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- (54) Benævnelse: **ANVENDELSE AF SAMMENSÆTNINGER MED ET INDHOLD AF KONDENSATIONSPRODUKT AF 1-AMINOPROPAN-2-OL OG FORMALDEHYD TIL FJERNELSE AF SVOVLFORBINDELSER FRA PROCESSTRØMME**
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DESCRIPTION

[0001] The present invention relates to the use of a composition that comprises a) one or more condensation products of 1-aminopropan-2-ol and formaldehyde and b) monoethylene glycol, in the removal of sulphur compounds from process streams. In addition, the invention relates to a corresponding method for removing one or more sulphur compounds from a process stream.

[0002] H₂S is an unpleasantly smelling and toxic gas that is a hazard to health to a great extent and furthermore leads in industrial systems to serious corrosion phenomena. The legislator has therefore enacted strict requirements for lowering the H₂S content in gaseous and liquid streams.

[0003] WO90/07467 A1 discloses condensation products of formaldehyde and ethanolamine (such as 3,3'-methylenebisoxazolidine and N,N',N''-tris(2-hydroxyethyl)hexahydrotriazine) and use thereof in gaseous and liquid hydrocarbon streams, in order to decrease therein the amount of hydrogen sulphide and organic sulphides. In addition, it is indicated that, in the case of hydrocarbon streams that contain water, glycols can be added in order at the same time to reduce the water content. An exemplary and preferred glycol is triethylene glycol.

[0004] WO2016/100224 A2 discloses compositions for removing sulphur compounds from moist or dry gaseous streams. The compositions, in addition to at least one compound for capturing the sulphur compound, further contain at least one hygroscopic agent. Preferred compounds for capturing the sulphur compounds are triazines or monoethanolamine, methylamine or methoxypropylamine. An exemplary hygroscopic agent is glycerol.

[0005] US 5,128,049 A describes a method for reducing the hydrogen sulfide content of hydrocarbon-containing fluids and aqueous solutions through a two-stage injection procedure whereby a dilute solution of a scavenging agent is injected into a hydrogen sulfide-containing fluid, followed by equilibration and a second injection of dilute solution of scavenging agent to further reduce the hydrogen sulfide content of the treated fluid.

[0006] WO 98/02501 A1 is directed to a method for scavenging sulphydryl compounds from sour hydrocarbon substrates, preferably crude oils, refined distillate streams, and natural gas, by mixing said substrates with preferably substantially water free bisoxazolidines.

[0007] US 4,978,512 A is directed to methods for selectively reducing the levels of hydrogen sulfide and organic sulfides from gaseous and/or liquid hydrocarbon streams, particularly natural gas streams, comprising contacting the streams with a composition comprising the reaction product of (i) a lower alkanolamine with (ii) a lower aldehyde.

[0008] Grotan[®] OX (i.e. 3,3'-methylenebis[5-methyloxazolidine]) is an anhydrous condensation product of formaldehyde and 1-aminopropan-2-ol (monoisopropanolamine, MIPA) in the molar

ratio 3:2, (Schülke & Mayr GmbH, Norderstedt, Federal Republic of Germany). The product Grotan[®] WS contains about 80% by weight of the formaldehyde donor compound α,α',α'' -trimethyl-1,3,5-triazine-1,3,5-(2H,4H,6H)triethanol (N,N',N''-tris(2-hydroxypropyl)hexahydrotriazine, hereinafter TTT). TTT is produced by condensation of 1-aminopropan-2-ol with formaldehyde (in the molar ratio 1:1). Grotan[®] OX and Grotan[®] WS show good efficacy in the chemical neutralization of H₂S.

[0009] The problem addressed by the present invention is to provide compositions that remove sulphur compounds from process streams, more precisely also from those process streams that preferably contain little or no water, including liquid and gaseous process streams (such as, in particular, hydrocarbon process streams). H₂S trapping compositions having improved efficiency and advantages in application which additionally are also more economical are sought.

[0010] It has now surprisingly been found that this problem is solved by using, in the removal of sulphur compounds from process streams

1. a) one or more condensation products of 1-aminopropan-2-ol and formaldehyde and
2. b) monoethylene glycol,

wherein the weight ratio used of a):b) is in the range from 5:95 to 70:30. The components a) and b) are preferably used according to the invention as a composition comprising a) and b), wherein component a) is present in an amount from 5 to 70% by weight and component b) is present in an amount from 30 to 95% by weight, in each case based on the weight of the composition.

