(19) Europäisches Patentamt / European Patent Office / Office européen des brevets

(11) EP 2 177 592 A1

(12) # EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
21.04.2010 Bulletin 2010/16

(21) Application number: **08777505.2**

(22) Date of filing: **17.06.2008**

(51) Int Cl.:
C10L 3/10 *(2006.01)*

(86) International application number:
PCT/JP2008/061388

(87) International publication number:
WO 2008/156191 (24.12.2008 Gazette 2008/52)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA MK RS

(30) Priority: **18.06.2007 JP 2007159861**
05.07.2007 JP 2007177102
12.07.2007 JP 2007182796

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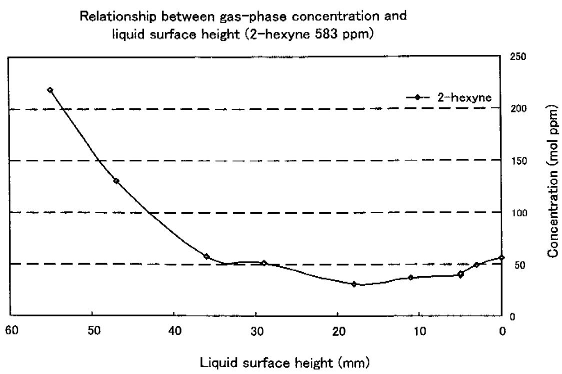
(54) **ODORANT FOR GAS AND PROCESS FOR PRODUCTION OF TOWN GAS WITH THE ODORANT**

(57) The present invention relates to a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, and to a method of manufacturing town gas that uses the gas odorizer.

The gas odorizer of the present invention contains no nitrogen, or even in cases in which it is included, is in a sufficiently low concentration, so that the combusting of fuel gas in which the gas odorizer of the present invention is blended does not produce sulfides, making it possible to prevent environmental pollution and making it suitable to use for fuel cell applications.

The method of manufacturing the town gas of the present invention comprises a gasifying step of gasifying liquefied natural gas, an LPG odorizing step of adding the gas odorizer of the present invention to liquefied petroleum gas, and a town gas generation step in which liquefied petroleum gas obtained by the LPG odorizing step is gasified and mixed with natural gas obtained by the gasification step and the heating value and combustibility adjusted to form the town

FIG.2



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Description

Technical field

[0001] The present invention relates to a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, and to a method of manufacturing town gas that uses the gas odorizer.

Background technology

[0002] In recent years, fuel gas has become indispensable to life, and its use is spreading to many fields. As such fuel gas, there are, for example, hydrocarbon system gas (liquefied petroleum gas) such as propane and butane and so forth, motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and DME (dimethyl ether), etc. Although they are each flammable and explosive, they have a very faint odor, so that if not modified, leaks can go unnoticed, so countermeasures are required to sufficiently prevent accidents such as ignition caused by leakage and explosion and the like.

[0003] Conventionally, the most simple such countermeasure method comprised adding to the fuel gas, as an odorizer (odorant), a compound having a distinctive odor, so that in the event of a gas leakage, it can readily be detected by the human sense of smell. The odorizers that have been used are mercaptans or sulfides.

[0004] However, because the mercaptans and sulfides that are general odorizers that have been conventionally used contain sulfur, combustion of the gas produces sulfur oxide, the emission of which, as-is, into the atmosphere has been a cause of environmental pollution.

[0005] Also, using an above-mentioned conventional odorizer in fuel gas (for example town gas, DME) used for fuel cells has problems, such as that, since the odorizer contains sulfur, the performance of the catalyst used in the fuel cells is lowered, reducing the cell voltage. So, a desulfurizer is provided to remove the sulfur, but that causes an increase in the cost of the fuel cell system.

[0006] Also, if the odorizer contains a high concentration of nitrogen, it is reformed, changing to ammonia, again lowering the catalyst performance and reducing the cell voltage.

[0007] Also, when the above conventional odorizers (mercaptans and sulfides) are used in liquefied petroleum gas (LP gas), because due to their properties mercaptans and sulfides have properties that are different from those of LP gas, even when the LP gas in a gas container decreases through use, the residue in the gas container increases. Therefore, when the LP gas in the gas container runs low, the concentration of the odorizer in the LP gas becomes very high. For example, when 99% of the LP gas has been consumed, the concentration of the odorizer in the LP gas container will be 77 times the initial concentration. When in this way the concentration of odorizer in the gas container became high, the problem arose that when the gas leaked out it produced an abnormally strong odor.

[0008] With the object of eliminating such problems, as disclosed, for example, in Unexamined Patent Application Publication 2002-294261 (hereinafter referred to as Patent Document 1) and Unexamined Patent Application Publication 2002-356688 (hereinafter referred to as Patent Document 2), in recent years odorizers are being developed that do not include sulfur, but there is a desire for further improvements. That is, there are expectations for the appearance of a fuel gas odorizer that enables environmental pollution to be further reduced, has a high detection concentration even in minute amounts, can be used for fuel cells, and in which the residual concentration of the odorizer barely changes even when there is little fuel gas left in the gas container, and does not give rise to the problem of an abnormal odor being produced.

[0009] Odorizers are being studied that even in trace amounts can securely impart an odor in the case not only of fuel gas but of other gases the odor of which can barely be detected when leakage occurs, for example leakages of oxygen gas, nitrogen gas, argon gas and toxic gases that cannot be perceived and therefore lead to wasteful consumption of the gas and danger to life, to which there is therefore a rising desire to impart an odor.

[0010] The present invention was made to solve the above problems, and has as its object to provide a gas odorizer that even when combusted does not produce sulfides and pollute the environment.

[0011] It is also an object of the present invention to provide a gas odorizer that has no problems even when used in fuel cells.

[0012] It is also an object of the present invention to provide a gas odorizer in which the residual concentration of the odorizer barely changes even when there is little fuel gas left in the gas container, and does not give rise to the problem of an abnormal odor being produced.

Disclosure of the Invention

[0013] To attain the above object, in accordance with a first aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises a mixture of normal butyl isocyanide and 2-hexyne.

[0014] In a second aspect of the invention of the present application, in the mixture ratio of the composition of the above first aspect, the 2-hexyne has 1 ~ 20 times the molarity of the normal butyl isocyanide.

[0015] In a third aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises a mixture of normal butyl isocyanide and 1-penthyne.

[0016] In a fourth aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises a mixture of normal butyl isocyanide and 2-hexyne and 1-penthyne.

[0017] In a fifth aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises a mixture of ethyl isocyanide and 2-hexyne.

[0018] In a sixth aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises a mixture of ethyl isocyanide and 1-penthyne.

[0019] In a seventh aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises a mixture of ethyl isocyanide and 2-hexyne and 1-penthyne.

[0020] In an eighth aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises a mixture of normal butyl isocyanide and ethyl isocyanide and 2-hexyne and 1-penthyne.

[0021] In a ninth aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises 2-hexyne.

[0022] In a tenth aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises 1-penthyne.

[0023] In an eleventh aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises 1-butyne.

[0024] In a twelfth aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises at least two or more selected from among 2-hexyne, 1-penthyne and 1-butyne.

[0025] In a thirteenth aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises a mixture of 2-hexyne and at least one of 3-methylbutanal and tertiary butyl mercaptan.

[0026] In a fourteenth aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises a mixture of 1-penthyne and at least one of 3-methylbutanal and tertiary butyl mercaptan.

[0027] In a fifteenth aspect of the invention of the present application, in a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, the odorizer comprises a mixture of 2-hexyne and 1-penthyne and at least one of 3-methylbutanal and tertiary butyl mercaptan.

[0028] In a sixteenth aspect of the invention of the present application, a gas odorizer according to any of the above first to fifteenth aspects that imparts to at least any fuel gas from among hydrocarbon system gas (liquefied petroleum gas) formed of propane and butane and so forth, motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and dimethyl ether (DME), a warning odor for awareness of gas leakage.

[0029] In a seventeenth aspect of the invention of the present application, a gas odorizer according to any of the above first to sixteenth aspects that imparts a warning odor for awareness of gas leakage to oxygen, nitrogen, argon gas, toxic gas, and so forth, to which a warning odor needs to be imparted.

[0030] In an eighteenth aspect of the invention of the present application, a method of manufacturing town gas by gasifying liquefied natural gas (LNG), mixing the gasified LNG with liquefied petroleum gas (LPG), adjusting the heating value and combustibility and imparting a distinctive odor, comprising a step of gasifying LNG to form natural gas (NG), an LPG odorizing step of adding the gas odorizer according to any of the above first to fifteenth aspects of the invention to liquid-state LPG, and a town gas generation step in which liquid-state LPG obtained by the LPG odorizing step is gasified and mixed with the NG obtained by the above gasification step and the heating value and combustibility adjusted to form the town gas.

[0031] In a nineteenth aspect of the invention of the present application, the LPG odorizing step of the eighteenth aspect of the invention is carried out by adding the above gas odorizer to liquid-state LPG in a tank lorry.

[0032] In a twentieth aspect of the invention of the present application, in the eighteenth or nineteenth aspect of the invention, the addition ratio of the gas odorizer with respect to the liquid-state LPG is made 5~15 times greater than the addition ratio to ordinary commercial LPG.

[0033] In the present invention, the gas odorizer (gas odorant) comprises a mixture of normal butyl isocyanide and 2-hexyne, a mixture of normal butyl isocyanide and 1-penthyne, a mixture of normal butyl isocyanide and 2-hexyne and

1-penthyne, a mixture of ethyl isocyanide and 2-hexyne, a mixture of ethyl isocyanide and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne and 1-penthyne, a mixture of normal butyl isocyanide and ethyl isocyanide and 2-hexyne and 1-penthyne, 2-hexyne, 1-penthyne, 1-butyne, or a mixture of two or more thereof, a mixture of 2-hexyne and at least one of 3-methylbutanal and tertiary butyl mercaptan, a mixture of 1-penthyne and at least one of 3-methylbutanal and tertiary butyl mercaptan, or a mixture of 2-hexyne, 1-penthyne and at least one of 3-methylbutanal and tertiary butyl mercaptan.

[0034] Thus, the gas odorizer of the present invention can be formed without including sulfur. Therefore, even when combusted the fuel gas with which the gas odorizer of the present invention is combined does not produce sulfides, enabling pollution of the environment to be prevented.

[0035] Also, as the gas odorizer (gas odorant) that imparts to gas a warning odor required for awareness of gas leakage, the present invention uses a mixture of normal butyl isocyanide and 2-hexyne, a mixture of normal butyl isocyanide and 1-penthyne, a mixture of normal butyl isocyanide and 2-hexyne and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne, a mixture of ethyl isocyanide and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne and 1-penthyne, a mixture of normal butyl isocyanide and ethyl isocyanide and 2-hexyne and 1-penthyne, 2-hexyrie, 1-penthyne, 1-butyne, or a mixture of two or more thereof, a mixture of 2-hexyne and at least one of 3-methylbutanal and tertiary butyl mercaptan, a mixture of 1-penthyne and at least one of 3-methylbutanal and tertiary butyl mercaptan, or a mixture of 2-hexyne and 1-penthyne and at least one of 3-methylbutanal and tertiary butyl mercaptan (TBM ($(CH_3)_3CSH$)), so that as with the conventionally used TBM, it is possible to impart a distinctive gas odor to the gas, making it appropriately applicable to hydrocarbon system gas (liquefied petroleum gas) such as propane and butane and so forth, motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and DME fuel gas and gases such as oxygen, nitrogen, argon gas, toxic gas, and so forth, to which a warning odor needs to be imparted.

[0036] Since the gas odorizer of the present invention can be formed without including sulfur, even if it is added to natural gas or DME and the like used in fuel cells, it enables a good fuel gas odorizer to be provided for fuel cell applications that does not give rise to problems such as lowering of the performance of the fuel cell catalyst and lowering of the cell voltage.

Brief description of the drawings

[0037]

Fig. 1 is a graph showing the gas phase concentration of normal butyl isocyanide in a propane gas container in the case of a mixture in which the molar ratio of 2-hexyne is three times that of the normal butyl isocyanide.
Fig. 2 is a graph showing the gas phase concentration of 2-hexyne in a propane gas container in the case of a mixture in which the molar ratio of 2-hexyne is three times that of the normal butyl isocyanide.
Fig. 3 is a graph showing the gas phase concentration of normal butyl isocyanide in a propane gas container in the case of a mixture in which the molar ratio of 2-hexyne is six times that of the normal butyl isocyanide.
Fig. 4 is a graph showing the gas phase concentration of 2-hexyne in a propane gas container in the case of a mixture in which the molar ratio of 2-hexyne is six times that of the normal butyl isocyanide.
Fig. 5 is a diagram that systematically shows the town gas manufacturing procedure at an LNG satellite base that applies the town gas manufacturing method of the present invention.
Fig. 6 is a diagram that systematically shows an outline of the manufacturing procedure at a conventional LNG satellite base.

