ODORANT MIXTURE FOR AN ODOURLESS GASEOUS FUEL

[0001] The present invention relates to the field of odorants for gaseous fuels, in particular odourless gaseous fuels, and has more especially as subject matter a composition comprising at least one alkyl sulphide and at least two alkyl acrylates which makes possible the detection of gas leaks and the prevention of the risks of explosion which result therefrom.

[0002] Town gases and coke oven gases, which were obtained by thermal processes, were used for a long time in the past as gaseous fuels, both for public lighting and for domestic requirements. These gases comprised highly odoriferous components. Consequently, they had a strong specific odour, so that a gas leak could be easily detected.

[0003] In contrast, the gaseous fuels currently used, whether natural gas, propane, butane, liquefied petroleum gas (or LPG) or even oxygen (for example for welding operations), are essentially odourless, either because of their origin or because of the purification treatment which they have received.

[0004] Thus, if leaks are not noticed in time, the rapid formation occurs of mixtures of gaseous fuels and of air which can explode, with consequently a high risk potential.

[0005] For these safety reasons, the natural gas moving in gas pipelines is odorized by injection (in specialized stations) of appropriate additives known as odorants.

[0006] Natural gas is generally conveyed odourless, after an appropriate purification treatment, from the production sites to the consuming countries, either via gas pipelines or (in liquid state) in specialized ships (methane carriers). In France, for example, natural gas is thus received in a limited number of injection stations where the odorant is injected, so that the natural gas, both that which moves through the French gas pipeline network and that which is stored in underground tanks, is odorized, which makes possible easy detection in the event of a leak, wherever in the network it occurs.

[0007] In other countries, natural gas may be distributed over the area of the country by a network of pipelines in which it moves without odorant, the natural gas then being odorized as it enters the towns in which it is consumed, which requires an even higher number of injection stations.

[0008] Storage tanks are generally maintained under an atmosphere of nitrogen or of natural gas in order to limit, at this stage, the risks of explosion.

[0009] Alkyl sulphides, used as odorants, alone or as a mixture, are known. Mention may be made, for example, of diethyl sulphide, dimethyl sulphide, methyl ethyl sulphide or tetrahydrothiophene, which are widely used for their excellent properties, in particular which are capable of triggering a feeling of alarm in people in the event of an accidental leak of natural gas thus odorized and of initiating the necessary protective operations.

[0010] However, during the combustion of natural gas, these products generate an amount of sulphur dioxide which, however low it might be, becomes not insignificant when an overall balance is carried out on the scale of a country or of a region, in particular with a high level of industrialization or urbanization. Thus, by way of example, the combustion of a natural gas odorized with tetrahydrothiophene at a concentration of 10 mg/Sm^3 (or number of m^3 of the gas, measured under standard temperature and pressure conditions) generates 7.3 mg/Sm^3 of sulphur dioxide.

[0011] In the general context of better consideration of environmental constraints, it is therefore desirable to reduce the amounts of SO_2 discharged to the ecosphere via odorants based on alkyl sulphides present in natural gas during the combustion of the latter.

[0012] Furthermore, the use of alkyl acrylates as components of gas odorant mixtures is disclosed in the literature.

[0013] As an example, Patent Application DE 19837066 mentions a process for the odorization of natural gas by addition of a mixture comprising an alkyl acrylate, a nitrogenous compound of pyrazine type and an antioxidant. However, this mixture exhibits the disadvantage of not having an odour characteristic of gas and is thus capable of being misinterpreted in the event of

a gas leak. The risk is, of course, the non-detection of this leak and an explosion, if the concentration of gas in the air reaches its lower explosive limit.

[0014] Patent JP 55-137190 also discloses an odorant mixture combining ethyl acrylate with a specific sulphur compound, in this instance tert-butyl mercaptan (or TBM). However, the major disadvantage of this mixture is that, because of the chemical reactivity of TBM with ethyl acrylate, the 2 components of the odorant mixture have to be stored in the various injection stations in separate tanks and also require separate injection pumps and heads for introduction into the gas pipeline. This results, in view of the complex logistics for the odorization of natural gas set out above, in a considerable increase in the costs of the injection stations resulting from the necessary multiplication in the storage tanks and injection pumps and heads.

