine grit sand (300 mesh) in place of the coarse grit material used in that example. The borders of the plates are each treated with one of eight different silanes and cured at 200°F for 15-30 min. After cooling, the mask is removed to reveal that fine grit sandblasting provides a fine visible border. The height of water retained on the plates by the silanized borders is measured. The data for water retention is shown Table 4.

[00110] As with coarse sandblasting in Example 3, the use of fine materials to etch and activate the surface of the glass plates produces a visible border. Sandblasting with fine mesh also provides a means by which to form spill-resistant border or barriers on glass with the ability to retain greater than about 4 mm of water for a number of silanes. See table 4.

Table 4: Fine-Blasted and Eight Different Silanes

Etchant	pH	Border Appearance	Silane	Molecular Formula	Water Height (mm)
Fine Grit Sandblast	N/A	Nice Visible	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.86
	N/A	Nice Visible	SIT 8175 (Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trimethoxysilane	$C_{14}H_{19}F_{13}O_3Si$	3.92
	N/A	Nice Visible	SIT 8176 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Triethoxysilane	$C_{11}H_{13}F_{13}O_3Si$	3.90
	N/A	Nice Visible	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	4.01
	N/A	Nice Visible	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.32
	N/A	Nice Visible	SIH 5840.5 Heptadecafluorotetrahydrodecyldimethyl (dimethylamino) silane	$C_{14}H_{16}F_{17}NSi$	3.86
	N/A	Nice Visible	SIH 5841.7 Heptadecafluoro-1,1,2,2,-Tetrahydrodecyltris (dimethylamino) silane	$C_{16}H_{22}F_{17}N_3Si$	4.51
	N/A	Nice Visible	SIT 8173 Tridecafluoro-1,1,2,2-Tetrahydrooctyl silane	$C_8H_7F_{13}Si$	3.85

Example 5 Spill-resistant border formation with tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane after activation of glass surfaces by chemical etching, abrasion, and combined treatments

[00111] A series of 4 inch by 4 inch glass plates are masked as described in Example 1 leaving a 0.5 inch border exposed around their outer margin, washed with water, and dried. The plates are then subject to one of the treatments described below

to activate the border region. After activation the plates are treated with tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (product reference SIT 8174 from Gelest), cured at 200°F for 15 to 30 minutes. After cooling the mask are removed, and the height of water retained by the border applied to those plates is measured. See Table 5 which correlates the height of water retained with the appearance of the border resulting from the treatment listed below:

1. 5% HF etching for 30 seconds produces a clear or invisible border;
2. Treatment with "New Improved Armour Etch" (Armour Products, Hawthorn, NJ), which is an inorganic fluoride, titanium dioxide, and citric acid composition, for 2-5 minutes produces a visible border;
3. Treatment with GALLERY GLASS® etching medium (Plaid Enterprises, Inc., Norcross, GA) for 1-3 minutes produces a clear border that is not visible, very similar to that produced by 5% HF;
4. Treatment with Professional 30second Glass Etching Cream (Martronic Corp, Salkum, WA) for 30 seconds produces a visible border;
5. Treatment with ETCHALL® Etching Cream (B & B Products, Inc., Peoria, AZ) for up to 15 minute produces a visible border;
6. 1 N NaOH etching for 5-7 minutes produces a clear or invisible border;
7. 5% aqueous sodium silicate, for 2-5 minutes also known as water glass, etches glass and produces a clear invisible border;
8. The hydroxyl radical generating system, VTX catalyst (Advanced Oxidation Technology, Inc., Fredericksburg, VA) (amount used) and H_2O_2 (3%??? w/w) when used in combination to activate glass prior to silanization produces a clear or invisible border;
9. Treatment by coarse grit sandblasting (43 mesh sand) produced a highly visible border with a rough appearance;
10. Treatment by coarse grit sandblast followed by sodium silicate etching is conduced by coarse grit sandblasting (43 mesh sand) as in treatment 9, *supra*, to produce a highly visible border with a rough appearance. The border produced by the sandblasting is subsequently etched using 5% aqueous sodium silicate for 2 minutes and 30 seconds;
11. Treatment by fine grit sandblasting (300 grit SiC particles) produced a visible border;

12. Treatment by etching with 5% HF in the presence of 20 % w/v of thermoplastic powder (512 powder, 10-100micron size, XIOM Corp. and NY) for 1-2 minutes produced a clear border;
13. Treatment by fine grit sandblast followed by sodium silicate etching is conduced by fine grit sandblasting as in treatment 11, *supra*, to produce a visible border. The border produced by the sandblasting is subsequently etched using 5% aqueous sodium silicate for 2 minutes and 30 seconds;
14. Treatment by fine grit sandblast followed by aqueous sodium hydroxide (NaOH 5% w/v) etching is conduced by fine grit sandblasting as in treatment 11, *supra*, to produce a visible border. The border produced by the sandblasting is subsequently etched using 5% aqueous sodium hydroxide for 2 minutes and 30 seconds.

[00112] The height of water retained by the various glass plates are plotted as a function of pH of the etchant used in Fig. 4. That plot indicates that the water height data are basically independent of the etchant's pH.

Table 5: Silane SIT8174

Broader Etchants	pH	Border Appearance	Silane	Molecular Formula	Water Height (mm)
5% HF Etch	1	Clear	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.69
New Improved Armour Etch	3	Nice Visible	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.80
Gallery Glass window etch	9	Clear	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.78
Professional 30s glass etching	3	Nice Visible	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.70
Etchall etching cream	3	Nice Visible	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	3.98
1N NaOH	14	Clear	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	3.89
Sodium Silicate	12.5	Clear	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.50
VTX	7	Clear	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.15
Coarse Grit Sandblast	N/A	Nice Visible	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.78
Coarse Grit Sandblast with Sodium Silicate	N/A	Nice Visible	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.27
Fine Grit Sandblast	N/A	Nice Visible	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.86
5% HF (with 512 Power coat	1	Clear	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.47
Fine Grit Sandblast with Sodium Silicate	12.5	Nice Visible	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.57
Fine Grit Sandblast with NaOH	14	Nice Visible	SIT 8174 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trichlorosilane	$C_8H_4Cl_3F_{13}Si$	4.02

Example 6 Spill-resistant border formation with tridecafluoro-1,1,2,2-tetrahydrooctyl trimethoxysilane after activation of glass surfaces by chemical etching, abrasion, and combined treatments

[00113] The ability of plates having borders prepared with tridecafluoro-1,1,2,2-tetrahydrooctyl trimethoxysilane (Gelest product reference SIT8176) under the conditions described in Table 6 to retain water is conducted using six glass plates. The plates are masked leaving a 0.5 inch border at their edge and treated using SIT8176 as the silanizing agent using the methods employed in Example 5. The height of water retained on these plates and the pH of the etchant, where applicable, is listed in Table 6.

Table 6 Silane SIT8176

Broader Etchants	pH	Border Appearance	Silane	Molecular Formula	Water Height (mm)
VTX	7	Clear	SIT8176 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trimethoxysilane	$C_{14}H_{19}F_{13}O_3Si$	3.16
Coarse Grit Sandblast	N/A	Nice Visible	SIT8176 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trimethoxysilane	$C_{14}H_{19}F_{13}O_3Si$	3.83
Coarse Grit Sandblast with Sodium Silicate	N/A	Nice Visible	SIT8176 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trimethoxysilane	$C_{14}H_{19}F_{13}O_3Si$	3.32
Fine Grit Sandblast	N/	Nice Visible	SIT8176 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trimethoxysilane	$C_{14}H_{19}F_{13}O_3Si$	3.92
Fine Grit Sandblast with Sodium Silicate	12.5	Nice Visible	SIT8176 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trimethoxysilane	$C_{14}H_{19}F_{13}O_3Si$	3.92
Fine Grit Sandblast with NaOH	14	Nice Visible	SIT8176 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Trimethoxysilane	$C_{14}H_{19}F_{13}O_3Si$	2.97

Example 7 Spill-resistant border formation with tridecafluoro-1,1,2,2-tetrahydrooctyl triethoxysilane after activation of glass surfaces by chemical etching, abrasion, and combined treatments

[00114] Spill-resistant borders are prepared on glass plates as in example 6 using tridecafluoro-1,1,2,2-tetrahydrooctyl triethoxysilane (Gelest reference SIT8175) in place of tridecafluoro-1,1,2,2-tetrahydrooctyl trimethoxysilane. Data for this example are summarized in Table 7. tridecafluoro-1,1,2,2-tetrahydrooctyl triethoxysilane

produce lower water heights than tridecafluoro-1,1,2,2-tetrahydrooctyl trimethoxysilane (SIT8176). Post-blast etching reductions in water height are similar to those in Examples 5 and 6.

Table 7: Silane SIT8175

Broader Etchants	pH	Border Appearance	Silane	Molecular Formula	Water Height (mm)
VTX	7	Clear	SIT 8175 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Triethoxysilane	$C_{11}H_{13}F_{13}O_3Si$	2.85
Coarse Grit Sandblast	N/A	Nice Visible	SIT 8175 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Triethoxysilane	$C_{11}H_{13}F_{13}O_3Si$	3.77
Coarse Grit Sandblast with Sodium Silicate	N/A	Nice Visible	SIT 8175 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Triethoxysilane	$C_{11}H_{13}F_{13}O_3Si$	3.12
Fine Grit Sandblast	N/A	Nice Visible	SIT 8175 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Triethoxysilane	$C_{11}H_{13}F_{13}O_3Si$	3.90
Fine Grit Sandblast with Sodium Silicate	12.5	Nice Visible	SIT 8175 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Triethoxysilane	$C_{11}H_{13}F_{13}O_3Si$	3.78
Fine Grit Sandblast with NaOH	14	Nice Visible	SIT 8175 Tridecafluoro-1,1,2,2-Tetrahydrooctyl Triethoxysilane	$C_{11}H_{13}F_{13}O_3Si$	3.12

Example 8 Spill-resistant border formation with n-octadecyl trimethoxysilane after activation of glass surfaces by chemical etching, abrasion, and combined treatments

[00115] The ability of plates having borders prepared with n-octadecyl trimethoxysilane (Gelest product reference SIO 6645) to retain water under the conditions described in Table 8 is conducted using six glass plates. The plates are masked leaving a 0.5 inch border at their edge and treated using SIO 6645 as the silanizing agent using the indicated methods in Example 5. The height of water retained on these plates and the pH of the etchant, where applicable, is listed in Table 8.

Table 8: Silane SIO6645

Broader Etchants	pH	Border Appearance	Silane	Molecular Formula	Water Height (mm)
New Improved Armour Etch	3	Nice Visible	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	3.91
Gallery glass window etch	9	Clear	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	3.97
Professional 30s glass etching	3	Nice Visible	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	4.07
Etchall etching cream	3	Nice Visible	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	3.94
10N NaOH	14	Clear	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	3.96
Sodium Silicate	12.5	Clear	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	3.96
VTX	7	Clear	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	3.91
Coarse Grit Sandblast	N/A	Nice Visible	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	4.09
Coarse Grit Sandblast with Sodium Silicate	N/A	Nice Visible	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	3.86
Fine Grit Sandblast	N/A	Nice Visible	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	4.01
Fine Grit Sandblast with Sodium Silicate	12.5	Nice Visible	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	4.03
Fine Grit Sandblast with NaOH	14	Nice Visible	SIO 6645 n-Octadecyl Trimethoxysilane	$C_{21}H_{46}O_3Si_3$	3.16

Example 9 Spill-resistant border formation with n-octadecyl triethoxysilane after activation of glass surfaces by chemical etching, abrasion, and combined treatments

[00116] The ability of plates having borders prepared with n-octyl triethoxysilane (Gelest product reference SIO 6715) to retain water is assessed using twelve glass plates treated with one of the conditions set forth in Table 9. The plates are masked leaving a 0.5 inch border at their edge and treated using SIO 6715 as the silanizing agent using the methods employed in Example 5. The height of water retained on these plates and the pH of the etchant, where applicable, is listed in Table 9.