Best mode for carrying out the invention

[0038] Details of embodiments of the present invention are described below.

(First embodiment)

[0039] First, a first embodiment is described. In the first embodiment of the present invention, as the gas odorizer (gas odorant) that imparts to gas a warning odor required for awareness of gas leakage, there are used a mixture of normal butyl isocyanide and 2-hexyne, a mixture of normal butyl isocyanide and 1-penthyne, and a mixture of normal butyl isocyanide and 2-hexyne and 1-penthyne.

[0040] In the first embodiment of the present invention, also, as the gas odorizer (gas odorant), there are used a mixture of ethyl isocyanide and 2-hexyne, a mixture of ethyl isocyanide and 1-penthyne, and a mixture of ethyl isocyanide, 2-hexyne and 1-penthyne.

[0041] In the first embodiment of the present invention, also, as the gas odorizer (gas odorant), there is used a mixture of normal butyl isocyanide and ethyl isocyanide and 2-hexyne and 1-penthyne.

[0042] The structural formula of normal butyl isocyanide is expressed by the following structural formula (1).

$CH_3(CH_2)_3N = C$ Structural formula (1)

[0043] The structural formula of ethyl isocyanide is expressed by the following structural formula (2).

$CH_3CH_2N = C$) Structural formula (2

[0044] The structural formula of 2-hexyne is expressed by the following structural formula (3).

$CH_3CH_2CH_2C = CCH_3$ Structural formula (3)

[0045] The structural formula of 1-penthyne is expressed by the following structural formula (4).

$CH_3CH_2CH_2C =$ CH Structural formula (4)

[0046] In the following description of each embodiment, the gas to which the odorizer is added is hydrocarbon system gas (liquefied petroleum gas) such as propane and butane and so forth, motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and DME fuel gas and oxygen, nitrogen, argon gas, toxic gas, and so forth, to which a warning odor needs to be imparted.

[0047] Also, the gas to which the above warning odor needs to be imparted is used ultimately in a gasified state, but in the stages to reach that state may take the form of a solid or liquid, and here is referred to as a gas regardless of its state.

[0048] As can be understood from the above structural formulas, the normal butyl isocyanide, ethyl isocyanide, 2-hexyne and 1-penthyne used as the gas odorizer do not contain sulfur.

[0049] Table 1 shows the results of comparative measurements relating to odor intensity, gas affinity, Ames test and acute oral toxicity of normal butyl isocyanide, ethyl isocyanide, 2-hexyne, 1-penthyne and the tertiary butyl mercaptan (TBM($(CH_3)_3CSH$) normally used as a fuel gas odorizer.

(Table 1)

No.	Odorizer	Odor recognition threshold value A (vol ppm)	Gas affinity	Ames test	Acute oral toxicity (LD50)
1	Normal butyl isocyanide	3.3E-05	0.6	Negative	50~300
2	Ethyl isocyanide	2.7E-04	1.2	Negative	50~300
3	2-hexyne	7.5E-03	1.7	Negative	Over 2000
4	1-penthyne	2-6E-02	1.6	Negative	300~2000
5	t-butyl mercaptan (TBM) (Conventional)	7.3E-05	1.8	Negative	7300

[0050] In Table 1, the recognition threshold value refers to the intensity (odor intensity) of the level of an odor that can be detected by the sense of smell that is indicated as a stage 2 level (a weak odor that can be recognized) in the method of indicating odor intensity. The recognition threshold value and odor intensity have an inversely proportional relationship, in which the smaller the recognition threshold value, the stronger the odor intensity.

[0051] Gas affinity is when an odor sense test is used to investigate the odor of a target odorizer and find the affinity with respect to gas odor and the affinity with other types of odors (tobacco, gasoline, raw garbage, etc.), and the result used to obtain the value (gas odor affinity) - (average affinity of other odors), and is a minimum of -3.0 and a maximum of 3.0.

[0052] The Ames test refers to a representative test method developed by Professor Ames of the University of California to screen mutagenic material (material having the property of acting on the chemical and physical factors that form genes that carry DNA and chromosomes, and inducing mutations) by detecting reversions in a bacterium (rat typhus bacterium).

[0053] A drug is orally administered to rats or mice and the weight of the drug given to animals that die over a two-week period is used to calculate the acute oral toxicity of the dosage per kilogram of body weight, a value that is indicated as the LD50.

[0054] With respect to the recognition threshold value, that of normal butyl isocyanide is about half that of the conventionally used TBM, and is a strong odor intensity. The recognition threshold value of ethyl isocyanide is about four times that of TBM, a somewhat weak odor intensity. The recognition threshold value of 2-hexyne is about 100 times that of TBM and that of 1-penthyne is about 360 times, each having a weak odor intensity.

[0055] Normal butyl isocyanide, ethyl isocyanide, 2-hexyne and 1-penthyne each had about the same odor quality (gas affinity) as the conventionally used TBM, and mutagenicity (Ames test) is negative as well as TBM. Each had a higher toxicity (acute oral toxicity) than the conventionally used TBM, but it was not a problem level.

[0056] Thus, on their own, none of normal butyl isocyanide, ethyl isocyanide, 2-hexyne and 1-penthyne had a problem level, therefore there was no problem using a mixture of normal butyl isocyanide and 2-hexyne, a mixture of normal butyl isocyanide and 1-penthyne, a mixture of normal butyl isocyanide and 2-hexyne and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne, a mixture of ethyl isocyanide and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne and 1-penthyne, and a mixture of normal butyl isocyanide and ethyl isocyanide and 2-hexyne and 1-penthyne as an odorizer.

[0057] Next, a case in which normal butyl isocyanide and 2-hexyne are mixed in a prescribed proportion with propane of liquefied petroleum gas (LP gas) is described in the following.

[0058] When normal butyl isocyanide and 2-hexyne are added to propane, each are put into the propane in a liquid state.

[0059] The description is made in the case of a mixture in which the molar ratio of the 2-hexyne is three times that of the normal butyl isocyanide. Here, the normal butyl isocyanide was 195 mol ppm, and the 2-hexyne was 583 mol ppm.

[0060] Fig. 1 and Fig. 2 are graphs showing gas phase concentrations in a propane gas container in the case of a mixture in which the molar ratio of 2-hexyne is three times that of the normal butyl isocyanide, with Fig. 1 showing the gas phase concentration of the normal butyl isocyanide and Fig. 2 showing the gas phase concentration of the 2-hexyne.

[0061] In Fig. 1, the horizontal axis shows the propane liquid surface height, and the vertical axis shows the mol concentration of the normal butyl isocyanide in the gas phase. As can be seen from this figure, when the liquid surface height is 64 mm, the concentration of the normal butyl isocyanide in the gas phase is 34 mol ppm, and that as subsequent use of the propane gas lowers the liquid surface, after a slight increase it gradually decreases, and when the liquid surface level is at 0, it is 18 mol ppm.

[0062] In Fig. 2, the horizontal axis shows the propane liquid surface height, and the vertical axis shows the mol concentration of the 2-hexyne in the gas phase. As can be seen from this figure, when the liquid surface height is 55 mm the concentration of the 2-hexyne in the gas phase is 218 mol ppm, and decreases as the subsequent use of the propane gas lowers the liquid surface, stabilizing at 25~55 mol ppm when the liquid surface height is 40 mm or below, going to 56 mol ppm at a liquid surface level of 0.

[0063] From Fig. 1 and Fig. 2, when the propane is used and gasifies, it facilitates the gasification of the normal butyl isocyanide and 2-hexyne, so that even when little propane remains in the gas container, it does not give rise to the phenomenon of an abnormal rise in the concentration of the odorizer in the gasified propane gas, therefore eliminating the problem of an abnormal odor being produced when little fuel gas remains in a conventional gas container.

[0064] In Fig. 1, the normal butyl isocyanide mixed in the propane was 195 mol ppm, and the overall average concentration of normal butyl isocyanide in the gas phase was 28 mol ppm. Therefore, the gas-liquid vaporization ratio (gas-liquid concentration ratio) was 28/195 = 0.14. This numerical value is twice the gas-liquid equilibrium ratio of the conventionally used TBM (0.07), which shows that the gasification of the normal butyl isocyanide from liquid phase to gas phase occurs more rapidly.

[0065] Moreover, the gas-liquid equilibrium ratio is the equilibrium ratio in the gas-liquid equilibrium state (in a state in which a solution is put into a sealed container, a state in which there is no change in temperature, pressure, and the composition of the gas phase and liquid phase); here, it refers to the ratio of the molar fraction ya of the normal butyl isocyanide in the gas phase to the molar fraction xa of the normal butyl isocyanide in the liquid phase (ya/xa) in a state in which normal butyl isocyanide is put into propane in a sealed container.

[0066] The gas-liquid vaporization ratio (gas-liquid concentration ratio) is the gas-liquid concentration ratio in a vaporization state, for example, the ratio of the molar fraction of an odorizer in a gas phase to the molar fraction of the odorizer in a liquid phase in a container in a state in which propane in the container is being used by an end gas burner. Compared to the gas-liquid equilibrium ratio, the gas-liquid vaporization ratio is a value that is closer to a state of actual use.

[0067] In Fig. 2, the 2-hexyne mixed in the propane was 583 mol ppm, and the overall average concentration of 2-hexyne in the gas phase was 56 mol ppm. Therefore, the gas-liquid vaporization ratio of the 2-hexyne was 56/583 = 0.1. This numerical value is 1.4 times the gas-liquid equilibrium ratio of the conventionally used TBM (0.07), which shows that the gasification of the 2-hexyne from liquid phase to gas phase occurs rapidly.

[0068] The normal boiling point of normal butyl isocyanide is 124°C while the normal boiling point of TBM is 65°C, so usually normal butyl isocyanide can be predicted to have a lower gas-liquid equilibrium ratio than that of TBM, but using it mixed with 2-hexyne may improve the actual gas-liquid equilibrium ratio.

[0069] The addition amounts of the normal butyl isocyanide and 2-hexyne having this gas-liquid equilibrium ratio are as follows.

[0070] First, to determine the addition amount of 2-hexyne, the addition amount for diluting the odor 200 times was obtained. The following is the reason for diluting the odor 200 times.

[0071] With LEL (%) as the lower explosive limit of propane in air, a gas detector alarm has an LEL of 25%, so if B is the number of dilutions, 1/B = (LEL/100) x 0.25 = (LEL) x 2.5E-3. Therefore, B = 400/LEL is obtained. Here, if the LEL (%) of propane is 2, then B = 400/LEL = 400/2 = 200. That is, even in a case in which propane gas leaks and is diluted 200 times, the propane gas will still be detected by a gas detector, which would ensure that as the gas concentration is 25% of the lower explosive limit, it is safe enough. To make the gas concentration detectable by the human sense of smell, the odorizer (here, 2-hexyne) in the propane, it only has to be ensured that there is an odor even when diluted 200 times.

[0072] The recognition threshold value of 2-hexyne is 7.5E-3, so 0.0075 x 200 = 1.5 (mol ppm) is required for it to be smelled even when diluted 200 times.

[0073] In order for there to be 1.5 mol ppm of 2-hexyne in the gasified propane gas, using 2-hexyne with three times the molarity with a gas-liquid vaporization ratio of 0.1, the concentration of the 2-hexyne to be added to the propane liquid will be 1.5/0.1 = 15 (mol ppm). Normal butyl isocyanide is 15/3 = 5 (mol ppm). Overall the odorizer would be 15 + 5 = 20 mol ppm. The respective molecular weights of 2-hexyne, normal butyl isocyanide and propane are 82, 83, 44, so if 20 mol ppm of odorizer is converted into mass ppm, taking the molecular weight of the odorizer as more or less 82, we get 20 x (82/44) = 37 (mass ppm). This 37 mass ppm is more or less the same as the 30 ~ 40 mass ppm of a conventional odorizer.

[0074] Using normal butyl isocyanide with three times the molarity with a gas-liquid vaporization ratio of 0.14, the concentration of 5 mol ppm of normal butyl isocyanide added to propane liquid that gasifies in the propane gas will be 5 x 0.14 = 0.70 (mol ppm).

[0075] Here, we will consider the addition amount of normal butyl isocyanide, the odor of which can be detected by a human being even when diluted 1000 times by a leakage of the propane gas. For the normal butyl isocyanide to be smelled even when it is gasified and diluted 1000 times, the concentration of the normal butyl isocyanide at the time of said dilution (0.70/1000 = 7.1E-4) must be over the recognition threshold value of the normal butyl isocyanide. 7.1E-4 > recognition threshold value (= 3.3E-5), and (7.1E-4)/(3.3E-5) = 21.5, so the concentration with just normal butyl isocyanide is about 20 times the recognition threshold value.

