

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
17 February 2005 (17.02.2005)

PCT

(10) International Publication Number
WO 2005/014192 A1

- (51) International Patent Classification⁷: **B09B 1/00**, B65G 5/00
- (21) International Application Number: PCT/EP2004/007565
- (22) International Filing Date: 6 July 2004 (06.07.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
MI2003A001469 18 July 2003 (18.07.2003) IT
- (71) Applicants (for all designated States except US): **ENI S.p.A.** [IT/IT]; Piazzale E. Mattei 1, I-00144 Rome (IT). **ENITECNOLOGIE S.p.A.** [IT/IT]; Via F. Maritano 26, I-20097 San Donato Milanese (MI) (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **DE ANGELIS, Alberto** [IT/IT]; Via Flli Cairoli, 16, I-20025 Legnano (MI) (IT). **POLLESEL, Paolo** [IT/IT]; Via Dossetti, 11/D, I-20097 San Donato Milanese (MI) (IT). **BELLUSSI, Giuseppe** [IT/IT]; Via E. Millo 14, I-29100 Piacenza (IT). **LOCKHART, Thomas, Paul** [US/IT]; Corso Mazzini 45, I-26900 Lodi (IT).
- (74) Agents: **DE GREGORI, Antonella** et al.; Via Borgonuovo, 10, I-20121 Milan (IT).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE DISPOSAL OF SULFUR IN THE FORM OF COMPOUNDS LIQUID AT ROOM TEMPERATURE

(57) Abstract: Process for the disposal of sulfur in the liquid state which comprises: a) transforming elemental sulfur into sulfanes having the general formula H_2S_{n+1} , wherein n is a number from 1 to 7; b) optionally mixing elemental sulfur in powder form with the liquid sulfanes, up to such a concentration as to guarantee the pumpability of the mixture; c) injecting the sulfanes liquid at room temperature into geological formations having a temperature lower than 150°C.



WO 2005/014192 A1

5

PROCESS FOR THE DISPOSAL OF SULFUR IN THE FORM OF COMPOUNDS
LIQUID AT ROOM TEMPERATURE

The present invention relates to a new process for the
10 disposal of sulfur in the form of derivatives in the liquid
state at room temperature.

More specifically, the present invention relates to a
new process for the disposal of sulfur coming from the pu-
rification treatment of hydrocarbons of a fossil nature,
15 for example crude oil or natural gas.

It is well known that sulfur can be present in consid-
erable quantities in both extracted crude oil and natural
gas. In this gas, the sulfur can be present in the form of
 H_2S in a molar percentage quantity which can reach 10% and
20 in certain particular cases it can even exceed 20%, refer-
ring to gas.

When present in high concentrations in gas, the hydro-
gen sulfide is separated using various systems, of which
the most widely used is absorption in solutions of ethanol-
25 amines. Once it is in the concentrated state, hydrogen sul-

fide is transformed into elemental sulfur by means of the Claus process. At this point, it is necessary to allocate the sulfur which, for the last few years and potentially for tens of years to come, has a market characterized by an excessive offer with respect to the demand. Sulfur is normally stored in elemental form as huge blocks which require continual monitoring and treatment of the run off water to avoid the acidification of the ground and surrounding underground water. In addition to this, there is an increasingly strict legislation on the part of states containing oil fields or natural gas reservoirs, which in some cases impose heavy penalties for the storage of recovered sulfur.

The Applicants have now found an innovative process for the elimination of said large quantities of sulfur which envisages its injection by pumping it into adequate geological structures in the form of compounds, more specifically as sulfanes, which are in the liquid state at room temperature. Sulfanes are compounds characterized by an extremely high weight content of sulfur, which varies from 97% (H_2S_2) to 99.2% (H_2S_8).

In another embodiment it is possible to use synthesized sulfanes as a solvent for dissolving additional elemental sulfur, in order to reduce the quantity of sulfur to be converted into sulfanes for its elimination.

The structures, to which the accumulation of sulfur in

the form of sulfanes is destined, can consist of the field itself from which the crude oil or associated gas has been extracted or other adequate deep geological structures, such as abandoned mines or saline aquifers. With the use of sulfanes, it is also possible to adopt, as structures for the storage of sulfur, geological formations whose temperature is much lower than the melting point of sulfur (119°C). As they are already liquid at room temperature, they can, in fact, also be stored in structures in which, if molten sulfur in the pure state were pumped, this would immediately solidify causing the obstruction of the pumps and pipe-lines.

