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(54) Title: CARRIER WITH ANISOTROPIC WETTING SURFACES

(57) Abstract: A carrier with an anisotropic wetting surface including a substrate with a multiplicity of asymmetric substantially uniformly shaped asperities thereon. Each asperity has a first asperity rise angle and a second asperity rise angle relative to the substrate. The asperities are structured to present a desired retentive force ratio (f_1/f_2) greater or less than unity caused by asymmetry between the first asperity rise angle and the second asperity rise angle according to the formula: $f_3/f_2 = \sin(\omega_3 + 1/2\Delta\Theta_0)/\sin(\omega_2 + 1/2\Delta\Theta_0)$. Entire surfaces or portions of surfaces of the carrier may be provided with the anisotropic wetting surfaces. The anisotropic wetting qualities may ensure that small droplets of liquid drain fully from the surface or, alternately, may ensure that droplets are retained in areas where they dry so that any contaminants are unlikely to cause harm.



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CARRIER WITH ANISOTROPIC WETTING SURFACESRELATED APPLICATIONS

This application claims the benefit of U.S. Utility Patent Application No. 11/228,897, entitled CARRIER WITH ANISOTROPIC WETTING SURFACES, filed September 16, 2005, and hereby fully incorporated herein by reference. NOTE: A petition has been filed to convert the above referenced utility application to a provisional application, however, such conversion is intended to have no effect on the claim to priority to the above referenced application.

FIELD OF THE INVENTION

The present invention relates generally to carriers for delicate electronic components, and more particularly to a carrier having drainable surfaces formed thereon.

BACKGROUND OF THE INVENTION

The process of forming semi-conductor wafers or other delicate electronic components into useful articles requires high levels of precision and cleanliness. As these articles become increasingly complex and miniaturized, contamination concerns grow. Contamination problems are reduced by providing controlled fabrication environments known as "clean rooms". Such clean rooms are protected from chemical and particulate contamination to the extent technically and economically feasible.

While clean rooms substantially remove most contaminants found in ambient air, it is often not possible or advisable to completely process components in the same clean room environment. Moreover, not all contamination and contaminants are eliminated. For that and other reasons, delicate electronic components are transported, stored, and fabricated in bulk using protective carriers. Examples of specialized carriers are disclosed in U.S. Patent Nos. 6,439,984; 6,428,729; 6,039,186; 6,010,008; 5,485,094; 5,944,194; 4,815,601; 5,482,161; 6,070,730; 5,711,427; 5,642,813; and 3,926,305, all assigned to the owner of the present invention, and all of which are hereby fully incorporated herein by reference. For the purposes of the present application, the term "carrier" includes, but is not limited to: semiconductor wafer carriers such as H-bar wafer carriers, Front Opening Unified Pods (FOUPs), and Standard Mechanical Interface Pods (SMIFs); reticle carriers;

tray carriers; carrier tapes; substrate carriers, and other carriers used in the micro-electronic industry for storing, transporting, fabricating, and generally holding small electronic components such as hard drive disks and other miscellaneous mechanical devices.

5 Contamination and contaminants can be generated in many different ways. For example, particulates can be generated mechanically by wafers as they are inserted into and removed from wafer carriers, and as doors are attached and removed from the carriers, or they can be generated chemically in reaction to different processing fluids. Contamination can also be the result of out-gassing on the carrier itself, biological in
10 nature due to human activity, or even the result of improper or incomplete washing of the carrier. Contamination can also occur on the exterior of a carrier as it is transported from station to station during processing.

 Process contaminants and contamination may be reduced by periodically washing and/or cleaning carriers. Typically, a carrier is cleaned of contaminants and contamination
15 by placing it in a cleaning apparatus, which subjects the exterior and interior surfaces to a flood or spray of cleaning fluids. After the washing step, a considerable amount of fluid may remain on the carrier. This residual fluid is typically dried with a stream of dry gas or by centrifugal spinning.

 Carriers often have intricate arrangements of surfaces that are difficult to dry. In
20 addition, a residual amount of the cleaning fluid may adhere to the surfaces of a carrier as a film or in a multiplicity of small droplets after the washing step. Any contaminants suspended in the residual cleaning fluid may be redeposited on the surface as the fluid dries, leading to contaminant carryover when the carrier is reused. Consequently, process efficiency and effectiveness is diminished overall.

25 Drainable surfaces are of special interest in commercial and industrial applications for a number of reasons. In nearly any process where a liquid must be dried from a surface, significant efficiencies result if the surface sheds the liquid without heating or extensive drying time. Often an appliance has a desired orientation for drying such that fluids are not retained in cavities or low spots due to the influence of gravity.

It is now well known that surface roughness has a significant effect on the degree of surface wetting. It has been generally observed that, under some circumstances, roughness can cause liquid to adhere more strongly to the surface than to a corresponding smooth surface. Under other circumstances, however, roughness may cause the liquid to
5 adhere less strongly to the rough surface than the smooth surface. In some circumstances, surface roughness may cause the surface to demonstrate directionally biased wetting.

Efforts have been made previously at introducing intentional roughness on a surface to produce an ultraphobic surface. The roughened surface generally takes the form of a substrate member with a multiplicity of microscale to nanoscale projections or
10 cavities, referred to herein as “asperities”.

What is still needed in the industry is a carrier with features that promote more effective cleaning and drying of the carrier with reduced levels of residual process contamination.

SUMMARY OF THE INVENTION

15 In an embodiment, the present invention includes a carrier with anisotropic wetting surfaces for promoting more effective cleaning and drying of the carrier. According to the invention, entire surfaces or portions of surfaces of a carrier are made to effect anisotropic wetting so that fluids flow off of the surface readily in a desired draining orientation. The anisotropic wetting surfaces of the carrier cause liquids that may come in contact with the
20 surface, such as may be used in cleaning, to quickly and easily “roll off” without leaving a liquid film or substantial number of liquid droplets. As a result, less time and energy is expended in drying the surfaces, and redeposited residue is minimized, thereby improving overall process quality. In addition, the anisotropic wetting surfaces may be resistant to initial deposition of contaminants, where the contaminants may be in liquid or vapor form.

25 In an embodiment of the invention, the anisotropic wetting surface includes a multiplicity of closely spaced asymmetric microscale to nanoscale asperities formed on a substrate. For the purpose of the present application, “microscale” generally refers to dimensions of less than 100 micrometers, and “nanoscale” generally refers to dimensions of less than 100 nanometers.

The invention is a carrier having a durable generally lyophobic or ultraphobic surface that has anisotropic wetting qualities. That is, fluids will demonstrate a variable resistance to flow across the surface depending on the direction in which they flow. The anisotropic wetting surface generally includes a substrate portion with a multiplicity of projecting asymmetrical regularly shaped microscale or nanoscale asperities.

The asperities may be formed in or on the substrate material itself or in one or more layers of material disposed on the surface of the substrate. The asperities may be any regularly or irregularly shaped three dimensional solid or cavity and may be disposed in any regular geometric pattern or randomly.

Microscale asperities according to the invention may be formed using known molding and stamping methods by texturing the tooling of the mold or stamp used in the process. The processes could include injection molding, extrusion with a textured calendar roll, compression molding tool, or any other known tool or method that may be suitable for forming microscale asperities. Smaller scale asperities may be formed using photolithography, or using nanomachining, microstamping, microcontact printing, self-assembling metal colloid monolayers, atomic force microscopy nanomachining, sol-gel molding, self-assembled monolayer directed patterning, chemical etching, sol-gel stamping, printing with colloidal inks, or by disposing a layer of parallel carbon nanotubes on the substrate.

The creation of asymmetric asperities can directionally bias the retentiveness of a surface. This approach can be applied to flat surfaces as well as curved surfaces such as tubes or troughs. Directionally biased fluid retention can be incorporated into conventionally wetting surfaces as well as ultraphobic surfaces. The asymmetric features can be random or periodic in design. Periodic asperities may vary in two dimensions such as structured stripes, ridges, troughs or furrows. Periodic asperities may also vary in three dimensions such as posts, pyramids, cones or holes. The size, shape, spacing and angles of the asperities can be tailored to achieve a desired anisotropic wetting behavior.

Generally, anisotropic wetting qualities are effective with droplets on surfaces and slugs within tubes, troughs or channels. Surfaces having anisotropic wetting qualities can be used to ensure that small droplets of liquid drain fully from the surface or, alternately,

can be used to help ensure that droplets are retained in areas where when they dry any contaminants are unlikely to cause harm.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view of an embodiment of a carrier with anisotropic wetting surfaces thereon according to the present invention;

Fig. 2 is a perspective view of an "H-bar" carrier with anisotropic wetting surfaces thereon according to the present invention;

Fig. 3 is a perspective view of a SMIF pod carrier with anisotropic wetting surfaces thereon according to the present invention;

Fig. 4 is a perspective view of a wafer shipper with anisotropic wetting surfaces thereon according to the present invention;

Fig. 5 is a perspective view of the base and cassette portions of the shipper depicted in Fig. 4;

Fig. 6 is a perspective view of a reticle pod with anisotropic wetting surfaces thereon according to the present invention;

Fig. 7 is a perspective view of a magnetic disk shipper with anisotropic wetting surfaces thereon according to the present invention;

Fig. 8 is a perspective view of a tray carrier with anisotropic wetting surfaces thereon according to the present invention;

Fig. 9 is a cross-sectional view of the tray carrier of Fig. 8 taken at section 8-8 of Fig. 8;

Fig. 10 is a top plan view of a section of carrier tape with anisotropic wetting surfaces thereon according to the present invention;

Fig. 11 is a perspective view of a flat panel display carrier with anisotropic wetting surfaces thereon according to the present invention;

Fig. 12 is a perspective view of a transport box with anisotropic wetting surfaces thereon according to the present invention;

Fig. 13a is a cross-sectional view of a capillary tube with smooth wall surface;

Fig. 13b is a cross-sectional view of a capillary tube with a wall surface having symmetrical asperities;

Fig. 13c is a cross-sectional view of a capillary tube with a wall surface having asymmetrical asperities;

Fig. 14 is a cross-sectional view of a liquid slug in a capillary tube, where the slug is under the influence of an external force.

Fig. 15a is an enlarged side view of the contact line of a liquid slug interacting with a surface asperity or feature, wherein the contact line is advancing;

Fig. 15b is an enlarged side view of the contact line of a liquid slug interacting with a surface asperity or feature, wherein the contact line is receding;

Fig. 16a is an enlarged fragmentary cross-sectional view of a capillary tube wall having symmetrical, generally saw-tooth shaped asperities;

Fig. 16b is an enlarged fragmentary cross-sectional view of a capillary tube wall having asymmetrical, generally saw-tooth shaped asperities;

Fig. 16c is an enlarged fragmentary perspective view of an anisotropic fluid contact surface with asperities in the form of asymmetrical, generally saw-tooth shaped ridges;

Fig. 16d is an enlarged fragmentary perspective view of an anisotropic fluid contact surface with asymmetrical prismoid asperities;

Fig. 16e is an enlarged fragmentary perspective view of an anisotropic fluid contact surface with asymmetrical frusto-conical asperities;

Fig. 17 is a graph of the ratio of retention forces of a surface with symmetric saw-tooth features relative to a corresponding smooth surface;

Fig. 18 is a graph of the ratio of retention forces of a surface with asymmetric saw-tooth features versus rise angle;

5 Fig. 19 is a graph of the ratio of retention forces of a surface with asymmetric saw-tooth features versus rise angle; and

Fig. 20 is a side view of a sessile liquid drop at a critical condition where $F_i = f_i$.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 generally depicts a wafer container 22. Wafer container 22 has an enclosure portion 24, constructed of polycarbonate plastic. Enclosure portion 24 generally includes a closed top 26, a closed bottom 30, a pair of opposing closed sides 32, 34, and a closed back 36. A door 38 completes the enclosure by enclosing the open front 39 of enclosure portion 24. Door 38 fits into door recess 40. A pair of wafer supports 41 are provided in enclosure 24 to support semi-conductor wafers. Each wafer support 41 has a plurality of ribs 42, forming recesses 43, thereby defining slots or shelves for supporting the wafer disks when container 22 is in use. Each shelf defines a wafer seating position for a wafer. Anisotropic wetting fluid contact surface 28 may be formed on the entire surface of carrier 22 or on any desired portion thereof as depicted. Thus, anisotropic wetting fluid contact surfaces 28 may be placed in any desired location on the carrier 22 while other portions have conventional surfaces. Anisotropic wetting fluid contact surface 28 may be formed in any of a variety of configurations and using a variety of processes as described hereinbelow.

