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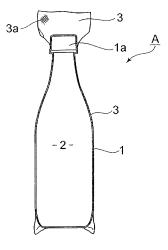
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## (54) CONTAINER WITH EXCELLENT AIRTIGHTNESS AND METHOD FOR HOLDING GAS MOLECULES OR VOLATILE COMPONENTS IN CONTAINER

(57) A bottle made of polyethylene terephthalate does likely undergo that a gas having a small molecular weight or volatile component escapes from the bottle in a short time in comparison with a glass bottle, steel can, and aluminum can. For a countermeasure, a simple operation prevents hydrogen molecules, helium gas, and volatile component from scattering and being lost.

A container filled with gas, or liquid or viscous fluid in which gas is dissolved, or metal granules adsorbing gas is given a cap, and then, the whole of the container including the cap is packed with a metal foil laminated film superior in gas-barrier properties to be vacuum packaged.

Fig. 1



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#### Description

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#### Field of the invention

[0001] The present invention relates to a container, such as a bottle or a film-use type container, which container is to be filled with gases such as hydrogen molecules (molecular hydrogen. Molecular formula H<sub>2</sub>), helium gas, or smell components, a liquid, a viscous fluid, or a solid body containing any of these gases, and is further given a cap or sealed, and the whole of the container including the cap or the seal is packed with a metal foil laminated film superior in gas-barrier properties to be vacuum packaged, thereby preventing permeable gases such as hydrogen molecules of small molecular weight from scattering and being lost. The invention does relate also to a method of keeping air-tightness of the container. Herein, keeping air-tightness includes also restraining specific molecules from scattering and being lost through permeation. Oxygen gas, carbonic acid gas, and, nitrogen gas larger in size than hydrogen molecules possibly evaporate and volatilize through apertures of unglazed earthenware and containers made of wood, bamboo, or paper which apertures of these materials are large in size. But, vacuum packaging with a metal foil laminated film superior in gas barrier properties prevents evaporation and volatilization of the gases. Here, evaporation and volatilization include also that gas molecules dissolved in a solution in a container permeate the container to scatter and be lost.

#### **BACKGROUND OF THE INVENTION**

[0002] (0002) A bottle made of resin (plastic), particularly, of polyethylene terephthalate is substantially excellent in gas barrier properties and is widely used as a container for drinks or beverages such as water, juice, liquors, carbonated drinks, seasonings such as soy sauce, etc. and liquid shampoo, liquid detergents. It is however widely known that gases or volatile components smaller in molecular weight than base materials (barrier layer) of the container (i.e., the polyethylene terephthalate bottles) could escape from the bottle in a short time in comparison with traditional glass or ceramic bottles, steel cans, and aluminum cans. Recently, alcoholic beverages such as wines are bottled in a polyethylene terephthalate bottle having coating with silica deposition or the like and are on the market. It is known to public that such bottle is not capable of keeping air-tightness at the same level as the traditional bottles.

[0003] (0003) The present inventors made such comparison and inspection regarding air-tightness, with hydrogen molecules-dissolved water (water dissolving hydrogen molecules in concentration of approximately 1000 ppb) being filled in a polyethylene terephthalate bottle which bottle then capped, followed by vacuum packaging the whole of the polyethylene terephthalate bottle entirely by use of an aluminum foil laminated film. We found that this bottle showed such result that concentration of remaining hydrogen molecules is dominantly high and shows a large difference in comparison with a polyethylene terephthalate bottle which bottle is packed using an aluminum foil laminated film but is not vacuum packaged.

**[0004]** (0004) Needless to say, it is broadly known to public that hydrogen molecules completely permeate a bottle made of resin, such as a polyethylene terephthalate bottle within several hours to several days and scatter to be lost since hydrogen molecule is smallest in mass as confirmed on the Earth.

**[0005]** (0005) When hydrogen molecules in the hydrogen dissolved water are capable of being kept in the container for some days, then, helium gas, oxygen gas, nitrogen gas, ethyl alcohol, and other organic component larger in molecular weight than hydrogen molecules can naturally be kept in the container for a longer time than conventional technological performance.

[0006] (0006) It has recently been found that hydrogen water is capable of reducing and eliminating hydroxy radical which is a typical reactive oxygen in vivo, and the fact that hydrogen water has effects on treatment and prevention of various diseases has been being clarified. Thus, hydrogen water is given attention in the field of beverages. Various goods using hydrogen water filled in containers are supplied on the market. The containers are generally a bag made of an aluminum foil laminated film. This is because a polyethylene terephthalate bottle, which although broadly used as a container for beverage, does merely allow hydrogen molecules to be lost from the bottle within several days. Moreover, for screw type or crown type metal cans such as aluminum or steel cans, and glass bottles or ceramic bottles, airtightness or water tightness is kept by disk or ring made of cork, resin (plastic) or rubber which fit on the inside of the cap to press edge of mouth of the cans and bottles. Hydrogen molecules do however volatilize and evaporate from the part of ring made of resin, and can be kept only in a short time. Otherwise even when kept longer, concentrations of hydrogen molecules gradually become lower, leading to be problematical in terms of quality. Meanwhile, the cap of screw type or crown type is metallic such as aluminum generally, but rather made of resin with its inside top having an integrally molded double steps. In the container having this cap, hydrogen molecules permeate the resin part. Thus, it is needed to provide vacuum-packaging using a metal foil laminated film which is low in gas permeation properties.

**[0007]** (0007) Moreover, in the medical field, it have been made studies of use of hydrogen molecules in a medicament drip infusion bag since it have been gradually found notable effects of performing drip infusion with hydrogen molecules with respect to a cerebral infarction and diseases of a circulatory organ. A container used for drip is generally made of

polyethylene and polyethylene resin is high in gas permeation rate, so that hydrogen molecules are completely lost from the container approximately within two days. Besides, aluminum foil cannot be applied to the container since a solution in the container must be seen through from the outside of the container. Thus, the fact that the container made of polyethylene is good in gas permeation properties at present is made use of in such manner that the container containing a to be dripped is soaked in a vessel having hydrogen water at high concentration and the container is then used. Naturally, the soaked container having therein the to be dripped is to be used immediately after addition of hydrogen molecules. In other words, at present, to apply hydrogen molecules into the to be dripped cannot be performed without a special apparatus and is not yet generalized but being still studied. If hydrogen molecules in the to be dripped are capable of being kept in a long time, studies and applications will progress by far, needless to say.

#### **Prior Art Documentation**

**Patent Documents** 

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[0008] (0008) Patent Document 1: Unexamined Patent Application 2004-124253, Patent Document 2: Unexamined Patent Application 2007-099365

[0009] (0009) As is mentioned above, it is a significant task to keep long hydrogen molecules in hydrogen water or in a to be dripped containing hydrogen molecules. A remarkable advance can be prospected if hydrogen molecules are capable of being kept in a long time by use of an ordinarily employed container such as a bottle made of polyethylene terephthalate. But, in the present scientific technology, a container made of resin (a container in the type of a bottle) does not have air-tightness at a level obtainable with traditional glass or ceramic bottles, steel cans, and aluminum cans. Even when competent air-tightness in the bottle type container is realized, it is difficult, as widely known, to keep air-tightness at a mouth cap (a cap) of the bottle-type container, since the mouth cap (cap) is made of resin which is low in air-tightness such as polyethylene, polypropylene, and so on.

**[0010]** (0010) A proposal has been made regarding an apparatus for forming a membrane having gas-barrier properties on the inner peripheral surface of the bottle made of resin (the patent document 1). The apparatus provides that gas component serving as a membrane-forming material is connected, in a vacuum chamber, to a high frequency power source or an ionization power source to thereby be brought into a state of plasma, whereby undergoing vapor deposition on the inner peripheral surface of the bottle made of resin to form a membrane.