[0076] That is, in a case in which the odorizer is a mixture of 15 mol ppm of 2-hexyne and 5 mol ppm of normal butyl isocyanide, the normal butyl isocyanide alone can ensure a sufficient odor intensity. An amount of 2-hexyne is added that can be smelled even when it is diluted 200 times, but here, this is to utilize the effect of raising to a gas-liquid vaporization ratio of 0.14 the gas-liquid equilibrium ratio of 0.0036 of the normal butyl isocyanide on its own.

[0077] When 20 mol ppm is added as an odorizer, the addition amount is more or less the same as in the conventional case, in addition to which it can be added to the propane as a liquid, so conventional adding equipment can be used as-is, making it possible to be readily added at a low cost.

[0078] Next is described the case of a mixture in which the molar ratio of 2-hexyne is six times that of the normal butyl isocyanide. Here, the normal butyl isocyanide was 216 mol ppm and the 2-hexyne 1291 mol ppm.

[0079] Fig. 3 and Fig. 4 are graphs showing the gas phase concentrations in a propane gas container in the case of a mixture in which the molar ratio of 2-hexyne is three times that of the normal butyl isocyanide, with Fig. 3 showing the gas phase concentration of the normal butyl isocyanide and Fig. 4 showing the gas phase concentration of the 2-hexyne.

[0080] In Fig. 3, the horizontal axis shows the propane liquid surface height, and the vertical axis shows the mol concentration of the normal butyl isocyanide in the gas phase. As can be seen from this figure, when the liquid surface height is 63 mm, the concentration of the normal butyl isocyanide in the gas phase is 2 mol ppm, and that as subsequent use of the propane gas lowers the liquid surface, it gradually increases, and when the liquid surface level is at 0, it is 15 mol ppm.

[0081] In Fig. 4, the horizontal axis shows the propane liquid surface height, and the vertical axis shows the mol concentration of the 2-hexyne in the gas phase. As can be seen from this figure, when the liquid surface height is 63 mm the concentration of the 2-hexyne in the gas phase is 446 mol ppm, and decreases as the propane gas is used, lowering the liquid surface, stabilizing at around 70 mol ppm when the liquid surface height is 30 mm or below, going to 90 mol ppm at a liquid surface level of 0.

[0082] From Fig. 3 and Fig. 4, it can be understood that, as in the above case of a mixture with three times the molar ratio, the normal butyl isocyanide and 2-hexyne readily gasifies. Therefore even when little propane remains in the gas container, it does not give rise to the phenomenon of an abnormal rise in the concentration of the odorizer in the gasified propane gas, therefore eliminating the problem of an abnormal odor being produced when little fuel gas remains in a conventional gas container.

[0083] In Fig. 3, the normal butyl isocyanide mixed in the propane was 216 mol ppm, and the overall average concentration of normal butyl isocyanide in the gas phase was 10 mol ppm. Therefore, the gas-liquid vaporization ratio was 10/216 = 0.05. This numerical value is 0.7 times the gas-liquid equilibrium ratio of the conventionally used TBM (0.07), which shows that the gasification of the normal butyl isocyanide from liquid phase to gas phase does not occur very readily.

[0084] In Fig. 4, the 2-hexyne mixed in the propane was 1291 mol ppm, and the overall average concentration of 2-hexyne in the gas phase was 144 mol ppm. Therefore, the gas-liquid vaporization ratio of the 2-hexyne was 144/1291

= 0.11. This numerical value is 1.6 times the gas-liquid equilibrium ratio of the conventionally used TBM (0.07), which shows that the gasification of the 2-hexyne from liquid phase to gas phase occurs more rapidly.

[0085] The addition amounts of the normal butyl isocyanide and 2-hexyne having this gas-liquid vaporization ratio are as follows.

[0086] First, to determine the addition amount of 2-hexyne, the addition amount for diluting the odor 200 times was obtained. The recognition threshold value of 2-hexyne is 7.5E-3, so 0.0075 x 200 = 1.5 (mol ppm) is required for it to be smelled even when diluted 200 times.

[0087] In order for there to be 1.5 mol ppm of 2-hexyne in the gasified propane gas, using 2-hexyne with six times the molarity with a gas-liquid vaporization ratio of 0.11, the concentration of the 2-hexyne to be added to the propane liquid will be 1.5/0.11 = 13.6 (mol ppm). Normal butyl isocyanide will be 13.6/6 = 2.3 (mol ppm). Overall the odorizer would be 13.6 + 2.3 = 15.9 mol ppm. The respective molecular weights of 2-hexyne, normal butyl isocyanide and propane are 82, 83, 44, so if 15.9 mol ppm of odorizer is converted into mass ppm, taking the molecular weight of the odorizer as more or less 82, we get 15.9 x (82/44) = 29.6 (mass ppm). This 29.6 mass ppm is more or less the same as the 30 ~ 40 mass ppm of a conventional (present) odorizer.

[0088] Using normal butyl isocyanide with six times the molarity with a gas-liquid vaporization ratio of 0.05, the concentration of 2.3 mol ppm of normal butyl isocyanide added to propane liquid that gasifies in the propane gas will be 2.3 x 0.05 = 0.12 (mol ppm).

[0089] Here, we will consider the addition amount of normal butyl isocyanide, the odor of which can be detected by a human being even when diluted 1000 times by a leakage of the propane gas. For the normal butyl isocyanide to be smelled even when it is gasified and diluted 1000 times, 0.12/1000 = 1.2E-4 must be over the recognition threshold value of the normal butyl isocyanide. 1.2E-4 > recognition threshold value (= 3.3E-5), and (1.2E-4)/(3.3E-5) = 3.6, so the concentration even with only normal butyl isocyanide is about 3~4 times the recognition threshold value.

[0090] That is, in a case in which the odorizer is a mixture of 13.6 mol ppm of 2-hexyne and 2.3 mol ppm of normal butyl isocyanide, the normal butyl isocyanide alone can ensure a sufficient odor intensity. An amount of 2-hexyne is added that can be smelled even when it is diluted 200 times, but here, this is to utilize the effect of raising to a gas-liquid vaporization ratio of 0.15 the gas-liquid equilibrium ratio of 0.0036 of the normal butyl isocyanide on its own.

[0091] When 15.9 mol ppm is added as an odorizer, the addition amount is more or less the same as in the conventional case, in addition to which it can be added to the propane as a liquid, so conventional adding equipment can be used as-is, making it possible to be readily added at a low cost.

[0092] The description has been made with respect to a case in which, in the mixture ratios of normal butyl isocyanide and 2-hexyne, in terms of molar ratio the molarity of the 2-hexyne is three times and six times that of the normal butyl isocyanide. However, the same result as in the above cases of three times the molarity and six times the molarity can be obtained with a mixture ratio of one times the molarity to 20 times the molarity, which is applied to make it 1~20 times with respect to molar ratio.

[0093] It is inexpedient for the molar ratio of the 2-hexyne to be times one or lower, for reasons such as that the normal butyl isocyanide gas-liquid vaporization ratio will be too small and almost no gasification will occur, there will be too little 2-hexyne so it will have almost no effect, and that the addition amount as an odorizer will be too small, making it impossible to utilize conventional adding equipment.

[0094] It is also inexpedient for the molar ratio of the 2-hexyne to be 20 times or more, for the reasons that the gas-liquid vaporization ratio of the normal butyl isocyanide will be too low (almost no gasification) due to the concentration of the normal butyl isocyanide being too low, and that the addition amount as an odorizer will be too large making it impossible to utilize conventional adding equipment.

[0095] While the above description has been made with respect to cases in which normal butyl isocyanide and 2-hexyne are added to propane, it can be similarly applied to other gases, such as for example butane and other hydrocarbon system gas (liquefied petroleum gas), motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and to DME and gases such as oxygen, nitrogen, argon gas, toxic gas, and so forth, to which a warning odor needs to be imparted.

[0096] Moreover, while the above description was made with respect to the use of a mixture of normal butyl isocyanide and 2-hexyne as the gas odorizer (gas odorant), the same result can be obtained even when a combination other than that is used, such as a mixture of normal butyl isocyanide and 1-penthyne, or a mixture of normal butyl isocyanide and 2-hexyne and 1-penthyne.

[0097] The same result can also be obtained even when a mixture of ethyl isocyanide and 2-hexyne, a mixture of ethyl isocyanide and 1-penthyne, or a mixture of ethyl isocyanide and 2-hexyne and 1-penthyne is used.

[0098] The same result can also be obtained even when a mixture of normal butyl isocyanide and ethyl isocyanide and 2-hexyne and 1-penthyne is used.

[0099] As set forth in the foregoing, as the gas odorizer (gas odorant), the present invention uses a mixture of normal butyl isocyanide and 2-hexyne, a mixture of normal butyl isocyanide and 1-penthyne, a mixture of normal butyl isocyanide and 2-hexyne and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne, a mixture of ethyl isocyanide and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne and 1-penthyne, or a mixture of normal butyl isocyanide and ethyl isocyanide and 2-hexyne and 1-penthyne, enabling the gas odorizer to be formed without including sulfur, so that in cases where the gas is a fuel gas, even when the fuel gas is combusted it does not produce sulfides, enabling pollution of the environment to be prevented.

[0100] Also, by using a mixture of normal butyl isocyanide and 2-hexyne, a mixture of normal butyl isocyanide and 1-penthyne, a mixture of normal butyl isocyanide and 2-hexyne and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne, a mixture of ethyl isocyanide and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne and 1-penthyne, or a mixture of normal butyl isocyanide and ethyl isocyanide and 2-hexyne and 1-penthyne for the gas odorizer, as with the conventionally used TBM, it is possible to impart a distinctive gas odor to the gas, making it appropriately applicable to hydrocarbon system gas (liquefied petroleum gas) such as propane and butane and so forth, motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and DME fuel gas and gases such as oxygen, nitrogen, argon gas, toxic gas, and so forth, to which a warning odor needs to be imparted.

[0101] Also, since the gas odorizer can be formed without including sulfur, even if it is added to natural gas or DME and the like used in fuel cells, it enables a good fuel gas odorizer to be provided for fuel cell applications that does not give rise to problems such as lowering of the performance of the fuel cell catalyst and lowering of the cell voltage.

[0102] Also, if an odorizer contains a high concentration of nitrogen, it is reformed, changing to ammonia, lowering the catalyst performance and reducing the cell voltage. However, since 2-hexyne and 1-penthyne do not contain nitrogen, the overall nitrogen content of the normal butyl isocyanide or ethyl isocyanide is a small, adequately low concentration, so that even when used as a gas odorizer, it did not lower catalyst performance or lower cell voltage.

[0103] Also, by using a mixture of normal butyl isocyanide and 2-hexyne, a mixture of normal butyl isocyanide and 1-penthyne, a mixture of normal butyl isocyanide and 2-hexyne and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne, a mixture of ethyl isocyanide and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne and 1-penthyne, or a mixture of normal butyl isocyanide and ethyl isocyanide and 2-hexyne and 1-penthyne for the gas odorizer, the residual concentration of the odorizer barely changes even when there is little fuel gas left in the gas container and is much lower than a conventional one. Therefore, it does not produce an abnormal odor, which conventionally has been a problem.

[0104] The normal boiling point of normal butyl isocyanide is 124°C while the normal boiling point of TBM is 65°C, so usually normal butyl isocyanide can be predicted to have a lower gas-liquid vaporization ratio than that of TBM, but using it mixed with 2-hexyne can greatly improve the gas-liquid equilibrium ratio of the normal butyl isocyanide.

[0105] Also, 2-hexyne having a gas odor also functions as a normal butyl isocyanide solvent, enabling a desired odor intensity and gas odor extent and the like to be used by arbitrarily changing the mixture ratio from times one molarity up to times 20 molarity.

(Second embodiment)

[0106] Next, a second embodiment of the present invention is described. In the second embodiment of the present invention, as the odorizer that imparts to gas a warning odor required for awareness of gas leakage, there is used any one of 2-hexyne, 1-penthyne, 1-butyne.

[0107] The structural formula of the 2-hexyne has been shown by the above structural formula (3), and the structural formula of the 1-penthyne has been shown by the above structural formula (4).

[0108] The structural formula of the 1-butyne is expressed by the following structural formula (5).

$$HC = CCH_2CH_3 \qquad \text{Structural formula (5)}$$

[0109] As can be understood from the above structural formulas, the above 2-hexyne, 1-penthyne and 1-butyne used as an odorizer do not contain sulfur.

[0110] The following description is made with respect to cases in which the 2-hexyne, 1-penthyne and 1-butyne are each added to liquefied petroleum gas (LP gas) propane.

