



(51) International Patent Classification:

H01M 2/12 (2006.01) *H01G 9/12* (2006.01)

(21) International Application Number:

PCT/JP2017/025063

(22) International Filing Date:

03 July 2017 (03.07.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2016-141609 19 July 2016 (19.07.2016) JP

(71) Applicant: **W. L. GORE & ASSOCIATES, CO., LTD.**

[JP/JP]; 1-8-15, Konan, Minato-ku, Tokyo, 1080075 (JP).

(72) Inventor: **KOBAYASHI, Kotaro**; c/o W. L. Gore &

Associates, Co., Ltd., 1-8-15, Konan, Minato-ku, Tokyo, 1080075 (JP).

(74) Agent: **AOKI, Atsushi** et al.; SEIWA PATENT & LAW,

Toranomom 37 Mori Bldg., 5-1, Toranomom 3-chome, Minato-ku, Tokyo, 1058423 (JP).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,

MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

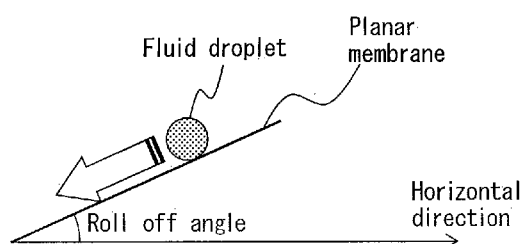
kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: VENT

FIG. 1



(57) **Abstract:** An object is to provide a vent which not only has fundamental performances possessed by vents (air-permeability, prevention from leakage), but also can inhibit decrease in air-permeability for a long period of time of use. There is provided a vent (ventilation hole) including a planar membrane, wherein the membrane has a roll off angle along a first direction and that along a second direction perpendicular to the first direction being different from each other by at least 5°, wherein the roll off angle is defined as a tilt angle of the membrane at which a fluid droplet of $v = 10\mu\text{L}$ of a solution having a surface tension of more than 50 mN/m starts rolling off the membrane plane at room temperature and a relative humidity of $50 \pm 30\%$, wherein the membrane is oriented in the vent so that the membrane plane may be tilted at an angle of $> 0^\circ$ with respect to a gravitational direction and the tilt direction may be parallel to the membrane direction having a minimum roll off angle.



- 1 -

DESCRIPTION

[Title of Invention]

VENT

5

[Technical Field]

[0001]

The present invention relates to a vent, and in particular, to a vent of a container containing liquid.

10

[Background Art]

[0002]

15

Since liquids have high fluidity, they are usually contained in a container. The container may be sealed in order to avoid leakage of liquid therefrom. On the other hand, a pressure increase in the container may be caused by, for example, vaporization or reaction of the liquid therein. A pressure increase in the container exceeding a pressure-resistance capability of the container may lead to breakage of the container. For this reason, the container may be provided with a vent (exhaust port) for releasing vapor in the container to the outside. The vent is also required to transmit the vapor, to prevent a pressure increase in the container, while preventing leakage of liquid.

20

25

[0003]

30

35

One example of the specific container includes a container such as that for lead storage batteries. Lead storage batteries, especially lead storage batteries for automobiles widely utilize a so-called open type structures in which electrolyte liquid such as dilute sulfuric acid can freely flow. Since lead storage batteries of this structure generate oxygen and hydrogen gases during charge, an exhaust port is required to release these gases toward the outside. Otherwise, gas pressure may increase in the battery, possibly leading to deformation or breakage of the battery. On the other hands, when a lead storage battery having an exhaust port

overturns, electrolyte liquid may leak from the exhaust port. Further, in the case of lead storage batteries for automobiles, violent fluctuation of the electrolyte liquid level also caused by jolt during driving an
5 automobile may result in ejection of small particulate splashes of electrolyte liquid from the exhaust port.

Various efforts have been done for this problem.

[0004]

PTL 1 discloses that an evacuation hole shielded by
10 a water-repellent porous membrane such as PTFE is made to be positioned higher than the liquid level in a battery upon overturn of the battery, in order to provide a battery easy to handle without spilling of liquid even when the battery overturns. PTL 1 says that this
15 disclosure can prevent spilling of liquid even upon the overturn of the battery and expands the use application of lead storage batteries.

[0005]

PTL 2 discloses an evacuation structure having an
20 evacuation hole on the upper surface thereof and a tilted gas-permeable membrane on the bottom surface thereof, in order to provide an evacuation structure of lead storage batteries which prevents spilling of liquid caused by jolt and is free from deformation or breakage caused by
25 pressure increase. Actions arising from this structure are explained as follows: When jolt is added to a battery, dilute sulfuric acid in the battery fluctuates and collides vigorously with the evacuation structure (gas-permeable membrane), but a tilted bottom surface of
30 the evacuation structure (gas-permeable membrane) divides the momentum of the obliquely colliding dilute sulfuric acid into a momentum added to the gas-permeable membrane and that of the deflected flight of the acid. In other words, the pressure increase of the dilute sulfuric acid
35 on the gas-permeable membrane is reduced and permeation can be controlled. The document also describes that the dilute sulfuric acid adhered to the tilted bottom tends

to be collected at the lowest point of the gas-permeable membrane and fall onto the electrolyte liquid.