Fig. 2 depicts an "H-bar" wafer carrier 44 having anisotropic wetting fluid contact surfaces 28. Carrier 44 has a first "H-bar" upright front end member 45, a second upright member 46 having an intermediate section 47 and sidewalls 48 with slots 49 for holding the wafers. Carrier 44 has an open top 50 for receiving wafers and an open bottom 51. Again, anisotropic wetting fluid contact surface 28 may be formed on the entire surface of carrier 44 or on any desired portion thereof

Fig. 3 is an exploded view of a standardized mechanical interface (SMIF) pod 52 having anisotropic wetting fluid contact surfaces 28. Pod 52 generally includes box 53 with open bottom 54, and door 55 to sealingly close the open bottom 54. Wafer cassette 56 rests on door 55 and provides slots 57 for holding wafers. Other details of SMIF pods are generally disclosed in U.S. Patent No. 5,482,161, hereby fully incorporated herein by reference. Anisotropic wetting fluid contact surface 28 may be formed on the entire surface of pod 52 or on any desired portion, such as cassette 56 or door 55.

Figs. 4 and 5 depict a wafer shipper 58 with anisotropic wetting fluid contact surfaces 28. Wafer shipper 58 generally includes base portion 59, cover portion 60, and cassette 61 for holding a plurality of wafers 62. Other details of wafer shippers are generally disclosed in U.S. Patent No. 5,992,638, hereby fully incorporated herein by reference. Anisotropic wetting fluid contact surface 28 may be formed on the entire surface of shipper 58 or on any desired portion thereof.

Fig. 6 depicts a reticle pod 63 with anisotropic wetting fluid contact surfaces 28. Reticle pod 63 generally includes base 64 with reticle supports 65 for holding a reticle (not depicted) for use in photolithography, and cover 66. Other details of reticle pods are generally disclosed in U.S. Patent No. 6,825,916, hereby fully incorporated herein by reference. Anisotropic wetting fluid contact surface 28 may be formed on the entire surface of pod 63 or on any desired portion thereof.

Fig. 7 depicts a magnetic disk shipper 67 with anisotropic wetting fluid contact surfaces 28. Disk shipper 67 generally includes base 68 defining a plurality of slots 69, each for receiving a magnetic disk 70, and cover 71. Other details of disk shippers are generally disclosed in U.S. Patent No. 6,070,730, hereby fully incorporated herein by reference. Anisotropic wetting fluid contact surface 28 may be formed on the entire surface of shipper 67 or on any desired portion thereof.

Figs. 8 and 9 depict a carrier tray 72 with anisotropic wetting fluid contact surfaces 28 for receiving and holding semiconductor devices or other electronic components such as circuit boards or magnetic hard drive components. Tray 72 generally includes body portion 73 defining a plurality of pockets 74 for receiving components. Anisotropic wetting fluid contact surface 28 may be formed on the entire surface of tray 72 or on any

portion thereof, including for example, only within pockets 74, or only on divider top surfaces 75 or bottom surface 76.

Fig. 10 depicts a component carrier tape 77 with anisotropic wetting fluid contact surfaces 28. Carrier tape 77 generally includes an elongate body 78 formed from thin polymer material and defining a plurality of pockets 79 for containing components. Other details of component carrier tapes are generally disclosed in U.S. Patent No. 6,981,595, hereby fully incorporated herein by reference. Anisotropic wetting fluid contact surface 28 may be formed on the entire surface of tape 77 or on any desired portion thereof, such as only within pockets 79 or only on surrounding surface 80

Similarly, Figs. 11 and 12 depict a flat panel display carrier 81 and a wafer transport box 82, respectively, with anisotropic wetting fluid contact surfaces 28 according to an embodiment of the invention. In sum, it will be appreciated that anisotropic wetting fluid contact surface 28 may be applied to any carrier where such properties may be desirable to facilitate drainage or to otherwise bias or direct fluid movement on surfaces of carriers.

Turning now to an understanding of the structure of anisotropic wetting fluid contact surfaces, cylindrical capillary tubes 136, each defining a flow channel 138 containing a liquid slug 140 are depicted in longitudinal cross-section in Figs. 13a-c for illustrative purposes. Fig. 13a depicts flow channel 138 of capillary 136 as having a relatively smooth wall surface 142. Fig. 13b depicts flow channel 138 with generally symmetrical saw tooth features 144 on wall 145, the saw tooth features 144 being greatly exaggerated in size for purposes of clarity. Fig. 13c depicts flow channel 138 with asymmetrical saw tooth features 146 on wall 147 forming an anisotropic wetting surface 28 according to an embodiment of the invention, with the asymmetrical saw tooth features 146 again being greatly exaggerated in size for purposes of clarity.

In the smooth tube 136 of Fig. 13a, the retention force— f_0 resisting movement of slug 140 to the left is equal to the retention force f_0 resisting movement to the right. Similarly, in the tube with symmetrical features 144 of Fig. 13b, the retention force — f_1 resisting movement of slug 140 to the left is equal to the retention force f_1 resisting movement to the right. For the tube with asymmetrical features 146 depicted in Fig. 13c, however, with fluid flow generally transverse to the peaks and valleys formed by the

features 146, the retention force f_3 resisting movement of slug 140 to the left is less by a measurable degree than the retention force f_2 resisting movement to the right. As will be discussed in more detail hereinbelow, this difference in retention force is determined by the geometry of the surface features. By disposing asymmetrical surface features according to predetermined relationships as described herein, the difference in retention force produces an anisotropic wetting fluid contact surface.

It will be appreciated that the liquid slugs 140 of Figs. 13a-c, if free from the influence of external forces, will tend to remain stationary in the tubes 136 since there is no energy being applied to overcome inertia and friction. When an external force F is applied to slug 140, depicted in Fig. 14 in capillary tube 136 which has a radius R , the fluid-liquid interfaces 148, 150, distort with both interfaces 148, 150, deflecting in the direction of the applied force. This external force F could arise from, for example, inclination of the tube or fluid pressure applied to end 152 of the tube. Capillary forces present at the leading 154 and trailing 156 contact lines will tend to anchor slug 140, inhibiting movement, until the applied external force F exceeds a critical value, F_i . When this threshold is reached so that F_i equals the retention force f_i , the distorted interfaces 148, 150, of slug 140 exhibit an advancing contact angle, θ_a , at leading contact line 154 and a receding value, θ_r , at trailing contact line 156. If the external force F is further increased such that $F_i > f_i$, slug 140 will begin to move in the direction urged by external force F .

The magnitude of the retention force, f_i , that resists incipient motion within a cylindrical capillary tube of radius R is determined by the fluid-liquid interfacial tension, γ , and the advancing and receding contact angles,

$$f_i = k\gamma R(\cos\theta_r - \cos\theta_a), \quad (1)$$

where

$$k = 2\pi. \quad (2)$$

If the surface is clean, smooth and free of defects, then the retention force can be expressed in terms of inherent contact angles, $\theta_{a,0}$ and $\theta_{r,0}$,

$$f_0 = k\gamma R(\cos\theta_{r,0} - \cos\theta_{a,0}). \quad (3)$$

Surface roughness generally increases retention force over that of a smooth surface. This increase arises from change in the contact angles due to their geometric interaction with surface asperities or features. Consider the contact line of a slug 140 interacting with a surface asperity or feature 146 on a substrate surface 158 as depicted in Figs. 15a and 15b. The rise angle of feature 146 from the substrate surface 158 is denoted ω_i . Fig. 15(a) depicts contact line 162 advancing across feature 146 with an apparent advancing contact angle of θ_a . The liquid exhibits its true advancing contact angle value, $\theta_{a,0}$, on face 164 of feature 146. The difference between the apparent advancing contact angle, θ_a , relative to the substrate surface 158 and true advancing angle, $\theta_{a,0}$, depends on the rise angle subtended by the feature, ω_i . Interaction with feature 146 causes θ_a to increase such that,

$$\theta_a = \theta_{a,0} + \omega_i. \quad (4)$$

Figure 15(b) depicts a contact line 166 retreating across the same feature 146 with an apparent receding contact angle of θ_r . The liquid exhibits its true receding value, $\theta_{r,0}$, on face 164 of feature 146. In contrast to the advancing case, interaction with the feature causes θ_r to decrease so that,

$$\theta_r = \theta_{r,0} - \omega_i. \quad (5)$$

For purposes of example, it may be assumed that the features 144, 146, on the inner surface of capillary tube 136 takes the form of a saw tooth or ratchet pattern depicted in Figs. 16a and 16b, and that the roughness in these tubes is radially symmetric (the features extend around the entire perimeter without variation in their cross-sectional shape). For symmetric features 144 with a rise angle of ω_1 as portrayed in Figure 16(a), the retention forces, $-f_1$ and f_1 are equal and wetting is isotropic. An expression for estimating f_1 comes from the combination of equations (1), (4) and (5),

$$f_1 = k\gamma R[\cos(\theta_{r,0} - \omega_1) - \cos(\theta_{a,0} + \omega_1)], \quad (6)$$

If the inner surface of the capillary tube 136 has the asymmetric features 146 depicted in Figure 16(b), then the magnitude of a retention force differential, Δf , or the difference between f_3 and f_2 , may be expressed in terms of ω_2 and ω_3 :

$$\Delta f = f_3 - f_2 = k\gamma R [\cos(\theta_{r,0} - \omega_3) - \cos(\theta_{a,0} + \omega_3) - \cos(\theta_{r,0} - \omega_2) + \cos(\theta_{a,0} + \omega_2)]. \quad (7)$$

Due to geometric limitations, $\theta_{r,0} - \omega_i$ must be $\geq 0^\circ$ and $\theta_{a,0} + \omega_i$ must be $\leq 180^\circ$. A number of trigonometric functions can be applied to separate terms and simplify these expressions. A general form of the retention force, f_i ,

$$f_i/k\gamma R = 2 \sin[\frac{1}{2}(\theta_{r,0} + \theta_{a,0})] \sin(\omega_i + \frac{1}{2}\Delta\theta_0), \quad (8)$$

can be framed in terms of inherent hysteresis, $\Delta\theta_0$,

$$\Delta\theta_0 = \theta_{a,0} - \theta_{r,0}, \quad (9)$$

and rise angles, ω_i , where $i = 0$ for a clean, smooth surface, with $\omega_0 = 0$; $i = 1$ for a surface with symmetric saw tooth features where $\omega_1 > 0$; and $i = 2$ or 3 for a surface with asymmetric features, $\omega_2 \neq \omega_3$. The retention force differential, Δf , from equation (7) that describes the tube with asymmetric roughness can be rewritten as

$$\Delta f = f_3 - f_2 = 2 k\gamma R \sin[\frac{1}{2}(\theta_{r,0} + \theta_{a,0})] [\sin(\omega_3 + \frac{1}{2}\Delta\theta_0) - \sin(\omega_2 + \frac{1}{2}\Delta\theta_0)]. \quad (10)$$

Equation (8) also can be used to express retention forces as ratios. For example, retention forces of a capillary tube with symmetric saw tooth features to the corresponding tube contrasted with a smooth surface yields the ratio,

$$f_1/f_0 = \sin(\omega_1 + \frac{1}{2}\Delta\theta_0)/\sin(\frac{1}{2}\Delta\theta_0). \quad (11)$$

In another example, a ratio of retention forces in a tube with asymmetric saw tooth features where the retention forces are diametrically opposed may be expressed as,

$$f_3/f_2 = \sin(\omega_3 + \frac{1}{2}\Delta\theta_0)/\sin(\omega_2 + \frac{1}{2}\Delta\theta_0). \quad (12)$$

It will be appreciated that whenever this f_3/f_2 , also known as retentive force ratio, exceeds or is less than unity, the surface will exhibit anisotropic wetting behavior, forming anisotropic wetting surface 28. The degree of anisotropic wetting decreases as the retentive force ratio approaches unity. At unity, wetting is isotropic.