[0111] In cases in which 2-hexyne, 1-penthyne and 1-butyne are each added to propane, they are put into the propane in a liquid state.

[0112] Table 2 shows the results of comparative measurements relating to recognition threshold value, gas-liquid equilibrium ratio and addition amount index of 2-hexyne, 1-penthyne, 1-butyne and the tertiary butyl mercaptan (TBM($(CH_3)_3CSH$) normally used as a fuel gas odorizer.

[0113] In Table 2, the recognition threshold value refers to the intensity (odor intensity) of the level of an odor that can be detected by the sense of smell that is indicated as a stage 2 level (a weak odor that can be recognized) in the method of indicating odor intensity. The recognition threshold value and odor intensity have an inversely proportional relationship, in which the smaller the recognition threshold value, the stronger the odor intensity.

(Table 2)

Odorizer		Odor recognition threshold value A (vol ppm)	Recognition threshold value compared to TBM (conventional (times)	Gas-liquid equilibrium ratio B	Gas-liquid equilibrium ratio compared to TBM (conventional) (times)	Addition amount index C (A/B) x 10^3	Addition amount index compared to TBM (convention -al) (times)
1	2-hexyne	7.50E-03	103	0.016	1.6	469	64
2	1-penthyne	2.60E-02	356	0.064	6.4	406	56
3	1-butyne	7.40E-01	10137	0.25	25	2960	405
4	t-butyl mercaptan	7.30E-05	1	0,01	1	7.3	1

[0114] The gas-liquid equilibrium ratio is the equilibrium ratio in the gas-liquid equilibrium state (in a state in which a solution is put into a sealed container, a state in which there is no change in temperature, pressure, and the composition of the gas phase and liquid phase); here, it refers to the ratio of the molar fraction ya of the odorizer in the gas phase to the molar fraction xa of the odorizer in the liquid phase (ya/xa) in a state in which the odorizer (2-hexyne, 1-penthyne, 1-butyne) is put into propane in a sealed container.

[0115] The addition amount index is an evaluation item that is peculiar to the present invention, a value that is obtained by the following numerical formula (1).

$$\text{Addition amount index C} = (\text{recognition threshold value A/gas-liquid equilibrium ratio B}) \times 10^3 \qquad \text{Numerical formula (1)}$$

[0116] The odor intensity of an odorizer, and whether the odorizer readily gasifies are major factors in a gas odor. That is, the smaller the recognition threshold value A, the easier it is to gasify from the liquid phase and the larger the gas-liquid equilibrium ratio B is, the smaller the addition amount can be made, so the smaller the value of the addition amount index C, the smaller the addition amount can be made.

[0117] The TBM used as a conventional odorizer has a recognition threshold value of 7.3 x 10^{-5} vol ppm, a gas-liquid equilibrium ratio of 0.01, and an addition amount index of 7.3.

[0118] A case will now be described in which an odorizer comprised of 2-hexyne is added to propane. In the case of 2-hexyne, the recognition threshold value is 7.5 x 10^{-3} vol ppm, 103 times more than the recognition threshold value of the conventionally used TBM.

[0119] The gas-liquid equilibrium ratio at the time the 2-hexyne was added to the propane is 0.016. This numerical value is 1.6 times the gas-liquid equilibrium ratio of the conventionally used TBM (0.01), which indicates that 2-hexyne gasifies from the liquid phase more rapidly than TBM.

[0120] That is, the 2-hexyne has 103 times the recognition threshold value and 1.6 times the gas-liquid equilibrium ratio of the conventionally used TBM, and while it has a weaker odor, it readily gasifies. Considered in terms of the addition amount index, the addition amount index of 2-hexyne is 469, 64 times that of the conventionally used TBM. Therefore, an odor on the same order as that of TBM can be obtained by adding to the propane an amount that is 64 times that of the conventional TBM.

[0121] The results of a comparison with the conventionally used TBM in respect of odor quality, toxicity and mutagenicity showed them to be about the same.

[0122] Also, even in a case in which the propane in the gas container is used, lowering the liquid surface height, the concentration of the 1-penthyne in the propane was about the same as the initial concentration, so there was no problem of an abnormal odor being produced.

[0123] A case will now be described in which an odorizer comprised of 1-penthyne is added to propane. In the case of 1-penthyne, the recognition threshold value is 2.6 x 10^{-2} vol ppm, 356 times *more than* the recognition threshold value of the conventionally used TBM.

[0124] The gas-liquid equilibrium ratio at the time the 1-penthyne was added to the propane is 0.064. This numerical value is 6.4 times the gas-liquid equilibrium ratio of the conventionally used TBM (0.01), which indicates that 1-penthyne gasifies from the liquid phase more rapidly than TBM.

[0125] That is, the 1-penthyne has 356 times the recognition threshold value and 6.4 times the gas-liquid equilibrium ratio of the conventionally used TBM, and while it has a weaker odor, it readily gasifies. Considered in terms of the addition amount index, the addition amount index of 1-penthyne is 406, 56 times that of the conventionally used TBM. Therefore, an odor on the same order as that of TBM can be obtained by adding to the propane an amount that is 56 times that of the conventional TBM.

[0126] The results of a comparison with the conventionally used TBM in respect of odor quality, toxicity and mutagenicity showed them to be about the same.

[0127] Also, even in a case in which the propane in the gas container is used, lowering the liquid surface height, the concentration of the 2-hexyne in the propane was about the same as the initial concentration, so there was no problem of an abnormal odor being produced.

[0128] Continuing on, a case will now be described in which an odorizer comprised of 1-butyne is added to propane. In the case of 1-butyne, the recognition threshold value is 7.4×10^{-1} vol ppm, 10137 times more than the recognition threshold value of the conventionally used TBM.

[0129] The gas-liquid equilibrium ratio at the time the 1-butyne was added to the propane is 0.25. This numerical value is 25 times the gas-liquid equilibrium ratio of the conventionally used TBM (0.01), which indicates that 1-butyne gasifies from the liquid phase quite a bit faster than TBM.

[0130] That is, the 1-butyne has 10137 times the recognition threshold value and 25 times the gas-liquid equilibrium ratio of the conventionally used TBM, and while it has a weaker odor, it readily gasifies. Considered in terms of the addition amount index, the addition amount index of 1-butyne is 2960, 405 times that of the conventionally used TBM. Therefore, an odor on the same order as that of TBM can be obtained by adding to the propane an amount that is 405 times that of the conventional TBM.

[0131] The results of a comparison with the conventionally used TBM in respect of odor quality, toxicity and mutagenicity showed them to be about the same.

[0132] Also, even in a case in which the propane in the gas container is used, lowering the liquid surface height, the concentration of the 1-butyne in the propane was about the same as the initial concentration, so there was no problem of an abnormal odor being produced.

[0133] While the above description has been made with respect to a case in which 2-hexyne, 1-penthyne and 1-butyne are each added to propane, it can be similarly applied to other gases, such as for example butane and other hydrocarbon system gas (liquefied petroleum gas), motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and to various types of DME fuel gases and to oxygen, nitrogen, argon gas, toxic gas, and so forth, to which a warning odor needs to be imparted.

[0134] As set forth in the foregoing, as the gas odorizer (gas odorant) the second embodiment of the present invention uses any of 2-hexyne, 1-penthyne, and 1-butyne, enabling the gas odorizer to be formed without including sulfur, so that in cases where the gas is a fuel gas, even when the fuel gas is combusted it does not produce sulfides, enabling pollution of the environment to be prevented.

[0135] Also, using any of 2-hexyne, 1-penthyne, and 1-butyne for the odorizer makes it possible to impart a distinctive gas odor by adding an amount that is in the order of 50 times to 400 times the amount of the conventionally used TBM, making it appropriately applicable not only in the case of the above propane, but also to hydrocarbon system gas (liquefied petroleum gas) other than propane such as butane and so forth, motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and various DME fuel gases and gases such as oxygen, nitrogen, argon gas, toxic gas, and so forth, to which a warning odor needs to be imparted.

[0136] Also, since the gas odorizer of the present invention can be formed without including sulfur, even if it is added to natural gas or DME and the like used in fuel cells, it enables a good fuel gas odorizer to be provided for fuel cell applications that does not give rise to problems such as lowering of the performance of the fuel cell catalyst and lowering of the cell voltage.

[0137] Also, if an odorizer contains a high concentration of nitrogen, it is reformed, changing to ammonia, lowering the catalyst performance and reducing the cell voltage. However, since 2-hexyne, 1-penthyne and 1-butyne do not contain nitrogen, so that even when used as a gas odorizer for a fuel cell, it lowering catalyst performance or lowering cell voltage caused by nitrogen contents can be precented..

[0138] Also, even when any of 2-hexyne, 1-penthyne, and 1-butyne is used for the gas odorizer, the residual concentration of the odorizer barely changes even when there is little fuel gas left in the gas container and is much lower than a conventional one. Therefore, it does not produce an abnormal odor, which conventionally has been a problem.

[0139] Also, while in the above second embodiment 2-hexyne, 1-penthyne and 1-butyne are each used singly as the odorizer, instead of singly, a mixture of at least two or more of 2-hexyne, 1-penthyne and 1-butyne may be used. A comparison showed 2-hexyne, 1-penthyne and 1-butyne to have about the same odor quality, toxicity and mutagenicity as the conventionally used TBM, so a desired mixture ratio may be selected according to the purpose.

(Third embodiment)

[0140] Next, a third embodiment of the present invention is described. In the third embodiment of the present invention, as the odorizer that imparts to gas a warning odor required for awareness of gas leakage, there is used a mixture of 2-hexyne and at least one of 3-methylbutanal and tertiary butyl mercaptan (TBM), a mixture of 1-penthyne and at least one of 3-methylbutanal and TBM, a mixture of 1-penthyne and at least one of 3-methylbutanal and TBM, or a mixture of 2-hexyne and 1-penthyne and at least one of 3-methylbutanal and TBM.

[0141] The structural formula of the 2-hexyne has been shown by the above structural formula (3), and the structural formula of the 1-penthyne has been shown by the above structural formula (4).

[0142] As stated above, the above 2-hexyne and 1-penthyne used as the odorizer do not contain sulfur. The chemical formula of the 3-methylbutanal mixed with these is ($(H_3C)_2CHCH_2CHO$), which does not contain sulfur. Also, the chemical formula of TBM is $(CH_3)_3CSH$, which contains sulfur.

[0143] The following description is made with respect to cases in which the above mixtures are added in a liquid state to liquefied petroleum gas (LP gas) propane.

[0144] Table 3 shows the results of comparative measurements relating to recognition threshold value A, gas-liquid vaporization ratio M and addition amount index C1 of 2-hexyne, 1-penthyne, 3-methylbutanal, TBM and various mixtures.

(Table 3)

Odorizer		Odor recognition threshold value A (vol ppm)	Recognition threshold value compared to TBM (conventional) (times)	Gas-liquid vaporization ratio M	Gas-liquid vaporization ratio compared to TBM (conventional) (times)	Addition amoun index C1 (A/M) x 10^3	Addition amount index C1 compared to TBM (conventional) (times)
1	2-hexyne	7.50E-03	103	0.10	0.8	75	123
2	1-penthyne	2.60E-02	356	0.16	1.3	163	267
3	3-methylbutanal	4.80E-05	0.7	0.11	0.9	0.44	0.72
4	t-butyl mercaptan (TBM)	7.30E-05	1	0.12	1	0.61	1
5	2-hexyne 50% 3-methylbutanal 50%	3.77E-03	52	0.11	0.9	36	59
6	2-hexyne 50% TBM 50%	3.79E-03	52	0.11	0.9	34	57
7	1-penthyne 50% 3-methylbutanal 50%	1.30E-02	178	0.14	1.1	96	159
8	1-penthyne 50% TBM 50%	1.30E-02	179	0.14	1.2	93	153

[0145] Table 3 shows the measurement results of the various mixtures, which are 3-methylbutanal and TBM each mixed with 2-hexyne, and 3-methylbutanal and TBM each mixed with 1-penthyne. The mixture ratio of 3-methylbutanal and TBM with respect to the 2-hexyne, and the mixture ratio with respect to the 1-penthyne, are 50%, respectively.

[0146] In the third embodiment, the mixing ratios of the 3-methylbutanal and TBM to the 2-hexyne and 1-penthyne, respectively, are 0 ~ 50%, and Table 3 shows the results of measurements made when the maximum 50% was used. The recognition threshold value A, gas-liquid vaporization ratio M and addition amount index C1 value between 0 and 50% are taken from between the value of 2-hexyne when used alone and the value of the 50% mixture shown in Table 3, and from between the value of 1-penthyne when used alone and the value of a 50% mixture shown in Table 3.

