United States Patent [19]

Tsunemi

[11] **3,879,176**

[45] **Apr. 22, 1975**

[54] **LIQUEFIED PETROLEUM GAS COMPOSITIONS**

[75] Inventor: **Masaaki Tsunemi,** Kawasaki, Japan

[73] Assignee: **Nippon Oil Company, Limited,** Tokyo, Japan

[22] Filed: **Aug. 20, 1973**

[21] Appl. No.: **390,112**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 205,745, Dec. 7, 1971, abandoned.

[30] **Foreign Application Priority Data**

Dec. 11, 1970 Japan 45-109734

[52] **U.S. Cl.** **44/52;** 44/66

[51] **Int. Cl.** **C10l 1/14**

[58] **Field of Search** 44/56, 70, 52, 66

[56] **References Cited**

UNITED STATES PATENTS

2,236,590 4/1941 Backoff et al. 44/70

Primary Examiner—Daniel E. Wyman
Assistant Examiner—Y. H. Smith
Attorney, Agent, or Firm—Ostrolenk, Faber, Gerb & Soffen

[57] **ABSTRACT**

Liquefied petroleum gas compositions characterized by containing 1 – 500 ppm., based on the liquefied petroleum gas, of one or more carboxylic acid esters boiling at a temperature above 200°C which are liquids at ambient temperatures.

9 Claims, No Drawings

LIQUEFIED PETROLEUM GAS COMPOSITIONS

This is a continuation-in-part of application Ser. No. 205,745 filed Dec. 7, 1971, and now abandoned.

The present invention relates to detergent, liquefied petroleum gas compositions. More particularly, the present invention relates to liquefied petroleum gas compositions for keeping apparatus or machinery in which a liquefied petroleum gas fuel is used, especially an apparatus for gasification of liquefied petroleum gases, clean.

When a liquefied petroleum gas is used as motor fuel or industrial fuel, an apparatus for gasifying liquefied petroleum gas has been required for the purpose of gasification, pressure reduction or pressure control. However, these apparatuses have complicated constructions. It has been known that, if a solid substance or a highly viscous substance adheres to the inside of such an apparatus, smooth operation is hindered and sometimes the apparatus becomes not usable.

In most apparatuses for gasifying a liquefied petroleum gas, particularly motor gasification apparatuses [motor gasification apparatuses in this specification indicate those shown in, for example, journal of Japan Machinery Society 67, No. 545,865 (1965) or Journal of Petroleum Society, 12, No. 12, 24 (1969)], the liquefied petroleum gas is gasified by heat of engine-cooling water. In short, the structure of such an apparatus comprises primary and secondary reducing chambers. The pressure is reduced in two separate states in the primary and secondary reducing chambers, pressures in the primary and secondary reducing chambers are regulated to around 1.35 Kg/cm^2 and atmospheric or a slightly lower pressure, respectively. The liquefied petroleum gas is introduced in the primary reducing chamber through a primary reducing valve at the inlet of the chamber and gasified therein. The resulting gas is then introduced in the secondary reducing chamber through a secondary reducing valve at the inlet of the chamber, pressure-controlled therein and then introduced in a mixer through a gas fuel supplier. Opening and closing operations of the reducing valves are performed by a diaphragm and a spring. In the motor gasification apparatus, as accumulation of a sediment is increased, the diaphragm is hardened and the liquefied petroleum gas supply valves (particularly the primary reducing valve) are fastened and the regular supply of the fuel to a combustion device is inhibited. In order to eliminate said trouble caused by the sediment, frequent control of the gasification apparatus is necessary. Finally, exchange of the gasification apparatus or complete cleaning of respective pieces of the dismantled apparatus become necessary.

In general, a liquefied petroleum gas contains solid substances, reactive components and other impurities, though in very small amounts. The contents comprise mainly impurities which cannot be removed completely in the preparation of the liquefied petroleum gas, corrosion inhibitors for the apparatus, impurities attached to some parts of the apparatus and impurities resulted substantially from every part of the apparatus. If the liquefied petroleum gas containing these impurities is used practically, a considerable amount of sediment occurs in the gasification apparatus during a long period operation and causes troubles.