**[0011]** (0011) However, that apparatus requires many vacuum chambers and has a quite complicated structure. Besides, the specification of the patent document 1 does not disclose how much the gas-barrier properties is improved. And the cap part is made of polyethylene or polypropylene high in gas permeation properties, so that gas leakage from the cap part is not prevented.

[0012] The patent document 2 discloses such technology that a container such as a glass bottle is filled with sake or the like and given a top, followed by covering almost entirely the container's external surface (which external surface preliminarily having a label or others put thereon) by use of a sealing-up outer packaging bag, thereby generating such state of an inside air pressure 1 to 5 hPa (hectopascal) between the container's external surface and the inner surface of the sealing-up outer packaging bag. In this case, the sealing-up outer packaging bag is provided not for preventing evaporation and volatilization of gases from the inside of the glass bottle but for protecting the label or others put on the outside of the glass bottle. Thus, the sealing-up outer packaging bag is characterized in that covering the container is performed with a transparent film through which the label put on the container's outside is seen. The present application is quite different from the patent document 2 in that since the whole of the container including the cap is covered with the metal foil laminated film, the contents of the covering of the container, namely, a label or others put on the container cannot be seen through from the outside. It is so referred to in the patent document 2 that the external surface of the container on which a label or others is put on is almost entirely covered by use of a sealing-up outer packaging bag. The container or the like is not completely covered. For the invention of the present application, if the container is not covered completely, hydrogen molecules or others will leak from there. Both inventions differ from each other also in this point.

#### Gist of the Invention

Tasks the Invention is to solve

[0013] (0013) The present invention has a task to provide that the product, which employs not only a bottle made of polyethylene terephthalate but also a bottle type container low in gas barrier properties as made of polyethylene, polypropylene, or the like, can prevent volatilization and evaporation of gas components from the bottles made of resin (plastic) and also can prevent lowering of concentrations of gas components in fluids and viscous fluid in the bottle type containers. The invention can make use of the conventional manufacturing facilities (for bottling liquids, etc.) as they

are and can be realized merely by partially adding the packaging process (the packaging line) to be performed after the contents filling process into the bottle type containers. Hence, keeping air-tightness of the bottle type container made of resin can be achieved at a low cost and with ease. According to this method, application of the invention is enabled to the feature of aluminum pouch type container using, for a mouthpiece at a part of the container, resin such as polyethylene or polypropylene low in gas barrier properties.

[0014] (0014) If hydrogen water is sealed in aluminum can, hydrogen molecules must be long kept. But, aluminum cans require a small special space ("dead volume") for preventing a solution put in the can from spilling out of the can when opened. Moreover, when heating and sterilizing is performed for the solution put in the can, volume of the solution increases as temperature rises, needing gas for allowing the change of volume, and the dead volume is needed also for this purpose. Hydrogen molecules in saturation can be soluble and exist as gas (1 atm) merely in quantity of 10mL or less in water of 500mL. Thus, If the dead volume is 10mL, half of hydrogen molecules escapes into gaseous phase. As a result, hydrogen molecules do not escape to the outside from the aluminum can, but, for the above-mentioned reason, hydrogen water put in the aluminum can is not able to keep hydrogen molecules of high concentration. Practically, concentration of hydrogen molecules of hydrogen water product filled in aluminum cans is low. When an aqueous solution is filled in a bottle made of polyethylene terephthalate, (since the bottle is flexible differing from the aluminum can,) the bottle may be subjected to circumferentially slightly applied pressure to deform upon closing a cap of the bottle (without providing the dead volume in the bottle), so that the aqueous solution can be prevented from spilling out of the bottle when opened.

[0015] (0015) The invention provides also that a film-use type container such as a medical drip container (made of polyethylene) prevents gas components such as hydrogen molecules or the like from permeating the contents, scattering and being lost from the contents of the film-use type container, and concentration of gas components in fluid or viscous fluid in the film-use type container is prevented from lowering. The present invention can make use of the conventional manufacturing facilities (such as those for filling into bags) as they are, and can be realized merely by partially adding the packaging process (the packaging line) to be performed after the process of filling the contents into the film-use type containers. Hence, keeping air-tightness of a film-use type container made of resin can be achieved at a low cost and with ease.

**[0016]** (0016) As above-mentioned, hydrogen molecules may escape into gaseous phase of the dead volume when exists at the upper part of a container. Thus, a or viscous fluid containing hydrogen molecules when filled into a container such as a bottle made of polyethylene terephthalate or the medical drip bag is needed to be filled in fully to the mouth of the container in order to have no special space (the dead volume) at the upper part of the container.

**[0017]** (0017) For a manufacturing facility (packaging facility) and a metal foil laminated film required to realize the present invention, a newly development of technology is not necessary since the conventional technologies for them are made use of. Besides, design of packaging can be carried out in consideration of cost performance since the metal foil laminated film can be designed and selected according to product's permeability into specific components which product filled in the bottle made of resin (for example, to be designed and selected are such factors as thickness and/or kinds of metal foil, and kinds, number and/or thickness of resin film to be adhered to the metal foil).

[0018] (0018) According to the present invention, it is not necessary to add additives to the bottle-making resin and further not necessary to provide coating, etc. to the bottle made of resin. Thus, the container in type of a bottle made of resin can be readily recycled, so that an effect of lessening carbon dioxide can be expected. The "container" referred to in the present invention includes the mentioned bottle made of resin and film-use type container and also includes containers having screw type or crown type caps, such as aluminum cans, steel cans, and glass bottles and ceramic bottles, and other containers made of paper, wood, or bamboo.

#### **Means for Solving The Task**

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[0019] To attain the above-mentioned object, the present invention does provide that a container (a bottle type container, a film type container) in which filled in are gases such as hydrogen molecules, helium gas, components, oxygen gas, nitrogen gas, carbonic acid gas, or a liquid, viscous fluid, or, solid body each containing any of these gases, a metallic container in the type of screw-cap or crown, a glass bottle, a ceramic bottle, and a container made of wood or bamboo, those containers being first provided with a cap or sealing, and then, the whole of each container including the cap or sealing being packed with a metal foil laminated film superior in gas barrier properties to be vacuum packaged. To be noted is that gases referred to here are hydrogen molecules having a smallest molecular weight, helium gas and component such as wine. For unglazed earthenware, and a container made of paper, wood, or bamboo, the gases may be also oxygen gas, nitrogen gas, and carbonic acid gas larger than hydrogen molecules. The film superior in gas barrier properties may be also a film produced by metal vapor deposition additionally to the metal foil laminated film. As seen from the fact that a balloon using a film made by aluminum vapor deposition and filled with helium gas will begin deflating two days later, the aluminum vapor deposition film is substantially poor in gas barrier properties in comparison with the metal foil laminated film.

[0020] The container packed with the metal foil laminated film when vacuum packaged will become as if unified, whereby providing the gas barrier properties to the container. Degree of vacuum upon vacuum packaging is that a pressure gauge of a vacuum packaging apparatus shows about -760mmHg to -740mmHg (gauge pressure notation(indication)). The higher the degree of vacuum is, the higher the adhesion of the container and the metal foil laminated film becomes, and air-tightness of the container made of resin is kept high. Absolute vacuum is -760mmHg (gauge pressure). Even when reading of the pressure gauge is -760mmHg, an actual value may be about -759mmHg. Besides, it may be influenced by atmospheric pressure fluctuation. A preferable gauge pressure for operation is -760mmHg to -750mmHg. Upon vacuum packaging in an apparatus (using a chamber type apparatus) at this degree of vacuum for 20 to 40sec, the container and the metal foil laminated film adhere to each other, so that hydrogen molecules can be kept in the container for a long time.