Table 9: Silane SIO6715

Broader Etchants	pH	Border Appearance	Silane	Molecular Formula	Water Height (mm)
New Improved Armour Etch	3	Nice Visible	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.85
Gallery Glass window etch	9	Clear	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	4.06
Professional 30s glass etching	3	Nice Visible	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.96
Etchall etching cream	3	Nice Visible	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.86
10N NaOH	14	Clear	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.25
Sodium Silicate	12.5	Clear	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.48
VTX	7	Clear	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.59
Coarse Grit Sandblast	N/A	Nice Visible	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.28
Coarse Grit Sandblast with Sodium Silicate	N/A	Nice Visible	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.12
Fine Grit Sandblast	N/A	Nice Visible	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.32
Fine Grit Sandblast with Sodium Silicate	12.5	Nice Visible	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	4.14
Fine Grit Sandblast with NaOH	14	Nice Visible	SIO 6715 n-Octyl Triethoxysilane	$C_{14}H_{32}O_3Si_3$	3.12

Example 10 Abrasion with fine polishing powders as a means of activating glass surfaces for the formation of spill-resistant borders

[00117] Four 4 inch by 4-inch square glass plates are masked with electrical tape to create a 0.5-inch wide spill-resistant border at the outer edge. The area that will form the border is polished using slurry of about 60-70 gram of cerium oxide in water (3.5-3.7 micron particles, about 3,000-8,000 mesh or grit). Polishing is carried out by using a motorized wheel with the surface of the plate being polished soaked with the slurry.

[00118] Following abrasion/polishing with cerium oxide, two of the four plates are etched with 5% aqueous HF solution for 30 seconds. The polished and polished/etched plates are washed with water and dried first with a stream of air and then in a 200°F oven for 5 min.

[00119] One each of the polished and polished/etched plates is treated with the silanizing agent SIT8174 or silanizing agent SIH5841.7. The treated plates are cured by heating at 200°F for 15-30 min. Data for all four plates are summarized in Table 10. The agent SIT8174 performed slightly better than SIH5841.7 for both sets of plates.

Table 10: Spill- Resistant Borders Prepared by Cerium Oxide Polishing With and Without 5% HF Etch Employing Two Different Silane Treatments

Border Treatment	pH	Silane	Formula	Water Height (mm)	Border Appearance
Cerium oxide polish	N/A	SIT8174	$C_8H_4Cl_3F_{13}Si$	4.46	Clear
Cerium oxide & 5% HF etch	1	SIT8174	$C_8H_4Cl_3F_{13}Si$	4.53	Clear
Cerium oxide	N/A	SIH5841.7	$C_{16}H_{22}F_{17}N_3Si$	4.31	Clear
Cerium oxide & 5% HF etch	1	SIH5841.7	$C_{16}H_{22}F_{17}N_3Si$	4.38	Clear

Example 11 The ability of spill-resistant borders to retain alcohol containing liquids.

[00120] Four 4 inch x 4-inch glass plates with spill-resistant borders are prepared by four different methods indicated in Table 11 as described in Example 5 and silanated with tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (SIT8174). The plates are tested for their spill performance with two alcoholic beverages; a wine (Sutter Home Merlot, California, 2007) and vodka (Krasser's Vodka). Spill height data for those alcoholic drinks are summarized in Table 11. Wine with its lower alcohol content shows a higher retained liquid level than the vodka with its higher alcohol content. The coarse grit sandblasted borders show the highest retained liquid heights for both liquids.

[00121] Table 11: Spill Barrier Height for Two Alcoholic Beverages

Border Treatment	pH	Silane	Formula	Water Height (mm)	Border Appearance
Sutter Home Merlot (California, 2007)					
5% HF	1	SIT8174	$C_8H_4Cl_3F_{13}Si$	3.54	Clear
Sodium silicate	12.5	SIT8174	$C_8H_4Cl_3F_{13}Si$	3.69	Clear
Coarse grit blast	N/A	SIT8174	$C_8H_4Cl_3F_{13}Si$	4.02	Visible
Fine grit blast	N/A	SIT8174	$C_8H_4Cl_3F_{13}Si$	3.58	Visible
Krasser's Vodka					
5% HF	1	SIT8174	$C_8H_4Cl_3F_{13}Si$	2.53	Clear
Sodium silicate	12.5	SIT8174	$C_8H_4Cl_3F_{13}Si$	2.53	Clear
Coarse grit blast	N/A	SIT8174	$C_8H_4Cl_3F_{13}Si$	2.66	Visible
Fine grit blast	N/A	SIT8174	$C_8H_4Cl_3F_{13}Si$	2.63	Visible

Example 12: The ability of spill-resistant borders to retain various liquid food items after cleaning.

[00122] Four groups three of 4 inch by 4 inch square plates, having a 0.5 inch spill-resistant border formed by the application of tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane to their edges after one of the following four treatments. In the first treatment, three plates are masked leaving a 0.5 inch region at the edge exposed for the preparation of the spill-resistant border. The plate is etched with 5% aqueous HF for 30 seconds at room temperature. The second set of three plates is masked as described for the first treatment in this example and subject to sandblasting with 400 mesh abrasive particles and subsequently etched with 5% aqueous HF for 30 seconds at room temperature. The third set of three plates is masked as described for the first treatment in this example and subject to sandblasting with 35 mesh abrasive particles and subsequently etched with 5% aqueous HF for 30 seconds at room temperature. The fourth set of plates are masked as described for the first treatment in this example and subject to sandblasting with 35 mesh abrasive particles without subsequent etching.

[00123] After the above treatments, and before removing the masks, the plates are washed with water, and dried in an oven (about 200°F) for about 15 minutes. After cooling, the plates are treated tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane as a 1% solution in hexane. After the hexane has evaporated the plates are cured by baking in an oven at 150 to 250°F for 5 to 30 minutes (curing can also be accomplished by allowing the silanated plates to remain at room temperature for about 24 hours in a

controlled humidity environment). Following curing masks are removed. The ability of each set of three plates to retain water is measured and the average values for the height of water retained is plotted for each plate in the histogram shown in Figure 5 and the average for each treatment is shown Figure 6.

[00124] Using the following sequence of cleaning and filling with various food stuffs, the ability of the plates to retain liquids (resistance to spillage) is assessed for each type of plate and food stuff:

i) Cleaning with soap and water,
ii) Filling with water (see data for the height of retained water in Table 12a),
iii) Cleaning with soap and water,
iv) Filling with apple juice (see data for the height of retained apple juice in Table 12b),
v) Cleaning with soap and water,
vi) Filling with oil and vinegar salad dressing with spices (see data for the height of retained salad dressing in Table 12c),
vii) Cleaning with soap and water,
viii) Filling with milk (see data for the height of retained milk in Table 12d),
vii) Cleaning with soap and water,
ix) Cooling the plates and water to approximately 36°F overnight and filling the plates with the cooled water without removing any condensation from their surfaces (see data for the height of retained cooled water in Table 12e), and
x) Drying the condensation present on the plates and filling them with ice cold water (see data for the height of retained ice cold water in Table 12f).

Table 12a: Retention of water after one cleaning with soap and water

Treatment	Spill Area (mm)		Spill Area (cm^2)	Volume of Water Filled In Spill Area Prior to Spill (cm^3)	Water Height in Spill Area Water Volume/Spill Area (mm)
	Width	Length			
1	28.30	41.19	11.66	4.8	4.12
2	22.73	46.78	10.63	4.8	4.51
3	18.64	45.13	8.41	5.0	5.94
4	18.93	47.08	8.91	4.0	4.49

Table 12b: Retention of apple juice after cleaning with soap

Treatment	Spill Area (mm)		Spill Area (cm^2)	Volume of Water Filled In Spill Area Prior to Spill (cm^3)	Water Height in Spill Area Water Volume/Spill Area (mm)
	Width	Length			
1	28.30	41.19	11.66	4.8	4.12
2	22.73	46.78	10.63	4.8	4.51
3	18.64	45.13	8.41	5.0	5.94
4	18.93	47.08	8.91	4.0	4.49

Table 12c: Retention of salad dressing after cleaning with soap and water

Treatment	Spill Area (mm)		Spill Area (cm^2)	Volume of Water Filled In Spill Area Prior to Spill (cm^3)	Water Height in Spill Area Water Volume/Spill Area (mm)
	Width	Length			
1	29.59	54.52	16.13	5.8	3.60
2	28.30	41.19	11.66	4.7	4.03
3	22.73	46.78	10.63	4.8	4.51
4	18.64	45.13	8.41	4.4	5.23
5	18.93	47.08	8.91	3.0	3.37

Table 12d: Retention of milk after cleaning with soap and water

Treatment	Spill Area (mm)		Spill Area (cm^2)	Volume of Water Filled In Spill Area Prior to Spill (cm^3)	Water Height in Spill Area Water Volume/Spill Area (mm)
	Width	Length			
1	28.30	41.19	11.66	3.6	3.09
2	22.73	46.78	10.63	3.9	3.67
3	18.64	45.13	8.41	4.0	4.76
4	18.93	47.08	8.91	3.0	3.37

Table 12e: Retention of cooled water after cleaning with soap and water (without removing condensation)

Sample ID	Spill Area (mm)		Spill Area (cm^2)	Volume of Water Filled In Spill Area Prior to Spill (cm^3)	Water Height in Spill Area Water Volume/Spill Area (mm)
	Width	Length			
1	28.30	41.19	11.66	1.6	1.37
2	22.73	46.78	10.63	3.4	3.20
3	18.64	45.13	8.41	3.9	4.64
4	18.93	47.08	8.91	2.9	3.25

Table 12f: Retention of ice cold water after removing condensation

Sample ID	Spill Area (mm)		Spill Area (cm^2)	Volume of Water Filled In Spill Area Prior to Spill (cm^3)	Water Height in Spill Area Water Volume/Spill Area (mm)
	Width	Length			
1	28.30	41.19	11.66	4.7	3.99
2	22.73	46.78	10.63	4.6	4.32
3	18.64	45.13	8.41	4.2	4.99
4	18.93	47.08	8.91	3.8	4.26

Example 13 The effects of abrasion on the ability of spill-resistant borders to retain water.

[00125] **Part A** - A second of the glass plates are prepared using each of the four treatments described in Example 12, is assessed for their ability to retain water (see the middle bar for each treatment group in Figure 5. The plates are subject to abrasion using a glass jar by moving it back and forth over the border 5 times and the height of water retained by the border on those plates is measured again. From the data in Table 13 and Figure 7 it can be seen that rubbing can reduce the water height to some extent.

Table 13A: Testing water retention of a spill-resistant border after abrasion with a glass jar five times

Treatment	Spill Area (mm)		Spill Area (cm^2)	Volume of Water Filled In Spill Area Prior to Spill (cm^3)	Water Height in Spill Area Water Volume/Spill Area (mm)
	Width	Length			
1	15.45	38.78	5.99	2.3	3.84
2	18.95	43.15	8.18	3.8	4.65
3	17.30	43.17	7.47	3.4	4.55
4	18.39	45.53	8.37	4.1	4.90

[00126] **Part B** - A 0.5 inch spill-resistant borders is prepared on the edge three 4- by 4-in. glass plates using as activation treatments (i) 0 5% HF etching produced a clear border, (ii) sandblasting using find sand produced a visible border by abrasion, and (iii) Professional 30 Second Glass Etch to form a visible border. The activated borders regions of each plate are treated with silane SIT8174 from Gelest, Inc.

[00127] For each plate, border abrasion tests are carried with using a 32-oz. glass jar filled (a "Mason Jar") filled with 24 oz. of water. After an initial measurement of water fill height for each plate, the jar is rubbed over the border on one side of the plate 50, 100, 150, 200 and 300 times for with the height of water retained by the plate measured after each set of rubbing. Data are shown in Table 13B.

Table 13B

Glass Plate Sample No.	Border Type	Height of water retained in millimeter for the numbers of rubs indicated in parentheses					
		(control 0 rubs)	(50)	(100)	(150)	(200)	(300)
1	Invisible	4.7	4.65	4.33	4.33	4.33	4.17
3	Visible (Sand)	4.86	4.81	4.81	4.81	4.81	4.81
5	Visible Professional 30sec. Glass Etch	4.7	4.81	4.65	4.49	4.49	4.49

Example 14: The hydrophobic and oleophobic behavior treated surfaces.