However, a practical method for solving the aforesaid problem efficiently has not been found yet.

The object of the present invention is to provide new liquefied gas compositions for keeping apparatus and machinery clear to avoid the contamination due to reactive components and impurities contained in the liquefied petroleum gas and also for removing the contaminating sediments to keep the apparatuses and machinery clear. The object of the invention, i.e., prevention of contamination of removal and discharge of the sediments can be attained by incorporating in the liquefied petroleum gases one or more carboxylic acid esters boiling at a temperature above 200°C which are in liquid state at ambient temperatures.

If a liquefied petroleum gas composition containing one or more carboxylic acid esters boiling at a temperature below 200°C is used, as shown in an Example given below, operation of the primary reducing valve is not smooth and sediment in the primary reducing chamber is larger in amount than in the case of the liquefied petroleum gas composition of the present invention. If a carboxylic acid ester which is solid at ambient temperature is used, sometimes the carboxylic acid ester is solidified during suspension of operation of the apparatus, thereby disturbing start-up considerably. Accordingly, the carboxylic acid esters used in the present invention must be in liquid state at ambient temperature.

The liquefied petroleum gases of the present invention involve all the gases prescribed in JIS (JIS K–2240). No special limitation is provided in structure of the carboxylic acid esters to be incorporated in liquefied petroleum gas according to the present invention.

One or more esters of the following groups can be used:

a. carboxylic acid esters obtained from the reaction between aromatic carboxylic acids and C_1–C_8 aliphatic alcohols, such as methyl-, ethyl-, propyl- and butyl benzoate, methyl- and ethyl salicylate, ethyl phenyl acetate, methyl-and ethyl benzoylacetate, etc.;

b. carboxylic acid esters obtained from the reaction between C_2–C_{18} aliphatic mono-carboxylic acid and either C_1–C_{10} aliphatic alcohols or C_2–C_3 aliphatic polyhydric alcohols, such as benzyl-, linalyl acetate, glycerine-1, 3-diacetate, ethyl caprylate, ethyl caprate, ethyl pelargonate, methyl oleate, amyl stearate, ethyl glycerate, triacetin, triolein, acetopyruvic acid ethyl ester and ethyl levulinate, etc.;

c. carboxylic acid esters obtained from the reaction between C_3–C_{10} polybasic acids and either C_1–C_{10} aliphatic alcohols or C_2–C_3 aliphatic polyhydric alcohols, such as diethyl succinate, diethyl glutarate, diethyl adipate, dibutyl adipate, dibutyl sebacate, dimethyl- and diethyl maleate, diethyl fumarate, diethyl glutaconate, dimethyl-, diethyl-, dibutyl, di-2-ethylhexyl- and dioctyl phthalate, triethyl citrate, diethyl mesoxalate, acetone dicarboxylic acid diethyl ester and diethyl-l-malate, etc.

Preferred esters are those having stable chemical properties, for example, benzyl acetate, propyl benzoate, butyl benzoate, ethyl adipate, diethyl phthalate, dibutyl phthalate, dioctyl phthalate, amyl stearate and mixtures thereof. The amount of the carboxylic acid ester in the composition is generally in the range of 1 – 500 ppm., preferably 5 – 20 ppm. If the amount of carboxylic acid ester is less than said range, the aimed prevention of contamination of the apparatuses and machinery or removal and discharge of the sediments is hardly performed. On the other hand, if the amount

of carboxylic acid ester is more than said range, the carboxylic acid ester per se is precipitated to give unfavorable, ill effects to the gasification apparatus.

The liquefied petroleum gas compositions of the present invention may contain other ordinary additives for liquefied petroleum gas such as anti-freezing agent and smelling agent.