It will further be appreciated that an anisotropic wetting fluid contact surface 28 may include asymmetric features of a wide variety of shapes and disposed in a wide

variety of patterns. For example, as depicted in Fig. 16c, anisotropic wetting fluid contact surface 28 may be formed by a succession of saw tooth ridges 170 on a substrate 172. In another example, as depicted in Figs. 16d and 16e, prismoid 174 or frusto-conical 176 asperities may be disposed in a more or less regular pattern on the substrate 172. The asperities may also be virtually any other asymmetrical shape exhibiting opposing rise angles at variance with each other, including nearly any irregularly shaped three dimensional solid or cavity.

From the above examples, it will be appreciated by those of skill in the art that relations may be expressed for retention forces of any type of surface relative to any other type of surface. Fig. 17, for example depicts the ratio of the retention forces of a capillary tube with symmetric saw tooth features relative to the corresponding smooth tube for liquid/solid combinations with different levels of inherent hysteresis, $\Delta\theta_0$. Retention forces are present even if the surface of the tube is smooth and clean, *i.e.*, $|f_0|$ is always > 0 . As ω_1 increases and the surface of the tube becomes rougher, the relative retention force increases. For smaller ω_1 values, the increase in f_1/f_0 is linear. In mathematical terms, if $\omega_1 + \frac{1}{2}\Delta\theta_0 \ll 1$, then equation (11) reduces to

$$f_1/f_0 \approx 2\omega_1/\Delta\theta_0 + 1. \quad (13)$$

It will be appreciated from Fig. 17 and equation (13) that the larger the inherent hysteresis in a system, the less influence the roughness of the surface will exert on the retention force. For example, using Fig. 17 to compare two capillary tubes of equal diameter, one with a smooth inner surface and the other with saw tooth features where $\omega_1 = 10^\circ$, if the liquid and material of construction show an inherent hysteresis of $\Delta\theta_0 = 10^\circ$, then retention force ratio is much larger ($f_1/f_0 = 2.97$) than if $\Delta\theta_0 = 30^\circ$ ($f_1/f_0 = 1.63$).

In another example, Fig. 18 depicts retention force ratios of a tube with asymmetric saw tooth features, f_3/f_2 , plotted against ω_2 for various ω_3 values. Inherent hysteresis of the system is assumed to be $\Delta\theta_0 = 10^\circ$. For a tube with ratchet-like structure where $\omega_2 = 45^\circ$ and $\omega_3 = 90^\circ$, $f_3/f_2 = 1.30$. The greater the difference between ω_2 and ω_3 , the greater the disparity of the retention force in the two opposing directions; if $\omega_2 = 10^\circ$ and $\omega_3 = 90^\circ$, $f_3/f_2 = 3.85$. It is anticipated that a strong directional bias could also be created using

shallow rise angles. If $\omega_2 = 1^\circ$ and $\omega_3 = 10^\circ$, then $f_3/f_2 = 2.48$. Alternatively, if $\omega_2 = 1^\circ$ and $\omega_3 = 90^\circ$, then $f_3/f_2 > 9$.

In yet another example, Fig. 19 depicts the variation in retention force ratios of a surface with asymmetric saw tooth features, f_3/f_2 , versus rise angle, ω_2 , for different levels of inherent hysteresis, $\Delta\theta_0$. In this example, $\omega_3 = 90^\circ$. As with the symmetric features, the retention force ratios are diminished by increases in $\Delta\theta_0$. For instance, in a capillary tube with asymmetric saw tooth features where $\omega_2 = 10^\circ$ and $\omega_3 = 90^\circ$, if the inherent hysteresis is $\Delta\theta_0 = 10^\circ$, then retention force ratio of $f_3/f_2 = 3.85$. If $\Delta\theta_0$ increases to 30° , then f_3/f_2 falls to 2.29.

The above relations may also be practically used to gauge the absolute magnitude of retention forces of surfaces. For example, a water slug in a horizontal PTFE tube with smooth interior surfaces and a radius of $R = 1$ mm exhibits an advancing contact angle of $\theta_{a,0} = 108^\circ$ and inherent hysteresis of $\Delta\theta_0 = 10^\circ$. In the tube without features depicted in Fig. 13a, the retention force that impedes displacement of the slug would be $f_0 = 77 \mu\text{N}$. Therefore, incipient motion of the water slug in either direction would require an external force $> 77 \mu\text{N}$. If a fluid-liquid combination with a lower interfacial tension were employed, the retention forces would be less.

By introducing asymmetric saw tooth features with $\omega_2 = 10^\circ$ and $\omega_3 = 90^\circ$ on the inner surface of the PTFE tube as depicted in Fig. 13c, $\Delta f = 672 \mu\text{N}$. It is of course important to note that the external force to move the slug in either direction will be greater than the value for the smooth tube, $f_2 = 228 \mu\text{N}$ and $f_3 = 900 \mu\text{N}$. Since the smaller retention force, f_2 , is directed to the right, the slug will move easily to the left, Figure 13(c). If the tube is made sufficiently small, the pressure differential to initiate movement is relatively large. For the PTFE tube described above ($\theta_{a,0} = 108^\circ$, $\Delta\theta_0 = 10^\circ$, $\omega_2 = 10^\circ$ and $\omega_3 = 90^\circ$), if the tube diameter were shrunk to $20 \mu\text{m}$, then the pressure differential to move a water slug in one direction versus the other would be approximately 20 kPa.

The size of the features are anticipated to be relatively unimportant for static slugs. Small features should produce the same directionally-biased wetting behavior as large ones. Once a slug begins to move, however, smaller features may have an advantage over larger ones. Smaller features would be less likely to disrupt flow. If too large, surface

features could increase turbulence, thereby increasing flow resistance. Consequently, in some embodiments of the invention wherein anisotropic wetting fluid contact surfaces 28 may experience fluid flow, the average size of asperities forming anisotropic wetting fluid contact surfaces 28 may be generally less than 500 μm , in other embodiments generally less than 10 μm , and in still other embodiments less than 100 nm.

While the discussion above has focused primarily capillary tubes with circular cross-sections, it also applies to non-circular tubes and sessile drops on surfaces. Equations (1) and (12) differ only in the pre-factor k . Also, it will be appreciated by those of skill in the art that with the onset of flow, additional forces must be considered, such as those that arise from liquid viscosity, inertia or vertical displacement.

Fig. 20 is a side view of a stationary sessile drop 180 under the influence of an external force, F_i . The external force distorts the shape of drop 180, causing it to “lean” forward. As depicted, drop 180 has reached a critical state where the retention and external force are equal, $f_i = F_i$. In this critical configuration the contact angle of the drop at the leading edge exhibits advancing value, θ_a , and the trailing edge a receding value, θ_r . If F_i is increased slightly, drop 180 will begin to move. The general equation that describes the retention forces associated with a liquid slug in a capillary also describes the retention forces associated with sessile drops,

$$f_i = k\gamma R(\cos\theta_r - \cos\theta_a), \quad (1)$$

where in this case, $2R$ is the drop width and the pre-factor, k , depends on the shape of the contact line. If the contact line of the sessile drop is circular, then

$$k \approx 1.5 \quad (22)$$

If the drop elongates due to the external force, then k increases.

To initiate movement of a liquid slug or droplet, a minimum external force must be applied to overcome the retention force associated with interfacial tension acting at the contact lines. The magnitude of the retention force increases with the fluid-liquid interfacial tension and surface roughness. If the surface roughness consists of symmetric features, then the increased resistance to incipient motion acts equally in both directions along the axis of the capillary and wetting will be isotropic. If the features are

asymmetric, then the retention force is less in one direction, and wetting will be anisotropic. The greater the asymmetry of the surface features, the greater the disparity of the retention force in the two opposing directions. With the appropriate design of surface features, the retention force differential Δf could exceed 5X. Liquid-solid combinations
5 that show minimal inherent contact angle hysteresis would be expected to show the greater rectification.

This understanding can be applied to the manufacture of carriers as described above. It is often desirable that when liquids are emptied from a carrier that all fluid consistently exit the carrier to avoid retention of fluids that may contaminate the carrier. It
10 can be seen that the above-discussed mathematical relationships can be utilized to design a surface profile that includes asymmetric asperities that will minimize retention forces that tend to retain droplets or slugs within the carrier in a chosen orientation to facilitate drainage and drying.

Alternately, it may be desirable to design a carrier that has maximized retention
15 force in a certain orientation. Here an anisotropic wetting surface may be designed to retain droplets or slugs in portions of the carrier that isolate contaminants away from carried items where they can do no harm.

Generally, the substrate material from which the carrier is made may be any generally lyophobic or ultraphobic material upon which asymmetric micro or nano scale
20 asperities may be suitably formed. The asperities may be formed directly in the substrate material itself, or in one or more layers of other material deposited on the substrate material, by photolithography or any of a variety of suitable methods. Microscale asperities according to the invention may be formed using known molding and stamping methods by texturing the tooling of the mold or stamp used in the process. The processes
25 could include injection molding, extrusion with a textured calendar roll, compression molding tool, or any other known tool or method that may be suitable for forming microscale asperities.

Other methods that may be suitable for forming smaller scale asperities of the desired shape and spacing include nanomachining as disclosed in U.S. Patent Application
30 Publication No. 2002/00334879, microstamping as disclosed in U.S. Patent No. 5,725,788, microcontact printing as disclosed in U.S. Patent No. 5,900,160, self-assembled metal

colloid monolayers, as disclosed in U.S. Patent 5,609,907, microstamping as disclosed in U.S. Patent No. 6,444,254, atomic force microscopy nanomachining as disclosed in U.S. Patent 5,252,835, nanomachining as disclosed in U.S. Patent No. 6,403,388, sol-gel molding as disclosed in U.S. Patent No. 6,530,554, self-assembled monolayer directed
5 patterning of surfaces, as disclosed in U.S. Patent No. 6,518,168, chemical etching as disclosed in U.S. Patent No. 6,541,389, or sol-gel stamping as disclosed in U.S. Patent Application Publication No. 2003/0047822, all of which are hereby fully incorporated herein by reference. Carbon nanotube structures may also be usable to form the desired asperity geometries. Examples of carbon nanotube structures are disclosed in U.S. Patent
10 Application Publication Nos. 2002/0098135 and 2002/0136683, also hereby fully incorporated herein by reference. Also, suitable asperity structures may be formed using known methods of printing with colloidal inks. Of course, it will be appreciated that any other method by which micro/nanoscale asperities may be accurately formed may also be used. A photolithography method that may be suitable for forming micro or nano scale
15 asperities is disclosed in PCT Patent Application Publication WO 02/084340, hereby fully incorporated herein by reference.

Anisotropic wetting surface principles can be applied to ultraphobic surfaces as well. Ultraphobic surfaces are described in the following U.S. Patents and U.S. Patent Applications which are incorporated herein in their entirety by reference: U.S. Patent
20 Applications 10/824,340; 10/837,241; 10/454,743; 10/454,740 and U.S. Patent 6,845,788. The disclosures of the above referenced Applications and Patent can be utilized along with the present application to design surface that demonstrate both anisotropic wetting and ultraphobic properties.