[00128] Water and mineral oil contact angle data are measured for on 2 inch by 2 inch glass plates that have been treated with one of nine different silanizing agents. Prior to treatment with silanizing agents the plates are activated by etching the surface with 5% aqueous HF for 30 seconds, drying at 200°F for 15-30 minutes, cooling, and treating the plates with one of nine the different silanes in Table 14(a). After treatment with silanes, the plates are cured at 200°F for 15 to 30 minutes and cooled. Ten measurements of the contact angles for water and mineral oil (Mineral Oil, Light Viscosity, Technical Grade, PTI Process Chemicals, Ringwood, IL) are made on each plate. The averages and standard deviations for those measurements are summarized in Table 14(a), which also includes data for glass that has not been treated with a silanizing agent as the "Control No Silanization" entry. All measurements are made at room temperature.

Table 14(a) Contact Angle for glass surfaces treated with one of nine different silanes to form a border region that is not visible

Silane ID:	Leaving Group	Terminal Functionality	Water Contact Angle (degrees)	
			Average	Std. Deviation
SIT8173.0	Trihydro	Fluorine (13)	91.569	6.1189
SIT8174.0	Trichloro	Fluorine (13)	116.212	3.2937
SIT8175.0	Triethoxy	Fluorine (13)	64.5037	8.0617
SIT8176.0	Trimethoxy	Fluorine (13)	91.722	6.8284
SIH5840.5	Dimethylamino	Fluorine (17)	81.006	8.5750
SIH5841.7	Tris(dimethylamino)	Fluorine (17)	85.491	8.6567
SIO6645.0	Trimethoxy	Methyl (18)	83.045	10.6766
SIO6715.0	Triethoxy	Methyl (18)	62.4912	0.9539
SIN6597.4	Dimethylamino	Fluorine (9)	59.7741	5.6127
Control No Silanization	--	--	18.395	1.4045

Silane ID:	Leaving Group	Terminal Functionality	Oil Contact Angle (degrees)	
			Average	Std. Deviation
SIT8173.0	Trihydro	Fluorine (13)	72.0708	7.0987
SIT8174.0	Trichloro	Fluorine (13)	108.7258	3.0468
SIT8175.0	Triethoxy	Fluorine (13)	33.1158	3.1323
SIT8176.0	Trimethoxy	Fluorine (13)	55.3158	7.2287
SIH5840.5	Dimethylamino	Fluorine (17)	41.068	2.8977
SIH5841.7	Tris(dimethylamino)	Fluorine (17)	56.337	3.7703
SIO6645.0	Trimethoxy	Methyl (18)	34.531	1.0548
SIO6715.0	Triethoxy	Methyl (18)	34.6855	1.0308
SIN6597.4	Dimethylamino	Fluorine (9)	27.0033	7.2239
Control No Silanization	--	--	12.341	3.6562

*Control measurement was made on the surface not subjected to HF treatment

[00129] Water and mineral oil contact angle data are measured on 2 inch by 2 inch glass plates prepared using one of the following three activating treatments:

1. Blasting with fine sand (57.5 μm);
2. Blasting with coarse sand (387.5 μm); and
3. Etching using 30 Sec Etching Cream

[00130] Following the activation treatment, the plates are treated with one of three different fluorinated alkyl silanizing agents (SIH 5840.5, SIH 5841.7, and SIT

8174.0) to convert the surface into hydrophobic or oleophobic surfaces such as would be used in a spill-resistant border. For plates blasted with coarse sand, a non-fluorinated silane (SIO 6715.0) is also employed to convert the surface into a spill resistant border. After treatment with the silanizing agents, the plates are cured at 200°F for 15 to 30 minutes and cooled. Five measurements of the contact angles for water and mineral oil are made on each plate. The averages and standard deviations for those measurements are summarized in Table 14(b), which also includes data for glass that has not been treated with a silanizing agent. All measurements are made at room temperature.

Table 14(b) Contact Angle for glass surfaces treated with silanes to form a visible border region

Silane ID:	Visible Border	Liquid	Contact Angle (degrees)	
			Average	Std. Deviation
SIH 5840.5	Fine Blast	water	76.93	5.797098
SIH 5840.5	Corse Blast	water	71.37	3.014489
SIH 5840.5	30 Sec. Etching Cream	water	46.41	4.425683
SIH 5841.7	Fine Blast	water	112.64	1.951766
SIH 5841.7	Corse Blast	water	106.79	2.053628
SIH 5841.7	30 Sec. Etching Cream	water	108.01	11.83157
SIT 8174.0	Fine Blast	water	123.74	2.899724
SIT 8174.0	Corse Blast	water	124.72	3.995871
SIT 8174.0	30 Sec. Etching Cream	water	110.87	1.73312
SIO 6715.0	Corse Blast		85.22	1.815218
Control No Silanization	Fine Blast	water	26.25	11.89606
Control No Silanization	Corse Blast	water	41.61	6.504281
Control No Silanization	30 Sec. Etching Cream	water	33.35	1.308337
SIH 5840.5	Fine Blast	mineral oil	29.71	4.563883
SIH 5840.5	Corse Blast	mineral oil	26.25	2.987117
SIH 5840.5	30 Sec. Etching Cream	mineral oil	38.13	5.513698
SIH 5841.7	Fine Blast	mineral oil	52.73	4.227723
SIH 5841.7	Corse Blast	mineral oil	79.85	3.850016
SIH 5841.7	30 Sec. Etching Cream	mineral oil	75.81	9.344477
SIT 8174.0	Fine Blast	mineral oil	88.22	4.614441
SIT 8174.0	Corse Blast	mineral oil	91.88	1.734779
SIT 8174.0	30 Sec. Etching Cream	mineral oil	85.75	4.597758
SIO 6715.0	Corse Blast	mineral oil	10.51	0.398026
Control No Silanization	Fine Blast	mineral oil	Less than 10	----
Control No Silanization	Corse Blast	mineral oil	13.66	1.212068
Control No Silanization	30 Sec. Etching Cream	mineral oil	16.21	2.340523

*Control measurements are made on the surface after blasting or etching

Example 15: Spill-resistant borders and their behavior with oils

[00131] The behavior of spill-resistant borders with oils is assessed by determining the height of a mineral oil layer that the border will cause to be retained without spillage. For the assessment, 0.5 inch borders are formed on the edge of masked 4 inch by 4 inch glass plates. The region that will form the border on three of the plates is activated with 5% aqueous HF, two of which are treated with a fluorine containing silanizing agents and one with a non-fluorine containing silanizing agent. The region that will form the border on the remaining three plates is activated by sandblasting with 60 mesh particles, followed by treatment with the same three silanes employed for the HF activated plates. The mineral oil height and contact angle data obtained for all six samples is summarized in Table 15.

Table 15 - Mineral Oil Height for Borders on Glass with Two Different Activators and Three Different Silanes

Plate ID	Silane Formula	Height (mm)	Contact Angle (Θ)	Standard Deviation
Sand Blast 8174	$C_8H_4Cl_3F_{13}Si$	2.38		
Sand Blast 5841.7	$C_{16}H_{22}F_{17}N_3Si$	2.06		
Sand Blast 6715.0 (Non-F)	$C_{14}H_{32}O_3Si_3$	0.95		
HF 8174	$C_8H_4Cl_3F_{13}Si$	1.91	108.7	3.04
HF 5841.7	$C_{16}H_{22}F_{17}N_3Si$	2.05	56.34	3.77
HF 6715.0 (Non-F)	$C_{14}H_{32}O_3Si_3$	1.17	34.7	1.03

*Non-F indicates the terminal functionality contained no fluorine atoms.

Example 16 The Effect of Leaving Silanizing Agent Groups on the Water Retention of Spill-Resistant Borders formed on Glass Surfaces

[00132] The effectiveness of silane leaving groups and terminal functionalities on the ability of spill-resistant borders to retain water is assessed for nine different silanes under controlled conditions. For the assessment, nine 4inch by 4 inch square glass plates are masked with electrical tape to create a 0.5-inch wide unmasked area around the outer edge as in Example 1. The unmasked area is etched with 5% HF for 1 minute, the acid is washed off with cold water, and the plates are dried at about 200°F for 15-30 minutes, followed by cooling, and treating separate plates with one of nine different silanes as a 1% solution of the silane in hexane. All of the plates are heat cured at about 200°F for 15-30 minutes, and after cooling are unmasked and the height of water retained by the spill-resistant border measured. All plates are processed at the same

time in order to minimize any treatment differences that might arise. Water-height data are summarized in Table 16.

Table 16: Water Height for Spill-Resistant Borders Created by Etching with 5% HF and using Nine Different Silanes

No.	Silane Name[a]	Water Height (mm)	Leaving Group	Terminal Functionality[b]
1	SIT8173	3.92	Trihydro	Fluorine (13)
2	SIT8174	4.59	Trichloro	Fluorine (13)
3	SIT8175	3.90	Triethoxy	Fluorine (13)
4	SIT8176	4.00	Trimethoxy	Fluorine (13)
5	SIH5840.5	4.30	Dimethylamino	Fluorine (17)
6	SIH5841.7	4.59	Tris(dimethylamino)	Fluorine (17)
7	SIO6645.0	4.08	Trimethoxy	Methyl (18)
8	SIO6715.0	3.69	Triethoxy	Methyl (8)
9	SIN6597.4	3.50	Dimethylamino	Fluorine (9)

[a]All silanes are from Gelest and the entry under "Silane Name" represents their Gelest references.
[b]Numbers in parenthesis represent the number of fluorine's in the terminal functional groups.

Example17 Sandblast Particle Size versus Feature Size of Glass Borders

[00133] Three different sand particle sizes are used to create different size features in glass borders. Sands are: fine, with particle size ranging from 45-70 μm; coarse, with particle sizes of 250-525 μm; or medium, which is composed of a 50:50 mixture of fine and coarse sands, and yielding a particle size ranging from 45-525 μm.

[00134] Feature sizes are measured by taking 200× magnification micrographs for each of the sandblasted borders made on 4- by 4-in. glass plates. The sand used and feature sizes observed are summarized in Table 17.

Table 17 Particle Sizes and Observed Feature Sizes

Sand Type	Sand Size Average in microns (μm)	Feature Size in Glass Border (μm)
Fine	57.5	60.4
Medium	222.5	109.6
Coarse	387.5	202.0

Claims

1. A method for forming a spill-resistant border on a surface comprising applying a composition to a surface that increases the hydrophobicity or oleophobicity of a portion of the surface that will server as a border, wherein said border forms a perimeter around at least one area that has a lower hydrophobicity and/or lower oleophobicity than the border.

2. The method of claim 1, further comprising activating at least one part of said portion of said surface prior to said applying a composition.

3. The method of claim 1 or claim 2, further comprising applying a mask to said surface either before said activating, or said applying a composition, or before both said activating and said applying a composition.

3. The method of any of claim 2 or claim 3, wherein said activating comprises etching the surface with a chemical agent.

4. The method of claim 3, wherein said chemical agent is hydrofluoric acid.

5. The method of claim 6, wherein said chemical agent is a composition comprising a glass etchant having a pH from about 0.1 to about 14.

6. The method of claim 5, wherein said chemical agent comprises sodium silicate, potassium hydroxide, or sodium hydroxide.

7. The method of any of claims 2 – 6, wherein said activating comprises abrading the surface.

8. The method of claim 7, wherein said abrading comprises sandblasting or polishing.

9. The method of claim any of claims 1-8, wherein at least a portion of said border is not visible.

10. The method of any of claims 1-8, wherein at least a portion of said border is selected from the group consisting of a visible but clear border, a fine visible border, and a coarse visible border.

11. The method of any of any of claims 1-10, wherein said surface is selected from a glass, metal, metalloid, ceramic, wood, plastic, resin, rubber, stone, and concrete surface.

12 The method of any of claims 1-11, wherein said spill resistant border resists the spreading of a liquid selected from the group consisting of water, an aqueous solutions, an aqueous suspension, and an aqueous emulsion.