Thanks to the solution, object of the present invention, a permanent sulfur storage is obtained without any risk of its leaving the surface and contaminating usable groundwater or negatively interfering with the extraction process of crude oil/gas. Large accumulations of sulfur do in fact exist in nature in deep geological structures which are indefinitely stable and do not have any negative impact on the surrounding environment.

An object of the present invention therefore relates to a process for the disposal of sulfur as derivatives, more specifically as sulfanes, which are in the liquid state at room temperature, and which comprises:

a) transforming elemental sulfur into sulfanes having the

general formula H_2S_{n+1} , wherein n is a number from 1 to 7;

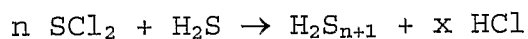
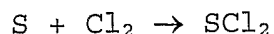
- b) optionally mixing elemental sulfur in powder form or in the molten phase, with the liquid sulfanes, up to such a concentration as to guarantee the pumpability of the mixture;
- c) injecting the sulfanes liquid at room temperature into geological formations which can also have a temperature lower than the melting point of sulfur ($119^{\circ}C$), to a temperature close to room temperature.

Preferably, the temperature of the geological formation is lower than $150^{\circ}C$ (boiling point of the lightest sulfane i.e. H_2S_2).

Sulfanes are products which are known in scientific literature and can be prepared according to at least two techniques. The first comprises the direct reaction between sulfur in the molten state and hydrogen sulfide wherein, depending on the molar ratios between the reagents, a mixture of sulfanes having different compositions, is obtained. Details on the synthesis of sulfanes according to this technique can be found in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A25, (1994), VCH.

A second preparation technique, described in Gmelin Handbuch der Anorganische Chemie Sulfur Vol. 4a/b (1983), Springer-Verlag Heidelberg, comprises at least two passages

according to the following reaction schemes:



wherein n represents a number ranging from 1 to 7 and x depends on the stoichiometry of the reaction.

As the hydrochloric acid produced can be difficult to dispose of, the HCl formed can, for example, be oxidized with air in the presence of a catalyst based on copper chloride and produce Cl_2 , according to what takes place, for example, in the Deacon process, which can be recycled to the preparation system of sulfanes.

Elemental sulfur in the molten state, or in the form of a finely ground powder to favour its solubility/dispersibility, can also be added to the sulfanes. For example, sulfur can be added in powder form with a particle size ranging from 1 to 100 μm up to a concentration corresponding to the solubility limits, in order to avoid excessively increasing the viscosity of the mixture.

The present invention implies pumping sulfanes in liquid form through surface pipes, well pipes and receiving geological structures. The elemental sulfur used in the synthesis of sulfanes can come directly from the Claus process or from a surface storage site.

The pressure necessary for pumping the liquid obtained from the transformation of elemental sulfur into sulfane

can be calculated with the general formula:

$$\Delta P = 2f \cdot \rho \cdot u_m^2 L / D_{eq}$$

wherein L is the length of piping used for injection into the geological structure, D_{eq} its equivalent diameter, u_m the average rate of the fluid pumped, ρ the density of the fluid pumped and f the friction factor which is a function of the roughness of the pipe and Reynolds number:

$$Re = D_{eq} \cdot u_m \cdot \rho / \mu$$

wherein μ is the kinematic viscosity of the fluid. The pumping device can be represented by a conventional pump.

In particular, the viscosity and density of the sulfanes liquid at room temperature, in relation to the number of sulfur atoms, are indicated in Table 1 enclosed.