The present invention may be embodied in other specific forms without departing
25 from the central attributes thereof, therefore, the illustrated embodiments should be considered in all respects as illustrative and not restrictive, reference being made to the appended claims rather than the foregoing description to indicate the scope of the invention.

CLAIMS

What is claimed is:

1. A carrier for articles having an anisotropic wetting surface portion, the anisotropic wetting surface portion comprising:

a substrate with a multiplicity of substantially uniformly shaped asperities thereon, each asperity having a first asperity rise angle and a second asperity rise angle relative to the surface, the asperities being structured to present a retentive force ratio (f_3/f_2) greater or less than unity when the retentive force ratio (f_3/f_2) is determined according to the formula:

$$f_3/f_2 = \sin(\omega_3 + \frac{1}{2}\Delta\theta_0)/\sin(\omega_2 + \frac{1}{2}\Delta\theta_0)$$

where ω_2 is the first asperity rise angle in degrees, ω_3 is the second asperity rise angle in degrees, and $\Delta\theta_0 = (\theta_{a,0} - \theta_{r,0})$ where $\theta_{a,0}$ is a true advancing contact angle of a fluid in contact with the surface in degrees, and $\theta_{r,0}$ is a true receding contact angle of the fluid on the surface in degrees.

2. The carrier of claim 1, wherein the asperities are projections.
3. The carrier of claim 2, wherein the asperities are polyhedrally shaped.
4. The carrier of claim 2, wherein the asperities are cylindrical or cylindroidally shaped.
5. The carrier of claim 1, wherein the asperities are cavities formed in the substrate.
6. The carrier of claim 1, wherein the asperities are positioned in a substantially uniform array.
7. The carrier of claim 6, wherein the asperities are positioned in a rectangular array.
8. The carrier of claim 1, wherein the carrier is a wafer container.

9. The carrier of claim 1, wherein the carrier is a SMIF pod.
10. The carrier of claim 1, wherein the carrier is tray.
11. The carrier of claim 1, wherein the carrier is an "H-bar" carrier.
12. The carrier of claim 1, wherein the carrier is a reticle pod.
13. The carrier of claim 1, wherein the carrier is a disk shipper.
14. The carrier of claim 1, wherein the carrier is a wafer shipper.
15. A method of making a carrier for articles with an anisotropic wetting surface, the method comprising:

providing a carrier presenting a surface; and

disposing a multiplicity of substantially uniformly shaped microscale or nanoscale asperities on the surface of the carrier to form the anisotropic wetting surface, each asperity having a first asperity rise angle and a second asperity rise angle relative to the surface, wherein the asperities are structured and disposed so as to present a retentive force ratio (f_3/f_2) greater or less than unity when the retentive force ratio (f_3/f_2) is determined according to the formula:

$$f_3/f_2 = \sin(\omega_3 + \frac{1}{2}\Delta\theta_0)/\sin(\omega_2 + \frac{1}{2}\Delta\theta_0)$$

where ω_2 is the first asperity rise angle in degrees, ω_3 is the second asperity rise angle in degrees, and $\Delta\theta_0 = (\theta_{a,0} - \theta_{r,0})$ where $\theta_{a,0}$ is a true advancing contact angle of a fluid in contact with the surface in degrees, and $\theta_{r,0}$ is a true receding contact angle of the fluid on the surface in degrees

16. The method of claim 15, wherein the asperities are formed by photolithography.
17. The method of claim 15, wherein the asperities are formed by a process selected from the group consisting of nanomachining, microstamping, microcontact printing, self-assembling metal colloid monolayers, atomic force microscopy

nanomachining, sol-gel molding, self-assembled monolayer directed patterning, chemical etching, sol-gel stamping, printing with colloidal inks, and disposing a layer of parallel carbon nanotubes on the substrate.

18. The method of claim 15, further comprising the step of selecting a geometrical shape for the asperities.

19. The process of claim 15, further comprising the step of selecting an array pattern for the asperities.

20. A method of cleaning a carrier for articles, comprising:

providing a carrier presenting an anisotropic wetting surface, the anisotropic wetting surface comprising a substrate with a multiplicity of asymmetric substantially uniformly shaped asperities thereon, each asperity defining a first asperity rise angle and a second opposing asperity rise angle relative to the substrate, the asperities being structured to present a retentive force ratio (f_3/f_2) greater or less than unity when the retentive force ratio (f_3/f_2) is determined according to the formula:

$$f_3/f_2 = \sin(\omega_3 + \frac{1}{2}\Delta\theta_0)/\sin(\omega_2 + \frac{1}{2}\Delta\theta_0)$$

where ω_2 is the first asperity rise angle in degrees, ω_3 is the second asperity rise angle in degrees, and $\Delta\theta_0 = (\theta_{a,0} - \theta_{r,0})$ where $\theta_{a,0}$ is a true advancing contact angle of a fluid in contact with the anisotropic wetting surface in degrees, and $\theta_{r,0}$ is a true receding contact angle of the fluid on the anisotropic wetting surface in degrees; and

contacting the anisotropic wetting surface with the fluid.

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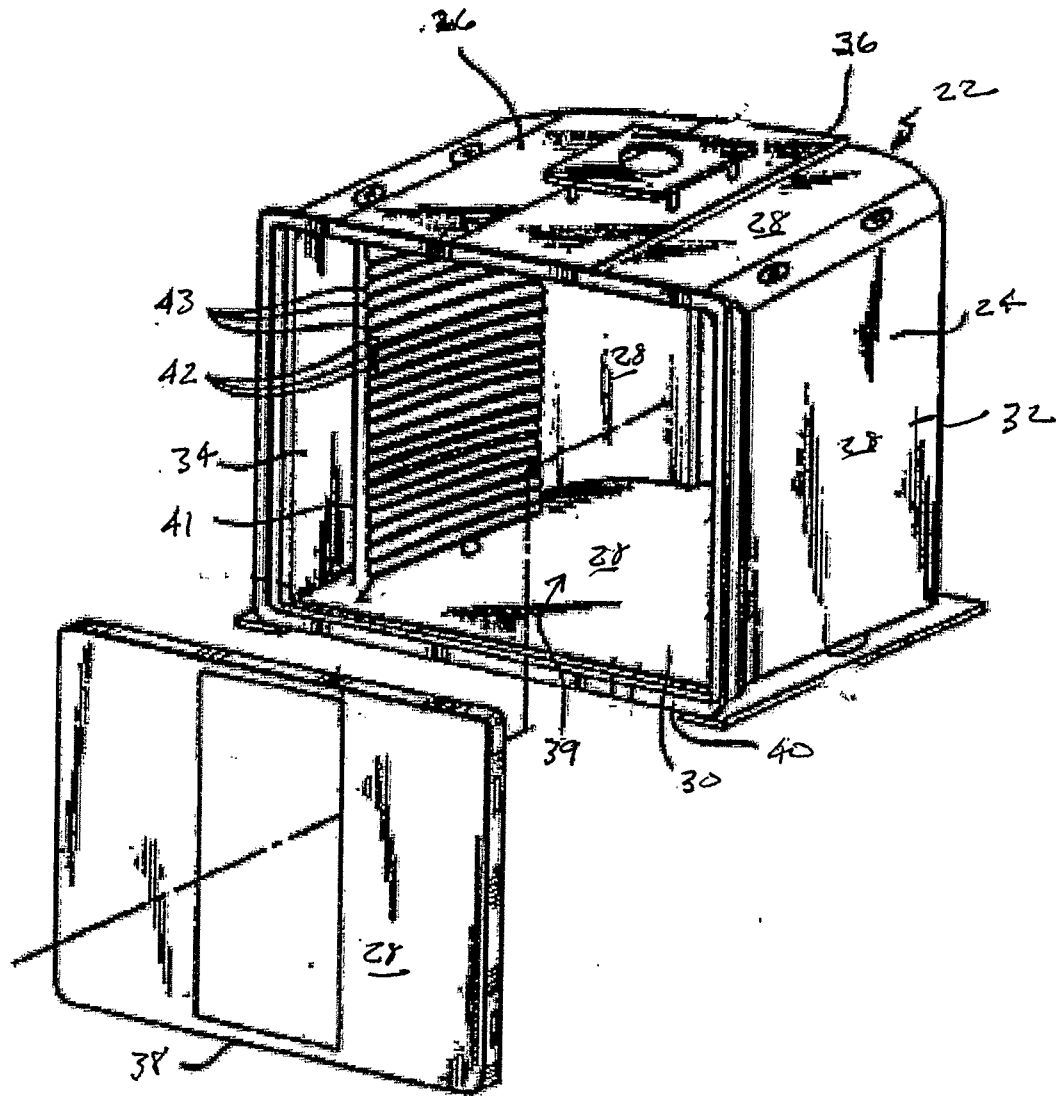


Fig. 1

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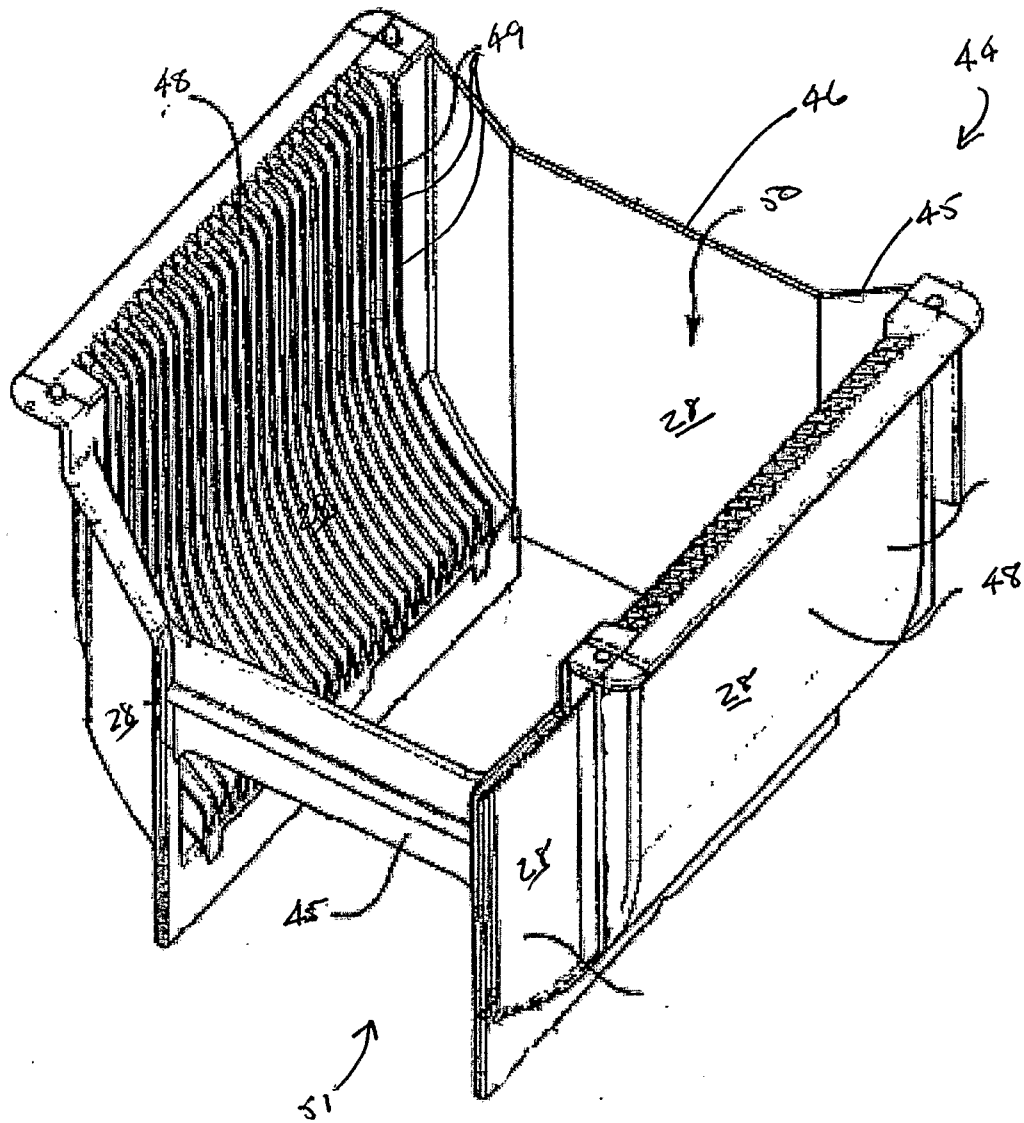