[0015] Furthermore, Patent Application WO 2004/024852 discloses an odorant consisting of four components, including an alkyl acrylate, an alkyl sulphide and an antioxidizing stabilizing agent, such as *tert*-butylhydroxytoluene, hydroquinone, and the like.

[0016] It is an aim of the present invention to provide a novel odorant mixture which overcomes in particular the disadvantages of the odorant mixtures of the prior art set out above.

[0017] A subject-matter of the present invention is thus a composition which can be used in particular as odorant for a gaseous fuel, more particularly natural gas, comprising:

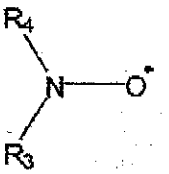
- from 0.1 to 49.9 parts by weight of at least one alkyl sulphide (I) of formula:

R^1-S-R^2

in which R^1 and R^2, which are identical or different, represent:

- an alkyl radical comprising from 1 to 4 carbon atoms; or
- R^1 and R^2, taken with the sulphur atom to which they are attached, represent a saturated or unsaturated ring comprising from 3 to 5 carbon atoms which is optionally substituted by a C_1-C_4 alkyl or C_1-C_4 alkenyl radical;

- from 50 to 99.8 parts by weight of at least two alkyl acrylates (II), the alkyl radicals of which comprise from 1 to 12 carbon atoms, preferably from 1 to 8;
- from 0.001 to 0.1 part by weight of at least one compound (III) which inhibits the polymerization of the alkyl acrylates (II) and which is active in the presence or in the absence of oxygen, preferably comprising a stable nitroxide radical of formula (IV):



in which:

- R^3 and R^4, which are identical or different, each represent a tertiary or secondary hydrocarbon radical comprising from 2 to 30 carbon atoms, preferably from 4 to 15, and optionally one or more heteroatoms chosen from sulphur, phosphorus, nitrogen or oxygen; or
- R^3 and R^4, taken with the nitrogen atom to which they are attached, represent a cyclic hydrocarbon radical comprising from 4 to 10 carbon atoms, preferably from 4 to 6, the said radical optionally being substituted.

[0018] The composition according to the invention confers on gaseous fuels, in particular on natural gas, after its injection into the latter, a high odorant power comparable to that obtained with the odorants based on alkyl sulphide of the prior art, allowing any person present in the vicinity of a leak to recognize the latter and to take the appropriate safety measures. This high odorant power is obtained at the same time as a significant reduction in the amounts of SO_2 discharged to the ecosphere after combustion of the gas thus odorized. Finally, this composition, because of the absence of reactivity between the compounds (I) and (II), can be employed in injection stations using a single storage tank, a single injection pump and a single injection head, which results in considerably simplified logistics.

[0019] According to a preferred alternative form of the composition according to the invention, the composition comprises from 5 to 14.95 parts by weight of compound(s) (I), from 85 to 94.95 parts by weight of compounds (II) and from 0.005 to 0.05 part by weight of compound(s) (III).

[0020] Preference is given to the use, as alkyl sulphide(s) (I), of tetrahydrothiophene (THT), methyl ethyl sulphide (MES), dimethyl sulphide (DMS) and/or diethyl sulphide (DES).

[0021] The acrylic acid esters (II) are chosen in particular from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, pentyl, hexyl, heptyl, octyl and dodecyl acrylates.

[0022] According to a preferred embodiment of the composition according to the invention, use is made of a combination of alkyl acrylates comprising in particular ethyl acrylate and advantageously of a combination of alkyl acrylates comprising in particular methyl acrylate and ethyl acrylate. The preferred combinations of alkyl acrylates comprising in particular methyl acrylate and ethyl acrylate generally comprise 20 to 40 parts by weight of methyl acrylate per 100 parts by weight of the methyl acrylate + ethyl acrylate total.