[0147] In Table 2 of the second embodiment, the gas-liquid equilibrium ratio which is a theoretical value was employed, but in the Table 3 of this third embodiment, the gas-liquid vaporization ratio is employed. As stated above, the gas-liquid vaporization ratio (gas-liquid concentration ratio) is the gas-liquid concentration ratio in the vaporization state, for example, the ratio of the molar fraction of an odorizer in a gas phase to the molar fraction of the odorizer in a liquid phase in a container in a state in which propane in the container is being used by an end gas burner. Compared to the gas-liquid equilibrium ratio, the gas-liquid vaporization ratio is a value that is closer to a state of actual use.

[0148] The TBM used as a conventional odorizer has a recognition threshold value of 7.3×10^{-5} vol ppm, a gas-liquid vaporization ratio of 0.12, and an addition amount index Cl of (= $(A/M) \times 10^3$) of 0.61.

[0149] In a case in which 2-hexyne was added singly to propane as an odorizer, as shown in Table 3, with a recognition threshold value A of 7.5×10^{-3} vol ppm and a gas-liquid vaporization ratio of 0.10, the addition amount index Cl was 123 times that of the conventional TBM. Also, in a case in which 1-penthyne was added singly to propane as an odorizer, with a recognition threshold value A of 2.6×10^{-2} vol ppm and a gas-liquid vaporization ratio M of 0.16, the addition amount index Cl was 267 times that of the conventional TBM. As mentioned in the second embodiment, with respect to addition amount, odor quality, toxicity and mutagenic gas, using 2-hexyne alone or 1-penthyne alone as an odorizer does not pose a problem. Also, there is no problem of an abnormal odor being produced even when the use of the propane in the container lowers the liquid surface height.

[0150] Next, a case of a 1:1 mixture of 50% 2-hexyne and 50% 3-mothylbutanal is described. The recognition threshold value A of 2-hexyne is 7.5×10^{-3} vol ppm, and the recognition threshold value A of 3-methylbutanal is 4.8×10^{-5} vol ppm, so as shown in Table 3, the recognition threshold value A of the 1:1 mixture is 3.77×10^{-3} vol ppm (= $(7.5 \times 10^{-3} + 4.8 \times 10^{-5})/2$). This numerical value is 52 times the recognition threshold value of the conventionally used TBM.

[0151] The gas-liquid vaporization ratio M of 2-hexyne is 0.1 and the gas-liquid vaporization ratio M of 3-methylbutanal is 0.11, so the gas-liquid vaporization ratio M of the 1:1 mixture is 0.11 (= (0.1 + 0.11)/2). This numerical value is 0.9 times the gas-liquid vaporization ratio M of the conventionally used TBM.

[0152] That is, a 1:1 mixture of 2-hexyne and 3-methylbutanal has 52 times the recognition threshold value A and 0.9 times the gas-liquid vaporization ratio of the conventionally used TBM, and while it has a slightly weaker odor, it has the same ready gasification. Considered in terms of the addition amount index, the addition amount index C1 of the 1:1 mixture of 50% 2-hexyne and 50% 3-methylbutanal is 36, 59 times that of the conventionally used TBM. Therefore, an odor on the same order as that of TBM can be obtained by adding to the propane an amount that is 59 times that of the conventional TBM.

[0153] The results of a comparison with the conventionally used TBM in respect of odor quality, toxicity and mutagenicity showed them to be about the same.

[0154] Also, even in a case in which the propane in the gas container was used, lowering the liquid surface height, the concentration of the 2-hexyne in the propane was about the same as the initial concentration, so there was no problem of an abnormal odor being produced.

[0155] While not shown in Table 3, when the mixture ratio of the 3-methylbutanal with respect to the 2-hexyne is between 0 and 50%, recognition threshold value A, gas-liquid vaporization ratio M and addition amount index Cl values, as stated above, are taken from between the value of 2-hexyne alone and the 50% mixture value shown in Table 3. Therefore the use as an odorizer does not pose a problem, even in a case in which the mixture ratio of the 3-methylbutanal with respect to 2-hexyne is between 0 and 50%.

[0156] Next, a case of a 1:1 mixture of 50% 2-hexyne and 50% TBM is described. The recognition threshold value A of 2-hexyne is 7.5×10^{-3} vol ppm, and the recognition threshold value A of TBM is 7.3×10^{-5} vol ppm, so as shown in Table 3, the recognition threshold value A of the 1:1 mixture is 3.79×10^{-3} vol ppm (= $(7.5 \times 10^{-3} + 7.3 \times 10^{-5})/2$). This numerical value is 52 times the recognition threshold value of the conventionally used TBM.

[0157] The gas-liquid vaporization ratio M of 2-hexyne is 0.1 and the gas-liquid vaporization ratio M of TBM is 0.12, so the gas-liquid vaporization ratio M of the 1:1 mixture is 0.11 (= (0.1 + 0.12)/2). This numerical value is 0.9 times the gas-liquid vaporization ratio M of the conventionally used TBM.

[0158] That is, a 1:1 mixture of 50% 2-hexyne and 50% TBM has 52 times the recognition threshold value A and 0.9 times the gas-liquid vaporization ratio of the conventionally used TBM, and although, as in the case of the 1:1 mixture of 2-hexyne and 3-methylbutanal, it has a slightly weaker odor, it has the same ready gasification. Considered in terms of the addition amount index, the addition amount index Cl of the 1:1 mixture of 2-hexyne and TBM is 34, 57 times that of the conventionally used TBM. Therefore, an odor on the same order as that of TBM can be obtained by adding to the propane an amount that is 59 times that of the conventional TBM.

[0159] The results of a comparison with the conventionally used TBM in respect of odor quality, toxicity and mutagenicity showed them to be about the same.

[0160] Also, even in a case in which the propane in the gas container was used, lowering the liquid surface height, the concentration of the 2-hexyne in the propane was about the same as the initial concentration, so there was no problem of an abnormal odor being produced.

[0161] While not shown in Table 3, when the mixture ratio of the TBM with respect to the 2-hexyne is between 0 and 50%, recognition threshold value A, gas-liquid vaporization ratio M and addition amount index Cl values, as stated above, are taken from between the value when 2-hexyne is used alone and when the mixture value is the 50% shown in Table 3. Therefore the use as an odorizer does not pose a problem, even in a case in which the mixture ratio of the TBM with respect to 2-hexyne is between 0 and 50%.

[0162] Next, a case of a 1:1 mixture of 50% 1-penthyne and 50% 3-methylbutanal is described. The recognition threshold value A of 1-penthyne is 2.6×10^{-2} vol ppm, and the recognition threshold value A of 3-methylbutanal is 4.8×10^{-5} vol ppm, so as shown in Table 3, the recognition threshold value A of the 1:1 mixture is 1.30×10^{-2} vol ppm (= $(2.6 \times 10^{-2} + 4.8 \times 10^{-5})/2$). This numerical value is 178 times the recognition threshold value of the conventionally used TBM.

[0163] The gas-liquid vaporization ratio M of 1-penthyne is 0.16 and the gas-liquid vaporization ratio M of 3-methylbutanal is 0.11, so the gas-liquid vaporization ratio M of the 1:1 mixture is 0.14 (= (0.16 + 0.11)/2). This numerical value is 1.1 times the gas-liquid vaporization ratio M of the conventionally used TBM.

[0164] That is, a 1:1 mixture of 50% 1-penthyne and 50% 3-methylbutanal has 178 times the recognition threshold value A and 1.1 times the gas-liquid vaporization ratio of the conventionally used TBM, and while it has a slightly weaker odor, it has the same ready gasification. Considered in terms of the addition amount index, the addition amount index C1 of the 1:1 mixture of 1-penthyne and 3-methylbutanal is 96, 159 times that of the conventionally used TBM. Therefore, an odor on the same order as that of TBM can be obtained by adding to the propane an amount that is 159 times that of the conventional TBM.

[0165] The results of a comparison with the conventionally used TBM in respect of odor quality, toxicity and mutagenicity showed them to be about the same.

[0166] Also, even in a case in which the propane in the gas container was used, lowering the liquid surface height, the concentration of the 1-penthyne in the propane was about the same as the initial concentration, so there was no problem of an abnormal odor being produced. While not shown in Table 3, when the mixture ratio of the 3-methylbutanal with respect to the 1-penthyne is between 0 and 50%, recognition threshold value A, gas-liquid vaporization ratio M and addition amount index Cl values, as stated above, are taken from between the value when 1-penthyne is used alone and when the mixture value is the 50% shown in Table 3. Therefore the use as an odorizer does not pose a problem, even in a case in which the mixture ratio of the 3-methylbutanal with respect to 1-penthyne is between 0 and 50%.

[0167] Next, a case of a 1:1 mixture of 50% 1-penthyne and 50% TBM is described. The recognition threshold value A of 1-penthyne is 2.6×10^{-2} vol ppm, and the recognition threshold value A of TBM is 7.3×10^{-5} vol ppm, so as shown in Table 3, the recognition threshold value A of the 1:1 mixture is 1.30×10^{-2} vol ppm (= $(2.6 \times 10^{-2} + 7.3 \times 10^{-5})/2$). This numerical value is 179 times the recognition threshold value of the conventionally used TBM.

[0168] The gas-liquid vaporization ratio M of 1-penthyne is 0.16 and the gas-liquid vaporization ratio M of TBM is 0.12, so the gas-liquid vaporization ratio M of the 1:1 mixture is 0.14 (= (0.16 + 0.12)/2). This numerical value is 1.2 times the gas-liquid vaporization ratio M of the conventionally used TBM.

[0169] That is, a 1:1 mixture of 50% 1-penthyne and 50% TBM has 179 times the recognition threshold value A and 1.2 times the gas-liquid vaporization ratio of the conventionally used TBM, and although, as in the case of the 1:1 mixture of 1-penthyne and 3-methylbutanal, it has a slightly weaker odor, it has the same ready gasification. Considered in terms of the addition amount index, the addition amount index Cl of the 1:1 mixture of penthyne and TBM is 93, 153 times that of the conventionally used TBM. Therefore, an odor on the same order as that of TBM can be obtained by adding to the propane an amount that is 153 times that of the conventional TBM.

[0170] The results of a comparison with the conventionally used TBM in respect of odor quality, toxicity and mutagenicity showed them to be about the same.

[0171] Also, even in a case in which the propane in the gas container was used, lowering the liquid surface height, the concentration of the 1-penthyne in the propane was about the same as the initial concentration, so there was no problem of an abnormal odor being produced. While not shown in Table 3, when the mixture ratio of the TBM with respect to the 1-penthyne is between 0 and 50%, recognition threshold value A, gas-liquid vaporization ratio M and addition amount index Cl values, as stated above, are taken from between the value when 1-penthyne is used alone and when the mixture value is the 50% shown in Table 3. Therefore the use as an odorizer does not pose a problem, even in a case in which the mixture ratio of the TBM with respect to 1-penthyne is between 0 and 50%.

[0172] While in the above third embodiment a mixture of 2-hexyne and either 3-methylbutanal or TBM was used as the odorizer, a mixture of both 3-methylbutanal and TBM may be used.

[0173] Also, while a mixture of 1-penthyne and either 3-methylbutanal or TBM was used, a mixture with both 3-methylbutanal and TBM may be used.

[0174] Furthermore, a mixture of 2-hexyne, 1-penthyne, and at least one of 3-methylbutanal and TBM may be used. A comparison showed that in each case, the odor quality, toxicity and mutagenicity was about the same as the conventionally used TBM, so a desired mixture ratio may be selected according to the purpose.

[0175] While the above descriptions were made with respect to cases in which the various mixtures were added to propane, they can be similarly applied to other gases, such as for example butane and other hydrocarbon system gas (liquefied petroleum gas), motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and to DME fuel gases and gases such as oxygen, nitrogen, argon gas, toxic gas, and so forth, to which a warning odor needs to be imparted.

[0176] As set forth in the foregoing, as the gas odorizer (gas odorant) the third embodiment of the present invention uses 2-hexyne mixed with 3-methylbutanal, 1-penthyne mixed with 3-methylbutanal, or a mixture of 2-hexyne and 1-penthyne and 3-methylbutanal, enabling the gas odorizer to be formed without including sulfur, so that in cases where the gas is a fuel gas, even when the fuel gas is combusted it does not produce sulfides, enabling pollution of the environment to be prevented.

[0177] Also, using a mixture of 2-hexyne and 3-methylbutanal, a mixture of 1-penthyne and 3-methylbutanal, or a mixture of 2-hexyne and 1-penthyne, and 3-methylbutanal for the odorizer makes it possible to impart a distinctive gas odor by adding an amount that is in the order of 50 times to 160 times the amount of the conventionally used TBM. It can be appropriately applied not only in the case of the above propane, but also to hydrocarbon system gas (liquefied petroleum gas) other than propane such as butane and so forth, motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and various DME fuel gases and gases such as oxygen, nitrogen, argon gas, toxic gas, and so forth, to which a warning odor needs to be imparted.