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[0021] A container for fluid or viscous fluid among the containers made of resin (plastic) (bottle-type) is almost a bottle made of polyethylene terephthalate. The polyethylene terephthalate bottle is a molded product made of PET resin (polyethylene terephthalate, a kind of saturated polyester), and non-reinforced PET has been enabled to manufacture a highly efficient polyethylene terephthalate bottle through development of stretch blow molding technology. And a polyethylene terephthalate bottle is rich of smoothness and shows appearance with gloss and an excellent dimensional stability. Meanwhile, polyethylene terephthalate resin itself does show substantial gas-barrier properties and smell-keeping properties and its gas barrier properties for oxygen and carbonic acid gas is at a level enough to be used practically. Thus, When the polyethylene terephthalate bottle is provided at its outside with vacuum for a short time, the bottle is not broken and a put in the bottle does not spill.

[0022] (0022) Accordingly, the present invention provides that a bottle type container or a film type container in which a fluid or viscous fluid is filled is first capped, covered or sealed, and then the whole of the container with the cap, cover or seal is packed by use of a metal foil laminated film superior in gas barrier properties to be then vacuum packaged. [0023] (0023) Any kinds of metal foil such as aluminum foil have a capacity of obstructing hydrogen molecules' permeating through the metal foil. Applicable metals for the metal foil may be aluminum, aluminum alloy, and titanium, stainless steel, nickel, permalloy, beryllium copper, phosphor bronze, nickel silver, molybdenum, brass, nichrome, tantalum, zinc, tin, silver solder, silver, copper, iron, lead, Kovar, or, zirconium. Practically, aluminum foil much commercially available is employed. Thickness of the metal foil may be about 6 to 30 μm for a packaging material, but about 12 to 18 μm practically.

[0024] (0024) But, metal foil is liable to have a pinhole. Hydrogen molecules possibly scatter to be lost through the pinhole when the metal foil's thickness is about 12 to 18  $\mu$ m. It is said that metal foil in thickness of more than 50  $\mu$ m is to be employed for zeroing the pinholes. But, aluminum foil in thickness of more than 50  $\mu$ m is hard and not suitable for use for packaging. Hence, the metal foil may be used doubly so that the pinholes can be completely covered, whereby enabling hydrogen molecules in hydrogen water to be preserved in a long time. And the feature is suitable for packaging any products such as medical supplies for which keeping concentration of hydrogen molecules is important.

[0025] (0025) The metal foil laminated film may use a multilayer laminate such as polyethylene terephthalate(PET)/metal foil/polyethylene, nylon/metal foil/polyethylene (or polypropylene), or PET/metal foil/high density polyethylene, or the like. The latter example of metal foil laminated film using aluminum foil is praisefully used for packaging retort food. Thickness of these films may be about 8 to 30  $\mu$ m. And laminating of the film with the metal foil may be performed mainly by dry laminate and otherwise performed through melt extrusion or calendering method.

[0026] (0026) Hydrogen water is excellent as is mentioned above but is very problematic in respect of preservation in view of such fact that even when hydrogen water is put in a polyethylene terephthalate bottle, hydrogen molecules in the hydrogen water completely come out of the bottle within few days. This bottle was vacuum packaged, for example, with aluminum foil laminated film comprising nylon/aluminum foil/polyethylene, so that there was found that hydrogen molecules in the hydrogen water were able to be kept for more than 40 days. Also, hydrogen water was filled in a medical drip bag made of polyethylene, and the drip bag was packed with aluminum foil laminated film comprising nylon/aluminum foil/polyethylene and vacuum packaged, so that hydrogen molecules were kept for more than 40 days similarly to the above-mentioned case.

[0027] (0027) Those examples relate to hydrogen molecules dissolved water. Meanwhile, it has been performed that hydrogen molecules are adsorbed to metal granules, so that hydrogen molecules can be generated from the metal granules to be fed to a fuel cell. In such case, since hydrogen molecules evaporate and volatilize from a container made of resin when applied, a metal container is employed, which metal container however has such defects that it is heavy and costs high. Thus, the container is made, for example, of a tough material such as resin, for example, polyethylene terephthalate, and packed with a film such as aluminum foil laminated film excellent in gas barrier properties and further vacuum packaged using a vacuum packaging apparatus, thereby enabling hydrogen molecules to be kept for a long time which merit was not obtained in the conventional feature of merely putting hydrogen molecules in the container made of resin.

[0028] (0028) To be noted is that upon use of the hydrogen molecules dissolved water, a film applied for vacuum packaging of the container will be broken. A film applied for vacuum packaging of a fuel cell will be kept as it is upon

use of the fuel cell.

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[0029] (0029) The above-mentioned explanation relates to a mineral water to which hydrogen molecules are added. Adding hydrogen molecules can be performed to any liquid or viscous fluid such as juice, carbonic acid drink, green tea drink, coffee drink, milk, yogurt, or the like. Meanwhile, oxygen and carbonic acid gas can be kept by use of a polyethylene terephthalate bottle, but it is hard for a specific kind of smell component such as of wine to be kept by the polyethylene terephthalate bottle. To be noted is that the smell component is defined as a volatile substance which is contained in food and has smell, and usually consists of many compounds. Some substances among those forming the smell component can permeate the bottle made of polyethylene terephthalate. This can be said from the fact that when wine is filled in a polyethylene terephthalate bottle, as time elapses, smell and taste of wine will change subtly and will do not taste good. Accordingly, taste and smell of wine or the like are also capable of being kept for a long time by first filling in a polyethylene terephthalate bottle, then packing the bottle with aluminum foil laminated film or the like superior in gas-barrier properties, followed by vacuum packaging using a vacuum-packaging apparatus.

[0030] (0030) In the meantime, when wine is bottled in the bottle made of polyethylene terephthalate, the bottle needs to be provided at its inside with a membrane having gas-barrier properties as mentioned previously. It is because smell changes due to that low molecular smell components evaporate and volatilize to the outside of the container when a bottle made of polyethylene terephthalate is merely used. The smell components may be ethyl acetate, acetoin, higher alcohol, various ester, or the like. These have higher molecular weight than oxygen and carbonic acid gas. But, it is said that smell components of wine are of 500 or more kinds, and it is so inferred or concluded that any smell component of wine evaporate or volatilize from the polyethylene terephthalate bottle. It is otherwise so inferred or concluded that smell components change and smell changes due to oxidization by oxygen which enters the bottle for a long time. This can also be prevented completely by vacuum packaging using the metal foil laminated film according to the present invention.

#### Effect of the Invention

**[0031]** (0031) The effect of the present invention does, as explained above, provide that there are filled in a container hydrogen molecules, helium gas, or smell component, or water, other liquids, or viscous fluid each dissolving therein any of these gases, or metal granules adsorbing gases, and the container is vacuum packaged with a metal foil laminated film superior in gas-barrier properties, whereby enabling gas molecules to be kept longer several or dozens of times than the feature merely filling the gas molecules or others in the container.

#### **Brief Description of the Drawings**

[0032] (0032)

[Figure 1] A front view of a bottle, according to an example of the present invention, made of polyethylene terephthalate and vacuum packaged with an aluminum foil laminated film (Example 1).

[Figure 2] A front view of a bottle made of polyethylene terephthalate, showing a comparative example (Comparative example 3).

[Figure 3] A front view of a bottle made of polyethylene terephthalate, showing another example of the present invention, vacuum packaged with an aluminum foil laminated film (Example 2).

[Figure 4] A front view of a bottle made of polyethylene terephthalate, the same bottle 1 as that of the example 1 vacuum packaged at a lower level of vacuum (Comparative Example 1).

[Figure 5] A graph showing concentration of hydrogen molecules in Table 1 (Example 1)

[Figure 6] A front view of a medical drip bag, showing other example of the present invention, vacuum packaged with an aluminum foil laminated film (Example 4).

[Figure 7] A front view of the drip bag with an aluminum foil laminated film shown in Figure 6 being partially broken (Example 4).