13. The method of claim 12, wherein said spill-resistant border provides a retention of ≥ 4.0 mm of said liquid.

14. The method claim 12, wherein said spill-resistant border provides a retention of ≥ 4.5 mm of said liquid.

15. The method of any of claims 1-12, wherein said spill resistant border resists the spreading of a liquid comprising an alcohol.

16. The method of claim 15, wherein said liquid comprises water and up to 95% by weight of an alcohol.

17. The method of claim 15 or claim 16, wherein said spill-resistant border provides a retention of ≥ 2.0 mm of said liquid.

18. The method of claims 15 or claim 16, wherein said spill-resistant border provides a retention of ≥ 2.5 mm of said liquid.

19. The method of claims 15 or claim 16, wherein said spill-resistant border provides a retention of ≥ 3.0 mm of said liquid.

20. The method of claims 15 or claim 16, wherein said spill-resistant border provides a retention of ≥ 3.5 mm of said liquid.

21. The method of any of claims 1-11, wherein said spill resistant border resists the spreading of a liquid comprising oil or lipid.

22. The method of claim 21, wherein said spill-resistant border provides a retention of ≥ 0.9 mm of said liquid.

23. The method of claim 21, wherein said spill-resistant border provides a retention of ≥ 1.0 mm of said liquid.

24. The method of claim 21, wherein said spill-resistant border provides a retention of ≥ 1.25 mm of said liquid.

25. The method of claim 21, wherein said spill-resistant border provides a retention of ≥ 1.5 mm of said liquid.

26. The method of claim 21, wherein said spill-resistant border provides a retention of ≥ 2.0 mm of said liquid.

27. The method of any of claims 1-26, wherein said composition comprises a silanizing agent having a terminal functionality that is selected from the group consisting of an alkyl, fluoroalkyl or perfluoroalkyl.

28. The method of claim 27, wherein said silanizing agent has at least one leaving group selected from the group consisting of chloro, -O-alkyl, -NH-(C_1-C_6alkyl), and –N-(C_1-C_6alkyl)$_2$.

29. The method of claim 27, wherein said silanizing agent has at least one leaving group selected from the groups consisting of chloro, -O-alkyl, -NH-(C_1-C_6alkyl), –N-(C_1-C_6alkyl)$_2$, and a combination thereof.

30. The method of claim 27, wherein said silanizing agent, is a compound of formula (I):

$$\mathbf{R_{4-n}Si\text{-}X_n} \quad \mathbf{(I)}$$

where n is an integer from 1-3;

and wherein each R is an independently selected from

(i) alkyl or cycloalkyl group optionally substituted one or more fluorine atoms,

(ii) $C_{1\text{ to }20}$ alkyl optionally substituted with one or more independently selected substituents selected from fluorine atoms and $C_{6\text{-}14}$ aryl groups, which aryl groups are optionally substituted with one or more independently selected halo, $C_{1\text{ to }10}$ alkyl, $C_{1\text{ to }10}$ haloalkyl, $C_{1\text{ to }10}$ alkoxy, or $C_{1\text{ to }10}$ haloalkoxy substituents,

(iii) $C_{6\text{ to }20}$ alkyl ether optionally substituted with one or more substituents independently selected from fluorine and $C_{6\text{-}14}$ aryl groups, which aryl groups are optionally substituted with one or more independently selected halo, $C_{1\text{ to }10}$ alkyl, $C_{1\text{ to }10}$ haloalkyl, $C_{1\text{ to }10}$ alkoxy, or $C_{1\text{ to }10}$ haloalkoxy substituents,

(iv) $C_{6\text{-}14}$ aryl, optionally substituted with one or more substituents independently selected from halo or alkoxy, and haloalkoxy substituents;

(v) $C_{6\text{ to }20}$ alkenyl or $C_{6\text{ to }20}$ alkynyl, optionally substituted with one or more substituents independently selected from halo, alkoxy, or haloalkoxy;

each X is independently selected from -H, -Cl, -I, -Br, -OH, -OR^2, -NHR^3, or -$N(R^3)_2$;

each R^2 is an independently selected $C_{1\text{ to }4}$ alkyl or haloalkyl group; and

each R^3 is an independently selected $C_{1\text{ to }4}$ alkyl or haloalkyl group.

31. The method of claim 30, wherein R is an alkyl, fluoroalkyl or perfluoroalkyl group comprising from 6 to 20 carbon atoms.

32. The method of claim 30, wherein R is an alkyl, fluoroalkyl or perfluoroalkyl group comprising from 8 to 20 carbon atoms

33. The method of claim 30, wherein R is an alkyl, fluoroalkyl or perfluoroalkyl group comprising from 10 to 20 carbon atoms.

34. The method of any of claims 30 - 33, wherein n is 3.

35. The method of any of claims 30 - 34, wherein R has the form $-Z-((CF_2)_q(CF_3))_r$, wherein Z is a C_{1-12} divalent radical derived from an alkane, alkene or alkyne, wherein q is an integer from 1 to 12, and wherein r is an integer from 1-4.

36. The method of any of claims 30 - 35, wherein, n is 2 or n is 1.

37. The method of any of claims 30 - 36, wherein all of the all halogen atoms present in any one or more said independently selected R groups are fluorine atoms.

38. The method of any of claims 30-37, wherein each X is independently selected from H, Cl, -OH $-OR^2$, $-NHR^3$, $-N(R^3)_2$, or combinations thereof.

39. The method of any of claims 30-37, wherein each X is independently selected from Cl, $-OR^2$, $-NHR^3$, $-N(R^3)_2$, or combinations thereof.

40. The method of any of claims 30-37, wherein each X is independently selected from, Cl, $-NHR^3$, $-N(R^3)_2$ or combinations thereof.

41. The method of claim 27, wherein said silanizing agent is tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane ($C_8H_4Cl_3F_{13}Si$), heptadecafluoro-1,1,2,2-tetrahydrodecycl tris(dimethylamino)silane ($C_{16}H_{22}F_{17}N_3Si$), or heptadecafluoro-1,1,2,2-tetrahydrodecylimethyl (dimethylamino)silane ($C_{14}H_{16}F_{17}NSi$).

42. The method of any of claims 1-41 wherein said spill-resistant border is a visible border produced by a process comprising sandblasting, chemical etching or a combination thereof.

43. The method of any of claims 1 – 8 or 10 - 42, wherein said spill-resistant border provides a contact angle of about 45° to about 125° with water on a glass surface that has a fine, medium or coarse visible border.

44. The method of any of claims 1 – 9 or 11 - 42, wherein said spill-resistant border provides a contact angle of about 60° to about 116° with water on a glass surface that has a border that is not visible.

45. The method of any of claims 1 – 8 or 10 - 42, wherein said spill-resistant border provides a contact angle of about 36° to about 91° with light mineral oil on a glass surface that has a fine, medium or coarse visible border.

46. The method of any of claims 1 – 9 or 11 - 42, wherein said spill-resistant border provides a contact angle of about 27° to about 109° with light mineral oil on a glass surface that has a border that is not visible.

47. A surface prepared by the method of any of claims 1-46.

48. The surface of claim 47, wherein said surface is selected from the group consisting of stone, glass and ceramic.

49. The surface of claim 47 or claim 48, wherein said surface is selected from the group consisting of a counter top, table top, cutting board, and a shelf for use in a refrigerated apparatus.

50. A surface comprising a hydrophobic or oleophobic spill-resistant border, wherein said border forms a perimeter around at least one area that has a lower hydrophobicity and/or lower oleophobicity than said border; or wherein said surface has a contact angle with water at about 68°F to 70°F that is less than about 120°, and wherein said spill resistant border has a contact angle with water at room temperature that is greater than the contact angle of water with the surface on which it is formed by greater than about 7°.

51. The surface of claim 50, wherein said border is a border that is not visible.

52. The surface of any of claims 50, wherein said border is a visible but clear border, a fine visible border, or a coarse visible border.

53. The surface of any of any of claims 50 - 52, where in said surface is selected from the group consisting of glass, metal, metalloid, ceramic, wood, plastic, resin, rubber, stone, and concrete.

54. The surface of any of any of claims 50 – 53, wherein said spill resistant border resists the spreading of a liquid selected from the group consisting of water, an aqueous solutions, an aqueous suspension, and an aqueous emulsion.

55. The surface of claim 54, wherein said spill-resistant border provides a retention of $\geq$ 4.0 mm of said liquid.

56. The surface of claim 54, wherein said spill-resistant border provides a retention of $\geq$ 4.5 mm of said liquid.

56. The surface of any of any of claims 50 – 53, wherein said spill resistant border resists the spreading of a liquid comprising an alcohol.

57. The surface of claim 56, wherein said liquid comprises water and up to 95% by weight of an alcohol.

58. The surface of claims 56 or claim 57, wherein said spill-resistant border provides a retention of $\geq$ 2.0 mm of said liquid.

59. The surface of claims 56 or claim 57, wherein said spill-resistant border provides a retention of $\geq$ 2.5 mm of said liquid.

60. The surface of claims 56 or claim 57, wherein said spill-resistant border provides a retention of $\geq$ 3.0 mm of said liquid.

61. The surface of claims 56 or claim 57, wherein said spill-resistant border provides a retention of $\geq$ 3.5 mm of said liquid.

62. The surface of any of any of claims 50 – 53, wherein said spill resistant border resists the spreading of a liquid comprising oil or lipid.

63. The surface of claim 62, wherein said spill-resistant border provides a retention of $\geq$ 0.9 mm of said liquid.

64. The surface of claim 62, wherein said spill-resistant border provides a retention of $\geq$ 1.0 mm of said liquid.

65. The surface of claim 62, wherein said spill-resistant border provides a retention of $\geq$ 1.25 mm of said liquid.

66. The surface of claim 62, wherein said spill-resistant border provides a retention of $\geq$ 1.5 mm of said liquid.

67. The surface of claim 62, wherein said spill-resistant border provides a retention of $\geq$ 2.0 mm of said liquid.

68. The surface of any of claims 50-67, wherein said spill-resistant border is formed by treating the surface with a silanizing agent having a terminal functionality that is selected from the group consisting of an alkyl, fluoroalkyl and prefluoroaklyl.

69. The surface of claim 68, wherein said silanizing agent has at least one leaving group selected from the group consisting of chloro, -O-alkyl, -NH-(C_1-C_6alkyl), and –N-(C_1-C_6alkyl)$_2$.

70. The surface of claim 68, wherein said silanizing agent has at least one leaving group selected from the group consisting of chloro, -O-alkyl, -NH-(C_1-C_6alkyl), –N-(C_1-C_6alkyl)$_2$, and a combination thereof.

71. The surface of claim 68, wherein said silanizing agent, is a compound of formula (I):

$$\mathbf{R_{4-n}Si\text{-}X_n} \quad \mathbf{(I)}$$

where n is an integer from 1-3;

and wherein each R is an independently selected from

(i) alkyl or cycloalkyl group optionally substituted one or more fluorine atoms,

(ii) $C_{1 \text{ to } 20}$ alkyl optionally substituted with one or more independently selected substituents selected from fluorine atoms and $C_{6\text{-}14}$ aryl groups, which aryl groups are optionally substituted with one or more independently selected halo, $C_{1 \text{ to } 10}$ alkyl, $C_{1 \text{ to } 10}$ haloalkyl, $C_{1 \text{ to } 10}$ alkoxy, or $C_{1 \text{ to } 10}$ haloalkoxy substituents,

(iii) $C_{6 \text{ to } 20}$ alkyl ether optionally substituted with one or more substituents independently selected from fluorine and $C_{6\text{-}14}$ aryl groups, which aryl groups are optionally substituted with one or more independently selected halo, $C_{1 \text{ to } 10}$ alkyl, $C_{1 \text{ to } 10}$ haloalkyl, $C_{1 \text{ to } 10}$ alkoxy, or $C_{1 \text{ to } 10}$ haloalkoxy substituents,

(iv) $C_{6\text{-}14}$ aryl, optionally substituted with one or more substituents independently selected from halo or alkoxy, and haloalkoxy substituents;

(v) $C_{6 \text{ to } 20}$ alkenyl or $C_{6 \text{ to } 20}$ alkynyl, optionally substituted with one or more substituents independently selected from halo, alkoxy, or haloalkoxy;

each X is independently selected from -H, -Cl, -I, -Br, -OH, $-OR^2$, $-NHR^3$, or $-N(R^3)_2$;

each R^2 is independently an independently selected $C_{1 \text{ to } 4}$ alkyl or haloaklyl group; and

each R^3 is independently an independently selected $C_{1 \text{ to } 4}$ alkyl or haloalkyl group.