The present invention will be illustrated below in detail. The accumulation of sediments in an apparatus in which liquefied petroleum gas is used is due to poor fluidity and hardness of the sediments per se in general. The carboxylic acid esters according to the present invention remove the sediments from sediment-sensitive parts of the apparatus such as the diaphragm and supply valve for liquefied petroleum gas in motor gasification apparatus by dissolving, suspending or dispersing such sediments in a medium to impart fluidity and then entraining the same in the gasified petroleum gas. The capacity of the usual apparatus for gasifying liquid petroleum is far smaller compared to the volume of liquefied petroleum gas to be gasified in the apparatus in a fixed period of time. Consequently, the flow velocity of the gasified petroleum gas is very high and, accordingly, the effect of removing the sediments according to the above mechanism is great. The mixture of carboxylic acid esters and sediments entrained in the petroleum gas is substantially burned directly.

Even if a small amount of sediment is attached to a part (in which gas flow velocity is low) of the apparatus or pipe, the sediment can be discharged easily from the combustion system through a condensate-discharging valve according to the effect of the present invention, i.e., the effect of dissolving, suspending or dispersing the sediments to impart fluidity.

Concrete effects obtainable by using the liquefied petroleum gas compositions of the present invention will be illustrated by way of examples. Various changes and modifications may be made without departing the spirit of scope of the invention.

EXAMPLE 1

An ordinary liquefied petroleum gas and a liquefied petroleum gas composition of the present invention were gasified by using a liquefied petroleum gas-gasifying apparatus for a motor car (hereinafter referred to as converter) under the same conditions as in the actual operation. Solidifications of primary reducing valves were as shown in Table 1.

Table 1

Test No.	Composition of Sample		Amount (Kg)	Average Flow Rate (kg/hr)	Condition of Primary Reducing Valve
1	Liquefied petroleum gas		45.1	5.0	X
2	Liquefied petroleum gas Isoamyl propionate	30 ppm	46.9	5.2	Δ
3	Liquefied petroleum gas Butyl acrylate	50 ppm	45.5	5.1	X
4	Liquefied petroleum gas Ethylene dibenzoate	100 ppm	47.0	5.2	X
5	Liquefied petroleum gas Butyl stearate	70 ppm	44.1	4.9	Δ
6	Liquefied petroleum gas Dibutyl phthalate	30 ppm	43.5	4.8	°
7	Liquefied petroleum gas Amyl stearate	30 ppm	44.7	5.0	°
8	Liquefied petroleum gas Ethyl benzoate	200 ppm	46.3	5.2	°
9	Liquefied petroleum gas Dibutyl adipate	50 ppm	42.0	4.7	°
10	Liquefied petroleum gas Ethyl glycerate	200 ppm	45.0	5.0	°
11	Liquefied petroleum gas Methyl benzoylacetate	50 ppm	45.0	5.0	°
12	Liquefied petroleum gas Linalyl acetate	250 ppm	48.2	5.3	°

Meanings of the symbols in Table 1 are as follows:
°: Valve, if released after 10 seconds holding, is opened directly.
Δ: Valve, if released after 10 seconds holding, is opened within 5 seconds.
X: Valve, if released after 10 seconds holding, is opened after a period longer than 5 seconds.

The above results suggest clearly that, if liquefied petroleum gas, per se, or a liquefied petroleum gas composition containing a low boiling carboxylic acid ester such as isoamyl propionate, butyl acrylate, etc. or containing a high boiling carboxylic acid ester, which is in solid state at ambient temperatures, such as ethylene dibenzoate and butyl stearate, etc. is used, the primary reducing valve in converter is apt to be fastened but, if liquefied petroleum gas composition containing a carboxylic acid ester boiling at a temperature above 200°C, which is liquid at ambient temperatures is used, the fixation or solidification of the primary reducing valve can be prevented.

EXAMPLE 2

Large quantities of an ordinary liquefied petroleum gas and a liquefied petroleum gas composition of the present invention were gasified in a motorcar converter under the same conditions as in the actual operation. Weights of sediments accumulated in the primary and secondary reducing chambers and operation conditions of primary reducing valve were as shown in Table 2.