Table 1

Density and viscosity of sulfanes (20°C) in relation to the sulfur atoms in the H_2S_n molecule

Nr. sulfur atoms in the molecule	ρ (g/cm ³)	μ (cPoise)
2	1.23	0.616
3	1.49	1.32
4	1.58	2.63
4.7	1.626	4.19
5	1.633	4.65
6	1.685	11.1
6.2	1.695	14.2
6.4	1.701	14.9
7.6	1.731	24.5

Geological structures which are appropriate for re-

ceiving the sulfur transformed into sulfane are preferably those forming the reservoir itself from which the crude oil or natural gas containing sulfur in the form of organic compound or hydrogen sulfide, are extracted. Alternatively, geological structures can be used, in a remote position with respect to the reservoir and having structural characteristics suitable for receiving and preserving the sulfanes. A particularly important aspect of the present invention is that geological structures whose temperature is much lower than the melting point of sulfur (119°C) can also be used for the storage of sulfur, in the form of sulfanes, reaching those reservoirs whose temperature is close to room value (25°C). In this way, it is therefore possible to use geological structures which are unsuitable for the accumulation of sulfur in the molten state in which the latter, due to the local temperature which is lower than its melting point, would solidify, thus blocking the pumps and pipes.

For the application of the present invention, either matrix geological structures or fractured structures, naturally or induced, can generally be used. In all cases, the pressure and maximum injection flow-rate of the fluid forming sulfanes in the liquid state, can be determined by calculations and measurements well known to experts in stimulation treatment of production wells or the production and

running of water re-injection wells.

Some illustrative and non-limiting examples are provided for a better understanding of the present invention and for its embodiment.

5 EXAMPLE 1 - Direct synthesis of sulfanes from H_2S and sulfur.

10 10 g (0.312 moles) of sulfur powder were placed in a 500 ml Hastelloy C autoclave, equipped with a mechanical stirrer, and 34 g (1 mole) of gaseous H_2S were charged. The closed autoclave was heated to $200^{\circ}C$ for 24 h, maintaining the internal contents under stirring.

The autoclave was then cooled to room temperature and degassed. The autoclave was subsequently flushed by the passage of a stream of nitrogen for 30 minutes, in order to
15 remove the non-reacted hydrogen sulfide.

The solid contained in the autoclave is melted at $120^{\circ}C$ and is distilled at reduced pressure (15 mmHg) collecting 0.15 g of an olive-yellow coloured oily liquid consisting of a mixture of sulfanes, which upon elemental
20 analysis proved to have an empirical formula of $H_2S_{3.4}$. Said mixture of sulfanes is characterized at room temperature by a density of 1.53 g/cm^3 and a viscosity of 1.84 CPoise. As the viscosity of a common crude oil (Brent) is about 30 CPoise, the pumping of the above mixture of sulfanes proved
25 to be a simple operation for conventional equipment for the

extraction of crude oil.

Sulfur in the molten state has a viscosity of about 12 CPoise, which is almost 7 times higher than the mixture of sulfanes. From an energy point of view, it is consequently
5 more convenient to pump sulfur in the form of sulfane rather than in the molten state.

EXAMPLE 2 - Synthesis in two passages of sulfanes from H_2S and sulfur using chlorine.

First passage: synthesis of sulfur chloride.

10 20 g of sulfur powder were placed in a 500 ml flask, equipped with a mechanical stirring anchor and reflux bubble cooler. Gaseous chlorine was then passed through the sulfur, perfectly anhydrified, until all the sulfur mass had melted producing a dark red-coloured liquid. 0.5 g of
15 $FeCl_3$ were subsequently added and anhydrified chlorine was continually passed for a further thirty minutes. The dark red liquid was then distilled, collecting the fraction which distills at between 55 and 62°C. 14.2 g of pure SCl_2 were obtained.

20 Second passage: synthesis of sulfanes.

32.37 g of H_2S (0.952 moles), to which 14 g of SCl_2 (0.136 moles) were slowly added, were charged into a 1 litre autoclave, previously anhydrified and cooled to -10°C, and the mixture was maintained under stirring for 30 min-
25 utes. The autoclave was subsequently degassed and flushed

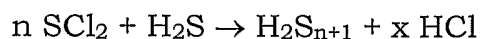
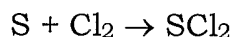
with nitrogen. The gas at the outlet consisted of a mixture of non-reacted H_2S and HCl formed during the reaction. A deep yellow-coloured liquid, having a weight of 13.6 g, was formed in the autoclave.

5 Upon elemental analysis, this liquid proved to consist of hydrogen and sulfur with an empirical formula of $\text{H}_2\text{S}_{4.5}$. In this compound, the chlorine is only present in traces demonstrating that the reaction has been completed. The mixture of sulfanes previously obtained is characterized at
10 room temperature by a density of 1.60 g/cm^3 and a viscosity of 3.64 CPoise. As the viscosity of a common crude oil (Brent) is about 30 CPoise, the pumping of the above mixture of sulfanes proved to be a simple operation for conventional equipment for the extraction of crude oil.