[0011] The invention is based, inter alia, on the fact that it has been found that the efficiency of condensation products of 1-aminopropan-2-ol and formaldehyde in the removal of sulphur compounds from process streams may be significantly increased by addition of monoethylene glycol. In addition, it is advantageous that, in the compositions according to the invention, the proportion of component b) does not impair those product properties such as handleability and flashpoint. Even in the case of the condensation product N,N',N''-tris(2-hydroxypropyl)hexahydrotriazine, that already acts well when used alone, there is an increase in activity when monoethylene glycol is added. Although, by addition of propylene glycol, a certain improvement in activity may be achieved, this improvement, however, is markedly less than compared with the effect with monoethylene glycol.

[0012] In a first aspect, the invention therefore relates to the use of a composition that comprises

1. a) one or more condensation products of 1-aminopropan-2-ol and formaldehyde and
2. b) monoethylene glycol,

wherein component a) is present in an amount from 5 to 70% by weight and component b) is

present in an amount from 30 to 95% by weight, in each case based on the weight of the composition,

[0013] in the removal of sulphur compounds from process streams. The component a) is a condensation product of 1-aminopropan-2-ol and formaldehyde, or a mixture of such condensation products. Preferably, the condensation product is produced by reacting 1-aminopropan-2-ol and formaldehyde in the molar ratio 1:0.8 to 1:1.8, preferably in the molar ratio 1:0.9 to 1:1.6.

[0014] In a first preferred embodiment, the condensation product is 3,3'-methylenebis[5-methyloxazolidine], i.e. the condensation product of formaldehyde and 1-aminopropan-2-ol in the molar ratio 3:2. In this case it is preferred that the component a) is 3,3'-methylenebis[5-methyloxazolidine]. In this first preferred embodiment, preferably component a) is present in an amount from 20 to 60% by weight, and component b) is present in an amount from 40 to 80% by weight.

[0015] Particularly preferably, in the first preferred embodiment, component a) is present in an amount from 30 to 50% by weight and component b) is present in an amount from 50 to 70% by weight, wherein, in particular, component a) is present in an amount of about 40% by weight and component b) is present in an amount of about 60% by weight.

[0016] This first preferred embodiment in which component a) comprises 3,3'-methylenebis[5-methyloxazolidine] and preferably, component a) is 3,3'-methylenebis[5-methyl-oxazolidine], wherein, particularly preferably, component a) is present in an amount from 30 to 50% by weight and component b) is present in an amount from 50 to 70%, is therefore particularly advantageous because the surprising effect in lowering the content of sulphur compounds already results after a short exposure time and the reinforcement of the effect by the content of monoethylene glycol is particularly pronounced (see Examples 6 to 8 and, in particular, Example 7).

[0017] In this first preferred embodiment, it is further preferred that the composition comprises less than 10% by weight of water, preferably less than 5% by weight of water, in particular less than 2% by weight of water, such as less than 1% by weight of water.

[0018] Particularly, preference is therefore given to the use of a composition that consists of a) about 40% by weight of 3,3'-methylenebis[5-methyloxazolidine] and b) about 60% by weight of monoethylene glycol.

[0019] In a second preferred embodiment, the condensation product is N,N',N''-tris(2-hydroxypropyl)hexahydrotriazine, i.e. the condensation product of formaldehyde and 1-aminopropan-2-ol in the molar ratio 3:3 (1:1), wherein component a) is preferably N,N',N''-tris(2-hydroxypropyl)hexahydrotriazine. In this second preferred embodiment, the composition preferably comprises 2 to 25% by weight of water, more preferably 5 to 20% by weight of water, in particular 10 to 15% by weight of water, such as 12% by weight of water.

[0020] In addition, in this second preferred embodiment, it is preferred that component a) is present in an amount from 35 to 60% by weight and component b) is present in an amount from 30 to 50% by weight, wherein preferably component a) is present in an amount from 40 to 55% by weight and component b) is present in an amount from 35 to 45% by weight, wherein, in particular component a) is present in an amount of about 48% by weight and component b) is present in an amount of about 40% by weight.

[0021] In all embodiments of the invention it is advantageous when the composition does not comprise a dialkylhydroxylamine of the formula $RR'NOH$, wherein R and R' independently of one another are selected from linear, branched and cyclic C_1 to C_{10} alkyl groups.

[0022] It is in addition advantageous when the composition does not contain an additive selected from urea, urea derivatives, amino acids, guanidine and guanidine derivatives.

[0023] The process stream is preferably selected from liquid and gaseous process streams.