Table 2

Test No.	Composition of sample		Amount (Kg)	Average Flow Rate (Kg/hr)	Weight of Sediment Prim. (g)	Weight of Sediment Sec. (g)	Condition of Primary Reducing Valve
1	Liquefied petroleum gas		1302	4.8	1.02	2.30	X
2	Liquefied petroleum gas Dioctyl phthalate	50 ppm	1253	5.0	0.58	2.87	°
3	Liquefied petroleum gas Dibutyl phthalate	30 ppm	1336	5.1	0.76	2.41	°
4	Liquefied petroleum gas Amyl stearate	50 ppm	1387	5.1	0.66	3.40	°
5	Liquefied petroleum gas Dimethyl maleate	100 ppm	1292	4.7	0.40	2.69	°
6	Liquefied petroleum gas Triolein	50 ppm	1314	4.9	0.81	3.03	°
7	Liquefied petroleum gas Ethyl caprate	100 ppm	1268	5.0	0.50	2.80	°
8	Liquefied petroleum gas Dioctyl phthalate Dimethyl maleate	10 ppm 50 ppm	1414	5.2	0.54	2.55	°

Meanings of the symbols in the right column in Table 2 are the same as in Table 1.

The above results suggest that if the liquefied petroleum gas composition of the present invention is used, the amount of sediment at issue in primary reducing chamber is reduced remarkably and operation conditions of the primary reducing valve is improved remarkably as compared with the case of using liquefied petroleum gas, per se.

As for the amount of sediment in the secondary reducing chamber, it was larger when the liquefied petroleum gas composition of the present invention was used. With respect to the properties, the sediment from the liquefied petroleum gas, per se, had a high tackiness and poor fluidity to make removal of the same difficult, whereas the sediment from the liquefied petroleum gas composition of the present invention was liquid, having a fluidity equivalent to that of carboxylic acid esters incorporated in the liquefied petroleum gas. In the latter case, accordingly, the sediment in the primary reducing chamber flowed into the secondary reducing chamber and it was easily discharged through a condensate-discharge valve of the second reducing chamber.

EXAMPLE 3

Detergent powers of an ordinary liquefied petroleum gas and a liquefied petroleum gas composition of the present invention for converters of motor engines in which a liquefied petroleum gas is used as fuel were evaluated. Accumulation of sediment and the operation condition of primary reducing valve after about 10,000 Km and 30,000 Km drive were as shown in Table 3.

As shown clearly by the above results, a distinct difference lies between non-treated, liquefied petroleum gas fuels and liquefied petroleum gas compositions of the present invention. Namely, if a liquefied petroleum gas, per se, is used as fuel, sediment in the primary reducing chamber is in a remarkably large amount and the sediment cannot be removed easily due to its hardness and viscosity. Consequently, smooth operation of the primary reducing valve is hindered. If drive is continued under such conditions, it is supposed that the drive becomes impossible finally owing to contamination of the device. On the other hand, if a liquefied petroleum gas composition of the present invention is used, contamination of the primary reducing chamber is little and operation of the primary reducing valve is kept always normal, since the small quantity of sediment comprises a liquid of a low viscosity. The sediment which was a liquid of a low viscosity in the secondary reducing chamber could be discharged from the converter, while sediment from the liquefied petroleum gas, per se, could not be removed easily due to its hardness and viscosity. As a result, the life of the diaphragm was prolonged considerably and driving distance per a fixed volume of the fuel was increased favorably according to smooth operation of the converter. In an experiment carried out simultaneously, it was found that if motor fuel of a liquefied petroleum gas, per se, in an already contaminated converter after about 30,000 Km drive was replaced with a liquefied petroleum gas composition of the present invention containing 30 ppm. of dioctyl phthalate and the drive was continued further about 10,000 Km, surprisingly, the hard sediment accumulated was dispersed and discharged whereby the

Table 3

Test No.	Composition of Sample	Drive Distance (Km)	Fuel Consumption (l)	Rate of Fuel Consumption (Km/l)	Weight of Sediment Primary Chamber (g)	Weight of Sediment Secondary Chamber (g)	Condition of Primary Reducing Valve
1	Liquefied petroleum gas	9,876	1,630	6.06	1.22*	1.37*	Δ
2	Liquefied petroleum gas	29,933	5,056	5.92	3.10*	3.56*	X
3	Liquefied petroleum gas Dioctyl phthalate 30 ppm	10,313	1,736	6.23	0.70**	2.25**	°
4	Liquefied petroleum gas Dioctyl phthalate 30 ppm	28,089	4,389	6.49	0.33**	4.26**	°

Note: Meanings of the symbols in the right column in Table 3 are the same as in Table 1.