[Citation List]

5 [Patent Literature]

[0006]

[PTL 1]

Japanese Laid-open Patent Publication No. S62-98559

[PTL 2]

10 Japanese Laid-open Patent Publication No. H11-345605

[Summary of Invention]

[Technical Problem]

[0007]

15 As described in PTLs 1, 2, a water-repellent porous membrane such as PTFE is well-known to be used for vents of containers containing liquid. In general, a vent provided with such water-repellent porous membrane degrades with time, and in particular, its air-
20 permeability decreases. The present inventors have extensively examined the cause. Jolt or tilt of a container may cause adhesion of liquid in the container to the surface of the water-repellent and air-permeable membrane. In addition, vaporized vapor generated by the
25 liquid vaporization in the container may be dew-condensed on the surface of the water-repellent and air-permeable membrane, and the dew-condensed liquid may adhere to the surface of the water-repellent and air-permeable membrane. The substance adhered to the surface of the
30 air-permeable membrane may obstruct at least a part of or all of the water-repellent and air-permeable membrane, causing decrease in air-permeability of the air-permeable membrane. Further, the adhered substance may become dry and fix to the air-permeable membrane. In this case, the
35 air-permeability of the air-permeable membrane is difficult to be recovered.

[0008]

The above-described problem arises also in the case that the container is a container for lead storage batteries. When the lead storage battery is transported or an automobile loaded with the lead storage battery is driven, electrolyte liquid in the battery may splash owing to jolt and may adhere to the surface of the water-repellent and air-permeable membrane. In addition, when the battery generates heat at the time of charge or discharge of the battery, electrolyte liquid evaporates owing to the heat and it may dew-condensate on the surface of the water-repellent and air-permeable membrane and adhere thereto. The adhered substance on the surface of the air-permeable membrane is a substance such as a sulfuric salt derived from electrolyte liquid in the battery, and it may obstruct the water-repellent and air-permeable membrane, resulting in decrease in the air-permeability of the air-permeable membrane. Further, when an adhered substance containing a substance such as sulfate salt becomes dry and fixes to the air-permeable membrane, the air-permeability of the air-permeable membrane is very difficult to be recovered.

[0009]

In view of the above description, a subject to be solved of the present invention is to provide a vent which not only has fundamental performances possessed by vents (air-permeability, prevention from leakage), but also enables inhibition of decrease in air-permeability in its use for a long period of time.

[Solution to Problem]

[0010]

The present invention provides the followings.

[0011]

[1] A vent (ventilation hole) provided with a planar membrane,

wherein the membrane has a roll off angle along a first direction and a roll off angle along a second

direction perpendicular to the first direction, which roll off angles being different from each other by at least 5°,

wherein the roll off angle is defined as a tilt
5 angle of the membrane at which a fluid droplet of $v = 10\mu\text{l}$ of a solution having a surface tension of more than 50 mN/m starts rolling off the membrane plane at room temperature and a relative humidity of $50\pm 30\%$,

wherein the membrane is oriented in the vent so that
10 the membrane plane is tilted at an angle of $> 0^\circ$ with respect to a gravitational direction, and the tilt direction is parallel to the membrane direction having a minimum roll off angle.

[0012]

15 [2] The vent according to item [1], wherein the solution is an aqueous solution.

[0013]

[3] The vent according to item [1] or [2], wherein the solution includes H_2SO_4 , KOH, or salt water.

20 **[0014]**

[4] The vent according to any one of the preceding items, which is a vent for a lead storage battery.

[0015]

25 [5] The vent according to any one of the preceding items, wherein the membrane is a porous PTFE membrane including fibrils having an average length of 40 μm or more and 80 μm or less.

[0016]

30 [6] The vent according to any one of the preceding items, wherein the membrane is a porous PTFE membrane including micro-pores defined by nodes and the fibrils, an average aspect ratio of which micro-pores is 15 or more and 40 or less.

[0017]

35 [7] The vent according to any one of the preceding items, wherein the membrane is a porous PTFE membrane

having an average porosity of 80% or more.

[0018]

5 [8] The vent according to any one of the preceding items, wherein the surface of the membrane consists solely of PTFE.

[0019]

10 [9] The vent according to any one of the preceding items, wherein the membrane is a porous PTFE membrane having a Gurley number of one second or less and a Water Endurance Pressure (WEP) of 5 kPa or more.

[0020]

15 [10] The vent according to any one of the preceding items, wherein the tilt angle of the membrane with respect to the gravitational direction is smaller than (90° - the minimum roll off angle).

[0021]

[11] The vent according to any one of the preceding items, wherein the tilt angle of the membrane with respect to the gravitational direction is 75° or less.

20 **[0022]**

[12] An open type lead storage battery using the vent according to any one of the preceding items.

[Advantageous Effects of Invention]

25 **[0023]**

The vent of the present invention has an air-permeability, which can release gas in the container to the outside and prevent pressure increase in the container and an associating damage.

30 Further, the vent of the present invention can also prevent leakage of liquid contained in the container to the outside.

35 Still further, the vent of the present invention has a planar membrane oriented in a specific direction, so that liquid droplets adhered to the planar membrane tend to roll off the planar membrane and tend not to adhere thereto. Accordingly, the liquid droplets can be

prevented from becoming dry and fixing to the planar membrane. This allows inhibition, for a long period of time, of decrease in the air-permeability of the planar membrane. In other words, the vent of the present invention can maintain high air-permeability for a long period of time.

[Brief Description of Drawings]

[0024]

10 [FIG. 1]

FIG. 1 is a drawing explaining a roll off angle.

[FIG. 2]

FIG. 2 is a drawing explaining an orientation of a planar membrane.

15 [FIG. 3]

FIG. 3 is a drawing explaining a tilt angle of a membrane with respect to a gravitational direction.

[Description of Embodiments]

20 **[0025]**

The vent according to the present invention is a vent provided with a planar membrane (ventilation hole), wherein the membrane has a roll off angle along a first direction and a roll off angle along a second direction perpendicular to the first direction, which roll off angles being different from each other by at least 5°,

wherein the roll off angle is defined as a tilt angle of the membrane at which a fluid droplet of $v = 10 \mu\text{l}$ of a solution having a surface tension of more than 50 mN/m starts rolling off the membrane plane at room temperature and a relative humidity of 50%,

wherein the membrane is oriented in the vent so that the membrane plane is tilted at an angle of $> 0^\circ$ with respect to a gravitational direction, and the tilt direction is parallel to the membrane direction having a

minimum roll off angle.