[0024] Preferably, the process stream contains at most 40% by weight of water, more preferably at most 35% by weight of water, particularly preferably at most 30% by weight of water, such as at most 25% by weight of water, or at most 20% by weight, or at most 15% by weight, for instance at most 10% by weight, or at most 5% by weight, for example at most 1% by weight, of water. Fields of use are, inter alia, biogas plants, the transport of petroleum and natural gas, the processing, storage and transport of fossil energy carriers and the removal of H_2S liberated by sulphate-reducing bacteria under anaerobic conditions. Examples of H_2S -containing streams or products are petroleum, crude oil, mineral oil, heating oil, diesel fuel, bitumen, distillation residues, drilling liquid and wastewater. Particular preference is given to the use according to the invention of the compositions in process streams that are hydrocarbon streams. Preferably, the process stream is a liquid or gaseous hydrocarbon stream.

[0025] The sulphur compound, for the removal of which the described composition is used, is selected from hydrogen sulphide, inorganic and organic sulphides, mercaptans and mercaptides, wherein the composition is preferably used in the removal of hydrogen sulphide from process streams. In a second aspect, the invention relates to a method for removing one or more sulphur compounds from a process stream, in which the process stream that contains the sulphur compound or sulphur compounds is contacted with a composition that comprises

1. a) one or more condensation products of l-aminopropan-2-ol and formaldehyde and
2. b) monoethylene glycol,

wherein component a) is present in an amount from 15 to 70% by weight and component b) is present in an amount from 30 to 85% by weight, in each case based on the weight of the composition.

[0026] The present disclosure further describes that it is possible to add components a) and b)

to the process stream separately in the said weight ratio. Correspondingly, described herein is also the use of a) one or more condensation products of l-aminopropan-2-ol and formaldehyde, and b) monoethylene glycol, wherein the weight ratio used of a) :b) is in the range from 5:95 to 70:30, in the removal of sulphur compounds from process streams.

[0027] According to the invention, it is used according to the first and second aspects, compositions which comprise the components a) and b). These compositions have a low viscosity and offer advantages with respect to cost savings, economic efficiency, cold stability and flow behaviour.

[0028] The advantages of the invention result, in particular, from the following examples. Percentages, unless stated otherwise, relate to the weight.

Examples

1. Condensation products used

Grotan® OX:

[0029] The reaction product of isopropanolamine and paraformaldehyde (91%) is formed in the molar ratio 2:3. In this case 3,3'-methylenebis(5-methyloxazolidine) is formed. The reaction water and the water from the paraformaldehyde are distilled off.

Grotan® WS:

[0030] The reaction product is formed from isopropanolamine and paraformaldehyde (91%) in the molar ratio 3:3 (1:1). This forms α,α',α'' -trimethyl-1,3,5-triazine-1,3,5-(2H,4H,6H)- triethanol (N,N',N''-tris(2-hydroxypropyl)hexahydrotriazine, TTT). The reaction water and the water from the paraformaldehyde remain in the product. The TTT content is about 80% by weight.

2. Method: Determination of the sulphide concentration (based on IP 570, determination of hydrogen sulphide in mineral oils)

[0031]

- Action of the differing sulphur capturing agents on the sample at various temperatures and for differing times

- Dilution of the sample with alkylbenzene in order to arrive at the linear working range of the analysis system
- Injection of the sample under investigation (including sulphur capturing agent) into the analysis system
- Addition of acid (2M H₃PO₄ in water) and optionally heating the analytical sample in the analysis system
- Quantitative expulsion of the resultant hydrogen sulphide in the analysis system by means of air and transfer of the hydrogen sulphide to an electrochemical measuring electrode in the analysis apparatus
- The hydrogen sulphide generates, at the electrochemical measurement electrode, a measurement signal that is proportional to the respective hydrogen sulphide amount
- By means of evaluation software, the resultant peak area (composed of measured signal intensity against time) is determined and converted to a sulphide content, on the basis of a calibration line

3. Study of various formaldehyde condensation products, glycols and mixtures thereof

[0032] In order to show the advantages of the compositions used according to the invention, a test was made as to what action various compositions have on the removal of H₂S in C₁₀₋₁₃ alkyl benzene (sulphide concentration 200 ppm). The samples were heated for this purpose to 50°C and the compositions were used in an amount in each case of 1000 ppm, wherein in the table hereinafter, for the mixtures of condensation product and glycol (monoethylene glycol and propylene glycol) in each case the weight ratio is stated. The results in the case of percentage reduction of H₂S content after exposure for 2 or 24 hours are given in Tab. 1.