[Figure 8] A front view of a medical drip bag showing a comparative example (Comparative Example 4).

[Figure 9] A perspective view showing a square cell-culturing container vacuum packaged with an aluminum foil laminated film (Example 6).

[Figure 10] A graph showing concentration of hydrogen molecules in Table 2 (Example 7).

[Figure 11] A front view of a tubular container made of polyethylene terephthalate, showing a further different other example according to the present invention, vacuum packaged with an aluminum foil laminated film, with metal granules (which adsorb hydrogen molecules) being filled in the tubular container (Example 5).

[Figure 12] A further other example is shown. Fig. 12(a) is a front view showing a transparent film type container filled with a beverage, and Fig. 12 (b) is also a front view of the container shown in Fig. 12(a) when formed with an aluminum foil laminated film (Example 8).

[Figure 13] A front view of other different transparent film type container filled with a beverage and vacuum packaged

with an aluminum foil laminated film (Example 9).

[Figure 14] An enlarged view of an example of a conventional metal can with a screw-type cap to be mounted to the can.

[Figure 15] A further different other example according to the present invention, showing a front view of a metal can type container vacuum packaged with an aluminum foil laminated film. (Example 10).

[Figure 16] An enlarged view of a crown cap to be put to a conventional glass bottle.

[Figure 17] A different example according to the present invention, showing a front view of a glass bottle vacuum packaged with an aluminum foil laminated film. (Example 11).

[Figure 18] A sectional view showing an example of a metal foil laminated film.

#### **Embodiments for Using the Invention**

**[0033]** (0033) A container is vacuum packaged with a metal foil laminated film superior in gas-barrier properties, so that the container's surface and the inner surface of the film are highly adhered to each other and unified, thereby preventing gas components from volatilizing and evaporating out of the inside of the container. Hereunder, the present invention will be detailed with referring to the Examples and Comparative Examples but is not limited to such Examples.

#### Example 1

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[0034] (0034) Fig. 1 shows an example of the present invention. Filled up to a mouth of a bottle 1(the container), capacity of 500cc, made of polyethylene terephthalate was a hydrogen molecules dissolved water 2 dissolving hydrogen molecules at concentration of approximately 1000 ppb. The polyethylene terephthalate bottle 1 was packed with an aluminum foil laminated film 3 and vacuum packaged, so that the film 3 was tightly adhered to the bottle 1, thereby achieving a container A containing hydrogen water and superior in air-tightness. Reference numeral la designates a cap (made of polyethylene) for the polyethylene terephthalate bottle 1.

[0035] Ten containers A superior in air-tightness were manufactured by packing the polyethylene terephthalate bottle 1 filled with the hydrogen water with an aluminum foil laminated film 3, and vacuum packaging the same. And the package was opened one by one every few days to measure concentration of hydrogen in the hydrogen water. Table 1 shows the result of the measurement. As seen from the table 1, concentration of hydrogen molecules did not change even after more than one month (32 days). Fig. 5 is a graph made based on the table 1.

[0036] (0036) ([Table 1] as shown)

#### Table 1

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35	PET bottle	PET bottle												
30	Test section	1/28, DH on manuf.	2/05 DH	2/15 DH	2/22 DH	3/01 DH	3/03 DH	3/15 DH	3/22 DH	3/29 DH	4/05 DH			
40	Example 1, packaged with aluminum foil film (-760 mmHg)	1,058	1,051	1,068	1,060	1,053	1,062	1,060	1,062	1,058	1,052			
45	Comparative Example 1, packaged with aluminum foil film (-740 mmHg)	1,063	310	45	0	0	0	0	0	0	0			
50	Comparative Example 2, packaged with aluminum foil film (Air-containing packaging)	1,060	280	0	0	0	0	0	0	0	0			

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(continued)

PET bottle										
Test section	1/28, DH on manuf.	2/05 DH	2/15 DH	2/22 DH	3/01 DH	3/03 DH	3/15 DH	3/22 DH	3/29 DH	4/05 DH
Comparative Example 3, without packaging (PET bottle alone)	1,067	0	0	0	0	0	0	0	0	0
Example 3, packaged with copper foil film (-760 mmHg)							1,059	1,060	1,059	1,055

The value shown in 1/28 is that obtained from measuring upon manufacturing. Other values are those obtained from measuring of hydrogen water taken out of containers.

**[0037]** (0037) The vacuum packaging apparatus is semi-automatic type Kashiwa Vacuum Equipment (NPC Incorporated) and did suction for 20 to 30 sec at vacuum of -760mmHg. Concentration of hydrogen molecules in hydrogen water was measured with a portable dissolved hydrogen meter ENH1000 (TRUSTLEX Incorporated). Hydrogen water subjected to measurement was around 300 cc for each case.

[0038] (0038) An aluminum foil laminated film 3 employed for the packaging consists of aluminum foil of  $16\mu m$  thickness and 20  $\mu m$  thick nylon and 50  $\mu m$  thick polyethylene each dry-laminated to the aluminum foil's respective sides. And the films 3 with the polyethylene surfaces being faced to each other are subjected to heat-seal for packaging. Although aluminum foil laminated film 3 is illustrated as being transparent in Fig. 1, the polyethylene terephthalate bottle 1 can in fact not be seen through from the outside as hindered by aluminum foil 3a. Aluminum foil 3a is seen through since each resin film on both sides is transparent.

#### Comparative Example 1

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[0039] (0039) Fig. 4 shows a comparative example of the present invention. In detail, ten bottles 1 manufactured, similarly to Example 1, made of polyethylene terephthalate and filled with hydrogen water were each packed with an aluminum foil laminated film 3 and vacuum packaged at vacuum of -740mmHg, forming containers C. In this example, the aluminum foil laminated film 3 and the bottle 1 had poor adhesion to each other, so that when the bottle 1 was forced to be turned, the bottle 1 turned as separating from the film 3. And the packages of the bottles were opened one by one on the same days as Example 1 to measure hydrogen concentration of hydrogen water. Result of the measurement is shown in Table 1. As seen, when eight days elapsed, hydrogen molecules quantity became about one forth. In half a month, dissolved hydrogen molecules quantity notably reduced to one twentieth.

#### **Comparative Example 2**

[0040] (0040) Ten containers B containing hydrogen water were manufactured using a bottle 1 made of polyethylene terephthalate and filling hydrogen water and having a polyethylene cap (Fig. 2), similarly to Example 1. The polyethylene terephthalate bottle filled with hydrogen water was packed with an aluminum foil laminated film 3 (not performing vacuum packaging: air-containing packaging). And the packages of the bottles were opened one by one on the same days as Example 1 to measure hydrogen molecules concentration in hydrogen water. Result of the measurement is shown in Table 1. As seen, when eight days elapsed, hydrogen molecules quantity became about one forth. In half a month, dissolved hydrogen molecules quantity became zero. The same reference numerals as of Fig. 1 are used here.

#### **Comparative Example 3**

[0041] (0041) Ten containers B containing hydrogen water were manufactured using a bottle 1 made of polyethylene terephthalate and filling hydrogen water and having a polyethylene cap (Fig. 2), similarly to Example 1. The containers were left as they were under normal temperature. And the caps of the bottles were taken off on the same days as Example 1 to measure hydrogen molecules concentration in hydrogen water in the container. Result of the measurement

<sup>\*</sup> DH: an amount of dissolved hydrogen (unit: ppb)

is shown in Table 1. As seen from Table 1, when eight days elapsed, hydrogen molecules concentration became 0 ppb. The same reference numerals as of Fig. 1 are used here.