72. The surface of claim 71, wherein R is an alkyl, fluoroalkyl or perfluoroalkyl group comprising from 6 to 20 carbon atoms.

73. The surface of claim 71, wherein In another embodiment, R is an alkyl, fluoroalkyl or perfluoroalkyl group comprising from 8 to 20 carbon atoms

74. The surface of claim 71, wherein R is an alkyl, fluoroalkyl or perfluoroalkyl group comprising from 10 to 20 carbon atoms.

75. The surface of any of claims 71 - 74, wherein n is 3.

76. The surface of any of claims 71 - 75, wherein R has the form $-Z-((CF_2)_q(CF_3))_r$, wherein Z is a $C_{1\text{-}12}$ divalent radical derived from an alkane, alkene or alkyne, and q is an integer from 1 to 12, and r is an integer from 1-4.

77. The surface of any of claims 71 - 76, wherein, n is 2 or n is 1.

78. The surface of any of claims 71 - 77, wherein all of the all halogen atoms present in any one or more independently selected R groups are fluorine atoms.

79. The surface of any of claims 71- 78, wherein each X is independently selected from the group consisting of H, Cl, -OH -OR^2, -NHR^3, -$N(R^3)_2$, and combinations thereof.

80. The surface of any of claims 71-78, wherein each X is independently selected from Cl, -OR^2, -NHR^3, -$N(R^3)_2$, or combinations thereof.

81. The surface of any of claims 71 - 78, wherein each X is independently selected from, Cl, -NHR^3, -$N(R^3)_2$ or combinations thereof.

82. The surface of claim 68, wherein said silanizing agent is tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane ($C_8H_4Cl_3F_{13}Si$), heptadecafluoro-1,1,2,2-tetrahydrodecycl tris(dimethylamino)silane ($C_{16}H_{22}F_{17}N_3Si$), or heptadecafluoro-1,1,2,2-tetrahydrodecylimethyl (dimethylamino)silane ($C_{14}H_{16}F_{17}NSi$).

83. The surface of any of claims 50 – 82 wherein said spill-resistant border is a visible border produced by a process comprising sandblasting, chemical etching or a combination thereof.

84. The surface of any of claims 50 or 52 – 83, wherein said spill-resistant border provides a contact angle of about 45° to about 125° with water on a glass surface that has a fine, medium or coarse visible border.

85. The surface of any of claims 50 – 51 or 53 – 83, wherein said spill-resistant border provides a contact angle of about 60° to about 116° with water on a glass surface that has a border that is not visible.

86. The surface of any of claims 50 or 52 – 83, wherein said spill-resistant border provides a contact angle of about 36° to about 91° with light mineral oil on a glass surface that has a fine, medium or coarse visible border.

87. The surface of any of claims 50 – 51 or 53 – 83, wherein said spill-resistant border provides a contact angle of about 27° to about 109° with light mineral oil on a glass surface that has a border that is not visible.

88. The surface of any of claims 50 – 83, wherein said surface has a contact angle with water less than about 90°, and wherein said spill resistant border has a contact angle with water at room temperature that is greater than the contact angle of water with the surface on which it is formed by greater than about 10°.

89.The surface of any of claims 50 – 83, wherein said surface has a contact angle with water less than about 80°, and wherein said spill resistant border has a contact angle with water at room temperature that is greater than the contact angle of water with the surface on which it is formed by greater than about 30°.

90. The surface of any of claims 50 – 83, wherein said surface has a contact angle with water less than about 70°, and wherein said spill resistant border has a contact angle with water at room temperature that is greater than the contact angle of water with the surface on which it is formed by greater than about 30°.

91. The surface of any of claims 50 – 83, wherein said surface has a contact angle with water less than about 60°, and wherein said spill resistant border has a contact angle with water at room temperature that is greater than the contact angle of water with the surface on which it is formed by greater than about 30°.

92. The surface of any of claims 50 – 83, wherein said surface has a contact angle with water less than about 50°, and wherein said spill resistant border has a contact angle with water at room temperature that is greater than the contact angle of water with the surface on which it is formed by greater than about 30°.

93. The surface of any of claims 50 – 83, wherein said surface has a contact angle with water less than about 30°, and wherein said spill resistant border has a contact angle with water at room temperature that is greater than the contact angle of water with the surface on which it is formed by greater than about 40°.

94. The surface of any of claims 50 – 83, wherein said surface has a contact angle with water less than about 20°, and wherein said spill resistant border has a contact angle with water at room temperature that is greater than the contact angle of water with the surface on which it is formed by greater than about 20°.

Figure 1

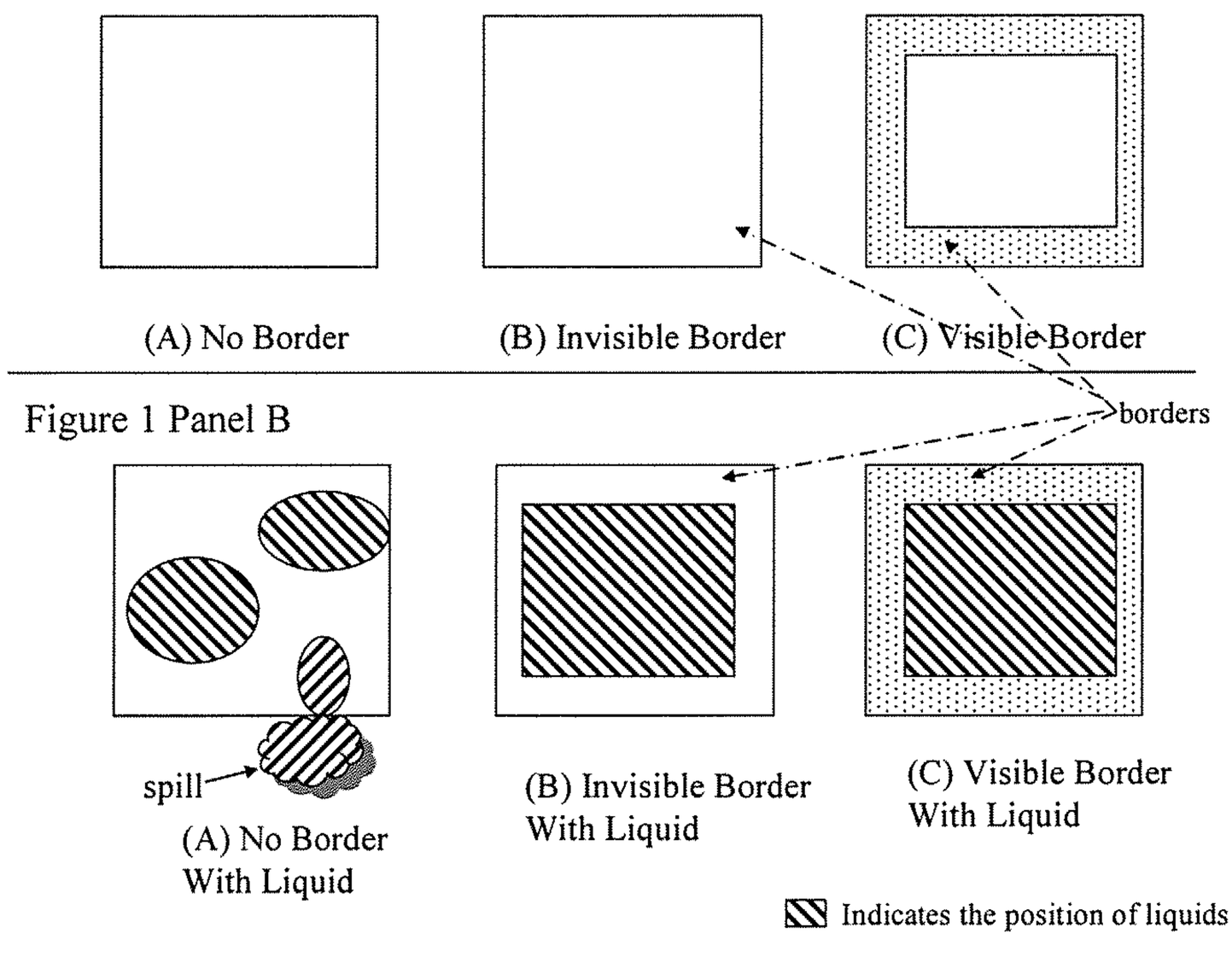
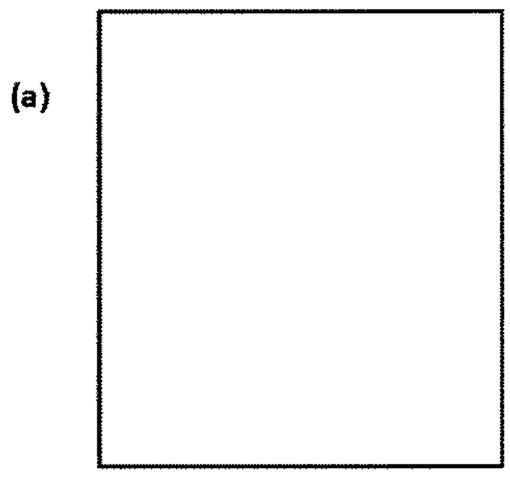
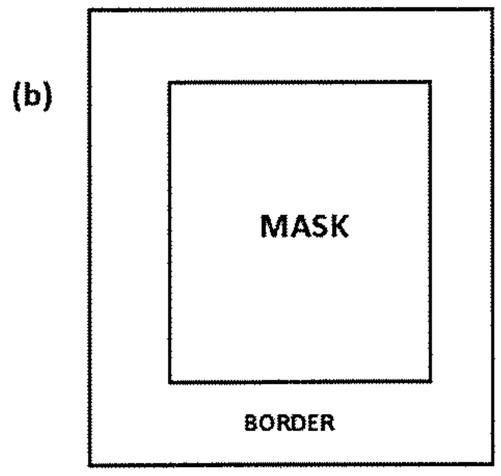

Figure 1 Panel A
(A) No Border
(B) Invisible Border
(C) Visible Border
borders
Figure 1 Panel B
spill
(A) No Border
With Liquid
(B) Invisible Border
With Liquid
(C) Visible Border
With Liquid
Indicates the position of liquids

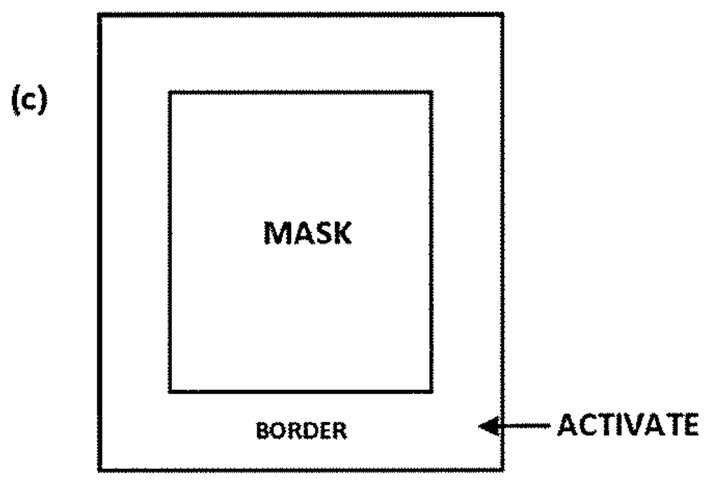
Figure 2



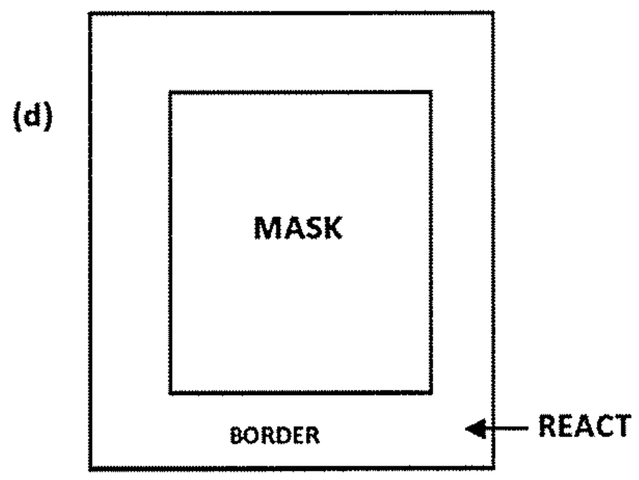
Flat glass (hydrophilic) water spreads easily and runs of edges. No water barrier.