Tab. 1

No.	Composition	2 h	24 h
1*	Monoethylene glycol	2.3%	5.8%
2*	Grotan [®] OX	7.9%	17.8%
3*	Grotan [®] OX + Monoethylene glycol (9:1)	9.7%	24.5%
4 *	Grotan [®] OX + Monoethylene glycol (8:2)	18.7%	-
5	Grotan [®] OX + Monoethylene glycol (6:4)	21.9%	82.6%
6	Grotan [®] OX + Monoethylene glycol (1:1)	23.3%	86.1%
7	Grotan [®] OX + Monoethylene glycol (4:6)	25.4%	88.0%
8	Grotan [®] OX + Monoethylene glycol (3:7)	21.5%	93.6%
9	Grotan [®] OX + Monoethylene glycol (2:8)	22.3%	97.5%
10	Grotan [®] OX + Monoethylene glycol (1:9)	14.6%	99.4%

No.	Composition	2 h	24 h
11*	Grotan [®] OX + Propylene glycol (4:6)	13.8%	34.0%
12*	Grotan [®] WS	14.0%	72.4%
13	Grotan [®] WS + Monoethylene glycol (6:4)	25.0%	88.9%
* Comparison - Experiment not carried out			

[0033] The results verify that monoethylene glycol and the condensation products of 1-aminopropan-2-ol and formaldehyde (Grotan[®] OX and Grotan[®] WS) in each case alone reduce the H₂S content only insufficiently, and more precisely not only for the exposure time of 2 h, but also for the exposure time of 24 h (comparative experiments 1, 2 and 12). The same applies to compositions consisting of Grotan[®] OX and monoethylene glycol in the weight ratios 9:1 and 8:2 (comparative experiments 3 and 4), that is to say having a small fraction of monoethylene glycol, and also to compositions consisting of Grotan[®] OX and propylene glycol (comparative experiment 11).

[0034] In contrast, the compositions according to the invention consisting of i) condensation product of 1-aminopropan-2-ol and formaldehyde (Grotan[®] OX or Grotan[®] WS) and ii) monoethylene glycol surprisingly act considerably better when the content of monoethylene glycol is higher than 20% by weight (experiments 5 to 10 and 13). In the case of compositions according to the invention consisting of i) Grotan[®] OX and ii) monoethylene glycol, for an exposure time of only 2 h, it is shown that a composition consisting of Grotan[®] OX and monoethylene glycol in the weight ratio 4:6 (experiment 7) already acts well (reducing the H₂S content by 25.4%), and for an exposure time of 24 h, the reduction is even 88%. In the case of the markedly longer exposure time of 24 h, in contrast, a mixture consisting of Grotan[®] OX and monoethylene glycol in the weight ratio 1:9 (experiment 10) acts excellently (reduction by 99.4%).

4. Particularly preferred composition

[0035] For production of the particularly preferred composition consisting of a) 40% by weight of 3,3'-methylenebis-[5-methyloxazolidine] and b) 60% by weight of monoethylene glycol, monoethylene glycol is charged and Grotan[®] OX is added. After brief stirring, a clear, colourless solution is obtained having the following properties (Tab. 2).

Tab. 2

Appearance	clear, colourless solution
Hazen colour number	11

Appearance	clear, colourless solution
Density at 20°C, g/ml	1.108
Refraction at 20°C	1.457
Cleavable HCHO, %	17.9

[0036] The storage stability of this composition was studied by storing samples for 1 month at 25°C or 40°C in PE bottles (Tab. 3):

Tab. 3

After 1 month of storage at	25°C	40°C
Appearance	clear, slightly yellowish	light yellow
Hazen colour number	29	70
Density at 20°C, g/ml	1.108	1.108
Refraction at 20°C	1.457	1.457
Cleavable HCHO, %	17.7	17.8
Reduction of H ₂ S content, 2 h, %	26.0	27.9
Reduction of H ₂ S content, 24 h, %	87.5	87.4

[0037] The results in Tab. 3 verify that this particularly preferred composition has not lost the activity in the reduction of H₂S content even after storage for one month at an elevated temperature of 40°C.

REFERENCES CITED IN THE DESCRIPTION

Cited references

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- [WO9007467A1 \[0003\]](#)

- WO2016100224A2 [0004]
- US5128049A [0005]
- WO9802501A1 [0006]
- US4978512A [0007]

Patentkrav

1. Anvendelse af en sammensætning, der omfatter

a) et eller flere kondensationsprodukter af 1-aminopropan-2-ol og formaldehyd og

5 b) monoethylenglycol,

hvor komponent a) er til stede i en mængde fra 5 til 70 vægt-%, og komponent b) er til stede i en mængde fra 30 til 95 vægt-%, i hvert tilfælde baseret på vægten af sammensætningen, ved fjernelse af svovlforbindelser fra processtrømme.