#### Example 2

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**[0042]** Fig. 3 shows a container A' containing hydrogen water and superior in air-tightness which container is provided by that a bottle 1 made of polyethylene terephthalate was, similarly to Fig. 1, packed with an aluminum foil laminated film 3 and then vacuum packaged at vacuum of -760mmHg. And a label 4 was put on at the upper part of the aluminum foil laminated film packaging 3 and there is written an indication 5 such as the name of contents of the polyethylene terephthalate bottle, the date of bottling, deadline for consumption, etc. Reference numeral 6 is a hole for suspending the whole package of bottle.

#### Example 3

**[0043]** (0043) A bottle 1 made of polyethylene terephthalate provided in a similar manner to Example 1 was packed with a copper foil laminated film and vacuum-packaged to cause the film to adhere to the bottle 1, thereby obtaining a container containing hydrogen water and superior in air-tightness. Ten such containers were prepared and dissolved hydrogen was measured in a similar manner to Example 1. As shown in table 1, concentration of hydrogen molecules did not change even after 20 days passed.

#### Example 4

**[0044]** Fig. 6 is a front view of a container (a film-use type container) D superior in air-tightness and containing hydrogen water, showing a further different other example according to the present invention, and provided by that a transparent bag 7 made of polyethylene to serve as a medical drip type container of 500 cc is filled, up to the mouth of the bag 7 without dead volume, with a drip water 8 in which hydrogen molecules dissolve at concentration of 1000 ppb, and the transparent bag 7 is packed with an aluminum foil laminated film 3 and vacuum packaged at vacuum of -760mmHg. Reference numeral 7a is a cap of the transparent bag and the cap also made of polyethylene. Also in this example, the aluminum foil laminated film 3 is illustrated as being transparent in the drawing. But, actually, the contents, i.e., the transparent bag 7 cannot be seen through from the outside due to aluminum foil 3a. In the drawing, the reference numeral 3a designates aluminum foil. To be noted is that upon use of the drip type container, it is necessary to completely remove the aluminum foil laminated film 3.

**[0045]** (0045) Ten containers D made of resin (plastic) and containing hydrogen water were manufactured provided by that the transparent bag 7 filled with a drip liquid having hydrogen molecules added was vacuum packaged with aluminum foil laminated film 3. And the packages were opened one by one cc of drip liquid to measure concentration of hydrogen molecules. Result of measurement is shown in Table 2, concentration of hydrogen molecules did not at all change even after one month (32 days). The same apparatuses were used as in Example 1 for vacuum packaging and measuring concentration of hydrogen molecules. Fig. 10 is a graph made based on Table 2.

[0046] (0046) (Table 2)

Table 2

Drip container										
Test section	3/04, DH on manuf.	3/07 DH	3/15 DH	3/22 DH	3/30 DH	4/06 DH	4/07 DH	4/08 DH	4/09 DH	4/10 DH
Example 4, packaged with aluminum foil film (-760 mmHg)	1,055	1,065	1,060	1,058	1,055	1,057	1,058	1,059	1,060	1,061
Comparative Example 4, packaged with aluminum foil film (-740 mmHg)	1,063	187	0	0	0	0	0	0	0	0

(continued)

Drip container										
Test section	3/04, DH on manuf.	3/07 DH	3/15 DH	3/22 DH	3/30 DH	4/06 DH	4/07 DH	4/08 DH	4/09 DH	4/10 DH
Comparative Example 5, packaged with aluminum foil film (Air-containing packaging)	1,065	85	0	0	0	0	0	0	0	0
Comparative Example 6, without packaging (Drip container alone)	1,058	0	0	0	0	0	0	0	0	0
Example 5, packaged with copper foil film (-760 mmHg)							1,061	1,059	1,062	1,055

The value shown in 3/04 is that obtained from measuring upon manufacturing. Other values are those obtained from measuring of hydrogen water taken out of the container.

[0047] (0047) However, for the container D containing hydrogen water, since the transparent bag 7 to be used as a medical drip container is covered with the aluminum foil laminated film 3 upon preservation or any other time for being dealt in any way, the contents of names of drugs and pharmaceutical manufacturers, use or application of drugs, and so on cannot be seen through from the outside. Thus, indication 3b of these matters is to be put on the aluminum foil laminated film 3. To be noted is that in Example 1 and this example, even when a seal or film indicating contents of drugs and names of pharmaceutical manufacturers is attached to the polyethylene terephthalate bottle 1 or drip container 7, there is no obstruction when vacuum packaging is performed with aluminum foil laminated film 3.

**[0048]** (0048) Fig. 7 is a front view of a container D made of resin (plastic) and containing hydrogen water in the state that the aluminum foil laminated film 3 is partially torn to expose the transparent bag 7. In Example 1 and this example, the aluminum foil laminated film 3 may be merely opened to be readily removed.

#### Comparative Example 4

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**[0049]** (0049) A transparent bag 7 obtained similarly to Example 4 and filled with drip water 8 dissolving hydrogen molecules was packed with an aluminum foil laminated film 3 and vacuum packaged at vacuum of -740mmHg. And the vacuum packaged containers were opened one by one on the same dates as those of Example 3 to measure concentration of hydrogen molecules in hydrogen water. As a result of the measurement, as seen in Table 2, the quantity of hydrogen molecules became about one fourth after eight days passed. And the quantity of dissolved hydrogen molecules became zero in half a month.

#### **Comparative Example 5**

[0050] (0050) Ten containers E containing hydrogen water (Fig. 8) were manufactured provided by a transparent bag 7 filled with hydrogen water manufactured similarly to Example 4 and provided with a cap 7a made of polyethylene. Each container E made of resin and filled with hydrogen water was packed with an aluminum foil laminated film 3 (without vacuum-packaging). The containers E were opened one by one on the same dates as of Example 3 to measure concentration of hydrogen molecules in hydrogen water. Result of the measurement is shown in Table 2. As seen from the Table 2, concentration of hydrogen molecules became almost less than ten percent after eight days passed, and hydrogen molecules had completely left after 18 days passed. Reference numeral 7b designates indication of names of drugs and pharmaceutical manufacturers and so on, as 3a in Fig. 6.

<sup>\*</sup> DH: an amount of dissolved hydrogen (unit: ppb)

#### **Comparative Example 6**

**[0051]** (0051) Ten containers E containing hydrogen water were manufactured provided by a drip container 7 filled with hydrogen water manufactured similarly to Example 4 and provided with a cap made of polyethylene (Fig. 7). The containers E were left as they were under normal temperature. The caps of the containers E were taken one by one on the same dates as of Example 4 to measure concentration of hydrogen molecules in hydrogen water inside the containers E. Result of the measurement is shown in Table 2. As seen from the Table 2, concentration of hydrogen molecules became 0 ppb after eight days elapsed. Reference numerals are the same as in Fig. 6.

#### 10 Example 5

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**[0052]** (0052) Ten containers (a film-use type container) containing hydrogen water and being superior in air-tightness were obtained provided by that a transparent bag 7 filled with hydrogen molecules dissolved drip water 8 provided similarly to Example 4 was packed with a copper foil laminated film and vacuum packaged at vacuum of -760mmHg. And the containers packages were opened one by one every few days on and after March 15 to take out 300 cc of drip liquid to measure concentration of hydrogen molecules. Result of the measurement is shown in Table 2. As seen in Table 2, concentration of hydrogen molecules did not at all fluctuate even when 20 days passed.

#### Example 6

[0053] (0053) Fig. 9 shows a further different other example according to the present invention which is a square container 9 for cell culture, the container 9 being vacuum packaged with an aluminum foil laminated film 3' and filled with medium 10 containing hydrogen molecules for culturing cells. The aluminum foil laminated film 3' consists of an aluminum foil laminated at each side with a film of nylon or polyethylene terephthalate, or, polypropylene or polyethylene. [0054] (0054) And the whole of the vacuum packaged container F is subjected to heating-processing (pressurizing and heating sterilization at more than 100°C or heating sterilization at less than 100°C by autoclave, etc.), whereby enabling manufacture of mediums containing hydrogen molecules which mediums are in a germ-free condition or have quite less number of germs. Shapes of the container may be round or polygonal as well as being square.