Fig. 2

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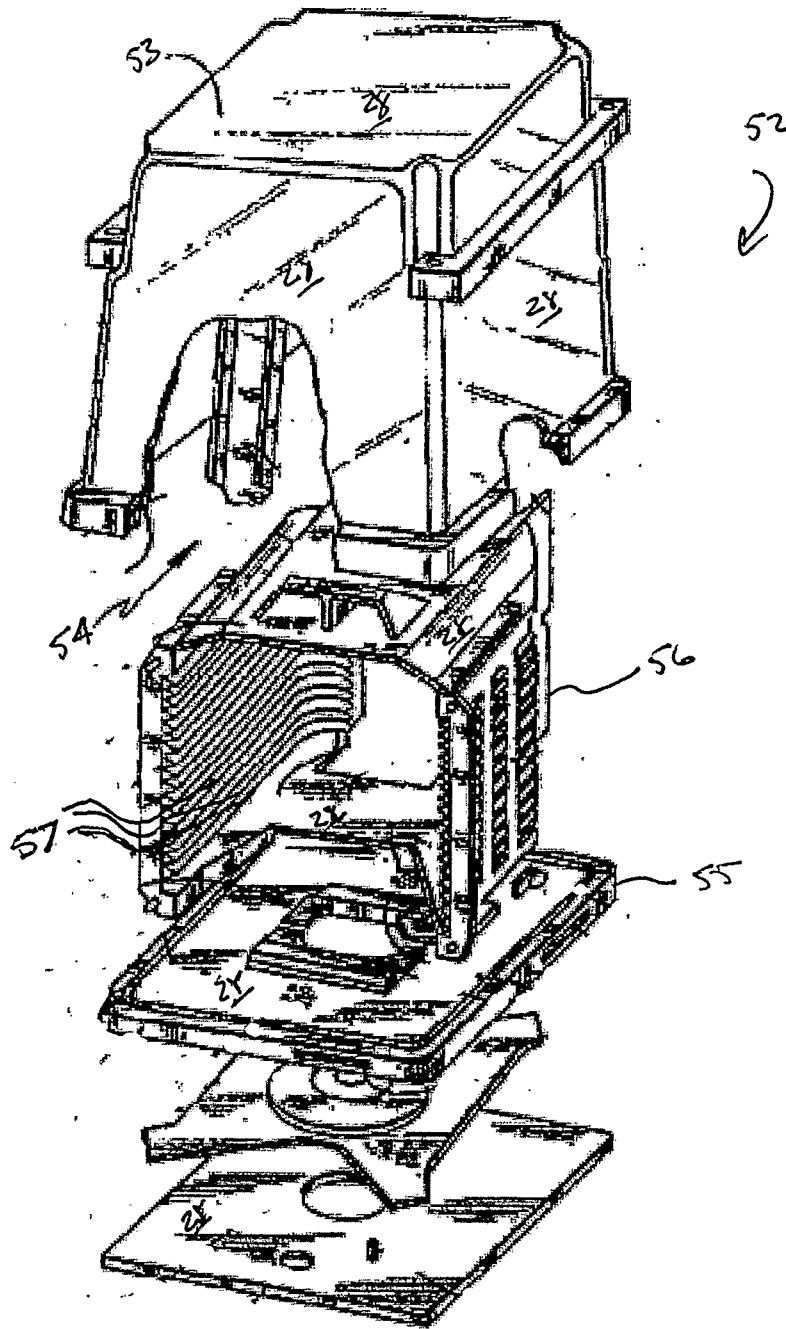


Fig. 3

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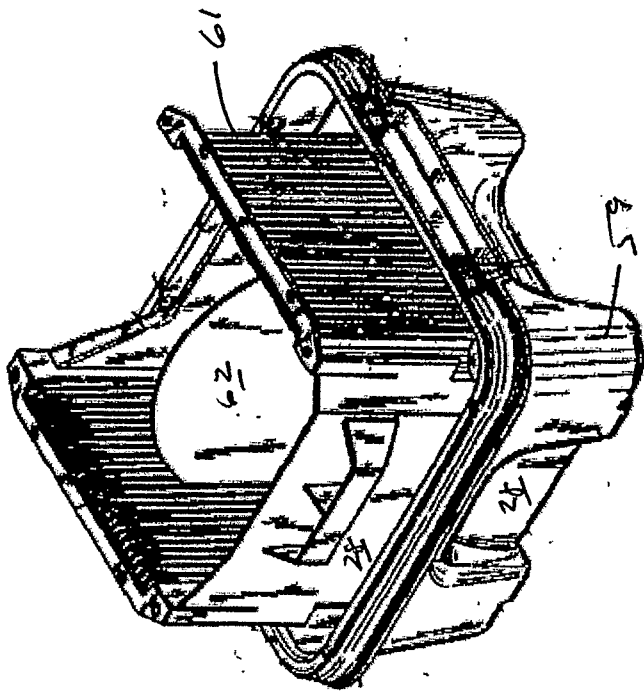


Fig. 5

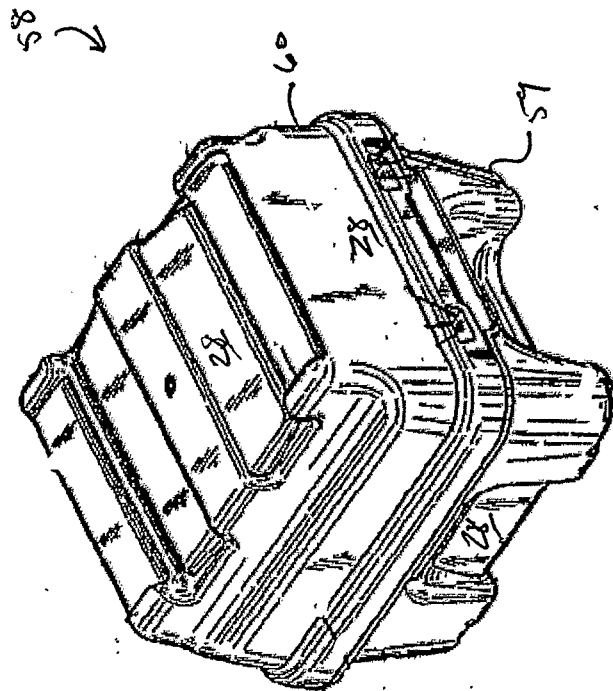


Fig. 4

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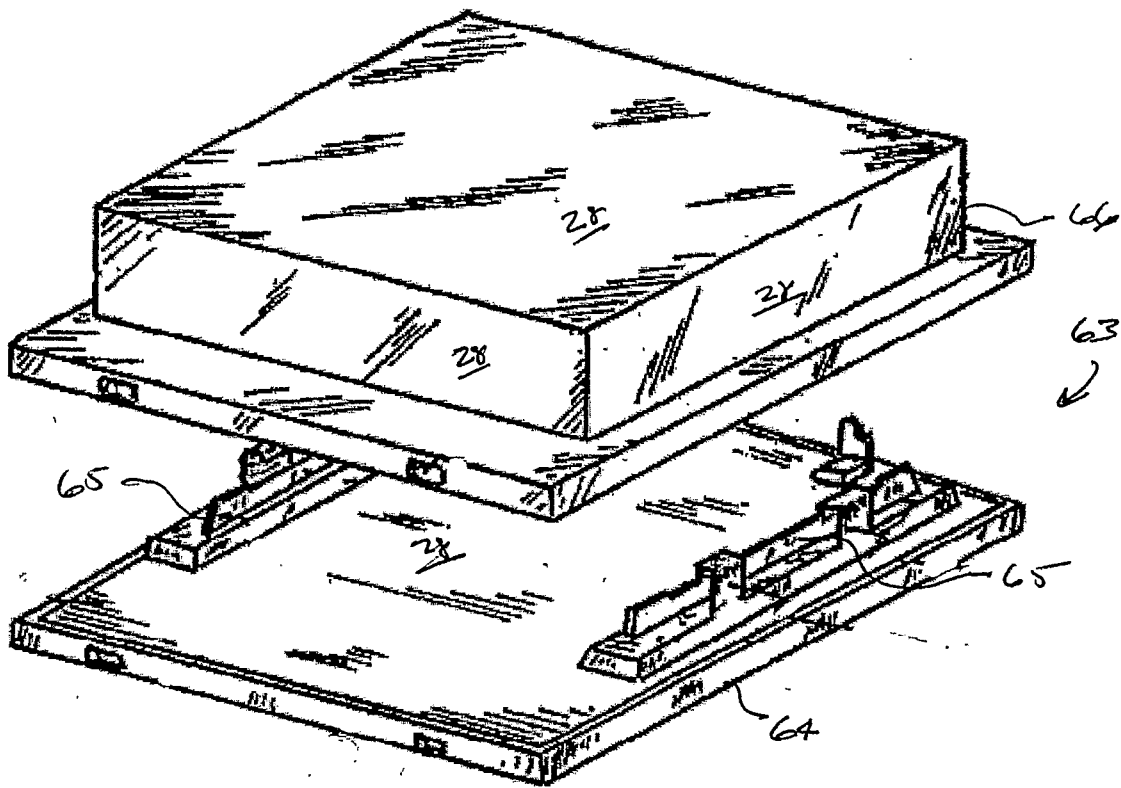


