Abstract:
The invention relates to the use of a composition comprising 3,3'-methylenebis(5-methyl oxazolidine) and b) one or more additives selected from among (i) urea, urea derivatives, amino acids, guanidine and guanidine derivatives and (ii) 1,2-diols in the removal of sulphur compounds from process streams. The composition is preferably used in the removal of hydrogen sulphide from process streams.
Use of compositions having a content of 3,3'-methylenebis(5-methyloxazolidine) in the removal of sulphur compounds from process streams

The invention relates to the use of a composition comprising a) 3,3'-methylenebis(5-methyloxazolidine) and b) one or more additives in the removal of sulphur compounds from process streams.

Hydrogen sulphide (H₂S) is an unpleasantly smelling, toxic gas which is a great hazard to health and in industrial plants leads to severe corrosion phenomena. Legislators have therefore imposed strict obligations for decreasing the H₂S content. Grotan®OX (3,3'-methylenebis(5-methyl oxazolidine), a water-free condensation product of formaldehyde and isopropanolamine in a molar ratio of 3:2) displays good effectiveness in the chemical neutralization of H₂S.

WO 02/051968 A1 discloses a process for decreasing the amount of hydrogen sulphide in a liquid or a gas by treatment with an H₂S-scavenging product. The H₂S-scavenging product is obtained by reaction of i) a compound having a carbonyl group with ii) an alcohol, thiol, amide, thioamide, urea or thiourea. The product is preferably prepared by reacting formaldehyde with an amine-free alcohol or urea. An example of an amine-free alcohol is ethylene glycol. The H₂S-scavenging agent can optionally be used together with amine, in particular monoethanolamine.

WO98/02501 discloses that bisoxazolidines can be used as scavenging agents for sulphphydryl compounds. An example of a bisoxazolidine is 3,3'-methylenebis(5-methyl oxazolidine), which is obtained by reaction of isopropanolamine with formaldehyde (in a molar ratio of 2:3). However, the scavenging action of 3,3'-methylenebis(5-methyl oxazolidine) (hereinafter MBO) for sulphur compounds is in need of improvement, especially in process streams having a low water content. Such process streams are frequently formulated on the basis of hydrocarbons.

According to DE 197 22 858 A1, compositions based on iodopropynylbutylcarbamate and formaldehyde depot compounds are used as preservatives. The addition of particular glycols, preferably 1,2-propylene glycol, has a positive effect on the odour of the compositions and reduces the emission of volatile materials (such as formaldehyde).

DE 102 44 442 A1 discloses a preservative which has a reduced formaldehyde emission and contains a) at least one formal and b) at least one emission-reducing additive selected from among urea, urea derivatives, amino acids, guanidine and guanidine derivatives.

The preservatives described in DE 10 2004 014 447 A1 comprise a) at least N-formal, b) at least one emission-reducing additive and c) monoethylene glycol.
DE 10 2012 203 003 A1 discloses a liquid preparation for reducing free oxygen and preserving water. The preparation comprises a) at least one N-formal and b) at least one dialkylhydroxylamine of the formula RR'NOH (where R and R' are selected independently from among Ci-Cio-alkyl groups).

It is accordingly an object of the present invention to provide compositions which remove sulphur compounds from process streams, including from process streams which preferably contain little or no water. In particular, H₂S-scavenger compositions which have improved efficiency and advantages in use and are additionally also more economical are sought. The compositions should also avoid or reduce precipitates.

These objects are achieved by the use of a composition comprising a) 3,3'-methylenebis(5-methyl oxazolidine) and b) one or more additives selected from among (i) urea, urea derivatives, amino acids, guanidine and guanidine derivatives and (ii) 1,2-diols. The composition is, according to the invention, used in the removal of sulphur compounds from process streams.

According to the invention, the composition is preferably used in the removal of hydrogen sulphide from process streams.

It has been found according to the invention that the addition of the additives mentioned improves the effectiveness of compositions containing 3,3'-methylenebis(5-methyl oxazolidine) in the removal of sulphur compounds from process streams compared to the use of 3,3'-methylenebis(5-methyl oxazolidine) alone (i.e. without the additives mentioned). Examples of sulphur compounds which are, according to the invention, removed from the process stream or whose content in the process stream is decreased, are H₂S, mercaptans, mercaptides, inorganic and organic sulphides and other thiol compounds.