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2. Anvendelse ifølge krav 1, **kendetegnet ved, at** kondensationsproduktet fremstilles ved at omsætte 1-aminopropan-2-ol og formaldehyd i molforholdet 1:0,8 til 1:1,8, fortrinsvis i molforholdet 1:0,9 til 1:1,6.

15 **3.** Anvendelse ifølge krav 2, **kendetegnet ved, at** komponent a) er 3,3'-methylenbis[5-methyloxazolidin].

4. Anvendelse ifølge krav 3, **kendetegnet ved, at** komponent a) er til stede i en mængde fra 20 til 60 vægt-%, og komponent b) er til stede i en mængde fra 40
20 til 80 vægt-%,

hvor komponent a) fortrinsvis er til stede i en mængde fra 30 til 50 vægt-%, og komponent b) er til stede i en mængde fra 50 til 70 vægt-%, hvor især komponent a) er til stede i en mængde på ca. 40 vægt-%, og komponent b) er til stede i en mængde på ca. 60 vægt-%.

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5. Anvendelse ifølge krav 4, **kendetegnet ved, at** sammensætningen omfatter mindre end 10 vægt-% vand, fortrinsvis mindre end 5 vægt-% vand, især mindre end 2 vægt-% vand, såsom mindre end 1 vægt-% vand.

30 **6.** Anvendelse ifølge krav 2, **kendetegnet ved, at** komponent a) er N,N',N''-tris(2-hydroxypropyl)hexahydrotriazin.

7. Anvendelse ifølge krav 6, **kendetegnet ved, at** sammensætningen omfatter 2 til 25 vægt-% vand, fortrinsvis 5 til 20 vægt-% vand, især 10 til 15 vægt-% vand,

såsom 12 vægt-% vand.

8. Anvendelse ifølge krav 6 eller krav 7, **kendetegnet ved, at** komponent a) er til stede i en mængde fra 35 til 60 vægt-%, og komponent b) er til stede i en mængde fra 30 til 50 vægt-%.

hvor komponent a) fortrinsvis er til stede i en mængde fra 40 til 55 vægt-%, og komponent b) er til stede i en mængde fra 35 til 45 vægt-%, hvor især komponent a) er til stede i en mængde på ca. 48 vægt-%, og komponent b) er til stede i en mængde på ca. 40 vægt-%.

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9. Anvendelse ifølge et af de foregående krav, **kendetegnet ved, at** sammensætningen ikke omfatter en dialkylhydroxylamin med formlen $RR'NOH$, hvor R og R' uafhængigt af hinanden er valgt fra lineære, forgrenede og cykliske C_1 - til C_{10} -alkylgrupper og/eller **kendetegnet ved, at** sammensætningen ikke omfatter et additiv valgt fra urinstof, urinstofderivater, aminosyrer, guanidin og guanidinderivater.

10. Anvendelse ifølge et af de foregående krav, **kendetegnet ved, at** processtrømmen er valgt fra flydende og gasformige processtrømme.

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11. Anvendelse ifølge et af de foregående krav, **kendetegnet ved, at** processtrømmen indeholder højst 40 vægt-% vand, fortrinsvis højst 35 vægt-% vand, særligt foretrukket højst 30 vægt-% vand, såsom højst 25 vægt-% vand, eller højst 20 vægt-%, eller højst 15 vægt-%, for eksempel højst 10 vægt-%, eller højst 5 vægt-%, for eksempel højst 1 vægt-% vand.

12. Anvendelse ifølge et af de foregående krav, **kendetegnet ved, at** processtrømmen er en carbonhydridstrøm.

13. Anvendelse ifølge et af de foregående krav, **kendetegnet ved, at** svovlforbindelsen er valgt fra hydrogensulfid, uorganiske og organiske sulfider, mercaptaner og mercaptider, hvor sammensætningen fortrinsvis anvendes til fjernelse af hydrogensulfid fra processtrømme.

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14. Fremgangsmåde til fjernelse af en eller flere svovlforbindelser fra en processtrøm, hvor processtrømmen, der indeholder svovlforbindelsen eller svovlforbindelserne, bringes i kontakt med en sammensætning, der omfatter

- 5 a) et eller flere kondensationsprodukter af 1-aminopropan-2-ol og formaldehyd og
- b) monoethylenglycol,

hvor komponent a) er til stede i en mængde fra 15 til 70 vægt-%, og komponent b) er til stede i en mængde fra 30 til 85 vægt-%, i hvert tilfælde baseret på vægten af sammensætningen.