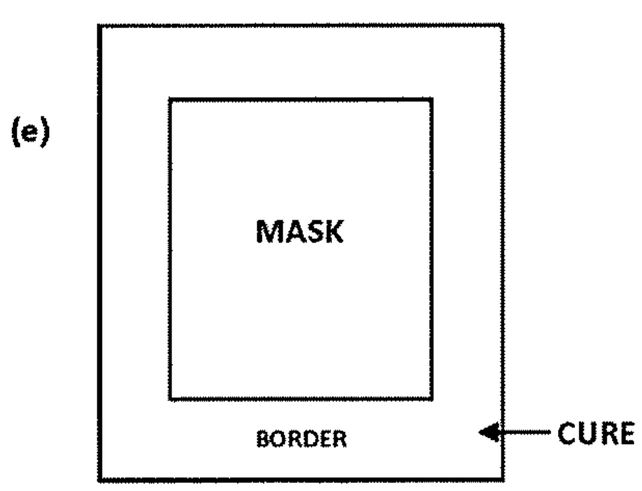
Masked area to hold liquids same as flat glass (hydrophilic) border to repel water (hydrophobic) and prevent run-off.



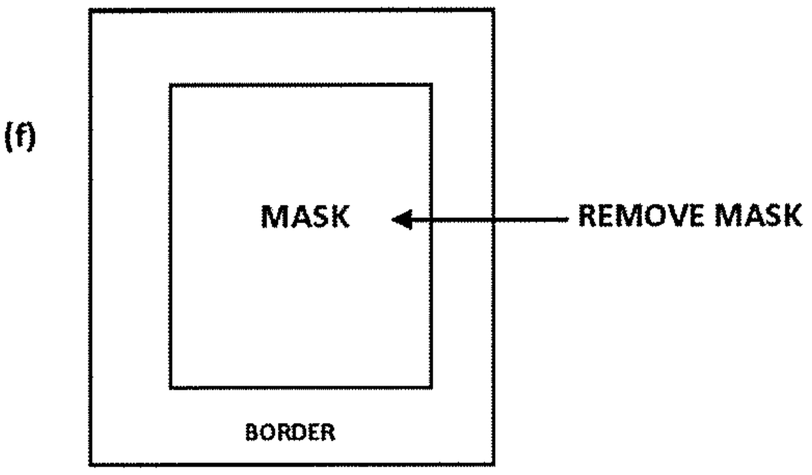
Step 1 in creating hydrophobic border is to activate border to reaction with silanes to make hydrophobic.



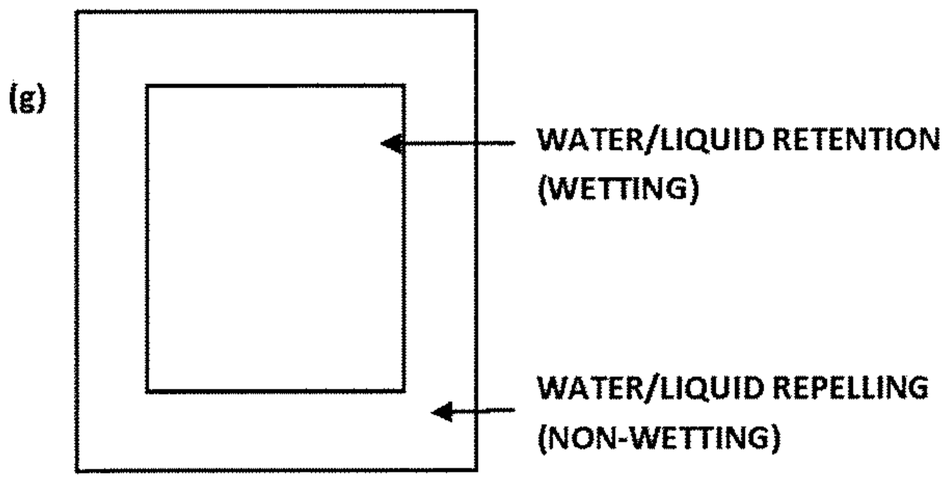
Step 2 in creating hydrophobic border is to react activated area with silanes.



Step 3 in creating hydrophobic border is to cure activated/reacted area.



Step 4 in creating hydrophilic center and hydrophobic border is to remove mask.



Glass completed to hold water/liquids in the center (hydrophilic) and repel liquid at borders (hydrophobic). Hydrophobic border can be visible or invisible, depending on activating method.

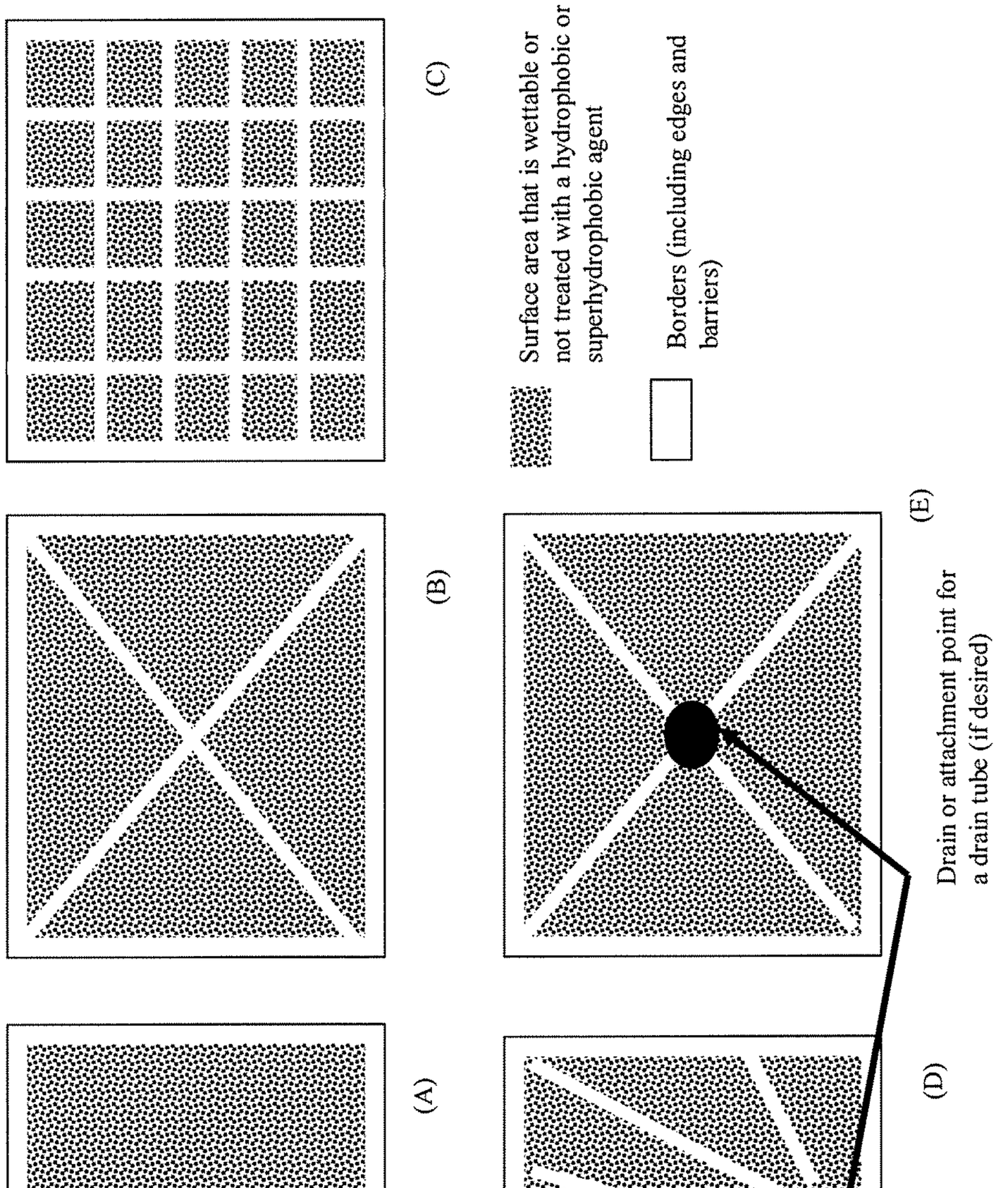

(C)
(B)
(A)
(E)
(D)
Surface area that is wettable or not treated with a hydrophobic or superhydrophobic agent
Borders (including edges and barriers)
Drain or attachment point for a drain tube (if desired)