#### Example 7

[0055] Fig. 11 shows a further different other example according to the present invention, showing a front view of a container G comprising a cylindrical container 11 made of PET (polyethylene terephthalate) filled with metal granules 13 adsorbing hydrogen molecules 12 and vacuum-packaged with an aluminum foil laminated film 3. Reference numeral 14 is a pipe for taking out hydrogen molecules, and 15 a cock, both metallic. To be noted is that examples 1 through 6 remove the aluminum foil laminated film 3 upon use of the contents. This example keeps intact the aluminum foil laminated film 3.

#### Example 8

**[0056]** (0056) Fig. 12(a) shows a film-use type container 16 unique in style, made of a transparent plastic and filled with something to drink 17 (medicament). Reference numeral 18 designates a mouthpiece made of plastic and in the shape of straw, and 19 a cap for the mouthpiece, and 16a a sleeve made of a tubular protection film extended from the film-use type container 16.

[0057] (0057) Now, Fig. 12(b) shows a film-use type container 20 made of an aluminum foil laminated film and filled with something to drink 21 (medicament). Extended part of the container 20 is a tubular sleeve 20a made similarly of an aluminum foil laminated film. Reference numeral 22 designates a mouthpiece and 23 a cap for the mouthpiece. And the film-use type container 20 may be placed in a vacuum-packaging apparatus to be vacuum packaged, whereby providing a container H superior in air-tightness with the tubular sleeve part 20a being vacuum packaged while packing the mouthpiece 21. If hydrogen molecules have been blown into the thing to drink 21, since the container body 20b is made of an aluminum foil laminated film, hydrogen molecules do not leak from the container body. Moreover, since the mouthpiece region 22 is vacuum packaged with the sleeve part 20a, hydrogen molecules do not leak from the mouthpiece region, too. Reference numeral 20c designates aluminum foil which can be seen through a transparent plastic film employed at both sides of the container.

#### Example 9

[0058] (0058) Fig.13 shows another pouch type container 24 whose upper part is cut at one lateral side 24a where a

mouthpiece 25 is provided. Reference numeral 26 designates a cap for the mouthpiece. The mouthpiece 25 and cap 26 are made of polyethylene, and the pouch body is made of aluminum foil laminated film. And both sides of the mouthpiece 25 region are covered with aluminum foil laminated films and vacuum packaging is performed. Then, hydrogen water 27 is filled into the container 24 through an opening 24b at its upper part, and the container 24 is sealed without having special space (the dead volume) at its upper part. Thus, hydrogen water is protected by the aluminum foil laminated film, and the mouthpiece 25 region is also vacuum packaged with aluminum foil laminated film, whereby enabling hydrogen water to be effectively kept in the container 24 for a long time.

#### Example 10

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**[0059]** (0059) Fig. 14 is an enlarged front view of a mouthpiece 28a of a metal can 28. Reference numeral 29 designates a screw cap on whose inner side fit is a pressure member 30 made of resin to pressure the edge 28b of the mouthpiece of the metal can 28 when the cap 29 is put on and tightened. The pressure member 30 made of resin functions for airtightness and water-tightness to prevent the contents 31 of the metal can from flowing out when the contents 31 is under normal pressure. But, when that the contents 31 is hydrogen water, hydrogen molecules leak from the pressure member 30 made of resin to the outside. The same problem arises when caps are screw type with respect to glass bottles or ceramic containers as well as the metal can 28.

**[0060]** (0060) Fig. 15 shows a further different other example according to the present invention, showing a front view of a container J consisting of a metal can 28 (having a screw cap 29) vacuum packaged with aluminum foil laminated film 3 and filled with water 31 containing hydrogen molecules. Vacuum packaging with aluminum foil laminated film 3 prevents hydrogen molecules from scattering and being lost from hydrogen water 31.

#### Example 11

[0061] (0061) Fig. 16 is an enlarged front view of a mouth 32a of a glass bottle 32. Reference numeral 33 designates a crown. A cap opening means 33a in a pull-top type is provided at a lateral side of the crown 33. A pressure member 34 made of resin (plastic) is fit inside the crown 33, so that the pressure member 34 pressures a mouth edge 32b of the glass bottle when the crown 33 is tightened. The pressure member 34 made of resin functions for being air-tight and water-tight to prevent the contents 35 from flowing out of the glass bottle when the contents 35 is under normal pressure.
But, when the contents 35 is hydrogen water, hydrogen molecules leak from the pressure member 34 made of resin to the outside. The same problems arise when the cap is a crown type with respect to a pottery type container as well as the glass bottle 32.

**[0062]** (0062) Fig. 17 shows a further different other example according to the present invention, showing a front view of a container K consisting of a glass bottle 32 (having a crown 33) vacuum packaged with aluminum foil laminated film 3 and filled with water 35 containing hydrogen molecules. Vacuum packaging with aluminum foil laminated film 3 prevents hydrogen molecules from scattering and being lost from hydrogen water 35.

[0063] (0063) Aluminum foil laminated film employed in those mentioned examples does consist of an aluminum foil in thickness of 16  $\mu$ m and nylon in thickness of 20  $\mu$ m and polyethylene in thickness of 15  $\mu$ m each dry-laminated on respective sides of the aluminum foil. But, not only aluminum foil, but also other metal foils in thickness of 30  $\mu$ m or less cannot escape a possibility of having pinholes. Besides, even when the metal foil is laminated with a film, the metal foil has a possibility of having pinholes at its parts being bent or scratched.

**[0064]** (0064) For fully ensuring to keep hydrogen molecules in a long time, it may be achieved, as shown in Fig. 18, by that aluminum foil or other metal foils 36, 37 are used double, a film made of resin (plastic) 38 is interposed between two metal foils, and films made of resin 39, 40 are laminated on the respective outside of the metal foils, whereby forming a four-fold metal foil laminated film 41 serving as more than enough feature.

#### **Industrial Usability**

[0065] (0065) A container made of resin such as a bottle made of polyethylene terephthalate or a medical drip bag is filled with a gas or a liquid or a viscous fluid in which a gas is dissolved, or metal granules adsorbing a gas, and is vacuum packaged with a metal foil laminated film superior in gas-barrier properties, whereby keeping air-tightness of the containers.

#### **Explanation of Reference Numerals**

[0066] (0066)

1: Bottle made of polyethylene terephthalate

	1a:	Cap for the polyethylene terephthalate bottle
	1a. 2:	Hydrogen molecules dissolved water
	3:	Aluminum foil laminated film
5	3a:	Aluminum foil
9	3b:	Indication of names of drugs, pharmaceutical manufacturers, and so on
	3":	Aluminum foil laminated film
	4:	Label
	5:	Indication
	6:	Hole
10	<b>7</b> :	Transparent bag made of polyethylene (Medical drip type container)
	7a:	Cap of the drip container
	7b:	Indication of names of drugs, pharmaceutical manufacturers, and so on
	8:	Hydrogen molecules dissolved drip water
	9:	Container for cell culture
15	10:	Medium
	11:	Tubular container made of polyethylene terephthalate
	12:	Hydrogen molecules
	13:	Metal granules
	14:	Pipe for taking out hydrogen molecules
20	15:	Cock
	16:	Film-use type container
	17:	Something to drink (medicament)
	18:	Mouthpiece
	19:	Cap for mouthpiece
25	20:	Film-use type container
	20a:	Sleeve
	20b:	Body of the container
	20c:	Aluminum foil
00	21:	Something to drink (medicament)
30	22:	Mouthpiece
	23:	Cap for mouthpiece
	24:	Pouch type container
	24a:	Lateral side at the upper part
25	25:	Mouthpiece
35	26:	Cap for mouthpiece
	27:	Hydrogen water
	28:	Metal can
	28a:	Mouthpiece
40	28b:	Edge of the mouthpiece
40	29:	Screw cap
	30: 31:	Pressure member made of resin
		Contents (hydrogen water) Glass bottle
	32: 32a:	Mouth
45	32a. 32b:	
40	32b. 33:	Mouth edge Crown
	33a:	Cap opening means
	33a. 34:	Pressure member made of resin
	3 <del>4</del> . 35:	Contents (hydrogen water)
50	36:	Metal foil
00	37:	Metal foil
	38:	Film made of resin (plastic)
	39:	Film made of resin (plastic)
	40:	Film made of resin
55	41:	Four-fold metal foil laminated film
	A:	Container containing hydrogen water and superior in air-tightness (bottle type container)
	Λ. Α':	Container containing hydrogen water and superior in air-tightness (bottle type container)
	B:	Container containing hydrogen water (bottle type container)
		The state of the s