[0178] Also, since the odorizer can be formed without including sulfur, even if it is added to town gas or DME and the like used in fuel cells, it enables a good fuel gas odorizer to be provided for fuel cell applications that does not give rise to problems such as lowering of the performance of the fuel cell catalyst and lowering of the cell voltage.

[0179] Also, as the gas odorizer (gas odorant) the third embodiment of the present invention uses TBM mixed with 2-hexyne, TBM mixed with 1-penthyne, or a mixture of 2-hexyne and 1-penthyne and TBM, which enables the content of the TBM that is the conventional odorizer to be greatly reduced to half or less, enabling the sulfur contained in the gas odorizer to be greatly reduced. Therefore, in cases where the gas is a fuel gas, even when the fuel gas is combusted it does not produce sulfides, enabling pollution of the environment to be prevented.

[0180] Also, using TBM mixed with 2-hexyne, TBM mixed with 1-penthyne, or a mixture of 2-hoxyne, 1-penthyne and TBM for the odorizer makes it possible to impart a distinctive gas odor by adding an amount that is in the order of 50 times to 160 times the amount of the conventionally used TBM. It can be appropriately applied not only in the case of the above propane, but also to hydrocarbon system gas (liquefied petroleum gas) other than propane such as butane and so forth, motor gas (taxi fuel), LNG (liquefied natural gas), town gas, industrial gas (acetylene, etc.), fuel cell gas (fuel cell fuel), hydrogen gas, and various DME fuel gases and gases such as oxygen, nitrogen, argon gas, toxic gas, and so forth, to which a warning odor needs to be imparted.

[0181] It also enables sulfur contained in the odorizer to be greatly reduced, so that even if it is added to town gas or DME and the like used in fuel cells, it enables the lowering of the performance of fuel cell catalysts and the lowering of cell voltage and the like to be suppressed compared to previously, enabling a good fuel gas odorizer to be provided for fuel cell applications.

[0182] Also, if an odorizer contains a high concentration of nitrogen, it is reformed, changing to ammonia, lowering the fuel cell catalyst performance and reducing the cell voltage. However, 2-hexyne, 1-penthyne, 3-methylbutanal and TBM do not contain nitrogen, so that even when used as gas odorizers, there was none of the lowering of catalyst performance or lowering of cell voltage caused by nitrogen.

[0183] Moreover, even when a mixture of 2-hexyne and one of either 3-methylbutanal and TBM, a mixture of 1-penthyne and one of either 3-methylbutanal and TBM, or a mixture of 2-hexyne and 1-penthyne and one of either 3-methylbutanal and TBM is used for the odorizer, the residual concentration of the odorizer barely changes even when there is little fuel gas left in the gas container, and is much lower than previously. Therefore, there is no problem of an abnormal odor being produced, which conventionally has happened.

(Fourth embodiment)

[0184] Next, a fourth embodiment of the present invention is described. This fourth embodiment is described with reference to a method of manufacturing town gas in a case in which the odorizer of the present invention is added to the town gas.

[0185] First, subjects of a method of manufacturing conventional town gas is described with reference to Fig. 6.

[0186] In recent years, gasified liquefied natural gas (LNG) is used for town gas. The LNG is carried from the Middle East and Southeast Asia and the like by tankers, stored in storage tanks at reception bases, after which, in the LNG state, it is transported by tank lorries to satellite bases located in regions near the places the town gas is consumed. At the satellite bases, it is stored in liquid form in tanks. After it is gasified, LPG is mixed with the natural gas, the heating value and combustibility are adjusted, odorization and suchlike processing is carried out and, via regional gas pipe networks, it is sent to customers. Although small- and medium-scale town gas manufacturing is done at satellite bases, large-scale town gas manufacturing is implemented at LNG reception bases, using the same method as satellite bases.

[0187] Fig. 6 is a diagram that systematically shows an outline of the manufacturing procedure at a conventional LNG satellite base. In Fig. 6, an LNG lorry 101 is charged with LNG from a storage tank of a reception base for transportation to a satellite base. At the satellite base, the LNG is transferred (unloaded) from the LNG lorry 101 to a LNG storage tank 102, via a line L10, and stored in the LNG storage tank 102. This transfer is carried out by using a pressure gasifier (not shown) provided on the LNG lorry 101 to raise the delivery pressure of the LNG lorry 101.

[0188] The LNG in the LNG storage tank 102 is delivered from the LNG storage tank 102 to an LNG gasifier 103, and is gasified by the LNG gasifier 103. The NG (gasified natural gas) is sent through NG line L11 to heating value adjusting equipment 105.

[0189] BOG (Boil-Off Gas) produced by vaporization in the LNG storage tank 102 that passes through line L12, and gas remaining in the LNG lorry 101 that passes through line L13, are each introduced into a BOG heater 107, and after being heated, pass through BOG line L14, join the NG of the NG line L11 and are sent to the heating value adjusting equipment 105.

[0190] The main reason for having the BOG line L14 join the NG line L11 is to prevent partialb of the NG brought on by the low temperature at the outlet of the LNG gasifier 103 bringing the NG in the NG line L11 to or below the dew point. That is, the flow and mixing of the high-temperature BOG is used to raise the temperature of the NG so it does not go to or below the dew point.

[0191] Pressure gasifier 106 is for adjusting the gas phase pressure of the LNG storage tank 102, adjusting the LNG delivery pressure. That is, the LNG storage tank 102 liquid (LNG) is gasified by the pressure gasifier 106, and the NG is returned via line L15 to the gas phase of the LNG storage tank 102. The gas phase pressure of the LNG storage tank 102 is adjusted by adjusting the return mass, that is, adjusting the LNG delivery pressure.

[0192] The pressure gasifier 106 can also be used when transferring (charging) the LNG of the LNG storage tank 102 to the LNG lorry 101. The LNG in the LNG storage tank 102 can be transferred (charged) back along the line L10 to the LNG lorry 101 by increasing the gasification amount of the pressure gasifier 106 to make the delivery pressure of the LNG storage tank 102 higher than the tank inlet pressure of the LNG lorry 101.

[0193] Because of variation in the composition of the LNG, at the heating value adjusting equipment 105 LPG (liquefied petroleum gas (propane, butane, etc.)) is added to (mixed with) NG, and the NG is supplied as gas having a heating value and combustibility prescribed by supply gas regulations. As an example of supply gas, there is the town gas standard called "13A".

[0194] The aims of managing the heating value and combustibility are to supply gas having a heating value and combustibility prescribed by supply regulations, so that the supply gas burns well in gas devices at the supply destination, and to comply with customer contracts specified by supply regulations. Indexes expressing combustibility include the Wobbe index (WI, a combustibility index that compensates for the effect the gas specific gravity has on the speed at which gas jets from the burner nozzle) and combustion speed (MCP). Due to variations in gas compositions, these indexes are greatly affected by manufacturing equipment operating conditions, starting and stopping operations, the combination of gas mixtures, and so forth.

[0195] The above heating value adjusting equipment 105 is equipment for adjusting the heating value and combustibility, mixing the NG of NG line L11 and LPG gas gasified by LPG storage tank 109 to make town gas. Because if unmodified the town gas is odorless so the danger posed by a leakage cannot be perceived, in the final manufacturing step an odorant such as a mercaptan or sulphide or the like is added from odorizing equipment 110, imparting a distinctive gas odor. After that, the town gas is sent to customers via the regional gas pipe network. In the following description, an additive for imparting an odor to gas is called an odorant, and an additive for adding an odor to liquid gas is called an odorizer.

[0196] In the manufacture of the above town gas, the step of adding the odorant comes last is because the odorization is done after confirming the gas has the heating value and combustibility prescribed by supply regulations, and because odorization is required by the Gas Business Act.

[0197] However, because odorants formed of the above conventional mercaptans and sulfides contain sulfur, they are a cause of environmental pollution when combusted, so there is a rising demand for a switch to sulfur-free odorants and odorizers.

[0198] In the manufacture of town gas, the LPG gas that is admixed at the heating value and combustibility adjustment step is odorless, but commercial LPG has odorizers added beforehand, giving it an odor. Therefore, the addition of an odorant after the adjustment of the heating value and combustibility can be omitted by using in the heating value and combustibility adjustment step LPG to which an odor has already been imparted.

[0199] Thus, the object of this fourth embodiment is to provide a method of manufacturing town gas that by switching to the system odorizer of the present invention comprised mainly of a sulfur-free system, as the town gas odorant, enables environmental pollution to be prevented and the town gas to be manufactured more easily by omitting the odorant addition step.

[0200] Fig. 5 is a diagram that systematically shows the town gas manufacturing procedure at an LNG satellite base that applies the town gas manufacturing method of the present invention. In Fig. 5, LNG lorry 1 is charged with LNG from a storage tank of a reception base for transportation to a satellite base. At the satellite base, the LNG is transferred (unloaded) from the LNG lorry 1 to an LNG storage tank 2, via a line L0, and stored in the LNG storage tank 2. This transfer is carried out by using a pressure gasifier (not shown) provided on the LNG lorry 1 to raise the delivery pressure of the LNG lorry 1.

[0201] The LNG in the LNG storage tank 2 is delivered from the LNG storage tank 2 to an LNG gasifier 3, and is gasified by the LNG gasifier 3. The NG (gasified natural gas) is sent through NG line L1 to heating value adjusting equipment 5 (gasification step).

[0202] BOG (Boil-Off Gas) produced by vaporization in the LNG storage tank 2 that passes through line L2, and gas remaining in the LNG lorry 1 that passes through line L3, are each introduced into a BOG heater 7, and after being heated, pass through BOG line L4, join the NG of the NG line L1 and are sent to the heating value adjusting equipment 5 (gasification step).

[0203] BOG line L4 is split into a first-stage BOG line L4a and a second-stage BOG line L4b, each of which join NG line L1.

[0204] The first-stage BOG line L4 is made to join the NG line L1 to prevent partial condensation of the NG brought on by the low temperature at the outlet of the LNG gasifier 3 bringing the NG in the NG line L1 to or below the dew point. That is, the flow and mixing of the high-temperature BOG is used to raise the temperature of the NG so it does not go to or below the dew point.

[0205] The second-stage BOG line L4b is made to join the NG line L1 on the downstream side of a pressure regulating valve 8 provided on the NG line L1. This is to prevent partial condensation occurring due to a drop in temperature caused by iso-enthalpy changes (pressure decrease) after the NG has passed through the pressure regulating valve 8 reducing the temperature of the NG to or below the dew point.

[0206] Pressure gasifier 6 is for adjusting the gas phase pressure of the LNG storage tank 2, adjusting the LNG delivery pressure. That is, the LNG storage tank 2 liquid (LNG) is gasified by the pressure gasifier 6, and the NG is returned via line L5 to the gas phase of the LNG storage tank 2. The gas phase pressure of the LNG storage tank 2 is adjusted by adjusting the return mass, that is, adjusting the LNG delivery pressure.

[0207] The pressure gasifier 6 can also be used when transferring (charging) the LNG of the LNG storage tank 2 to the LNG lorry 1. The LNG in the LNG storage tank 2 can be transferred (charged) back along the line L0 to the LNG lorry 1 by increasing the gasification amount of the pressure gasifier 6 to make the delivery pressure of the LNG storage tank 2 higher than the tank inlet pressure of the LNG lorry 1.

[0208] As described in the above, heating value adjusting equipment 5 is for mixing LPG with NG and adjusting the heating value and combustibility, mixing the NG of the NG line L1 and the LPG gasified at the LPG storage tank 9 to form town gas (town gas generation step).

[0209] The LPG storage tank 9 is charged with liquid LPG supplied from LPG lorry 11. In LPG plant 10, the LPG lorry 11 is charged with this liquid LPG from an LPG high-pressure storage tank 12, via an LPG supply line 13 and loading arm 14.

[0210] Line mixing is used to mix the liquid odorizer with the liquid LPG. That is, it is supplied via odorizer line 16 from odorizer tank 15 to the LPG supply line 13, and mixed with liquid LPG flowing in the LPG supply line 13. A small quantity at a time of liquid odorizer from the odorizer tank 15 is delivered to the LPG supply line 13 by a metering pump 17 disposed partway along the odorizer line 16 (LPG odorizing step).