Fig. 6

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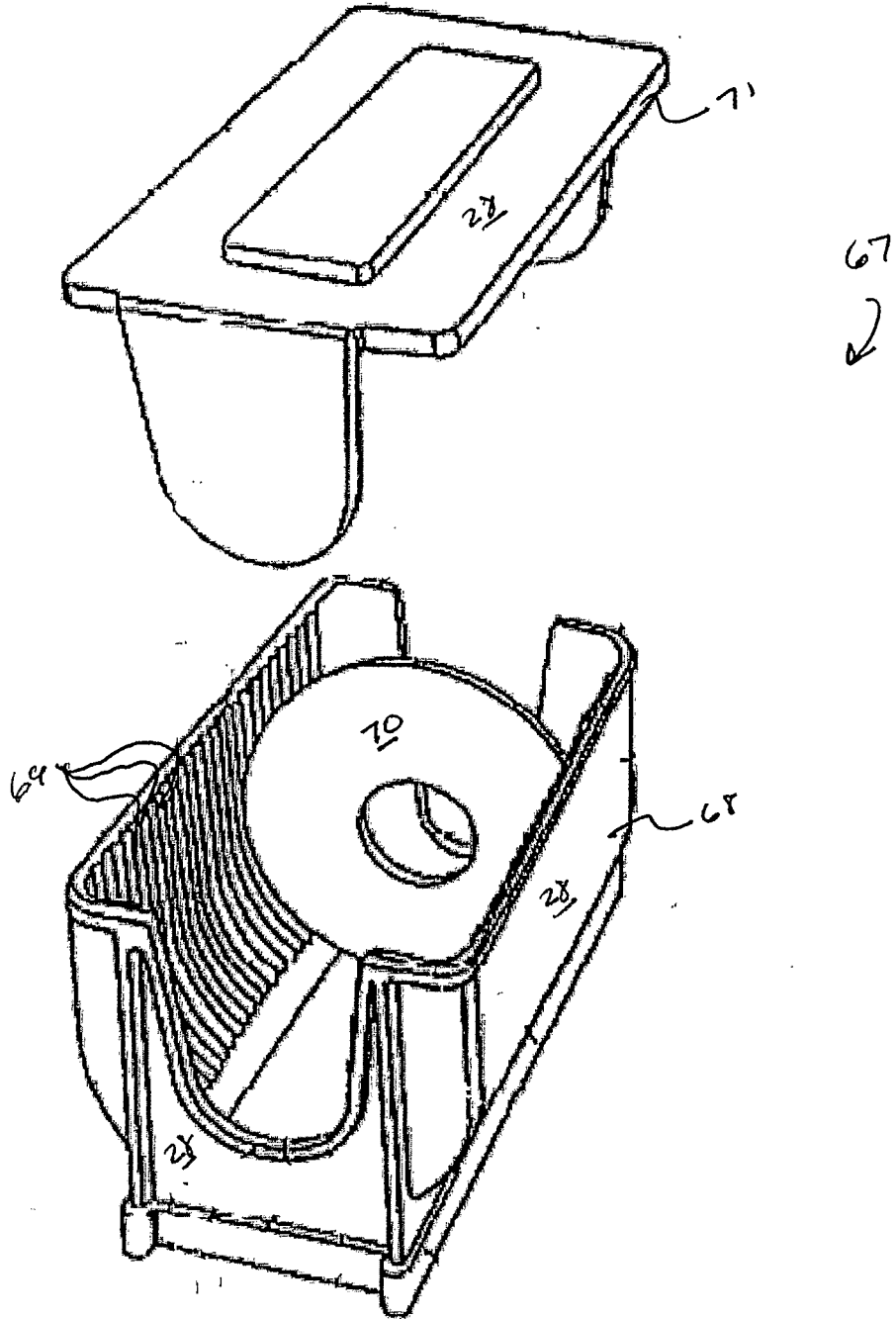


Fig. 7

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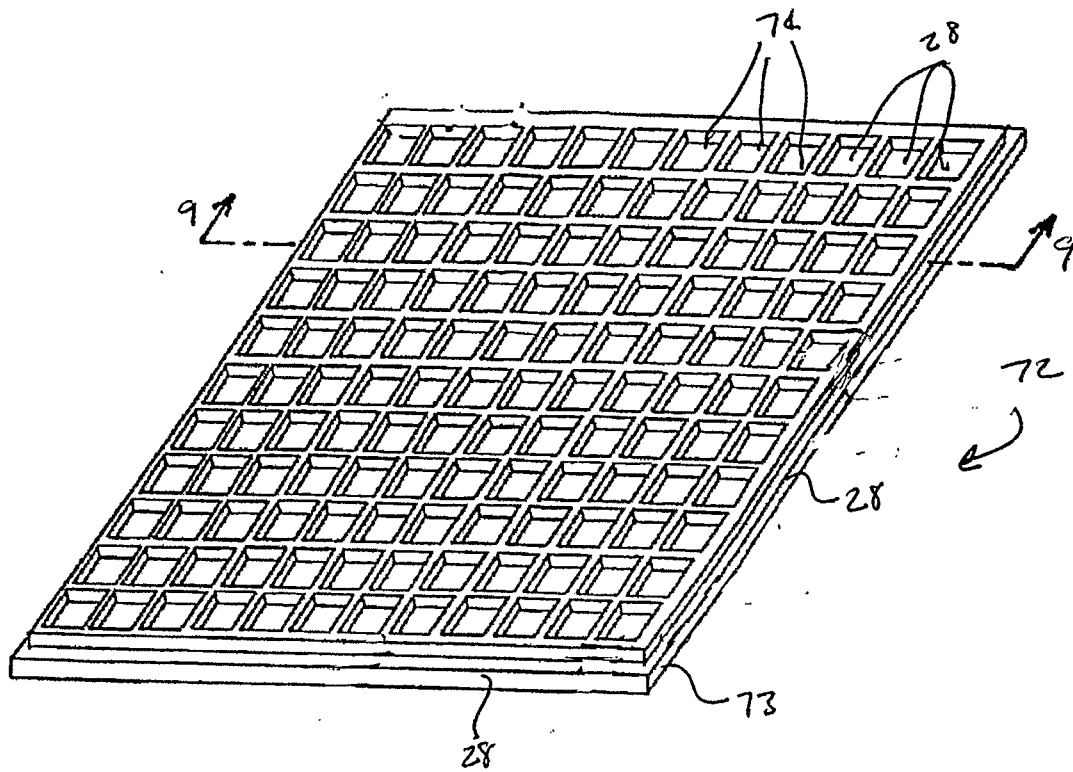


Fig. 8

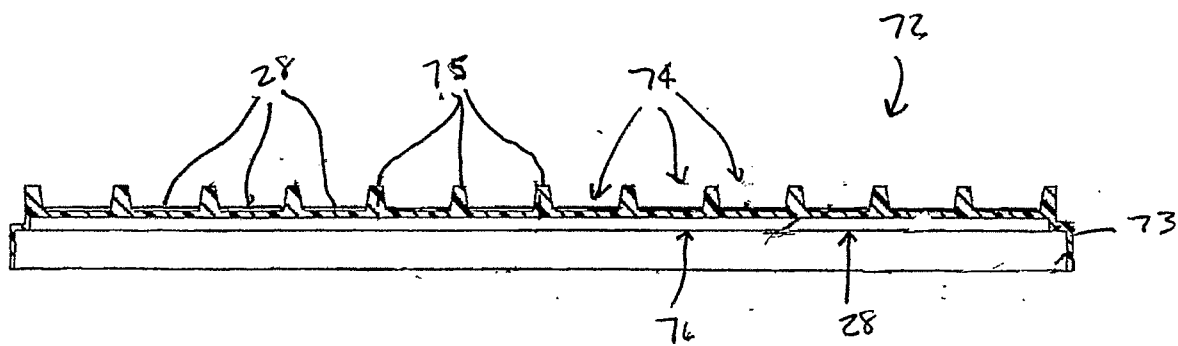


Fig. 9

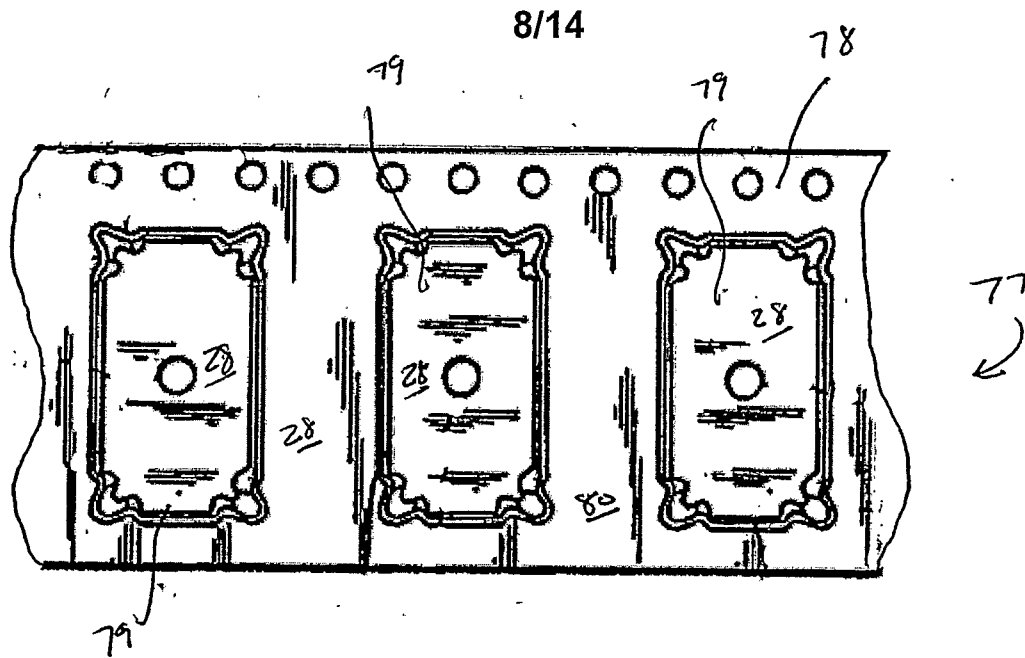


Fig. 10

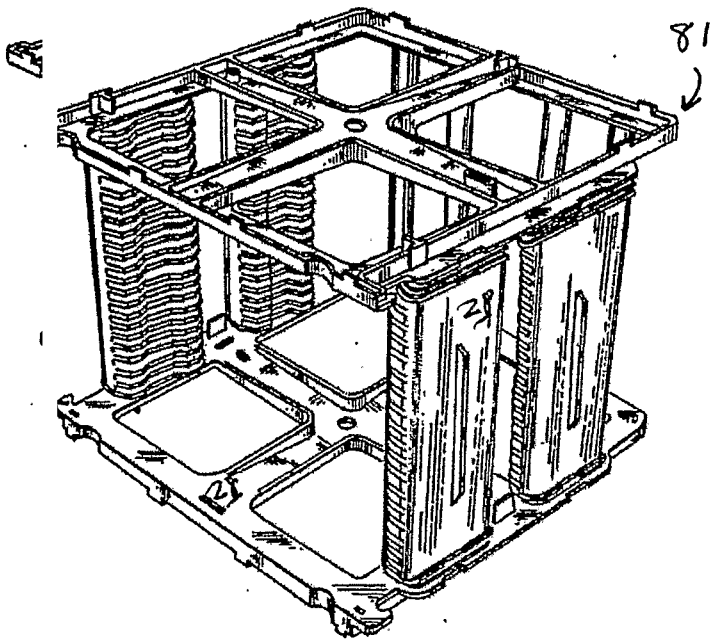


Fig. 11

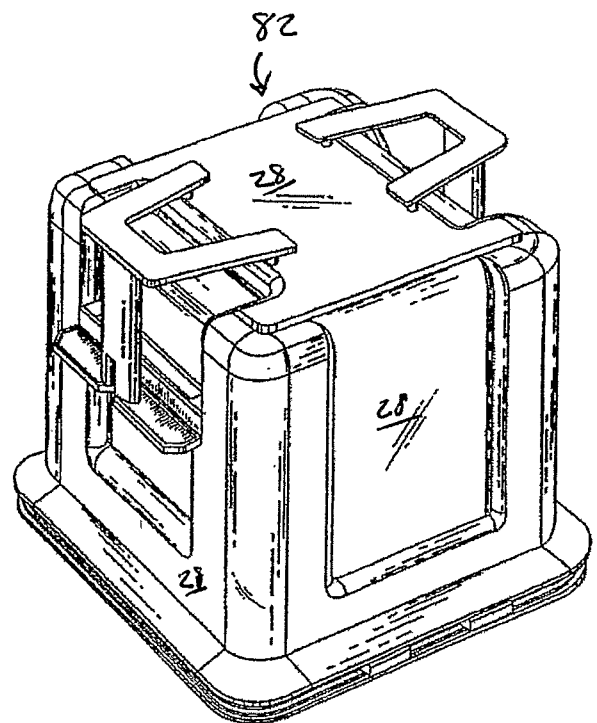


Fig. 12

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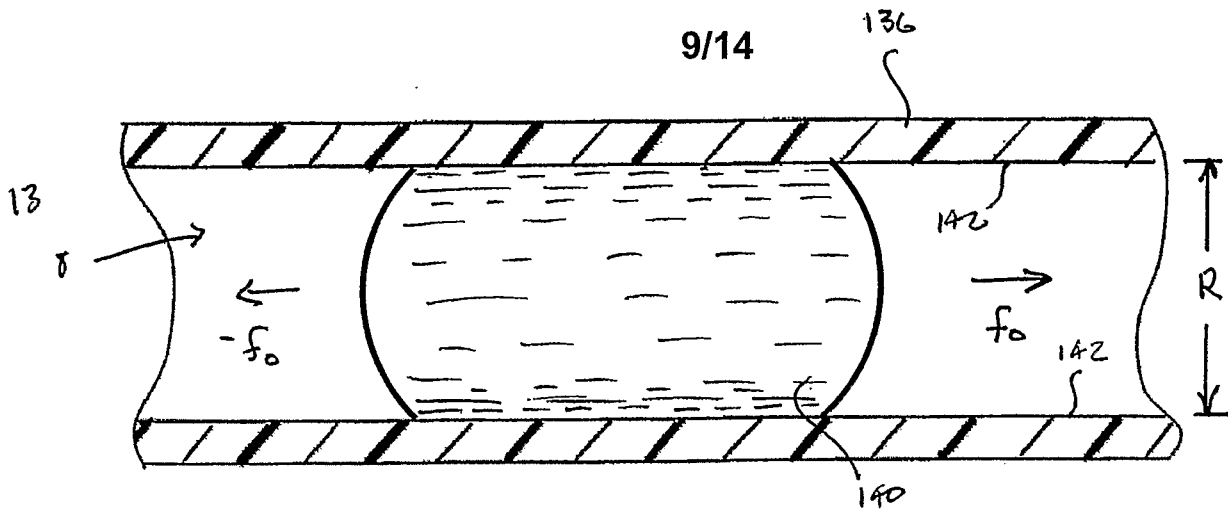