- C: Container containing hydrogen water poor in adhesion to aluminum foil laminated film
- D: Container containing hydrogen water and superior in air-tightness (Film-use type container)
- E: Container containing hydrogen water (film-use type container)
- F: Culturing container containing hydrogen molecules
- 5 G: Container (in tubular shape) superior in air-tightness and filled with metal granules
  - H: Container superior in air-tightness (film-use type container)
  - I: Container superior in air-tightness (film-use type container)
  - J: Container superior in air-tightness (metal can type container)
  - K: Container superior in air-tightness (glass bottle type container)

## Claims

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- 1. A container superior in air-tightness characterized in that the container is filled with hydrogen molecules, helium gas, smell component, or liquid, viscous fluid, or solid body each containing any of these gases and is given a cap or sealed, and the whole of the container including the cap or seal is then packed with a metal foil laminated film superior in resistance against gas permeability (gas-barrier properties) to be vacuum packaged.
- 2. A container superior in air-tightness as set forth in Claim 1 wherein the container is vacuum packaged with a film superior in gas-barrier properties, so that the surface of the container and the inner surface of the film high adhere to each other to unite the container and the film, thereby preventing the gas components from scattering and being lost from the inside of the container and improving the gas-barrier properties.
  - 3. A container superior in air-tightness as set forth in Claim 1 or 2 wherein when the container filled with hydrogen molecules, helium gas, smell component, or liquid, viscous fluid, or solid body each containing any of these gases is given a top or cap, and the whole of the container including the top or cap is then covered with a metal foil laminated film to be vacuum packaged, a pressure gauge of a vacuum packaging apparatus is -760mmHg to -740mmHg (gauge pressure notation/ absolute vacuum is -760mmHg).
- 4. A container superior in air-tightness as set forth in Claim 1, 2 or 3 wherein the liquid or viscous fluid containing hydrogen molecules is filled in the container up to its mouth without having any space (dead volume) at the upper part of the container.
- 5. A container superior in air-tightness as set forth in Claim 1, 2, 3 or 4 wherein the container may employ a container made of resin provided by molding a material among resin such as polyethylene terephthalate (PET), polyamide (nylon), polyethylene (PE), polypropylene (PP) into a solid in shape of a bottle having thickness of 150 μm or more; a container in form of a bag made using a film less than 200 μm thick, such as a medical drip bag having a mouth for coinjection and a discharge port; a stand pouch type container (including gazette pouch) having a mouth cap (mouthpiece), or three-way-sealed packaging bag (including three-way-sealed packaging bag having back-bonding part), or four-way-sealed packaging bag, etc.; a metal can having a screw cap or a crown; a glass bottle, a ceramic bottle, or a container made of paper, wood, or bamboo.
  - 6. A method for keeping gas molecules or volatile components in a container characterized in that the container filled with hydrogen molecules, helium gas, smell component, or liquid, viscous fluid, or solid body each containing any of these gases is given a cap or sealed, and the whole of the container including the cap or seal is then packed with a metal foil laminated film superior in resistance against gas permeability (gas-barrier properties) to be vacuum packaged.
  - 7. A method for keeping gas molecules or volatile components in a container as set forth in Claim 6 wherein the container is vacuum packaged with a film superior in gas-barrier properties, so that the surface of the container and the inner surface of the film high adhere to each other to unite the container and the film, thereby preventing the gas components from volatilizing and evaporating from the inside of the container and improving the gas-barrier properties.
- 8. A method for keeping gas molecules or volatile components in a container as set forth in Claim 6 or 7 wherein when the container filled with hydrogen molecules, helium gas, smell component, or liquid, viscous fluid, or solid body each containing any of these gases is given a top or cap, and the whole of the container including the top or cap is then covered with an aluminum foil laminated film to be vacuum packaged, a pressure gauge of a vacuum packaging

apparatus is -760mmHg to -740mmHg (gauge pressure notation/ absolute vacuum is -760mmHg).

- **9.** A method for keeping gas molecules or volatile components in a container as set forth in Claim 6, 7 or 8 wherein the liquid or viscous fluid containing hydrogen molecules is filled in the container up to its mouth without having any space (dead volume) at the upper part of the container.
- 10. A method for keeping gas molecules or volatile components in a container as set forth in Claim 6, 7, 8 or 9 wherein the container may employ a container made of resin provided by molding a material among resin such as polyethylene terephthalate (PET), polyamide (nylon), polyethylene (PE), polypropylene (PP) into a solid in shape of a bottle having thickness of 150 μm or more; a container in form of a bag made using a film less than 200 μm thick, such as a medical drip bag having a mouth for coinjection and a discharge port; a stand pouch type container (including gazette pouch) having a mouth cap (mouthpiece), or three-way-sealed packaging bag (including three-way-sealed packaging bag having back-bonding part), or four-way-sealed packaging bag, etc.; a metal can having a screw cap or a crown; a glass bottle, a ceramic bottle, or a container made of paper, wood, or bamboo.

Fig. 1

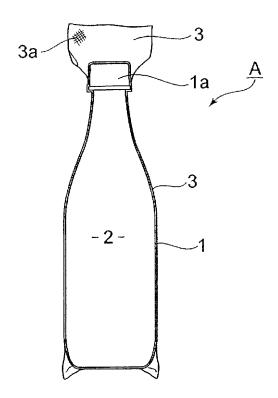


Fig. 2

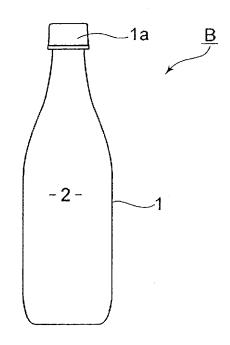


Fig. 3

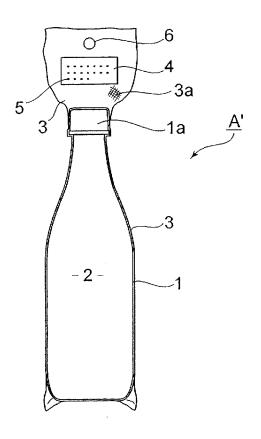


Fig. 4

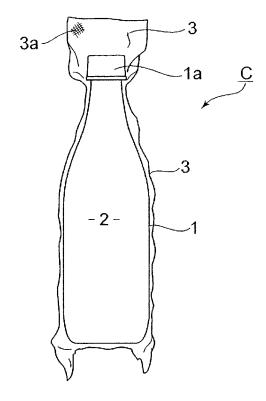


Fig. 5

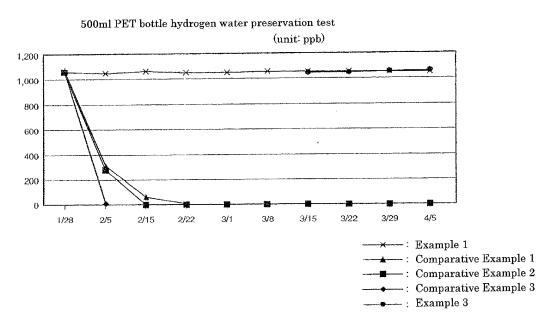


Fig. 6

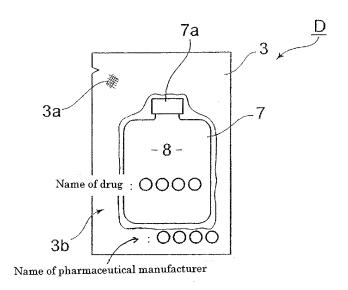
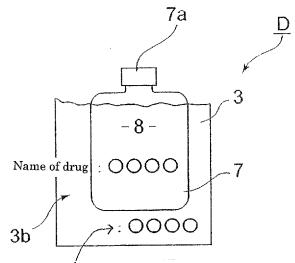