* Removal of marked sediment is difficult due to its hardness or viscosity.

**Marked sediment is oily liquid and easily discharged through a condensate-discharge valve.

content of the converter was made clean again. The reduced fuel combustion rate of the car could return to its initial, favorable condition in virtue of said effect.

Thus, it is apparent that liquefied petroleum gas compositions of the present invention exhibit excellent effects.

Various changes and modifications can be made in the present invention without departing from the spirit and the scope thereof. The various embodiments set forth herein serve to further illustrate the invention but were not intended to limit it.

I claim:

1. A liquefied petroleum gas composition containing 1–500 ppm, based on the liquefied petroleum gas, of at least one carboxylic acid ester boiling at a temperature above 200°C. and which is liquid at ambient temperature, said carboxylic acid ester being selected from the group consisting of (a) the ester of an aromatic carboxylic acid and a 1–8 carbon atom aliphatic alcohol, (b) the ester of a 2–18 carbon atom aliphatic monocarboxylic acid and a 1–10 carbon atom aliphatic alcohol, (c) the ester of a 2–18 carbon atom aliphatic monocarboxylic acid and a 2–3 carbon atom aliphatic polyhydric alcohol, (d) the ester of a 3–10 carbon atom polybasic carboxylic acid and a 1–10 carbon atom aliphatic alcohol, and (e) the ester of a 3–10 carbon atom polybasic carboxylic acid and a 2–3 carbon atom aliphatic polyhydric alcohol.

2. The liquefied petroleum gas composition of claim **1** wherein said carboxylic acid ester is a member of the group consisting of methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, methyl salicylate, ethyl salicylate, ethyl phenyl acetate, methyl benzoylacetate, ethyl benzoylacetate, benzyl acetate, linalyl acetate, glycerine-1,3-diacetate, ethyl caprylate, ethyl caprate, ethyl pelargonate, methyl oleate, amyl stearate, ethyl glycerate, triacetin, triolein, acetopyruvic acid ethyl ester, ethyl levulinate, diethyl succinate, diethyl glutarate, diethyl adipate, dibutyl adipate, dibutyl sebacate, dimethyl maleate, diethyl maleate, diethyl fumarate, diethyl glutaconate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di-2-ethylhexyl phthalate, dioctyl phthalate, triethyl citrate, diethyl mesoxalate, acetone dicarboxylic acid diethyl ester, and diethyl-1-malate.

3. The liquefied petroleum gas composition of claim **1** wherein said carboxylic acid ester is a member selected from the group consisting of benzyl acetate, propyl benzoate, butyl benzoate, ethyl adipate, diethyl phthalate, dibutyl phthalate, dioctyl phthalate and amyl stearate.

4. The liquefied petroleum gas composition of claim **1** wherein the amount of the said carboxylic acid ester contained therein is 5–250 ppm, based on the said liquefied petroleum gas.

5. The liquefied petroleum gas composition of claim **2** wherein the amount of the said carboxylic acid ester contained therein is 5–250 ppm, based on the said liquefied petroleum gas.

6. The liquefied petroleum gas composition of claim **3** wherein the amount of the said carboxylic acid ester contained therein is 5–250 ppm, based on the said liquefied petroleum gas.

7. The liquefied petroleum gas composition of claim **4** wherein the amount of said carboxylic acid ester is 30–200 ppm.

8. The liquefied petroleum gas composition of claim **5** wherein the amount of the said carboxylic acid ester is 30–200 ppm.

9. The liquefied petroleum gas composition of claim **6** wherein the amount of the said carboxylic acid ester is 30–200 ppm.

* * * * *