Fig. 13a

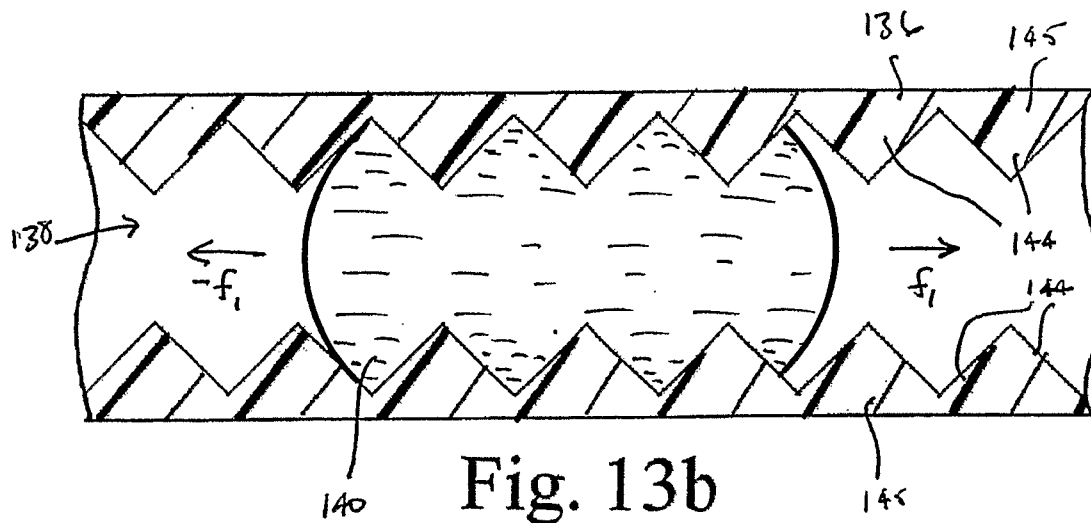


Fig. 13b

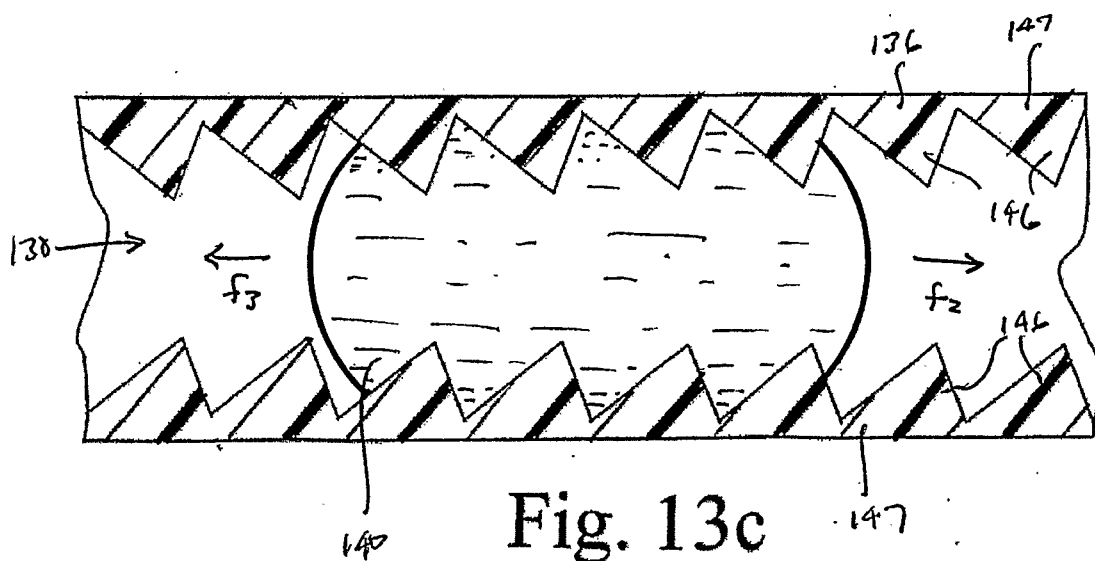


Fig. 13c

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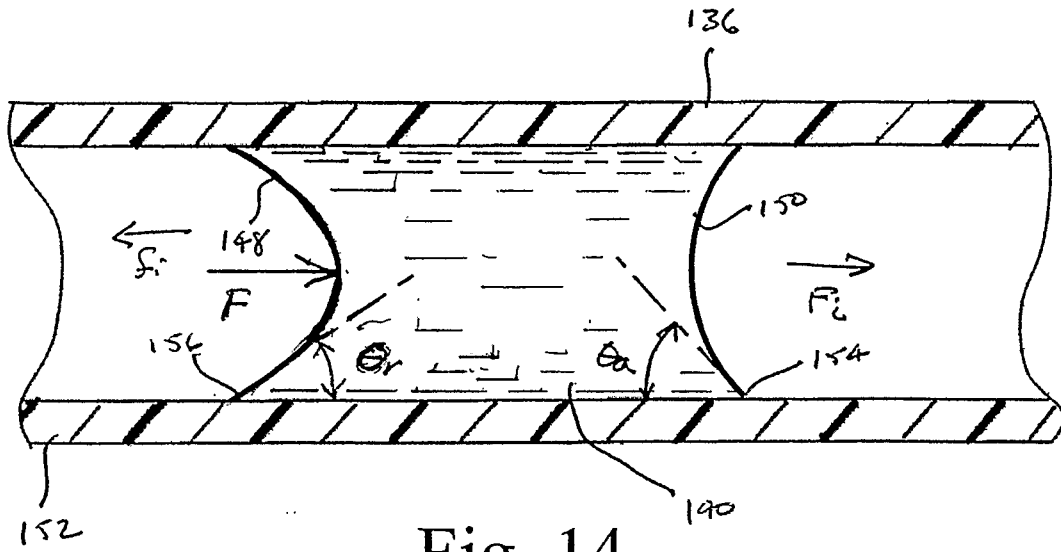


Fig. 14

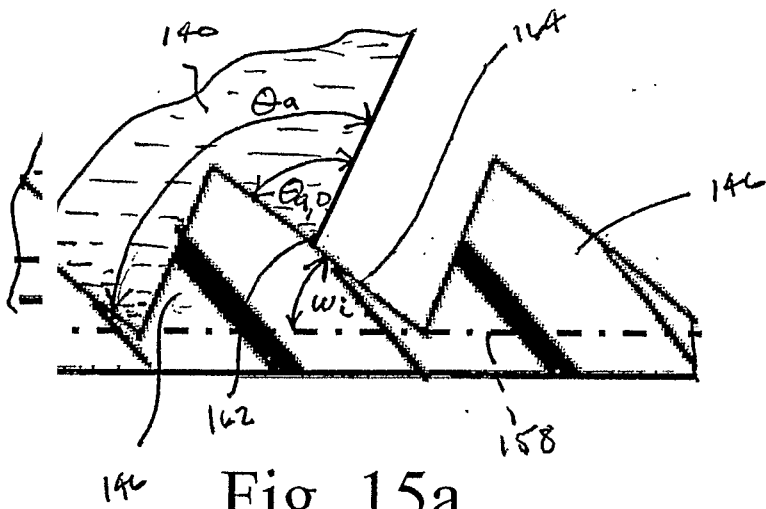


Fig. 15a

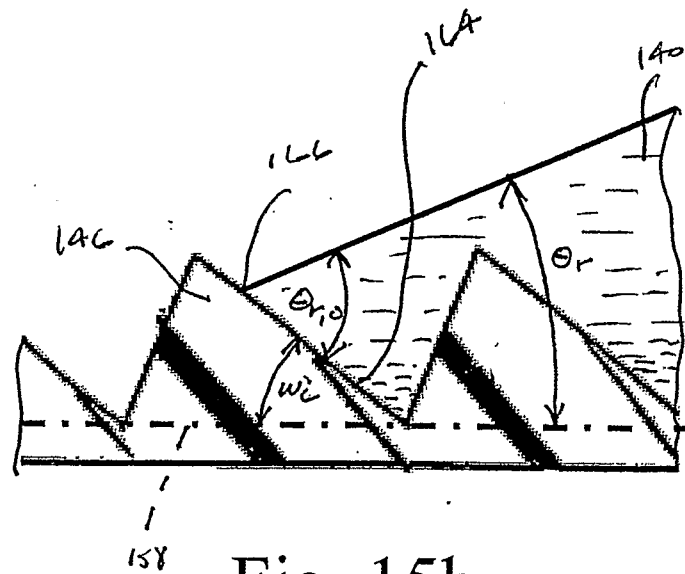
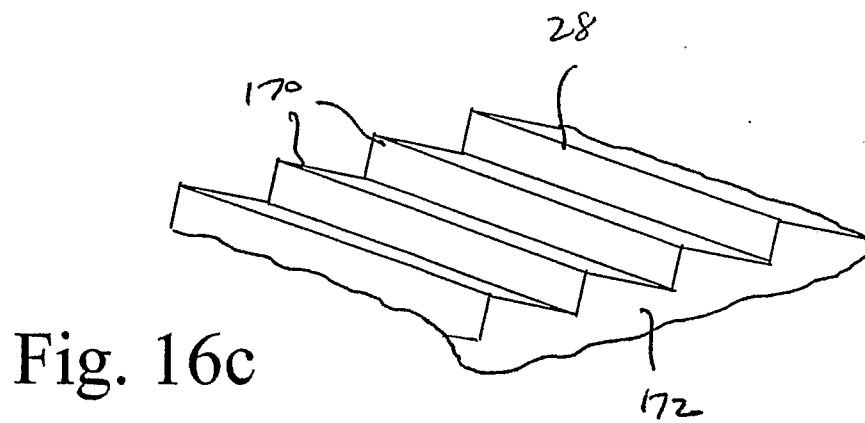
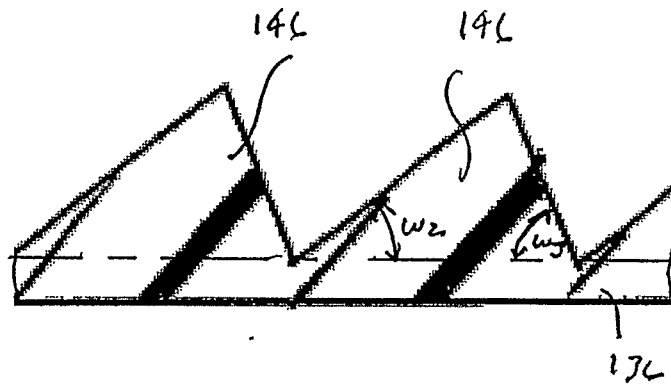
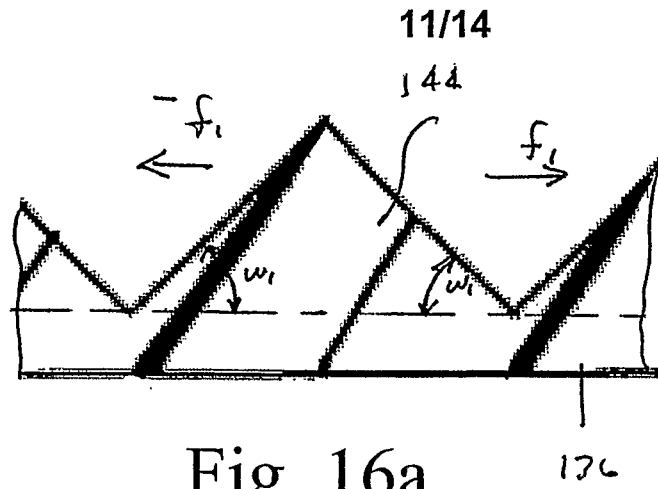