[0211] While in the above description line mixing was used to mix the liquid odorizer, another method may be used. For example, an injection system can be used in which the odorizer line 16 is connected to the LPG supply line 13 directly in front of the loading arm 14 and the liquid odorizer injected via the loading arm 14 to mix it with the liquid LPG in the LPG lorry 11 in which charging has been completed. In that case, nitrogen gas in the upper part of the odorizer tank 15 is pressurized and the liquid odorizer delivered to the odorizer line 16 by that pressure. Also, the injection amount of the odorizer is adjusted by a needle valve or the like disposed on the odorizer line 16. Regulating the addition amounts of the odorizer is considered to be easier with this method than with line mixing. Also, because it is necessary to add 5 to 15 times the amount added to LPG alone, the line mixing method might require modifications to be made to the equipment that includes the odorizer injection pump. Depending on the odorizer, it might be possible to inject it into the tank lorry before charging the LPG. While only tank lorries have been mentioned, the same can be said with respect to coastal tankers that should be odorized.

[0212] While in the above description the LPG lorry 11 was charged via LPG supply line 13 etc. with liquid LPG from the LPG high-pressure storage tank 12, it may be charged not from the LPG high-pressure storage tank 12 but from an LPG low-temperature storage tank.

[0213] The odorizer can readily be evenly mixed with the LPG while the LPG lorry 11 is transporting the LPG from the

LPG plant 10 to the satellite base.

[0214] In the present invention, an odorizer according to the present invention comprising mainly a sulfur-free system is used for the odorizer. As the odorizer, there may be used, for example, a mixture of normal butyl isocyanide and 2-hexyne, a mixture of normal butyl isocyanide and 1-penthyne, a mixture of normal butyl isocyanide, 2-hexyne and 1-penthyne, a mixture of ethyl isocyanide and 2-hexyne, a mixture of ethyl isocyanide and 1-penthyne, a mixture of ethyl isocyanide, 2-hexyne and 1-penthyne, a mixture of normal butyl isocyanide, ethyl isocyanide, 2-hexyne and 1-penthyne.

[0215] 2-hexyne, 1-penthyne, 1-butyne or a mixture of two or more thereof can also be used.

[0216] A mixture of 2-hexyne and at least one of 3-methylbutanal and TBM, a mixture of 1-penthyne and at least one of 3-methylbutanal and TBM, or a mixture of 2-hexyne, 1-penthyne and at least one of 3-methylbutanal and TBM may also be used.

[0217] The addition amounts of these odorizers are as follows. Here, the LNG is taken to be composed of methane and the LPG is taken to be composed of propane. First, to obtain the mixture ratio of the NG and propane gas admixed in the heating value adjusting equipment 5, the heating value of NG (methane gas) is 39.85 MJ/m^3N, the heating value of propane is 101.8 MJ/m^3N, the heating value of town gas (13A) is 46.1 MJ/m^3N. Therefore if it is nine-tenths NG and one-tenth propane, the heating value of town gas (46.1 MJ/m^3N) will be secured. And, a gas odor can be imparted to the town gas with the one-tenth propane by adding 10 times the amount of odorizer added to normal commercial propane to the propane carried by the LPG lorry 11. Depending on the above type of odorizer, this addition amount will be in the order of 5 times to 15 times, which will be the amount (5 times to 15 times the amount of odorizer added to normal commercial LPG) of odorizer injected into the LPG lorry 11. This odorizer addition amount is more or less the same as the amount added from the odorizing equipment in the conventional final step.

[0218] The above was calculated assuming the LNG composition was 100% methane, but in a case in which the LNG composition was 95% methane and 5% ethane, since the heating value of ethane is 70.0 MJ/m^3N, the town gas (13A) heating value (46.1 MJ/m^3N) can be secured by mixing 7.6% propane with the NG. Therefore, compared to when it is 100% methane, 1.3 times (= 10/7.6) the odorizer will have to be added to the LPG.

[0219] These odorizers are gasified together with the LPG and delivered to the heating value adjusting equipment 5, where they spread uniformly though the whole of the town gas during the adjustment of the heating value and combustibility, imparting a distinctive gas odor to the town gas. Following that, the town gas is sent as-is to customers via the regional gas pipe network, without going through the conventional odorant addition step. Therefore, it is possible to manufacture the town gas more easily.

[0220] The mutagenicity and acute oral toxicity of these odorizers were in the same order as those of a conventional odorant, giving rise to no particular problem.

[0221] Because these odorizers contain no sulfur at all, the only sulfur in the town gas is the trace amount included in the LPG, so sulfur can greatly reduced. Therefore, even in cases in which the town gas is combusted, virtually no sulfides are produced, making it possible to prevent environmental pollution caused by sulfides.

[0222] If synthesized, sulfur-free LPG is used for the LPG mixed in the adjustment of heating value and combustibility, the town gas would have zero sulfur, making it possible to perfectly prevent environmental pollution caused by sulfides.

[0223] In this way, it is possible to manufacture town gas that contains none of the sulfur that is admixed by a conventional odorant, enabling a good town gas to be provided for fuel cell applications that does not give rise to problems such as lowering of the performance of the fuel cell catalyst and lowering of the cell voltage.

[0224] Also, since the above odorizers contain no nitrogen, or even in cases in which it is included, it is in a sufficiently low concentration that in cases in which the town gas is used in fuel cells, lowering of the performance of fuel cell reformer catalysts and lowering of the cell voltage caused by the nitrogen reforming and changing into ammonia can be greatly reduced. From that point too, it enables the provision of good town gas for fuel cell applications.

[0225] While in the above description liquid LPG was charged into the LPG lorry 11, instead of the LPG lorry 11, it can be charged into a pressure-resistant gas container, and the gas container transported.

[0226] As stated in the foregoing, the invention of the fourth embodiment comprises the manufacture of town gas by mixing gasified liquid LPG obtained by the pre-addition of a liquid, sulfur-free-system odorizer with gasified LNG and adjusting the heating value and combustibility.

[0227] The odorant of the town gas manufactured by the invention of the fourth embodiment is a sulfur-free system, so that in accordance with the invention of the fourth embodiment, environmental pollution can be prevented. Also, the conventional odorant addition step can be omitted, making it easier to manufacture the town gas. Furthermore, it can provide a good town gas for fuel cell applications.

Industrial applicability

[0228] As described in the foregoing, the gas odorizer of the present invention can by formed without including sulfur, making it possible to provide a good fuel gas odorizer for fuel cell applications that even when added to natural gas or DME and the like used in fuel cells, does not give rise to problems such as the lowering of fuel cell catalyst performance and lowering of cell voltage.

[0229] Also, the method of manufacturing town gas of the present invention comprises manufacturing the town gas by gasifying and mixing liquid LPG obtained by the pre-addition of the gas odorizer of the present invention with gasified LNG, and then adjusting the heating value and combustibility. Thereby, the odorant of the town gas manufactured by the town gas manufacturing method of the present invention is a sulfur-free system, enabling environmental pollution to be prevented by using the town gas manufacturing method of the present invention. Also, the conventional odorant addition step can be omitted, making it easier to manufacture the town gas. Furthermore, it can provide a good town gas for fuel cell applications.

Claims

1. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising a mixture of normal butyl isocyanide and 2-hexyne.

2. The gas odorizer described in claim 1, in which the 2-hexyne has 1 ~ 20 times the molarity of the normal butyl isocyanide in the mixture ratio.

3. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising a mixture of normal butyl isocyanide and 1-penthyne.

4. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising a mixture of normal butyl isocyanide, 2-hexyne and 1-penthyne.

5. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising a mixture of ethyl isocyanide and 2-hexyne.

6. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising a mixture of ethyl isocyanide and 1-penthyne.

7. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising a mixture of ethyl isocyanide and 2-hexyne and 1-penthyne.

8. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising a mixture of normal butyl isocyanide and ethyl isocyanide and 2-hexyne and 1-penthyne.

9. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising 2-hexyne.

10. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, a said odorizer comprising 1-penthyne.

11. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising 1-butyne.

12. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising at least two or more selected from among 2-hexyne, 1-penthyne and 1-butyne.

13. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising a mixture of 2-hexyne and at least one of 3-methylbutanal and tertiary butyl mercaptan.

14. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said odorizer comprising a mixture of 1-penthyne and at least one of 3-methylbutanal and tertiary butyl mercaptan.

15. In a gas odorizer that imparts to gas a warning odor required for awareness of gas leakage, said gas odorizer comprising a mixture of 2-hexyne, 1-penthyne, and at least one of 3-methylbutanal and tertiary butyl mercaptan.

16. A gas odorizer according to any of claims 1 to 15, wherein the gas to which a warning odor needs to be imparted is at least any fuel gas from among liquefied petroleum gas, motor gas, liquefied natural gas, town gas, industrial gas, fuel cell gas, hydrogen gas, and dimethyl ether.

17. A gas odorizer according to any of claims 7, to 15, herein the gas is at least any gas from among oxygen, nitrogen, argon gas, toxic gas to which a warning odor needs to be imparted.

18. In a method of manufacturing town gas by gasifying liquefied natural gas, mixing the gasified liquefied natural gas with liquefied petroleum gas, adjusting the heating value and combustibility and imparting a distinctive gas odor,
a method of manufacturing town gas comprising,
a gasifying step of gasifying liquefied natural gas,
an LPG odorizing step of adding the gas odorizer according to any of claims 1 to 15 to liquefied petroleum gas, and
a town gas generation step wherein liquefied petroleum gas obtained by the LPG odorizing step is gasified and mixed with natural gas obtained by the gasification step and the heating value and combustibility adjusted to form the town gas.

19. The town gas manufacturing method described in claim 18 wherein the LPG odorizing step is carried out by adding the gas odorizer to liquefied petroleum gas charged in a tank lorry or gas container.

20. The town gas manufacturing method described in claim 18 or 19 wherein the addition ratio of the gas odorizer with respect to the liquefied petroleum gas is 5 ~ 15 times greater than the addition ratio to ordinary commercial liquefied petroleum gas.

FIG.1

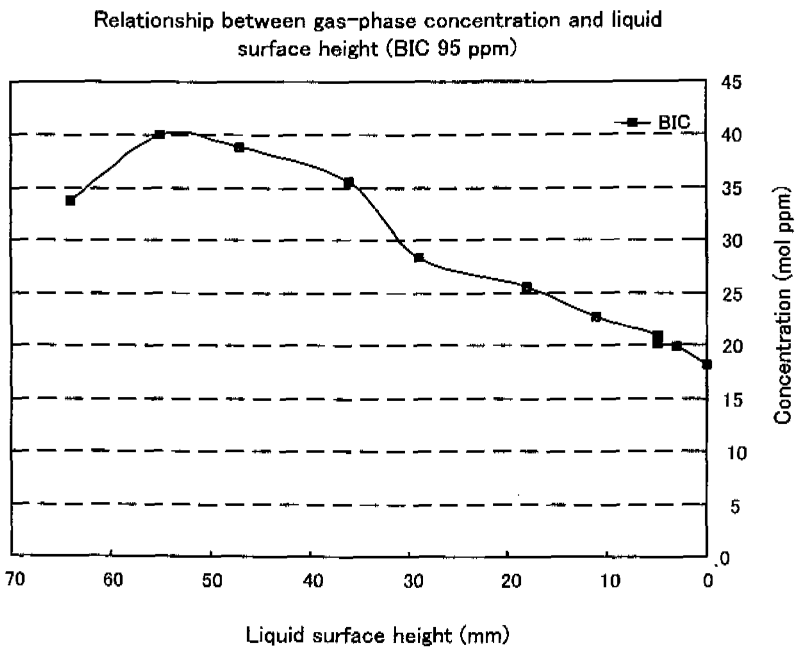

Relationship between gas-phase concentration and liquid surface height (BIC 95 ppm)
BIC
45
40
35
30
25
20
15
10
5
0
Concentration (mol ppm)
70
60
50
40
30
20
10
0
Liquid surface height (mm)

FIG.2

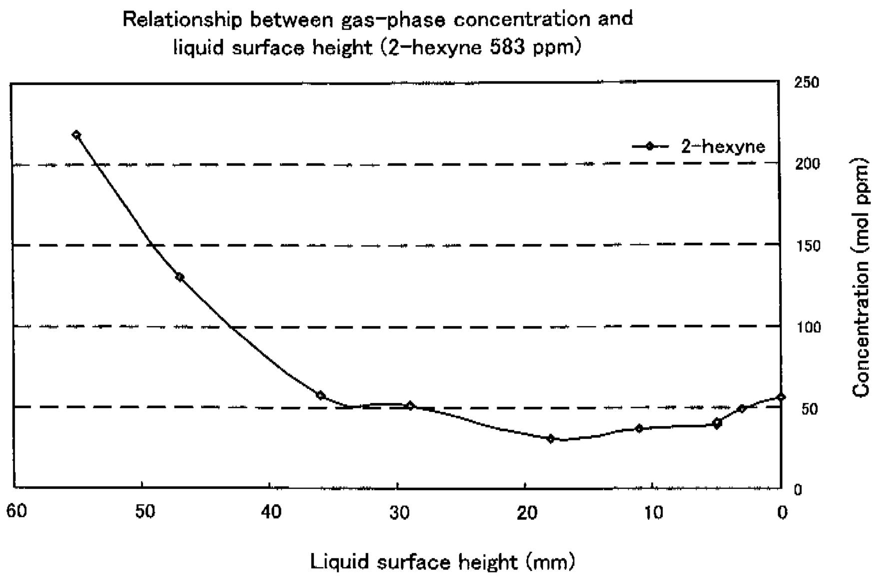

Relationship between gas-phase concentration and
liquid surface height (2-hexyne 583 ppm)
2-hexyne
250
200
150
100
50
0
Concentration (mol ppm)
60
50
40
30
20
10
0
Liquid surface height (mm)