Fig. 7



Name of pharmaceutical manufacturer

Fig. 8

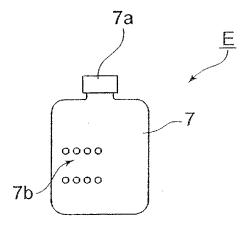


Fig. 9

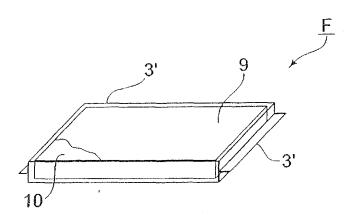
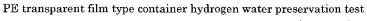


Fig. 10



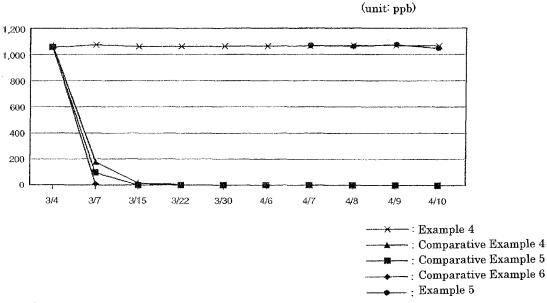


Fig. 11

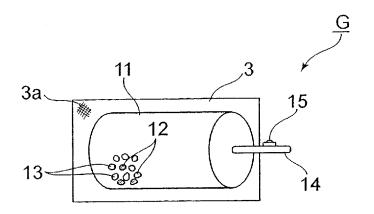


Fig. 12

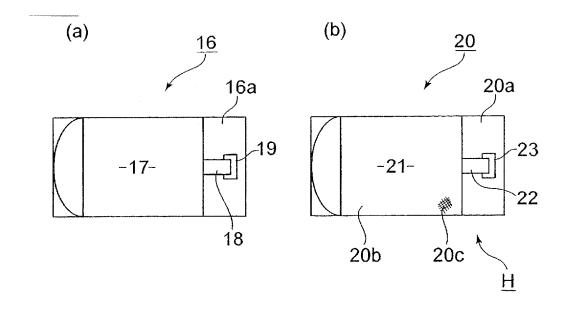


Fig. 13

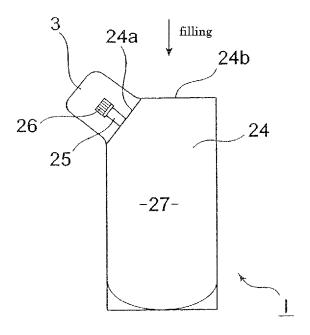


Fig. 14

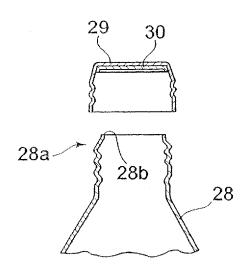


Fig. 15

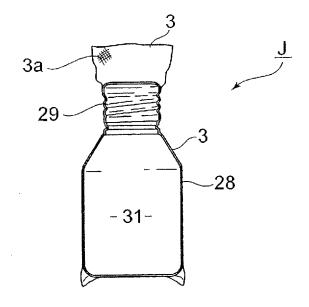


Fig. 16

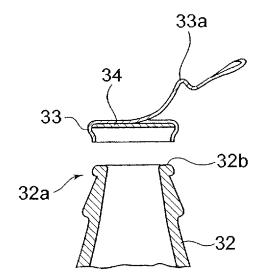


Fig. 17

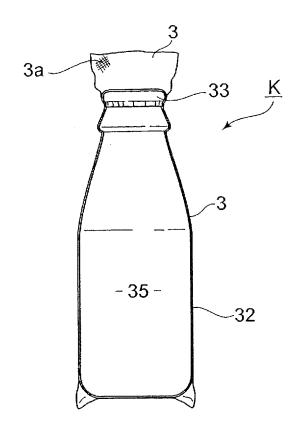
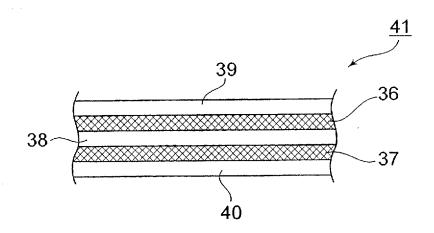


Fig. 18



#### International application No. INTERNATIONAL SEARCH REPORT PCT/JP2013/061757 CLASSIFICATION OF SUBJECT MATTER 5 B65D81/20(2006.01)i, B65B31/02(2006.01)i, B65D77/04(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED 10 Minimum documentation searched (classification system followed by classification symbols) B65D81/20, B65B31/02, B65D77/04 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched 15 1922-1996 Jitsuvo Shinan Koho Jitsuyo Shinan Toroku Koho 1996-2013 Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. 1-10 Υ JP 2009-292511 A (Makino Co,. Ltd.), 17 December 2009 (17.12.2009), 25 claims 1 to 3; paragraphs [0002] to [0011]; fig. 1 to 6 (Family: none) Υ JP 2004-42910 A (Toray Engineering Co., Ltd.), 1-10 12 February 2004 (12.02.2004), 30 paragraphs [0033] to [0035] (Family: none) JP 2011-136727 A (Doctorsman Co., Ltd.), Υ 1-10 14 July 2011 (14.07.2011), claims 1 to 5; paragraph [0016]; fig. 1 to 9 35 (Family: none) See patent family annex. Further documents are listed in the continuation of Box C. 40 Special categories of cited documents: 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 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 document of particular relevance; the claimed invention cannot be filing date considered novel or cannot be considered to involve an inventive step when the document is taken alone 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) 45 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 referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than "&" document member of the same patent family the priority date claimed Date of the actual completion of the international search Date of mailing of the international search report 50 08 July, 2013 (08.07.13) 23 July, 2013 (23.07.13) Name and mailing address of the ISA/ Authorized officer Japanese Patent Office Telephone No. 55 Form PCT/ISA/210 (second sheet) (July 2009)

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/061757

5	C (Continuation)	. DOCUMENTS CONSIDERED TO BE RELEVANT	2013/061/3/
	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
10	Y	JP 2011-177242 A (Miz Co., Ltd.), 15 September 2011 (15.09.2011), paragraphs [0039] to [0040], [0066] (Family: none)	4,9
15	Y	JP 2004-99168 A (Information Science Research Institute), 02 April 2004 (02.04.2004), paragraphs [0006], [0014] & WO 2004/024591 A1 & KR 10-2005-0061471 A & CN 1688496 A & AU 2003273581 A	4,9
20			
25			
30			
35			
40			
45			
50			
55	E DOTHE : 121	O (continuation of second sheet) (July 2009)	

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

#### REFERENCES CITED IN THE DESCRIPTION

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#### Patent documents cited in the description

• WO 2004124253 A [0008]

• WO 2007099365 A [0008]