Fig. 15b



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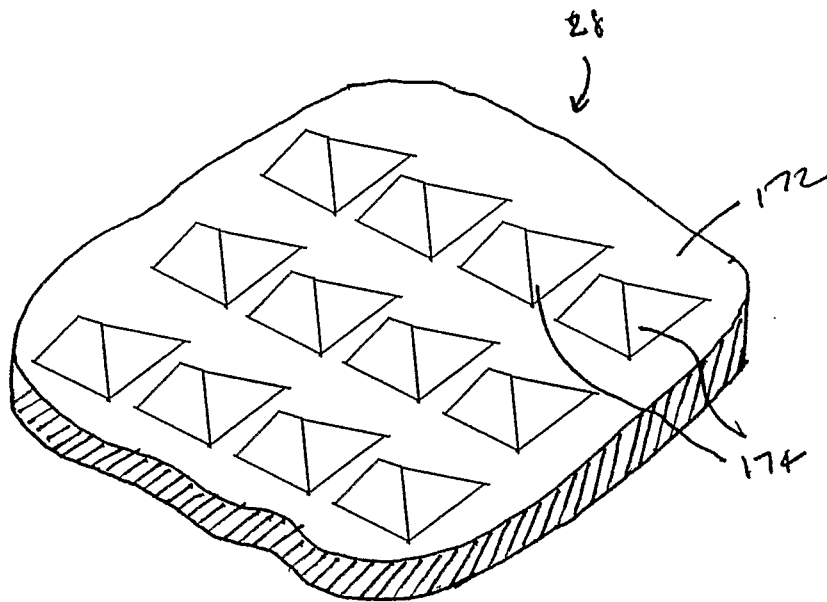


Fig. 16d

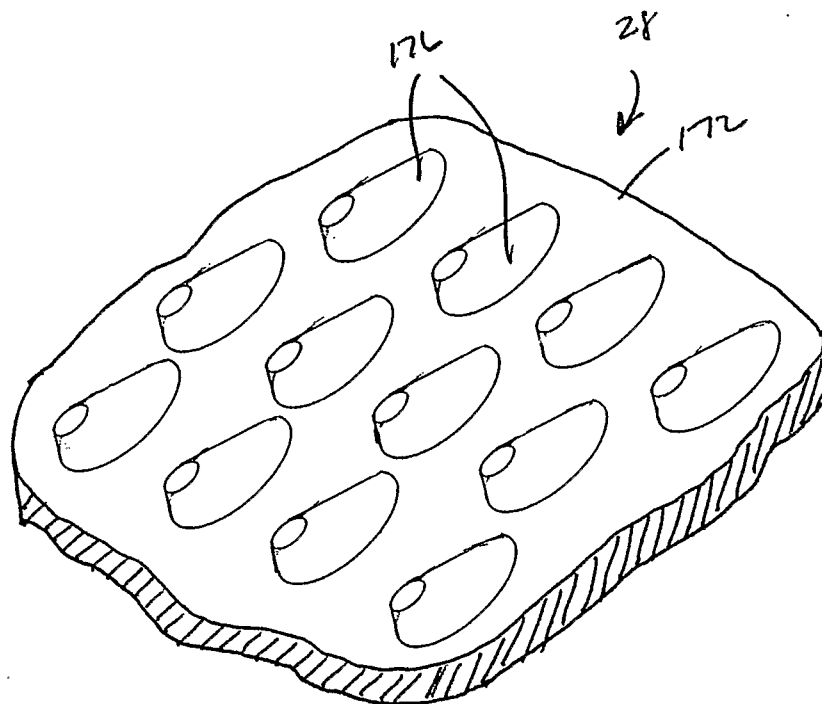


Fig. 16e

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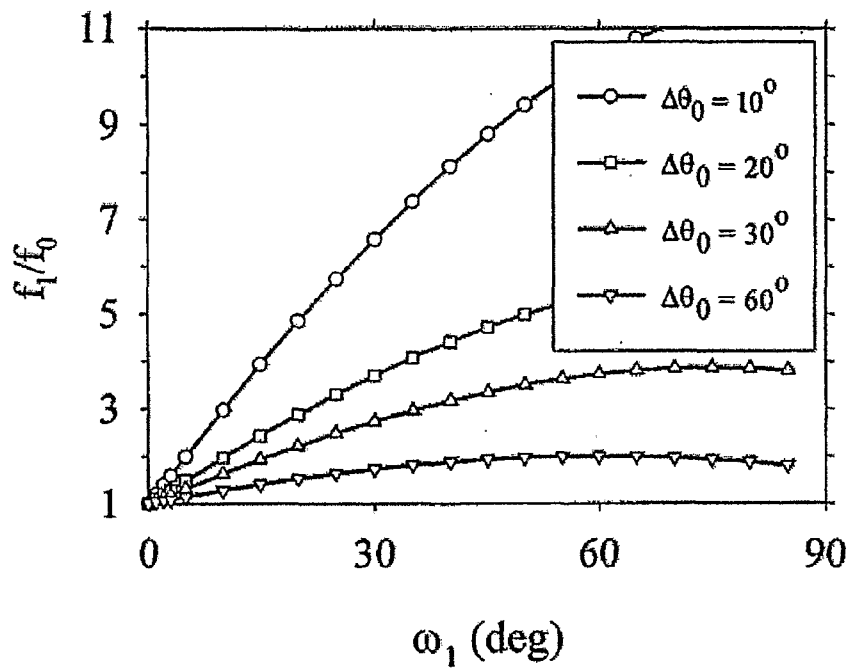


Fig. 17

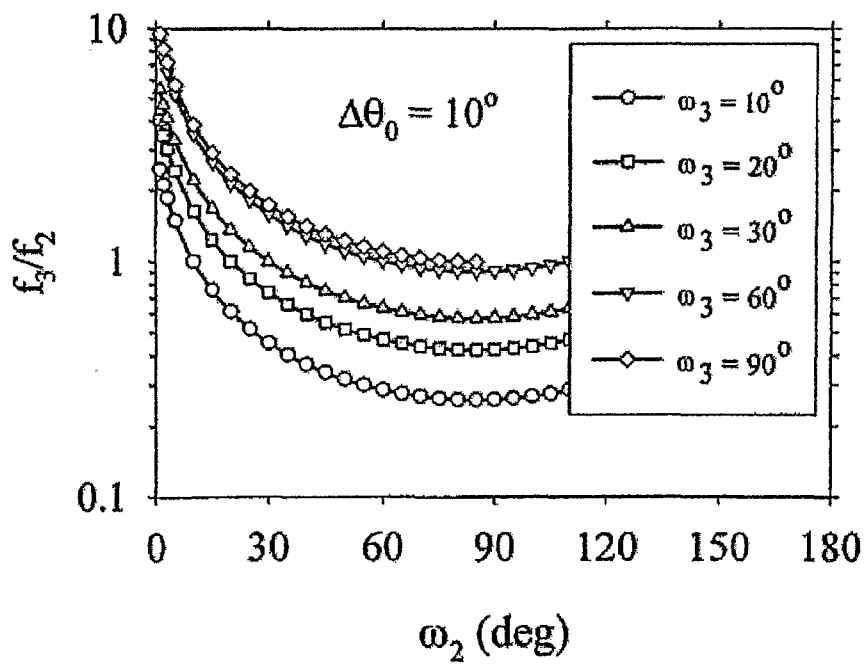


Fig. 18

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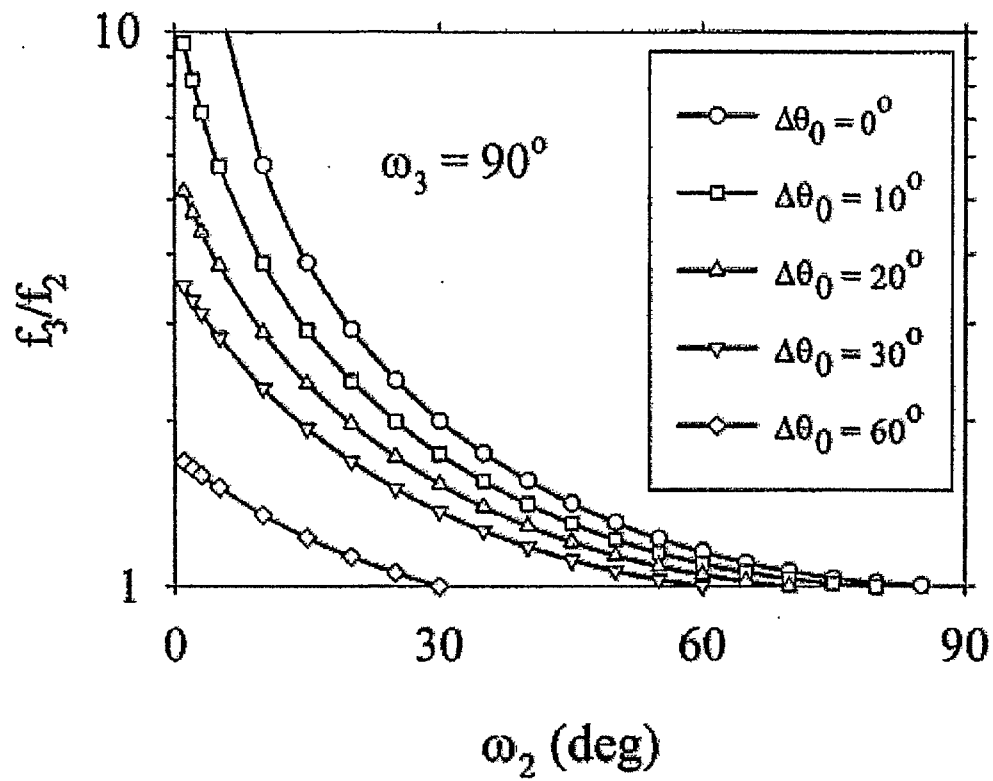


Fig. 19



Fig. 20

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US06/36065

A. CLASSIFICATION OF SUBJECT MATTER

IPC: B65D 85/30(2006.01)

USPC: 428/141

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/141

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,209,555 B1 (STRUVEN) 3 Apr. 2001 (03.04.2001), see whole document	1-20
X	US 2002/0149107 A1 (CHANG et al.) 17 Oct. 2002 (17.10.2002), see whole document	1-20

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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

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

"T"

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

"X"

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

"Y"

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

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document member of the same patent family

Date of the actual completion of the international search

07 January 2007 (07.01.2007)

Date of mailing of the international search report

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