[0023] According to a very particularly preferred alternative form of the invention, use is made of a composition comprising tetrahydrothiophene, methyl acrylate and ethyl acrylate.

[0024] The presence in the composition according to the invention of compound(s) (III) has the effect of inhibiting the polymerization of the acrylates, which are very reactive monomers which can spontaneously polymerize. Such an uncontrolled polymerization is capable of placing in danger people found close to injection stations, such as residents or workers in charge of maintenance, due to the risk of explosion. If this polymerization occurs during storage, including, for example, in storage tanks or vessels of injection stations, it can also result in rapid fouling, indeed even blocking, of the pipes between the storage tank and the injection point. Such a phenomenon can result in an uncontrolled fall in the concentration of the odorant in the natural gas, which increases the risk related to an undetected gas leak.

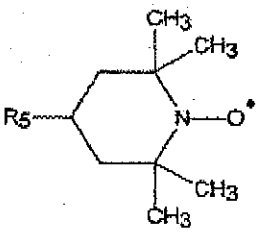
[0025] The compounds of formula (IV) are known *per se* and their preparation is, for example, described in the work "Synthetic Chemistry of Stable Nitroxides" by L. B. Volodarsky *et al.*, CRC Press, (1993), ISBN: 0-8493-4590-1.

[0026] Inhibitors of formula (IV) exhibit the advantage, in contrast to other inhibitors, such as radical inhibitors belonging to the family of the hydroquinones, of not requiring storage of the odorant mixture under air. This is because storage under air is rendered necessary for radical inhibitors of hydroquinone type owing to the fact that the active form of the inhibitor is a molecule comprising a radical which is formed following reaction with oxygen.

[0027] In point of fact, it is highly advantageous, in designing injection stations, to be able to store the odorant mixture in the appropriate vessel under natural gas pressure. Such an embodiment makes it possible advantageously to increase the efficiency of the injection pumps.

[0028] The inhibitors of formula (IV) also offer the advantage, for the same reason, of being able to be used in tanks for storage under nitrogen, encountered in some stations for the injection of natural gas.

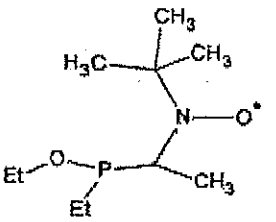
[0029] According to a particularly preferred alternative form, use is made, as inhibitor of formula (IV), of a compound derived from tetramethylpiperidine oxide (also denoted by the term TEMPO) of formula (IVa):



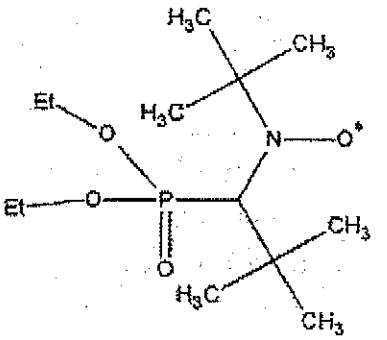
in which R^5 represents a hydroxyl, amino, R^6COO- or R^6CON- group where R^6 is a C_1-C_4 alkyl radical.

[0030] It is preferable advantageously to choose the compound of formula (III) from at least one of the following compounds:

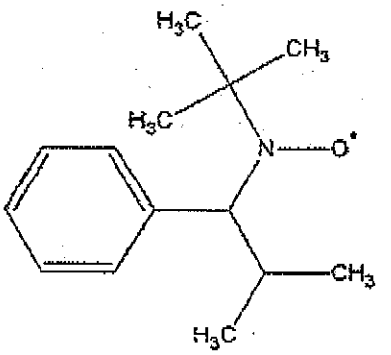
- compound (A), known as N-(*tert*-butyl)-N-(1-[ethoxy(ethyl)-phosphino]propyl)nitroxide, of formula:



- compound (B), known as N-(*tert*-butyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide, of formula:



- compound (C), known as N-(*tert*-butyl)-N-(2-methyl-1-phenyl-propyl)nitroxide, of formula:



[0031] Another subject-matter of the invention is a process for the odorization of an odourless gaseous fuel comprising the addition of an effective amount of the composition comprising at least one alkyl sulphide, at least two alkyl acrylates and at least one compound (III) which inhibits the polymerization of alkyl acrylates and which is stable in the presence and in the absence of oxygen, preferably of formula (IV). The amount of the said composition can be determined by a person skilled in the art by means of systematic tests, taking into account the specific characteristics of the gaseous fuel and of the

distribution networks. Purely by way of indication, this effective amount can be between 1 and 500 mg/Sm^3, preferably between 2 mg/Sm^3 and 50 mg/Sm^3.