Figure 3

Figure 4

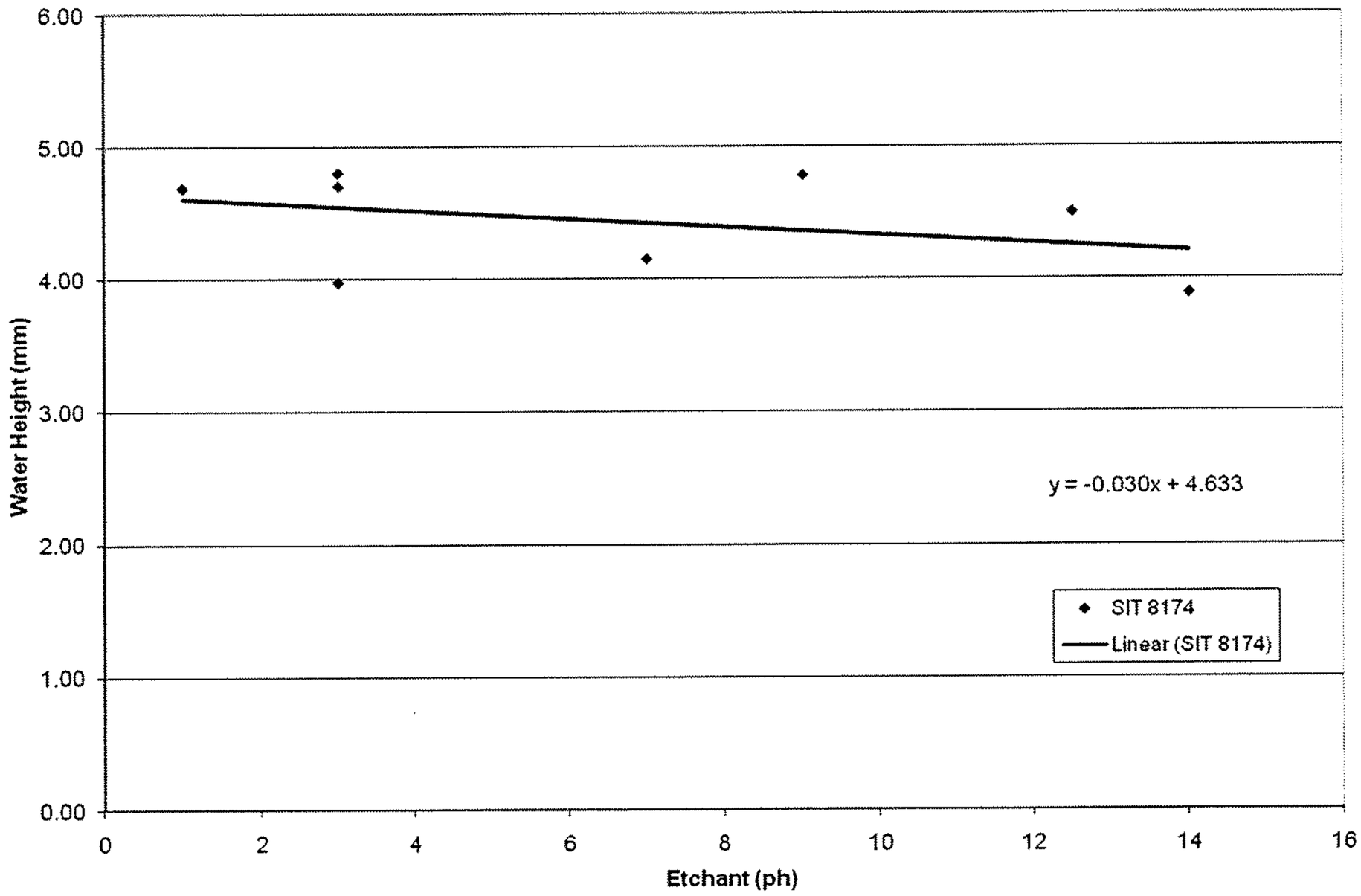


Figure 5

Figure 5

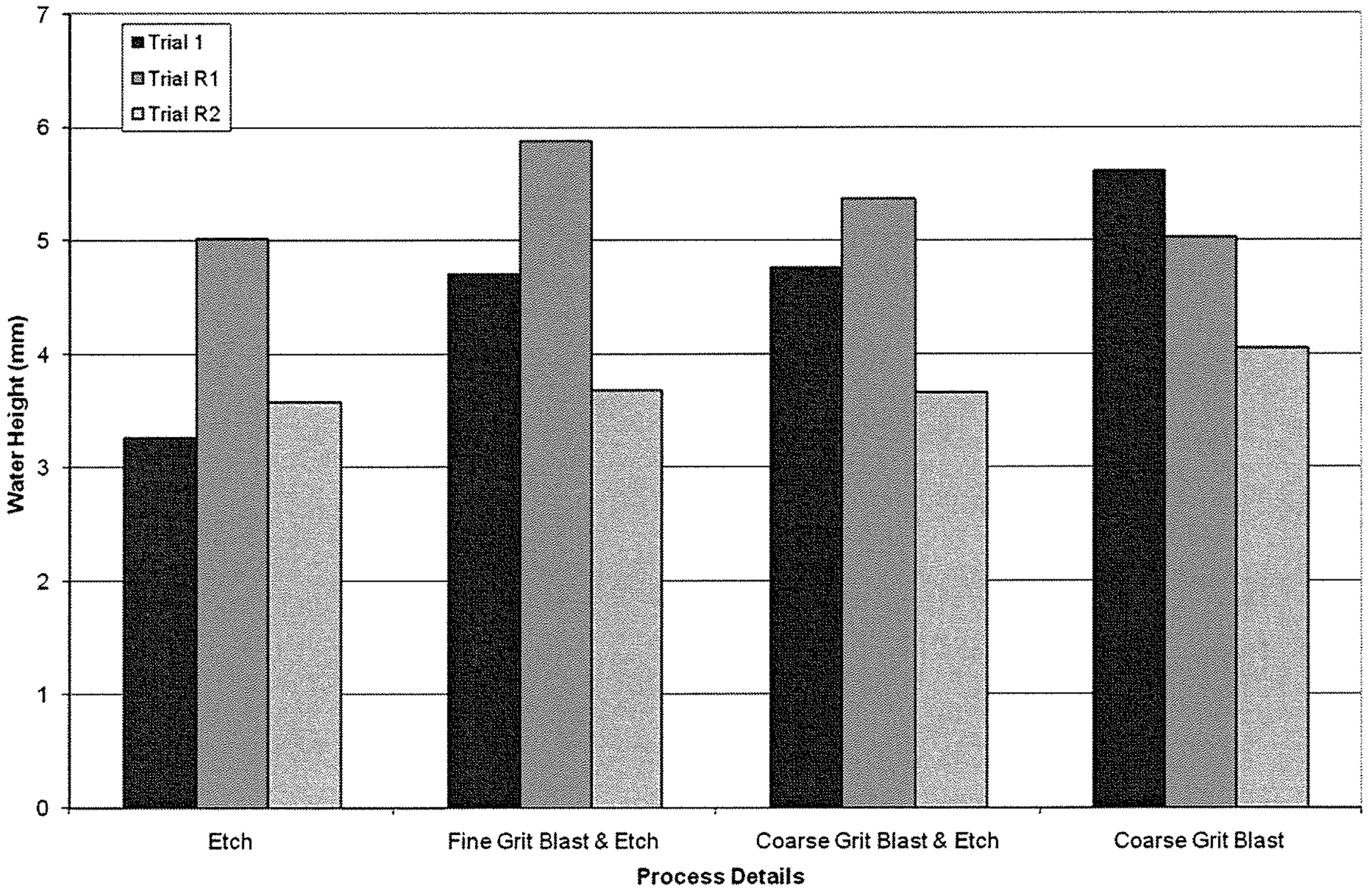

Trial 1
Trial R1
Trial R2
Water Height (mm)
0
1
2
3
4
5
6
7
Etch
Fine Grit Blast & Etch
Coarse Grit Blast & Etch
Coarse Grit Blast
Process Details

Figure 6:

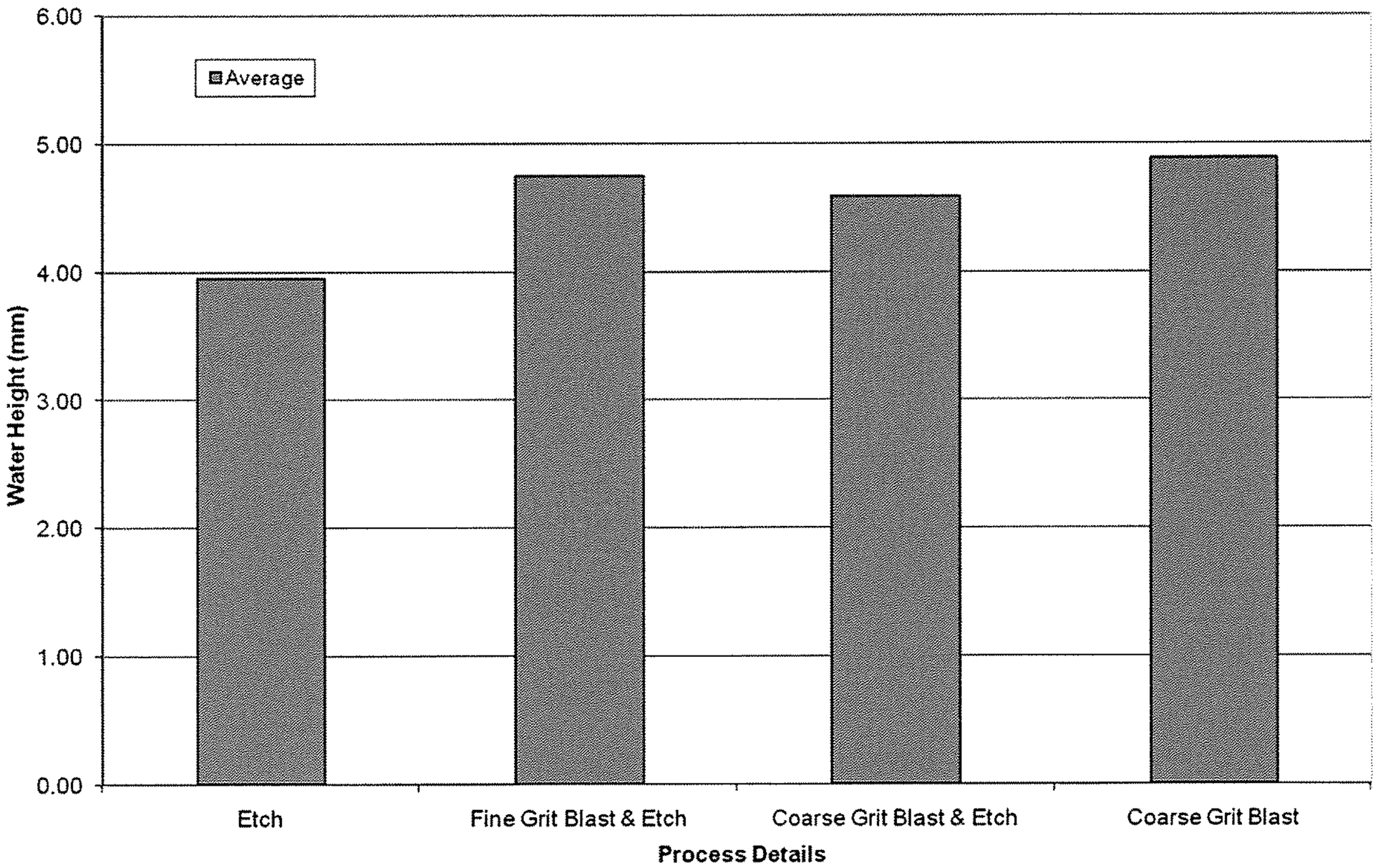
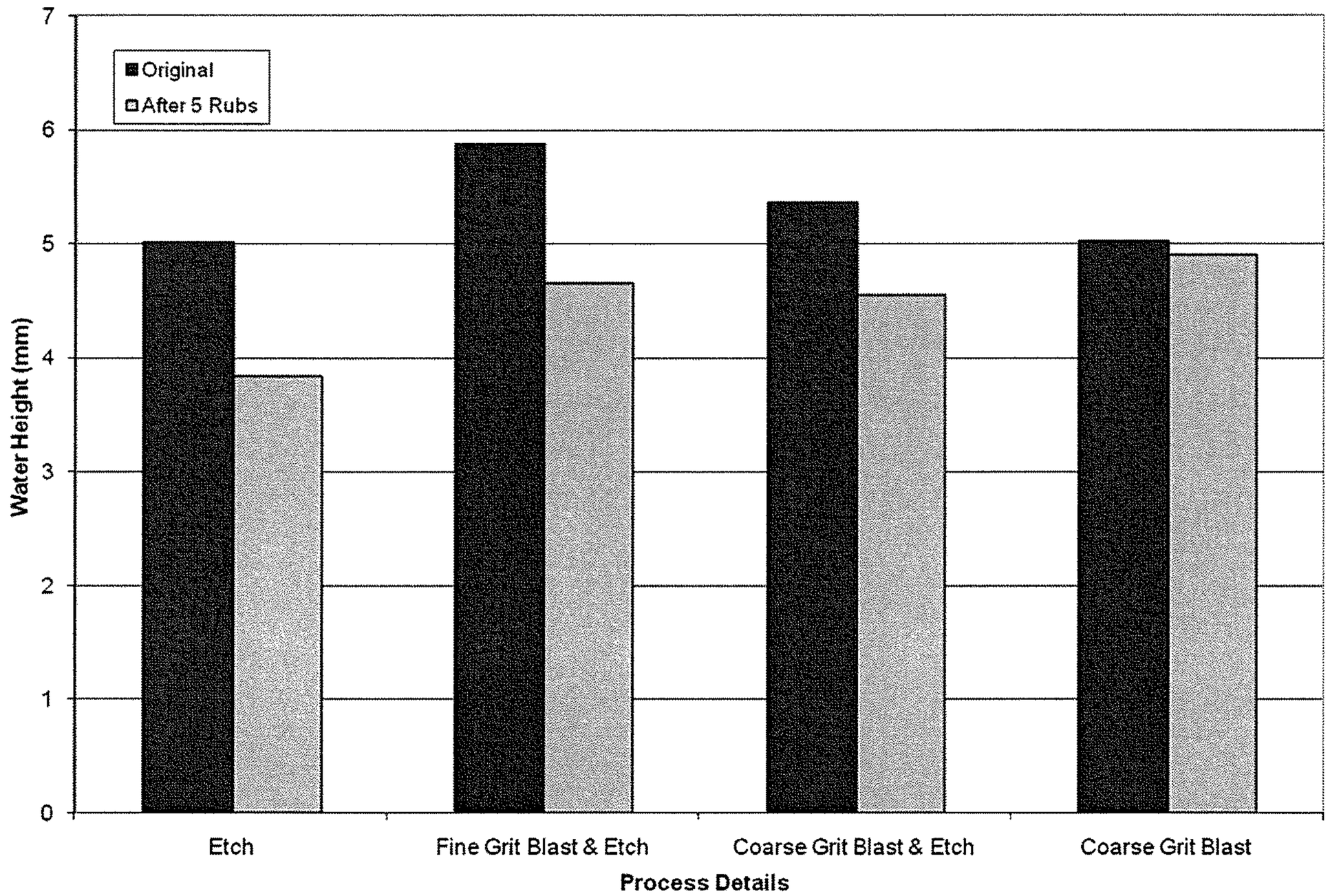
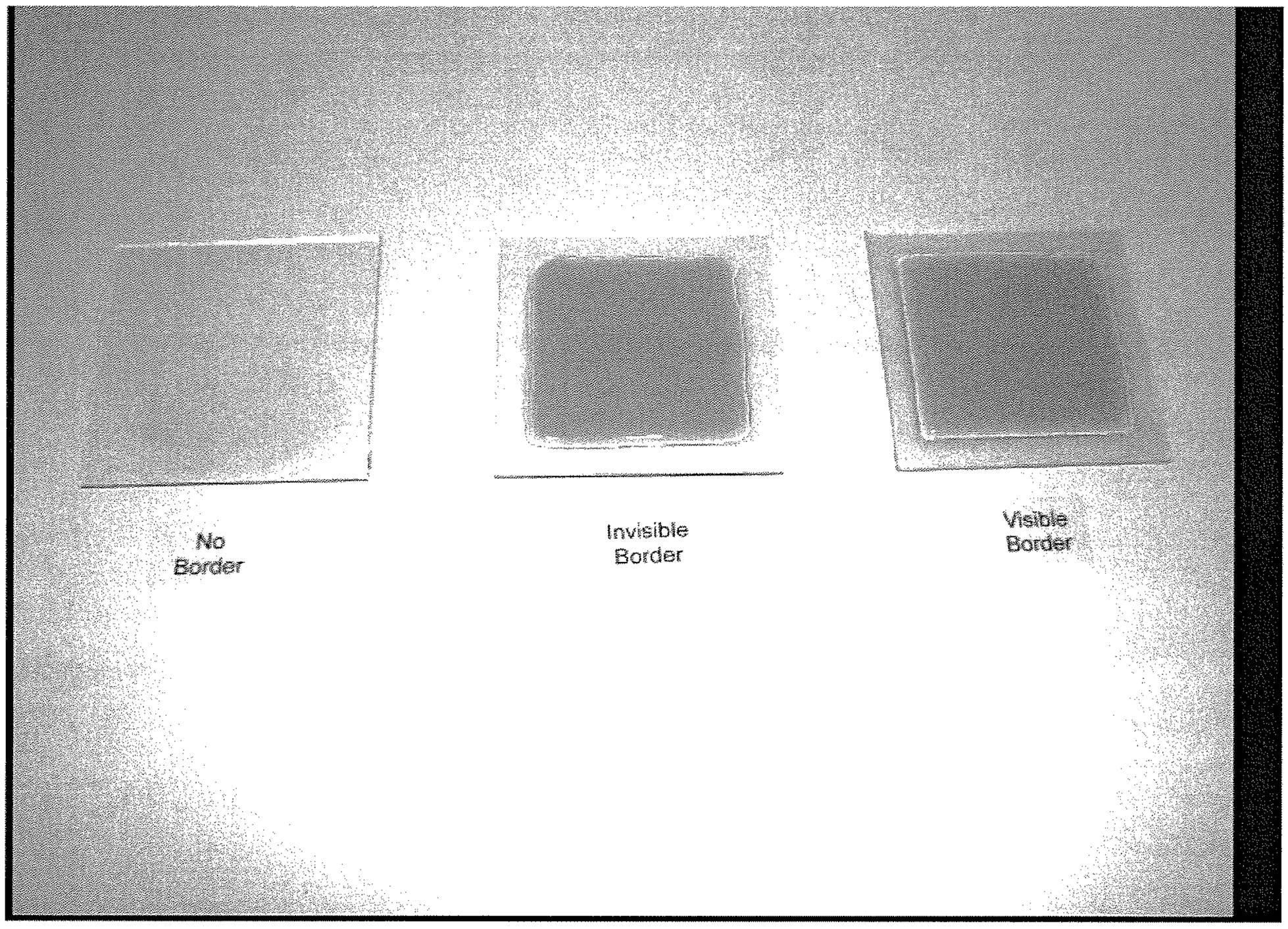
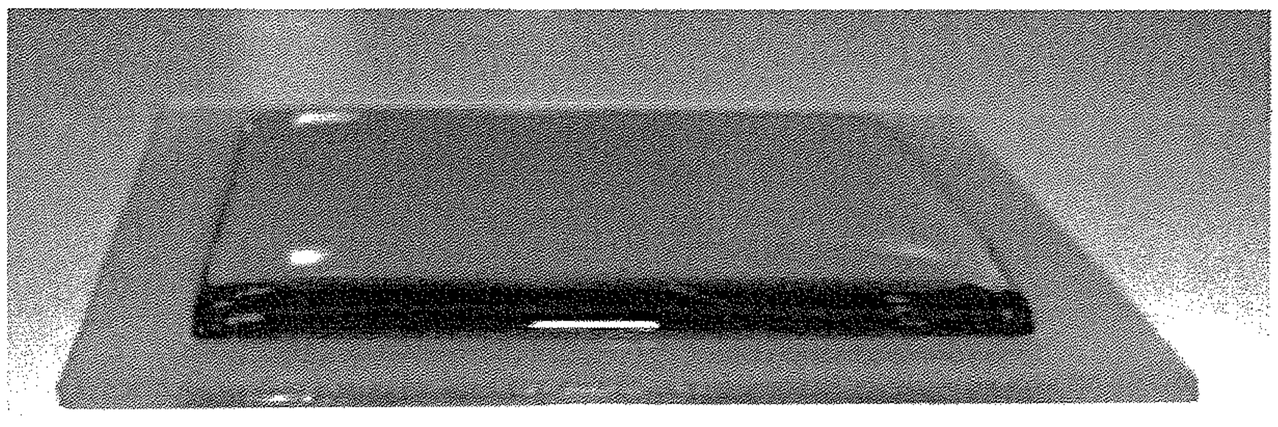