[0026]

The present inventors have found that when the planar membrane was tilted, there was a direction in which fluid droplets tended to roll off and a direction in which they tended not to roll off, depending on an in-plane direction in the planar membrane. In other words, the planar membrane may have a different roll off angle depending on the direction. Without wishing to be bound by a specific theory, this is attributed to a relation with a surface structure of the membrane. For example, when the planar membrane is produced by extension, fibers thereof are extended in the extension direction. When a liquid droplet is placed on the planar membrane, it generally tends to roll off along the extension direction of fibers.

[0027]

The planar membrane of the present invention has different roll off angles each corresponding to a first direction and a second direction, where the second direction is a direction perpendicular to the first direction. In addition, the roll off angle along the first direction and that along the second direction are different from each other by at least 5°. This means that the membrane has an in-plane direction in which liquid droplets tend to roll off and that in which the liquid droplets tend not to roll off. In other words, this means that the membrane has an in-plane direction in which the roll off angle becomes a minimum. Note that the first direction may be any in-plane direction of the membrane. The first direction may be a direction in which liquid droplets tend most to roll off the membrane plane or may be a direction in which liquid droplets tend most not to roll off the membrane plane. In addition, the first direction may be an extension direction in production of the membrane or may be a perpendicular direction to the extension direction.

[0028]

The roll off angle is defined as an tilt angle of membrane at which a fluid droplet of $v = 10 \mu\text{l}$ of a solution having a surface tension of more than 50 mN/m at room temperature and a relative humidity within the range of $50 \pm 30\%$ starts rolling off the membrane plane. This is explained with reference to FIG. 1. The roll off angle is measured by the following procedure.

A planar membrane is oriented in a state of 0° , i.e., to a horizontal direction. The horizontal direction is a direction perpendicular to the gravitational direction.

Fluid of volume $v = 10 \mu\text{l}$ is placed, so as to take a form of a droplet, on the membrane plane oriented horizontally. The fluid is a solution having a surface tension of more than 50 mN/m at room temperature and a relative humidity within the range of $50 \pm 30\%$. The room temperature may be a temperature within the range of $20 \pm 20^\circ\text{C}$, i.e., $0 - 40^\circ\text{C}$. The relative humidity is within the range of $50 \pm 30\%$, i.e., within the range of $20 - 80\%$. When the surface tension is 50 mN/m or less, the liquid may tend not to become a droplet and not to roll off the membrane surface. For this reason, a solution having a surface tension of 50 mN/m or less is used in the present invention.

The membrane plane is gradually raised from the horizontal direction (0°) to the perpendicular direction (90°). An angle between the membrane plane and the horizontal direction (tilt angle of the membrane) upon the start of rolling off of the droplet placed on the membrane plane is defined as a roll off angle of the liquid droplet. Usual apparatuses for measuring the tilt angle carry out the measurement until the rolling off starts or the tilt angle of the membrane reaches 90° .

[0029]

The planar membrane is oriented in the vent at a

tilt angle of $> 0^\circ$ with respect to the gravitational direction. (" 0° with respect to the gravitational direction" means a direction coinciding with the gravitational direction). The tilt of the planar membrane with respect to the gravitational direction makes droplets of the solution on the planar membrane tend to roll off. The planar membrane may be tilted at an angle of $< 90^\circ$ with respect to the gravitational direction. The reason of this is that the angle of 90° with respect to the gravitational direction means the membrane oriented horizontally and the droplet of the solution tends not to roll off.

[0030]

As described above, the planar membrane has different roll off angles depending on the direction in the membrane plane. In the present invention, the planar membrane is oriented so that the tilt direction of the membrane is parallel to a membrane direction having a minimum roll off angle. FIG. 2 is a drawing explaining conceptually the orientation of the planar membrane.

[0031]

As for the planar membrane, fluid droplets of liquid may adhere to the surface thereof owing to jolt of the liquid in a container or to evaporation and dew-condensation of the liquid. However, in the present invention, the planar membrane is tilted with respect to the gravitational direction, and thereby, fluid droplets adhered to the planar membrane tend to flow downward (gravitational direction) along the planar membrane and fall into the container. Accordingly, the fluid droplets tend not to generate obstructions in the planar membrane. Further, the fluid droplets also tend not to become dry and fix to the planar membrane. As a result, decrease in air-permeability of the planar membrane can be inhibited.

[0032]

Further, in the present invention, the tilt

direction of the planar membrane coincides with (i.e., is parallel to) the direction of the minimum roll off angle of the planar membrane. As described above, the roll off angle is referred to as a tilt angle of the planar
5 membrane at which a fluid droplet starts rolling off the membrane plane. The direction at which the roll off angle (tilt angle) is a minimum is a direction at which the fluid droplet tends most to flow downward (to gravitational direction) on the planar membrane. In other
10 words, the planar membrane of the present invention is oriented in a direction at which the fluid droplet tends most to flow downward (gravitational direction). Accordingly, fluid droplets adhered to the planar membrane particularly tend to flow and to fall into the
15 container. As a result, according to the present invention, obstructions in the planar membrane can be remarkably reduced and decrease in the air-permeability of the planar membrane can be remarkably reduced.

[0033]

20 The larger the difference of the roll off angle between the above-mentioned first direction and the second direction is, the larger the difference of flowability of fluid droplets therebetween is. Accordingly, when the tilt direction of the planar
25 membrane is made to be parallel to the direction having the minimum roll off angle of the planar membrane, the effect of reducing obstructions in the planar membrane differs greater in comparison to other cases. Accordingly, in the present invention, the difference of
30 roll off angle is 5° or more, and may be preferably 10° or more, more preferably 15° or more, still more preferably 20° or more.