[0032] The composition according to the invention described above can be used as is or else can be diluted in a solvent or a mixture of solvents which is inert with regard to acrylates. Mention may be made, as examples of solvents, of cyclohexane or n-hexane.

[0033] The dilution of the composition can reach 85%, i.e. 15 parts by weight of the composition according to the invention are diluted in 85 parts by weight of solvent.

[0034] The gaseous fuels to which the process according to the invention applies comprise: natural gas, propane, butane, liquefied petroleum gas (or LPG) or even oxygen or also hydrogen, such as that generated by fuel cells.

[0035] Natural gas is a preferred gaseous fuel according to the present invention due to its very widespread use and to the scale of the distribution networks, making it particularly desirable to reduce any danger resulting from the risk of leakage.

[0036] As regards natural gas, the composition which can be used as odorant is added by injection in specialized stations according to conventional techniques employedis this field.

[0037] Finally, a subject-matter of the invention is a gaseous fuel, preferably a natural gas, comprising an amount of between 1 mg/Sm^3 and 500 mg/Sm^3, preferably between 2 mg/Sm^3 and 50 mg/Sm^3, of the composition comprising at least one alkyl sulphide, at least two alkyl acrylates and at least one compound (III), preferably of formula (IV).

[0038] The following examples are given purely by way of illustration of the invention and should not under any circumstances be interpreted as limiting the scope thereof.

Example 1 (reference): Odorization of natural gas with tetrahydrothiophene

[0039] 10 mg per Sm^3 of tetrahydrothiophene are injected into natural gas using an appropriate laboratory device.

[0040] The content of sulphur dioxide formed, after combustion of the gas thus odorized which has a high odorant power, is equal to 7.3 mg/Sm^3.

Example 2:

[0041] The following composition is obtained by simple mixing of the weights of the components indicated in the liquid state, with the exception of hydroxy-TEMPO, which is a solid:

Ethyl acrylate	58.6 g	58.66 parts by weight
Methyl acrylate	29.3 g	29.33 parts by weight
Tetrahydrothiophene	120 g	12.00 parts by weight
Hydroxy-TEMPO	0.1 g	0.01 part by weight

[0042] Example 1 is subsequently repeated, the tetrahydrothiophene being replaced by the composition according to the invention thus prepared.

[0043] The gas thus odorized is subjected to an olfactory test, from which it emerges that the gas thus odorized has a good alerting power (high odorant power similar to that of the composition of Example 1).

[0044] The content of sulphur dioxide formed, after combustion of the gas thus odorized, is equal to 0.87 mg/Sm^3.

Example 3:

[0045] The following composition is obtained by simple mixing of the weights of the components indicated in the liquid state:

Ethyl acrylate	58.6 g	58.66 parts by weight
Methyl acrylate	29.3 g	29.33 parts by weight
Tetrahydrothiophene	120 g	12.00 parts by weight
N-(*tert*-Butyl)-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide	0.1 g	0.01 part by weight

[0046] Example 1 is subsequently repeated, the tetrahydrothiophene being replaced by the composition according to the invention thus prepared.

[0047] The gas thus odorized is subjected to an olfactory test, from which it emerges that the gas thus odorized has a good alerting power (high odorant power similar to that of the composition of Example 1).

[0048] The content of sulphur dioxide formed, after combustion of the gas thus odorized, is equal to 0.87 mg/Sm^3.