FIG.3

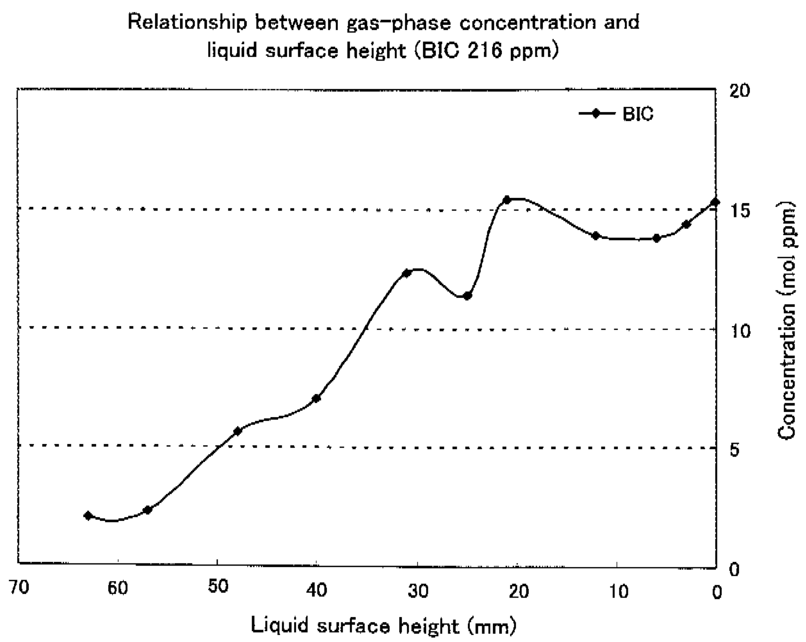

Relationship between gas-phase concentration and
liquid surface height (BIC 216 ppm)
BIC
20
15
10
5
0
Concentration (mol ppm)
70
60
50
40
30
20
10
0
Liquid surface height (mm)

FIG.4

Relationship between gas-phase concentration and liquid surface height (2-hexyne 1291 ppm)

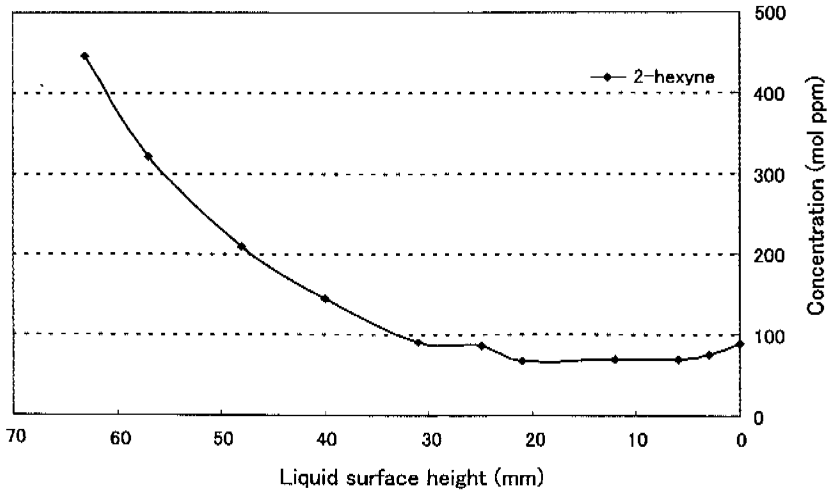


FIG.5

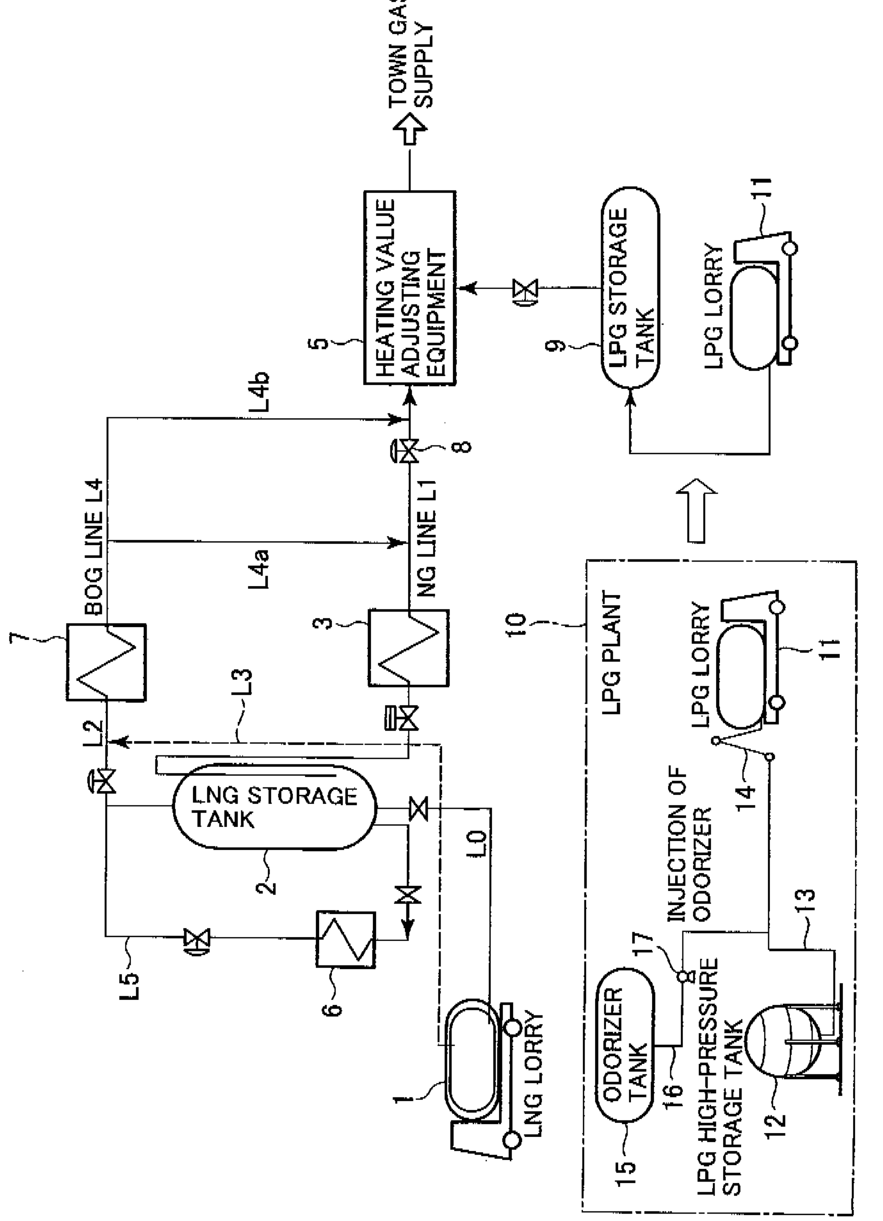
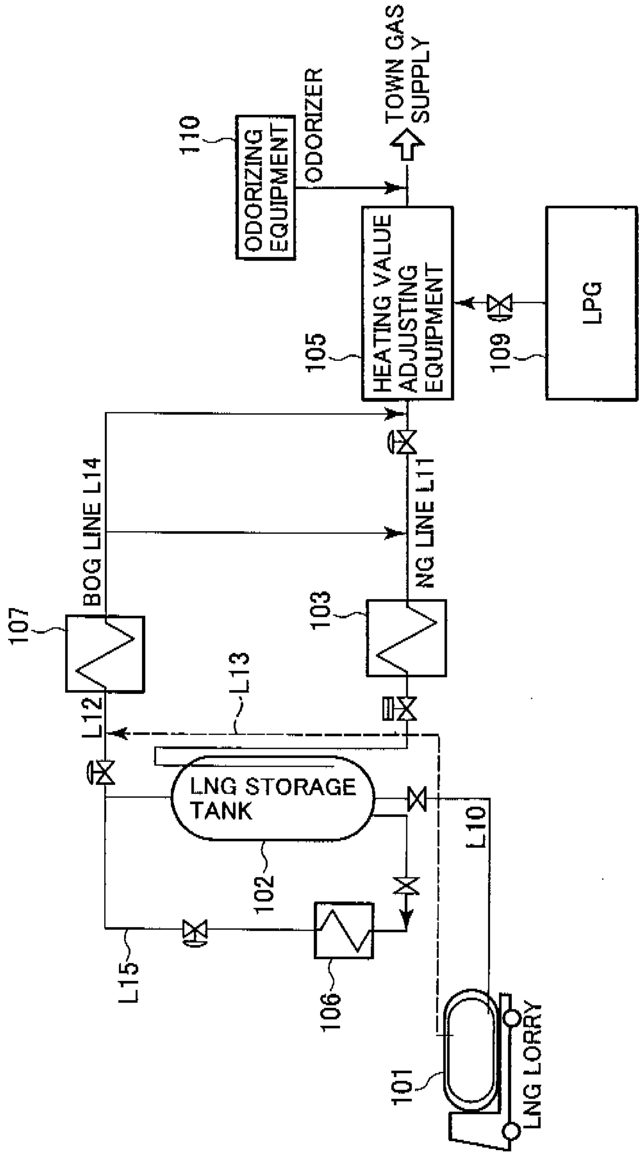

TOWN GAS SUPPLY
HEATING VALUE ADJUSTING EQUIPMENT
5
L4b
8
BOG LINE L4
NG LINE L1
L4a
7
3
L2
L3
LNG STORAGE TANK
2
L0
L5
6
1
LNG LORRY
9
LPG STORAGE TANK
LPG LORRY
11
10
LPG PLANT
LPG LORRY
11
14
INJECTION OF ODORIZER
13
17
ODORIZER TANK
15
16
LPG HIGH-PRESSURE STORAGE TANK
12

FIG.6


ODORIZING EQUIPMENT
110
ODORIZER
TOWN GAS SUPPLY
HEATING VALUE ADJUSTING EQUIPMENT
105
LPG
109
BOG LINE L14
NG LINE L11
107
103
L12
L13
LNG STORAGE TANK
102
L10
L15
106
101
LNG LORRY

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2008/061388

A. CLASSIFICATION OF SUBJECT MATTER
C10L3/10(2006.01)i

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)
C10L3/10

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2008
Kokai Jitsuyo Shinan Koho	1971-2008	Toroku Jitsuyo Shinan Koho	1994-2008

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 54-127404 A (Nippon Zeon Co., Ltd.), 03 October, 1979 (03.10.79), Full text; all drawings; particularly, Claims; page 2, lower left column, line 13 to lower right column, line 15; examples 1 to 4 (Family: none)	9-12,16, 18-20 1-8,13-15,17
X A	JP 2003-155488 A (Tokyo Gas Co., Ltd.), 30 May, 2003 (30.05.03), Claim 1; Par. No. [0036]; table 9 (Family: none)	11,16 1-10,12-15, 17-20
X A	JP 2005-203108 A (Soda Aromatic Co., Ltd.), 28 July, 2005 (28.07.05), Claims 1, 4, 6; Par. No. [0015]; example 2 (Family: none)	11,16 1-10,12-15, 17-20

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"E" earlier application or patent but published on or after the international filing date
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"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

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"&" document member of the same patent family

Date of the actual completion of the international search 04 July, 2008 (04.07.08)	Date of mailing of the international search report 15 July, 2008 (15.07.08)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2008/061388

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/015038 A1 (SYMRISE GMBH & CO. KG.), 19 February, 2004 (19.02.04), & DE 10235752 A1 & AU 2003258564 A1	1-20
A	JP 2004-200088 A (Hitachi, Ltd.), 15 July, 2004 (15.07.04), (Family: none)	1-20
A	JP 2007-515520 A (SYMRISE GMBH & CO. KG.), 14 June, 2007 (14.06.07), & WO 2005/061680 A1 & DE 10359743 A1 & EP 1694801 A1 & MX 2006006895 A1 & AU 2004303520 A1 & CN 1898366 A	1-20

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

REFERENCES CITED IN THE DESCRIPTION

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- WO 2002294261 A **[0008]**
- WO 2002356688 A **[0008]**