[0034]

35 The above-mentioned solution may be an aqueous solution. Since the surface tension of water is approximately 73 mN/m, many solutes can be made to be

aqueous solutions the surface tension of which is more than 50 mN/m.

[0035]

The solution may include H_2SO_4 , KOH, or salt water.
5 The solution is used for defining the roll off angle.
 H_2SO_4 , KOH, or salt water is very widely used for industrial applications, and often contained in a container. The vent of the present invention can be used as a vent of a container for these solutions, and the
10 vent can maintain high air-permeability for a long period of time.

[0036]

The vent of the present invention may be a vent for lead storage batteries. In general, lead storage
15 batteries are secondary batteries using lead dioxide as a positive electrode (anode plate), spongy lead as a negative electrode (cathode plate), and dilute sulfuric acid as an electrolyte liquid. Lead storage batteries are widely used as batteries for automobiles, light planes
20 among other things, and may be used in applications for backup power supply.

In general, aqueous sulfuric acid is used as an electrolyte liquid (electrolyte) for lead storage batteries. When the vent is a vent for lead storage
25 batteries, substances adhered to the planar membrane are thought to come mostly from the electrolyte liquid (aqueous sulfuric acid). When H_2SO_4 is selected as a fluid used for defining the roll off angle, the roll off angle (roll off angle of H_2SO_4 solution) can be expected
30 to be comparable to that of the adhered substances coming from the electrolyte liquid. In other words, the tilt direction of the planar membrane which leads to a minimum roll off angle by using H_2SO_4 is expected to lead to a minimum roll off angle also by using the adhered
35 substances coming from the electrolyte liquid. As a result, the air-permeability of the vent of the lead storage battery can be maintained to be high for a long

period of time.

[0037]

The planar membrane may have hydrophobic porosity, thereby preventing liquid in the container from leakage, and in addition, transmitting vaporized vapor to the outside of the container. Polyethylene, polypropylene, and PTFE (polytetrafluoroethylene) all of which can be made to be a porous membrane may be used materials of the planar membrane. In particular, PTFE (polytetrafluoroethylene) is suitable as a material applicable to vents, particularly as a material applicable to vents for batteries since it has intrinsically an excellent property, such as hydrophobicity, chemical resistance, resistance against ultraviolet-rays, oxidation resistance, and thermal resistance. A porous membrane can be easily obtained by extending PTFE. PTFE is intrinsically water-repellent, and can repel a solution such as aqueous sulfuric acid. In other words, a vent provided with a PTFE membrane can prevent leakage of a solution in a container by the PTFE membrane. (When the container is a container for a battery, electrolyte liquid in the battery (aqueous sulfuric acid) can be prevented from leakage). On the other hand, since PTFE membrane is porous, gas in the container can be released to the outside of the container through the porous part. For this reason, when gas pressure within the container increases, the gas is released to the outside of the container through this porous PTFE, enabling prevention of the pressure increase in the container and an associating damage of the container. (when the container is a container for a battery, the pressure increase in the battery and the associating damage of the battery can be prevented).

[0038]

The porous PTFE membrane (planar membrane) has an average length of fibrils which may be 40 μm or more and 80 μm or less. The porous PTFE obtained by extending

PTFE consists of nodes (nodules) and fibrils (small fibers). The nodes and the fibrils are each made of polytetrafluoroethylene and are different from each other presumably depending to the agglomerate or crystal state of polytetrafluoroethylene molecules. In general, the node is thought to be an agglomerate of polytetrafluoroethylene primary particles mutually connected by fine crystal ribbons, and the fibril is thought to be a bundle of fully extended crystal ribbons pulled from the primary particles. The average length of the fibrils can be obtained by observing the surface of the PTFE membrane by using an electron microscopy among other things. Since the fibrils generally extend along their extension direction, liquid droplets tend to roll off along the extension direction of the fibrils and they tend not to roll off in the direction perpendicular to the extended fibrils. In other words, the extended PTFE membrane tends to generate a difference of roll off angle, depending on the in-plane direction. However, when the average length of the fibrils is 40 μm or less, a large difference of roll off angle, for example, a difference of 5° or more tends not to occur between the extension direction of the fibrils and a direction perpendicular thereto. It is thought that a longer length of the fibrils makes liquid droplets tend to roll off in the extension direction of the fibrils. The average length of the fibrils may preferably be 50 μm or more, 60 μm or more. Excessive extension of the fibrils may lead to fracture thereof. When the average length of the fibrils is 80 μm or less, problems caused by the fracture of the fibrils among other things do not occur. In order to reduce the possibility of the fracture, the average length of the fibrils may be 70 μm or less, 60 μm or less.

35 **[0039]**

The porous PTFE membrane (planar membrane) has an

average aspect ratio of a micro-pore defined by nodes and fibrils which may be 15 or more 40 or less. The nodes and the fibrils can be obtained by extending PTFE. Divisions by these nodes and/or fibrils form micro-voids (micro-pores). The shape of the micro-pores changes depending on extension conditions (such as extension direction and extension ratio). The aspect ratio is a parameter indicating an extent of circularity of the shape of the micro-pore and is obtained from a ratio of the maximum length to the minimum length of the micro-pore. When the aspect ratio is one, it means that the shape of the micro-pore is largely circular. It is preferable to adopt an average value of aspect ratios obtained from a plurality of micro-pores because the membrane is a porous body. The average aspect ratio can be obtained by observing the surface of the PTFE membrane by using an electron microscopy among other things.