15 Under these conditions, the sulfur is solid and it cannot therefore be pumped, but also in the molten state its viscosity, equal to about 12 CPoise, is higher than the previous mixture of sulfanes and it was consequently more convenient, from an energy point of view, to pump the sul-
20 fur in the form of sulfane rather than in the molten state.

CLAIMS

1. A process for the disposal of sulfur, as derivatives which are in the liquid state at room temperature, which comprises:
- 5 a) transforming elemental sulfur into sulfanes having the general formula H_2S_{n+1} , wherein n is a number from 1 to 7;
- b) optionally mixing elemental sulfur in powder or molten form with the liquid sulfanes, up to such a concentra-
- 10 tion as to guarantee the pumpability of the mixture;
- c) injecting the liquid sulfanes at room temperature into geological formations.
2. The process according to claim 1, wherein the sulfanes are produced by the direct reaction of sulfur in the molten
- 15 state and hydrogen sulfide.
3. The process according to claim 2, wherein the elemental sulfur used in the synthesis of sulfanes comes directly from the Claus process.
4. The process according to claim 1, wherein the sulfur
- 20 comes from a surface storage site.
5. The process according to claim 1, wherein the sulfanes are produced according to the following reaction schemes:



- 25 wherein n represents a number ranging from 1 to 7 and x de-

depends on the stoichiometry of the reaction.

6. The process according to claim 4, wherein the hydrochloric acid produced is oxidized with air in the presence of a catalyst to produce Cl_2 which is recycled to the preparation system of sulfanes.

7. The process according to any of the previous claims, wherein the difference in pressure necessary for pumping the liquid obtained from the liquefaction of sulfur is provided by the formula:

$$\Delta P = 2f \cdot \rho \cdot u_m^2 L / D_{eq}$$

wherein L is the length of piping used for injection into the geological structure, D_{eq} its equivalent diameter, u_m the average rate of the fluid pumped, ρ the density of the fluid pumped and f the friction factor which is a function of the roughness of the pipe and Reynolds number:

$$Re = D_{eq} \cdot u_m \cdot \rho / \mu$$

wherein μ is the kinematic viscosity of the fluid.

8. The process according to any of the previous claims, wherein the disposed sulfur comes from the purification treatment of hydrocarbons of a fossil nature (crude oil) or natural gas.

9. The process according to any of the previous claims, wherein the geological structures suitable for receiving the molten sulfur are those forming the reservoir from which the crude oil or natural gas containing sulfur are

removed.

10. The process according to any of the previous claims,
wherein elemental sulfur, in the molten state or as a
finely ground powder with a particle size ranging from 1 to
5 100 μm , is added to the sulfanes, up to a concentration
corresponding to the solubility limit.

10

15

20

25

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/007565

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B09B1/00 B65G5/00

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)

IPC 7 B09B B65G E21B

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 582 025 B2 (R. PICKREN) 24 June 2003 (2003-06-24) column 1, line 14 - line 29 column 2, line 59 - column 4, line 40 column 5, line 63 - column 6, line 30 column 11, line 30 - line 47 column 12, line 35 - line 65 figures 1,3	1,3,8,10
A	----- "GMELIN HANDBOOK OF INORGANIC CHEMISTRY Supp. Vol. 4A/B, ed. 8." 1983, SPRINGER VERLAG, BERLIN, DE, XP002268680 cited in the application page 391, line 28 - page 394, line 9 ----- -/--	2,5



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *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

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* 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
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

9 November 2004

Date of mailing of the international search report

18/11/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Plontz, N

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/007565

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 428 700 A (W. LENNEMANN) 31 January 1984 (1984-01-31) claim 1	1
A	----- US 3 690 377 A (B. KNIGHT) 12 September 1972 (1972-09-12) abstract -----	

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/007565

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6582025	B2	06-02-2003	US 2003025381 A1	06-02-2003
			CA 2381103 A1	03-02-2003
			EA 4110 B1	25-12-2003
			US 2003132659 A1	17-07-2003
US 4428700	A	31-01-1984	NONE	
US 3690377	A	12-09-1972	NONE	