In a first aspect, the invention thus provides for the use of a composition comprising:

a) 3,3'-methylenebis(5-methyl oxazolidine) and
b) one or more additives selected from among:

(i) urea, urea derivatives, amino acids, guanidine and guanidine derivatives and

(ii) 1,2-diols,

in the removal of sulphur compounds from process streams.

The composition used according to the invention is preferably in the form of a concentrate and comprises from 60 to 99% by weight of 3,3'-methylenebis(5-methyl oxazolidine), preferably from 70 to 97% by weight, in particular from 80 to 92% by weight.
In a first preferred embodiment, the composition comprises:

b) one or more additives selected from among urea, urea derivatives, amino acids, guanidine and guanidine derivatives. Examples of such additives are glycoluril, tetramethylolglycoluril, dimethylhydantoin, dimethyldimethylhydantoin, dimethylol-urea, tetramethylolurea, imidazolidinylurea and diazolidinylurea.

The composition particularly preferably comprises b) urea. Here, preference is given to the composition being in the form of a concentrate and comprising b) from 1 to 20% by weight of urea, preferably from 2 to 14% by weight, in particular from 2.5 to 8% by weight, for example from 3 to 6% by weight, of urea.

In a second preferred embodiment, a composition comprising b) one or more 1,2-diols is used. In this embodiment, preference is given to the composition being in the form of a concentrate and comprising b) from 1 to 25% by weight of 1,2-diol, preferably from 3 to 20% by weight, in particular from 5 to 15% by weight, of 1,2-diol. Preferred 1,2-diols used according to the invention are selected from among ethylene glycol, propyleneglycol and mixtures thereof, with component b) preferably being ethylene glycol.

In a third preferred embodiment, the composition used according to the invention comprises b) at least one component (i) and at least one component (ii). In this embodiment, preference is again given to the composition being in the form of a concentrate and comprising b) (i) from 1 to 20% by weight of urea, preferably from 2 to 14% by weight, in particular from 2.5 to 8% by weight, for example from 3 to 6% by weight of urea. It is further preferred in this embodiment that the composition comprises b) (ii) from 1 to 25% by weight of 1,2-diol, preferably from 3 to 20% by weight, in particular from 5 to 15% by weight, of 1,2-diol.

Particular preference is thus given according to the invention to using compositions comprising:

a) from 60 to 99% by weight of 3,3'-methylenebis(5-methyl oxazolidine), (preferably from 70 to 97% by weight, in particular from 80 to 92% by weight, of 3,3'-methylenebis(5-methyl oxazolidine)),

b) (i) from 1 to 20% by weight of urea (preferably from 2 to 14% by weight, in particular from 2.5 to 8% by weight, for example from 3 to 6% by weight, of urea) and

b) (ii) from 1 to 25% by weight of 1,2-diol (preferably from 3 to 20% by weight, in particular from 5 to 15% by weight, of 1,2-diol).

Apart from the compulsory components a) 3,3'-methylenebis(5-methyl oxazolidine) and b) one or more of the additives mentioned, the composition can further comprise c) N,N-dialkyl hydroxylamine of the formula RR'NOH, where R and R'
are selected independently from among linear, branched and cyclic CrCl₁₀alkyl
groups. A preferred Ν,Ν-dialkyl hydroxylamine is Ν,Ν-diethyl hydroxylamine.

Process streams treated according to the invention are, for example, liquid and
and gaseous process streams.

Exemplary process streams contain not more than 40% by weight of water,
preferably not more than 35% by weight of water, particularly preferably not more than
30% by weight of water, for example not more than 25% by weight or not more than
20% by weight or not more than 15% by weight, for example not more than 10% by
weight or not more than 5% by weight, for example not more than 1% by weight, of
water.