In general, the direction of the maximum aspect ratio coincides with the extension direction of the fibrils. Liquid droplets tend to roll off along the direction of this maximum aspect ratio, and they tend not to roll off in the direction of the minimum aspect ratio. A larger aspect ratio is thought to make liquid droplets tend more to roll off in direction of the maximum aspect ratio. When the aspect ratio is less than 15, a large difference of the roll off angle, for example, a difference of 5° or more, tend not to occur between the direction of the maximum aspect ratio and that of the minimum aspect ratio. The aspect ratio may preferably be 20 or more, 25 or more, and 30 or more. A larger extension ratio enables a larger aspect ratio, but excessive extension of the PTFE membrane may lead to the fracture thereof. When the aspect ratio is 40 or less, a problem caused by the fracture of the PTFE membrane among other things does not occur. In order to reduce the possibility of the fracture, the aspect ratio may be 35 or less, and 30 or less.

[0040]

The porous PTFE membrane (planar membrane) has an average porosity which may be 80% or more. When the porosity is less than 80%, enough air-permeability may not be obtained. Higher porosity enables higher air-permeability, and the porosity may be 85% or more and 90% or more. However, excessive porosity may cause fracture of the PTFE membrane. In order to reduce the possibility of the fracture, the porosity may be 99% or less, 95% or less, and 90% or less.

The porosity of the porous PTFE can be calculated, from a bulk density ρ measured in accordance to a measurement method of bulk density defined in JISK 6885:2005, on the basis of the following formula,

$$\text{porosity (\%)} = [(2.2 - \rho) / 2.2] \times 100.$$
[0041]

The surface of the planar membrane may consist solely by PTFE. As described above, polyethylene, polypropylene, PTFE (polytetrafluoroethylene), and so on can be adopted as materials of the planar membrane. The planar membrane constituted by these materials may have a surface coated with PTFE so that the surface consists solely of PTFE. Further, the planar membrane itself may be constituted solely by PTFE. Although water-repellence and oil-repellence may be given by surface treatment of the surface of the planar membrane, such a surface treatment is not carried out in the case of a planar membrane having a surface consisting solely by PTFE. PTFE itself has intrinsically an excellent property, such as hydrophobicity, chemical resistance, resistance against ultraviolet-rays, oxidation resistance, and thermal resistance, and a planar membrane having a surface consisting solely of PTFE can make these properties exert directly to liquid or vapor in a container.

[0042]

The porous PTFE membrane (planar membrane) has a

Gurley number which may be one second or less and a Water Endurance Pressure (WEP) which may be 5kPa or more. The Gurley number is evaluated in accordance to JIS P 8117:2009. The Gurley number is referred to as a time
5 (second) required for air of 100 cm³ to pass through the sample having an area of 6.45 cm² in a direction perpendicular to the sample under a pressure of 1.29 kPa. The Gurley number is an index of air-permeability. When the Gurley number is one second or less, air-permeability
10 is generally sufficient for vents.

The Water Endurance Pressure (WEP) is an index of water-repellence of a planar membrane or an ability thereof to function as a water-barrier. In order to measure WEP, a test sample, i.e., a vent provided with a
15 planar membrane is prepared. The test sample is placed in a container containing liquid. The vent is kept for one hour or more, with the outward direction of the vent (outside direction of the container) oriented along the gravitationally downward direction. The quantity of
20 liquid in the container is adjusted so that a given pressure may be applied to the planar membrane. For example, when the given pressure is 3kPa and the liquid is water, the level of the liquid contained in the container is adjusted to be about 30 cm. In the above-described condition, leakage of the liquid from the vent
25 is visually observed. The pressure applied to the membrane is gradually increased until the leakage is observed, and a pressure at which the leakage is confirmed is defined as the Water Endurance Pressure of the membrane. The planar membrane of the present
30 invention has a WEP which may be 5kPa or more, preferably 8 kPa or more, and more preferably 10 kMPa or more. Although required WEPs are different depending on use applications, a WEP of approximately 3 kPa is a
35 sufficient leak-proof nature of a container for usual lead storage batteries. The above-described planar membrane can give sufficient air-permeability and

sufficient leak-proof nature to vents.

[0043]

By vibrating, at 10 GHz, the container in which the test sample is placed, leakage of the liquid from the vent may be visually observed as an index of water-resistance relating to WEP. The leakage after a long period of time, such as several days, several weeks, and several months may also be observed, with the container kept tilted by 45° with respect to the horizontal direction or the gravitational direction, i.e., with the liquid in the container kept constantly in contact to the planar membrane. These observations are based on an assumption that the container is a lead storage battery. One aspect of the planar membrane of the present invention can provide a vent which exhibit liquid-leakage neither in the above-described vibration test nor in the 45° tilting experiment for a long period of time.

[0044]

The tilt angle of the membrane with respect to the gravitational direction may be less than (90° - the minimum roll off angle). This situation is explained schematically in FIG. 3. As shown in FIG. 3, the membrane is tilted to the gravitationally downward direction more than to the minimum roll off angle α . For this reason, even liquid droplets in the container once adhered to the surface of the membrane roll off immediately without remaining on the surface. As will be understood, the liquid droplets do not become dry and fix to the surface of the membrane. Accordingly, the air-permeability of the membrane is maintained to be high for a long period of time.

The following may be noted with regard to the description of "tilt angle of the membrane" and "(90° - the minimum roll off angle)." The roll off angle is based on the horizontal direction, i.e., it is 0° in the horizontal direction and is 90° in the gravitational

direction. On the other hand, the tilt angle of the membrane is based on the gravitational direction, i.e., it is 0° in the gravitational direction and is 90° in the horizontal direction. The horizontal direction is a direction perpendicular to the gravitational direction. For this reason, this aspect specifies that the tilt angle of the membrane with respect to the gravitational direction may be less than (90° - the minimum roll off angle).