6.00
5.00
4.00
3.00
2.00
1.00
0.00
Average
Water Height (mm)
Etch
Fine Grit Blast & Etch
Coarse Grit Blast & Etch
Coarse Grit Blast
Process Details

Figure 7


Original
After 5 Rubs
Water Height (mm)
0
1
2
3
4
5
6
7
Etch
Fine Grit Blast & Etch
Coarse Grit Blast & Etch
Coarse Grit Blast
Process Details

Photographs of the plates shown in Figure 1B with water dyed blue and a close up of the plate with a visible border at a lower angle.





Micrographs of Borders produced by sandblasting with coarse, medium or fine abrasive particles followed by etching the borders with HF

Borders that are not visible (clear) can not be photographed.

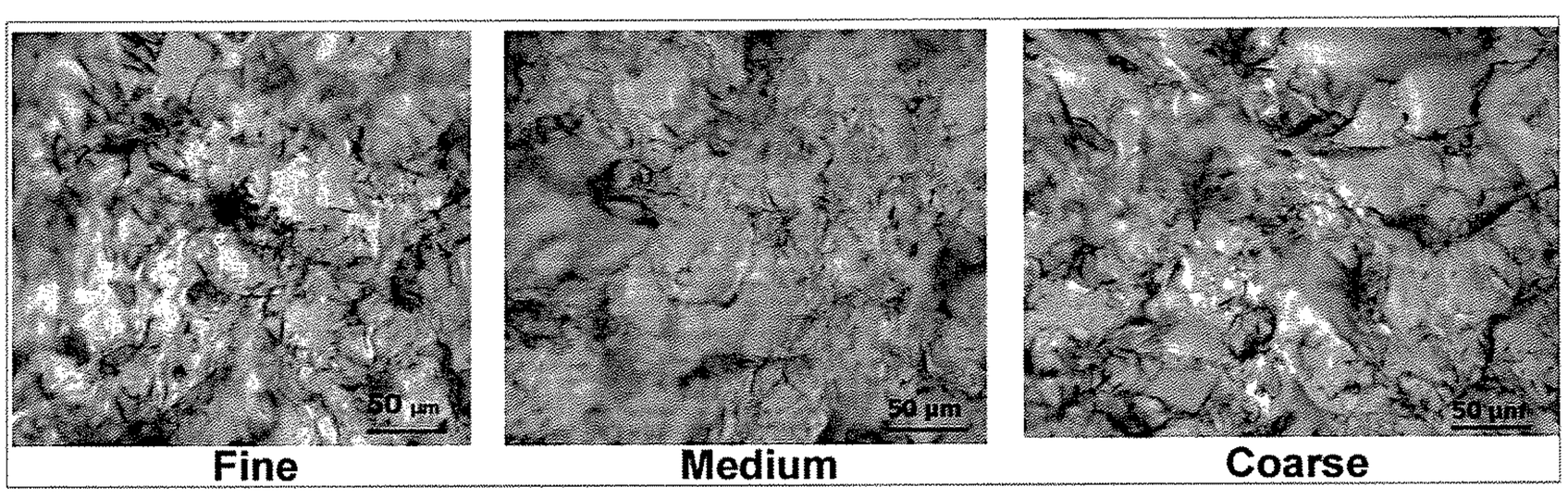


Figure 1

Figure 1 Panel A

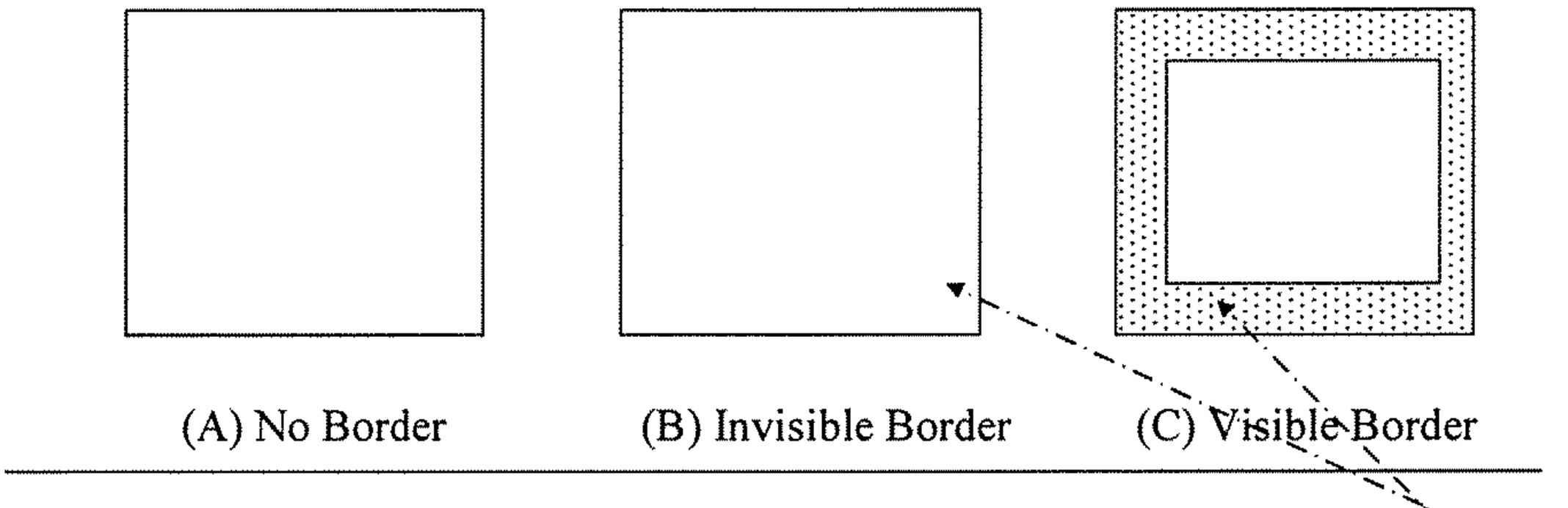


Figure 1 Panel B