CLAIMS

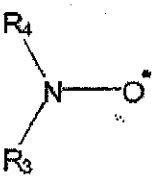
1. A composition which can be used in particular as odorant for a gaseous fuel, more particularly natural gas, comprising:

- from 0.1 to 49.9 parts by weight of at least one alkyl sulphide (I) of formula:

R^1-S-R^2

in which R^1 and R^2, which are identical or different, represent:

- an alkyl radical comprising from 1 to 4 carbon atoms; or
- R^1 and R^2, taken with the sulphur atom to which they are attached, represent a saturated or unsaturated ring comprising from 3 to 5 carbon atoms which is optionally substituted by a C_1-C_4 alkyl or C_1-C_4 alkenyl radical;
- from 50 to 99.8 parts by weight of at least two alkyl acrylates (II), the alkyl radicals of which comprise from 1 to 12 carbon atoms, preferably from 1 to 8;
- from 0.001 to 0.1 part by weight of at least one compound (III) which inhibits the polymerization of the alkyl acrylates (II) and which is stable in the presence or in the absence of oxygen, preferably comprising a stable nitroxide radical of formula (IV):



in which:

- R^3 and R^4, which are identical or different, each represent a tertiary or secondary hydrocarbon radical comprising from 2 to 30 carbon atoms, preferably from 4 to 15, and optionally one or more heteroatoms chosen from sulphur, phosphorus, nitrogen or oxygen; or

- R^3 and R^4, taken with the nitrogen atom to which they are attached, represent a cyclic hydrocarbon radical comprising from 4 to 10 carbon atoms, preferably from 4 to 6, the said radical optionally being substituted.

2. The composition of claim 1, comprising from 5 to 14.95 parts by weight of compound(s) (I), from 85 to 94.95 parts by weight of compounds (II) and from 0.005 to 0.05 parts by weight of compound(s) (III).

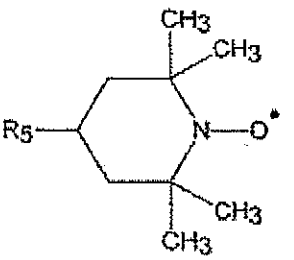
3. The composition of either of claims 1 and 2, wherein the alkyl sulphide or sulphides (I) is/are chosen from tetrahydrothiophene (THT), methyl ethyl sulphide (MES), dimethyl sulphide (DMS) and/or diethyl sulphide (DES), and is preferably THT.

4. The composition of any of claims 1 to 3, wherein the acrylic acid esters (II) are chosen from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, *tert*-butyl, pentyl, hexyl, heptyl, octyl and dodecyl acrylates.

5. The composition of any of claims 1 to 4, wherein the acrylic acid esters (II) comprise at least methyl acrylate and ethyl acrylate.

6. The composition of any of claims 1 to 5, comprising tetrahydrothiophene (I), methyl acrylate (II) and ethyl acrylate (II).

7. The composition of any of claims 1 to 6, wherein the inhibitor or one of the inhibitors of formula (IV) is a compound derived from tetramethylpiperidine oxide of formula (IVa):



in which R^5 represents a hydroxyl, amino, R^6COO- or R^6CON- group where R^6 is a C_1-C_4 alkyl radical.

8. The composition of any of claims 1 to 6, wherein the compound or at least one of the compounds of formula (III) is chosen from N-(*tert*-butyl)-N-(1-[ethoxy(ethyl)phosphino]propyl)nitroxide, N-(*tert*-butyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide and/or N-(*tert*-butyl)-N-(2-methyl-1-phenylpropyl) nitroxide.

9. A process for the odorization of an odourless gaseous fuel comprising the addition of an effective amount of the composition as defined in one of Claims 1 to 8, used either pure or diluted.

10. The odorization process of claim 9, wherein the gaseous fuel is natural gas.

11. A gaseous fuel comprising an amount of between 1 mg/Sm^3 and 500 mg/Sm^3, preferably between 2 mg/Sm^3 and 50 mg/Sm^3, of the composition as defined in one of claims 1 to 8.

12. The gaseous fuel of claim 11, characterized in that it consists of natural gas.