10 **[0045]**

The above-mentioned tilt angle of the membrane may be 75° or less. The tilt angle of the membrane is based on the gravitational direction, and liquid droplets tend more to adhere to the membrane as the angle gets closer to 0° . Even when the liquid droplets once adhere to the membrane, they tend to roll off. The tilt angle of the membrane may be preferably 70° or less, more preferably 65° or less, and still more preferably 60° or less. The upper limit of the tilt angle is not particularly limited, but it may be $< 90^\circ$ since the gravitational direction is 90° .

In addition, the minimum roll off angle of the planar membrane, based on the horizontal direction, is preferably smaller since liquid droplets tend more to roll off, i.e., liquid tends not to adhere to the membrane. For this reason, the minimum roll off angle of the planar membrane is preferably 35° or less, more preferably 25° or less, and it may be still more preferably 15° or less, and still more preferably 10° or less. The lower limit of the tilt angle is not particularly limited, but it may be $> 0^\circ$ since it does not become horizontal (0°).

30 **[0046]**

A vent provided with any one of the above-described planar membranes may be used for open type lead storage

batteries. Lead storage batteries have an electrolyte liquid such as dilute sulfuric acid therein. The vent of the present invention can release gas in a battery to the outside thereof while preventing leakage of the electrolyte liquid. Further, the planar membrane mounted on the vent of the present invention makes even adhered electrolyte liquid tend to roll off and is maintained to be highly air-permeable for a long period of time.

10 [Examples]

[0047]

The present invention will be explained by using Examples and Comparative examples. However, the present invention should not be construed to be limited to the Example.

15 **[0048]**

Membrane test

Various planar membranes listed in Table 1 were prepared. Table 1 lists thickness, a Gurley number, a WEP (Water Endurance Pressure), a porosity, an aspect ratio, and a fibril length, of these planar membranes. Aspect ratios were not measured for membranes #4 to #8 because their shape of micro-pore was not able to be clearly distinguished. Further, Gurley numbers were obtained at the start and the end of a series of data acquisitions, and the Gurley numbers obtained at the start were recorded as initial values (initial) and those obtained at the end were recorded as values after the test (after test). The Gurley numbers of the membranes after applying various loads for data acquisition were largely greater than the initial Gurley numbers.

30 **[0049]**

[Table 1]

Table 1 Properties of membrane

	Thickness	G No (initial)	WEP	Pore ratio	Pore aspect ratio (Ave)	Fibril length (Ave)	G No (after test)
	um	s	kPa	%	-	um	s
#1	300	12	90	60	10	8	50
#2	300	1	30	80	15	40	1.5
#3	100	0.2	20	90	18	50	0.3
#4	15	0.1	25	95	-	40	0.2
#5	30	0.1	10	95	-	50	0.2
#6	40	0.12	20	95	-	40	0.4
#7	20	0.13	40	92	-	75	0.5
#8	25	10	-	60	-	-	80

[0050]

Further, various liquids (classified with respect to surface tension) were prepared. These liquids had various surface tensions at room temperature and a relative humidity within the range of $50 \pm 30\%$. Aqueous sulfuric acid, and aqueous solutions of potassium hydroxide and sodium chloride had a concentration of 30% by mass, 30 % by mass, and 3.5 % by mass, respectively, and had a surface tension of 77 mN/m, 100 mN/m, and 74 mN/m, respectively. A coolant was used which was a commercially available cooling water for automobile engines, a main ingredient of which was ethylene glycol, and the surface tension of which was 50 mN/m. A window washer liquid was used which was commercially available aqueous detergent for washing automobiles, the surface tension of which was 40 mN/m. Brake oil and engine oil were used which were also commercially available for automobiles and each surface tension of which was 20 - 40 mN/m.

[0051]

The planar membranes of Table 1 were oriented in a state of 0° , i.e., in a horizontal direction. The horizontal direction was a direction perpendicular to the gravitational direction. A fluid of volume $v = 10 \mu\text{l}$ was placed on the membrane plane oriented horizontally so as to take a form of droplet. The membrane plane was gradually raised from the horizontal direction (0°) toward

the perpendicular direction (90°). A roll off angle was recorded which was an angle between the membrane plane and the horizontal direction (tilt angle of the membrane) upon the start of the roll off of the droplet placed on the membrane plane. The measurement was carried out until rolling off started or the tilt angle of the membrane became 90° . Table 2 depicts the result.

[0052]

[Table 2]

	liquid	30wt% H ₂ SO ₄ aq	30wt% KOH aq	3.5wt% NaCl aq	coolant	window washer liquid	brake oil	engine oil
membrane	surface tension (mN/m)	77	100	74	50	40	20-40	20-40
#1	minimum roll off angle	40	35	50	90	90	90	90
	maximum roll off angle	40	40	50	90	90	90	90
	difference between the roll off angles	0	5	0	0	0	0	0
#2	minimum roll off angle	35	30	40	50	90	90	90
	maximum roll off angle	50	50	55	70	90	90	90
	difference between the roll off angles	15	20	15	20	0	0	0
#3	minimum roll off angle	20	20	30	40	90	90	90
	maximum roll off angle	30	55	40	70	90	90	90
	difference between the roll off angles	10	35	10	30	0	0	0
#4	minimum roll off angle	25	20	45	50	90	90	90
	maximum roll off angle	30	35	55	60	90	90	90
	difference between the roll off angles	5	15	10	10	0	0	0
#5	minimum roll off angle	25	50	25	75	90	90	90
	maximum roll off angle	30	65	40	90	90	90	90
	difference between the roll off angles	5	15	15	15	0	0	0
#6	minimum roll off angle	30	30	45	-	90	90	90
	maximum roll off angle	45	40	55	-	90	90	90
	difference between the roll off angles	15	10	10	-	0	0	0
#7	minimum roll off angle	40	40	20	-	90	90	90
	maximum roll off angle	45	50	35	-	90	90	90
	difference between the roll off angles	5	10	15	-	0	0	0
#8	minimum roll off angle	35	30	45	90	90	90	90
	maximum roll off angle	38	35	50	90	90	90	90
	difference between the roll off angles	3	5	5	0	0	0	0