Fields of use are, inter alia, biogas plants, petroleum and natural gas extraction,
processing, storage and transport of fossil energy carriers and the removal of H₂S
liberated by sulphate-reducing bacteria under anaerobic conditions. Examples of H₂S-
containing streams or products are petroleum, crude oil, mineral oil, heating oil, diesel
fuel, bitumen, distillation residues, drilling fluids and wastewater. Particular preference
is given to the use according to the invention of the compositions in process streams
which are hydrocarbon streams.

In a second embodiment, the invention relates to a process for removing one or
more sulphur compounds from a process stream, wherein the process stream
containing the sulphur compound or sulphur compounds is brought into contact with a
composition comprising a) 3,3′-methylenebis(5-methyl oxazolidine) and b) one or more
additives selected from among (i) urea, urea derivatives, amino acids, guanidine and
guanidine derivatives and (ii) 1,2-diols.

The use is preferably at elevated temperature (for example 50°C or above, e.g.
70°C or above, 90°C or even 150°C or above). Subsequent liberation of H₂S
advantageously does not occur to the same extent as in the case of the sole use of
3,3′-methylenebis(5-methyl oxazolidine). The compositions used according to the
invention are better suited for binding the inherent H₂S which is gradually formed
subsequently during prolonged hot storage than is 3,3′-methylenebis(5-methyl
oxazolidine) alone.

The constituents according to the invention can be introduced individually into
the H₂S-containing process streams, either within a short time interval or at different
points in time. Surprisingly, there is reduced formation of troublesome insoluble
deposits or precipitates, sometimes such precipitates are even dissolved.

Compositions used according to the invention also have a very good short-term and in
particular long-term action. Rapid and efficient lowering of the H₂S content is achieved
at short contact times.
The advantages of the invention can be seen, in particular, from the following examples. Percentages are by weight, unless indicated otherwise.

**Examples**

**Composition OX (comparison):**

The reaction product of isopropanolamine and paraformaldehyde (91% strength) in a molar ratio of 2:3 is formed. 3,3'-Methylenebis(5-methyl oxazolidine) is formed here. The water of reaction and the water from the paraformaldehyde are distilled off.

**Composition OK (according to the invention):**

The reaction product of isopropanolamine and paraformaldehyde (91% strength) in a molar ratio of 2:3 is formed. 3,3'-Methylenebis(5-methyl oxazolidine) is formed here. The water of reaction and the water from the paraformaldehyde are distilled off. Urea and ethylene glycol are added (the mixture contains about 4.6% by weight of urea and about 9.5% by weight of ethylene glycol).

**Method of determining the sulphide concentration (based on IP 570, Determination of hydrogen sulphide in mineral oils)**

- Contacting of the various sulphur-scavenging agents with the sample at various temperatures and for different times
  - Dilution of the sample with alkylbenzene in order to bring it into the linear working range of the analytical system
  - Injection of the test sample (including sulphur-scavenging agent) into the analytical system
- Addition of acid (2M H₃PO₄ in water) and optionally heating of the analytical sample in the analytical system
  - Quantitative driving-off of the resulting hydrogen sulphide in the analytical system by means of air and transfer of the hydrogen sulphide to an electrochemical measuring electrode in the analytical instrument
- The hydrogen sulphide produces a measurement signal which is proportional to the respective amount of hydrogen sulphide at the electrochemical measuring electrode.
  - The peak area formed (made up of measurement signal intensity versus time) is determined by means of evaluation software and converted into a sulphide content on the basis of a calibration line.
a) \( \text{H}_2\text{S in C}_{10-i3}-\text{alkylbenzene (sulphide concentration 200 ppm), 20°C, 2 h} \)

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b) \( \text{H}_2\text{S in C}_{10-13}-\text{alkylbenzene (sulphide concentration 100 ppm), 50°C} \)

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c) \( \text{H}_2\text{S in C}_{10-13}-\text{alkylbenzene (sulphide concentration 200 ppm), 50°C, 2 h} \)

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These examples demonstrate that compositions used according to the invention not only decrease the sulphide content better than does 3,3'-methylenebis(5-methyloxazolidine) alone, but that this improved effect is even more pronounced at an elevated use temperature.
Claims

1. Use of a composition comprising:
   a) 3,3'-methylenebis(5-methyl oxazolidine) and
   b) one or more additives selected from among:
      (i) urea, urea derivatives, amino acids, guanidine and guanidine derivatives
      and
      (ii) 1,2-diols,
   in the removal of sulphur compounds from process streams.