[0053]

The surface tension of the window washer liquid was approximately 40 mN/m and that of the oils (brake oil and engine oil for automobile use, and so on) was approximately less than 20 - 40 mN/m, and they permeated through the membrane without taking a form of liquid droplet on the planar membrane. Even when the membrane was tilted perpendicularly (90°) with respect to the horizontal direction, the window washer liquid and the oils were not confirmed to have rolled off, and their roll off angles were recorded to be 90° in the Table 2.

[0054]

The liquids having a surface tension of 50 mN/m or more took a form of droplet on the planar membrane, and made it possible to measure their roll off angle. Further, the roll off angles of the liquid droplet were found to be different from each other depending on a direction in the membrane plane. In particular, difference between the maximum roll off angle and the minimum roll off angle seemed to correlate largely with the aspect ratio. The difference between the maximum roll off angle and the minimum roll off angle was confirmed to become largely greater with increase in the aspect ratio.

[0055]

Fouling test (adhesion test)

Three types of vents provided with the membrane #3 were fabricated. A first vent was provided with the planar membrane in the horizontal direction and was a vent having the planar membrane which was not tilted. A second vent was a vent having a planar membrane which was tilted in a direction of the maximum roll off angle (in a direction which tended to cause roll off). A third vent was a vent having the planar membrane which was tilted in a direction of the minimum roll off angle (in a direction which tended to cause roll off). The tilt angles of the

second and third vents were determined to be 65° (which were 0° in the gravitational direction).

A commercially available 12 V lead battery was prepared, and the above-described three types of vents were installed on the liquid plug part of this battery. Temperature in the container was kept to be 25°, and recharge was carried out under a constant electric current and a constant voltage of 14.4 V, to expose the membrane to overcharge for 30 days so that aqueous sulfuric acid might be volatilized and aerosolized. The Gurley number of the membrane of the vent was measured from day 0 to day 30. Table 3 depicts the aging of the Gurley number on the basis of the initial value of the Gurley number (Gurley number on day 0) which was set to be 100.

[0056]

[Table 3]

Table 3 fouling test

Gurley value (-)	Initial value	day 7	day 14	day 30
0°(without tilt)	100	109	118	125
tilted in a direction of maximum roll off angle	100	109	117	124
tilted in a direction of minimum roll off angle	100	106	110	115

* The initial value was set to be 100.

[0057]

The first vent (horizontal; without tilt) showed increase in the Gurley number with the elapse of day. The second vent (tilted in a direction of the maximum roll off angle) showed slightly inhibited increase in the Gurley number in comparison to the first vent, but this did not exhibited a significant effect. The third vent (tilted in a direction of the minimum roll off angle) showed significantly inhibited increase in the Gurley number in comparison to the second vent. Since the Gurley number is an index of air-permeability, the third vent was confirmed to maintain a high air-permeability

for a long period of time.

5 The surface of the planar membrane in addition to the Gurley number was observed by using a scanning electron microscopy. Although the first and second vents showed an adhered substance such as sulfate salt on the surface of the membrane, the third vent showed no adhered substance such as sulfate salt on the surface of the membrane.

CLAIMS

[Claim 1]

A vent comprising a planar membrane,

5 wherein the membrane has a roll off angle along a first direction and a roll off angle along a second direction perpendicular to the first direction, which roll off angles being different from each other by at least 5°,

10 wherein the roll off angle is defined as a tilt angle of the membrane at which a fluid droplet of $v = 10\mu\text{l}$ of a solution having a surface tension of more than 50 mN/m starts rolling off the membrane plane at room temperature and a relative humidity of $50 \pm 30\%$,

15 wherein the membrane is oriented in the vent so that the membrane plane is tilted at an angle of $> 0^\circ$ with respect to a gravitational direction, and the tilt direction is parallel to the membrane direction having a minimum roll off angle.

[Claim 2]

20 The vent according to claim 1, wherein the solution is an aqueous solution.

[Claim 3]

The vent according to claim 1 or 2, wherein the solution comprises H_2SO_4 , KOH, or salt water.

25 [Claim 4]

The vent according to any one of the preceding claims, which is a vent for a lead storage battery.

[Claim 5]

30 The vent according to any one of the preceding claims, wherein the membrane is a porous PTFE membrane comprising fibrils having an average length of 40 μm or more and 80 μm or less.

[Claim 6]

35 The vent according to any one of the preceding claims, wherein the membrane is a porous PTFE membrane comprising micro-pores defined by nodes and the fibrils,

an average aspect ratio of which micro-pores is 15 or more and 40 or less.

[Claim 7]

5 The vent according to any one of the preceding claims, wherein the membrane is a porous PTFE membrane having an average porosity of 80% or more.

[Claim 8]

10 The vent according to any one of the preceding claims, wherein the surface of the membrane consists solely of PTFE.

[Claim 9]

15 The vent according to any one of the preceding claims, wherein the membrane is a porous PTFE membrane having a Gurley number of one second or less and a Water Endurance Pressure (WEP) of 5 kPa or more.

[Claim 10]

20 The vent according to any one of the preceding claims, wherein the tilt angle of the membrane with respect to the gravitational direction is smaller than (90° - the minimum roll off angle).

[Claim 11]

25 The vent according to any one of the preceding claims, wherein the tilt angle of the membrane with respect to the gravitational direction is 75° or less.

[Claim 12]

An open type lead storage battery using the vent according to any one of the preceding claims.

$\frac{1}{2}$

FIG. 1

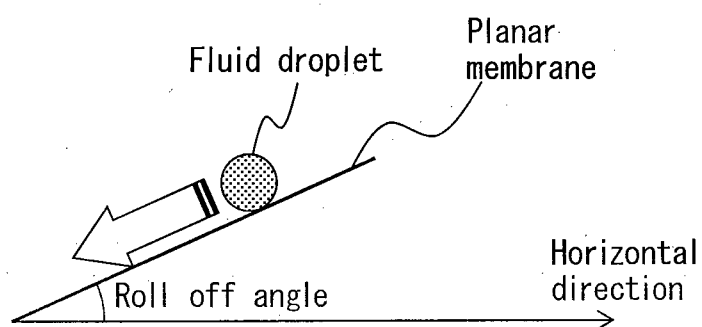
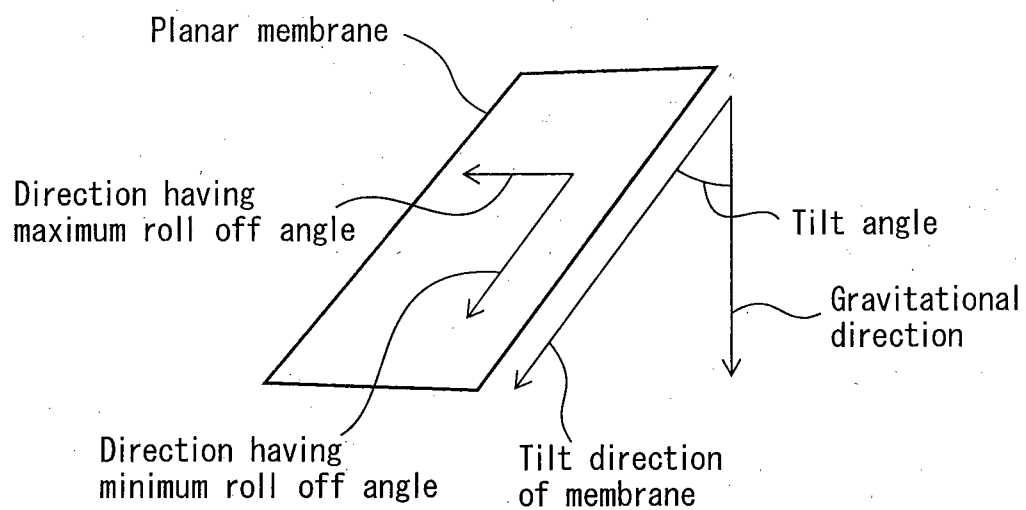
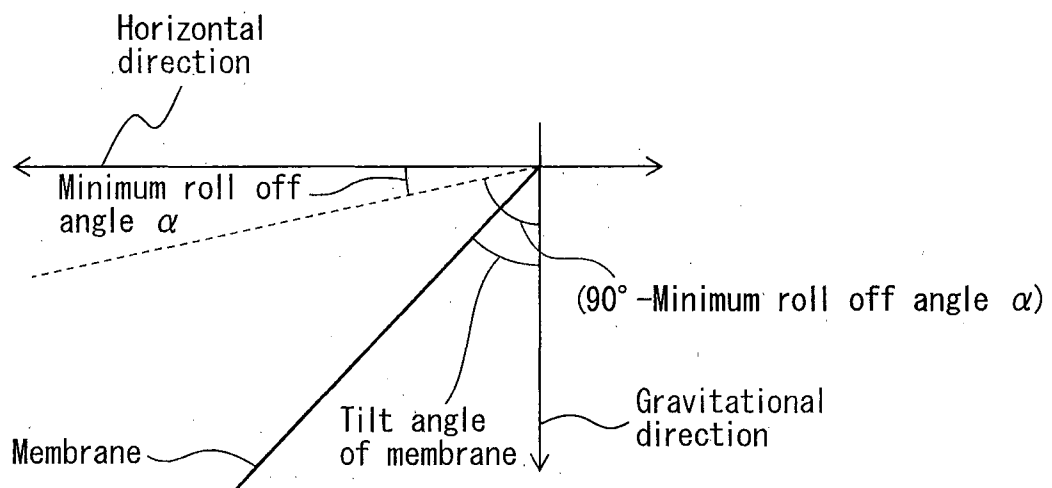


FIG. 2



$\frac{2}{2}$

FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/025063

A. CLASSIFICATION OF SUBJECT MATTER		
Int.Cl. H01M2/12 (2006.01) i, H01G9/12 (2006.01) n		
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)		
Int.Cl. H01M2/12, H01G9/12		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2017 Registered utility model specifications of Japan 1996-2017 Published registered utility model applications of Japan 1994-2017		
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.
A	JP 62-98559 A (PANASONIC CORPORATION) 1987.05.08, claims 1-3, Figs. 1-3 (Family:none)	1-12
A	JP 11-345605 A (PANASONIC CORPORATION) 1999.12.14, claims 1-2, Fig. 1 (Family:none)	1-12
A	JP 5-159765 A (W. L. GORE & ASSOCIATES, CO., LTD.) 1993.06.25, paragraph [0011] (Family:none)	1-12
A	Microfilm of the specification and drawings annexed to the written application of Japanese Utility Model Application No.39420/1984 (Laid-open No.152262/1985) (NITTO DENKO CORPORATION) 1985.10.09, claim 1, Fig. 2A (Family:none)	1-12
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
18.08.2017		29.08.2017
Name and mailing address of the ISA/JP		Authorized officer
Japan Patent Office		MAEDA, Hiroyuki
3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan		4X 2930
		Telephone No. +81-3-3581-1101 Ext. 3477