2. Use according to Claim 1, characterized in that the composition is in the form of a concentrate and comprises from 60 to 99% by weight of 3,3'-methylenebis(5-methyl oxazolidine).

3. Use according to Claim 2, characterized in that the composition is in the form of a concentrate and comprises from 70 to 97% by weight of 3,3'-methylenebis(5-methyl oxazolidine).

4. Use according to Claim 3, characterized in that the composition is in the form of a concentrate and comprises from 80 to 92% by weight of 3,3'-methylenebis(5-methyl oxazolidine).

5. Use according to anyone of Claims 1 to 4, characterized in that the composition comprises b) urea.

6. Use according to Claim 5, characterized in that the composition is in the form of a concentrate and comprises from 1 to 20% by weight of urea.

7. Use according to Claim 6, characterized in that the composition is in the form of a concentrate and comprises from 2 to 14% by weight of urea.

8. Use according to Claim 7, characterized in that the composition is in the form of a concentrate and comprises from 2.5 to 8% by weight of urea.

9. Use according to anyone of Claims 1 to 4, characterized in that the composition comprises b) one or more 1,2-diols.
10. Use according to Claim 9, **characterized in that** the composition **is** in the form of a concentrate and comprises from 1 to 25% by weight of 1,2-diol.

11. Use according to Claim 10, **characterized in that** the composition **is** in the form of a concentrate and comprises from 3 to 20% by weight of 1,2-diol.

12. Use according to Claim 11, **characterized in that** the composition **is** in the form of a concentrate and comprises from 5 to 15% by weight of 1,2-diol.

13. Use according to anyone of Claims 9 to 12, **characterized in that** the 1,2-diol is selected from among ethylene glycol, propylene glycol and mixtures thereof.

14. Use according to anyone of Claims 13, **characterized in that** the 1,2-diol is ethylene glycol.

15. Use according to anyone of Claims 1 to 14, **characterized in that** the composition further comprises c) N,N-dialkyl hydroxylamine of the formula RR'NOH, where R and R' are selected independently from among linear, branched and cyclic C₃- C₁₀-alkyl groups.

16. Use according to Claim 15, **characterized in that** the N,N-dialkyl hydroxylamine is N,N-diethyl hydroxylamine.

17. Use according to anyone of Claims 1 to 16, **characterized in that** the process stream is selected from among liquid and gaseous process streams.

18. Use according to anyone of Claims 1 to 17, **characterized in that** the process stream contains not more than 40% by weight of water.

19. Use according to anyone of Claims 1 to 18, **characterized in that** the process stream is a hydrocarbon stream.

20. Use according to any of Claims 1 to 19, **characterized in that** the sulphur compound is selected from among hydrogen sulphide, inorganic and organic sulphides, mercaptans and mercaptides.
21. Use according to Claim 20, characterized in that the sulphur compound is hydrogen sulphide.

22. Process for the removal of one or more sulphur compounds from a process stream, wherein the process stream containing the sulphur compound or sulphur compounds is brought into contact with a composition comprising:
   a) 3,3'-methylenebis(5-methyl oxazolidine) and
   b) one or more additives selected from among:
      (i) urea, urea derivatives, amino acids, guanidine and guanidine derivatives
      and
      (ii) 1,2-diols,
## INTERNATIONAL SEARCH REPORT

**International application No**

PCT/EP2016/080743

### A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G29/20 C10L3/10

**ADD.**

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)

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

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

EPO-Internal

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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See patent family annex.

- **Y** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- **O** document referring to an oral disclosure, use, exhibition or other means

**Date of the actual completion of the international search**

9 March 2017

**Date of mailing of the international search report**

05/04/2017

**Name and mailing address of the ISA/IB**

European Patent Office, P.B. 5818 Patentlaan 2
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Authorized officer

Klaas, Daphne

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