MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)
FORM 1
REGULATION 9

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952-1973
APPLICATION FOR A PATENT

We BRENNSTOFFINSTITUT FREIBERG
of Freiberg 9200 - DDR Halsbrucker Strasse 34, Germany

hereby apply for the grant of a Patent for an invention entitled:

"PROCESS FOR THE REMOVAL OF HYDROGEN SULPHIDE FROM TECHNICAL GASES"

which is described in the accompanying complete specification. This Application is a Convention Application and is based on the Application numbered: 313 158 3 for a Patent or similar protection made in Germany on 24th February, 1988.

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DATED this 6th day of February, 1989.

BRENNSTOFFINSTITUT FREIBERG
By their Patent Attorneys

GRIFFITH HACK & CO.

TO: THE COMMISSIONER OF PATENTS
COMMONWEALTH OF AUSTRALIA

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Process for the removal of hydrogen sulphide from technical and natural gases is characterised by the fact that the gas containing hydrogen sulphide together with a stoichiometric amount of sulphur dioxide and the solvent N-Methyl-\-Caprolactam (NMC) are fed into an absorption instrument where coarse, crystalline sulphur, which can be separated easily from the NMC through gravitational separation, is created in the solvent as a result of the reaction of the H\textsubscript{2}S with the SO\textsubscript{2}.

Process as per Claim 1 characterised by the separation of sulphur from the solvent N-Methyl-\-Caprolactam being carried out in the temperature range of 120 - 130 °C and thus leading to the production of liquid sulphur.
The following statement is a full description of this invention, including the best method of performing it known to us:-

"PROCESS FOR THE REMOVAL OF HYDROGEN SULPHIDE FROM TECHNICAL GASES"
Process for the removal of hydrogen sulphide from technical gases

Areas of application of the invention

The invention concerns a process for the removal of hydrogen sulphide from technical gases such as natural gas, coal gasification gas, synthetic gas or waste gases from conventional desulphuration processes.

Characteristics of the known technical solutions

Hydrogen sulphide has to be removed from technical gases because of its toxic effect on the environment, its corrosive effect on and toxicity to many technical catalysts. A large number of processes or combinations of processes for this task are known in the technology.

In the majority of the cases of application, the hydrogen sulphide is removed absorptively from the gases through solvents acting either physically or chemically and with the re-use of the heat energy released from the solvents (F.C. Riesenfeld; A.L. Kohl; Gas Purification; Gulf Publ. Co. Houston-Texas; 2nd Edition, 1974). In the course of this process, waste gases containing H₂S are created
which, depending on the quality of the crude gas and the type of the desulphuration process used, contain still more gaseous elements which render the further transformation of \( \text{H}_2\text{S} \) in conventional Claus plants difficult, both technologically and energywise or even prevent it if the hydrogen sulphide content is too low or if the proportion of higher hydrocarbons in the waste gases is too high.

Further processes are known for the removal of hydrogen sulphide where the hydrogen sulphide is oxidised to elementary sulphur through aqueous solutions containing oxidising compounds and whereby these oxidising compounds are reduced. Examples of this type of processes are, for instance, the Sulfint process (H. Mackinger; Sulfint Process, Hydrocarb. Proc. (1982) 3, p. 98 - 101), the LO-CAT Process (L.C. Hardison; Go from \( \text{H}_2\text{S} \) to \( \text{S} \) in one unit, Hydrocarbon Proc. (1985) 4, p. 70 - 71) and the Stretford Process (Nicklin, T.; The Application of the Stretford Process to the Purification of Natural Gas; IGU/A 13 - 73; 12th World Gas Conference, Nice (1973)).

The processes mentioned above have the disadvantages that the so-called Redox compounds have to be re-oxidised by means of an equipment intensive regeneration using air, that the sulphur develops in a very fine form due to the aqueous solutions and requires large volume gravitational containers or filtration plants, that the complex chemical absorption solutions require a very precise examination of the chemical composition and effectiveness and that toxic waste brines are created which require a costly separation of liquid wastes.
Processes are also known for the removal of hydrogen sulphide by means of a reaction with sulphur dioxide in organic solvents that contain a catalyst (H. Fischer; Reduktion des Auswurfs von Schwefelverbindungen aus Schwefelrückgewinnungsanlagen (Reduction of the Recrement from Sulphur Compounds from SulphurExtraction Plants); Erdöl und Kohle 27 (1974) 6, p. 292 - 296); (Lynn, S.U. et al; The Removal of H2S from Coal-Derived Gases; Proceedings of the 9th Annual Contractors Meeting on Containment Control in Coal-Derived Gas Streams, Morgantown, 9.5.1985); (DE-OS 2156072); (DE-AS 191445); 9DE-SS 2313148) or sulphuric acid in methanol (Polish patent specification no. 98843) or also made from a mixture of water with methanol (Polish patent specification no. 98432).

The necessity of using a catalyst requires an intensive examination of the chemical composition and effectiveness while the use of volatile methanol as a liquid reactive medium requires a higher level of effort for the absorptive extraction of methanol vapours.

Furthermore, processes with organic solvents such as sulfoxide (DE-85 2188285), phosphine oxide (DE-08 2188284), derivatives of urea (DE-08 2188282), polyglycols (DE-85 2165646) or the triamine of orthophosphoric acid (DE-OS 2105643) were recommended but which have not established themselves on an industrial scale because the solvents are either cost intensive or not sufficiently available for industrial production or are difficult to use technically.
Object of the invention

The object of the invention is a process for the removal of hydrogen sulphide from technical gases where crystalline sulphur capable of good precipitation is produced by means of a single phase process control and without the use of an additional catalyst and the gas is desulphurated in the range of a few ppm to zero.

Description of the nature of the invention

The invention is based on the task of removing hydrogen sulphide from technical gases in a single phase process and to simultaneously produce elementary sulphur.

According to the invention the task is performed as follows:

The crude gas to be desulphurated is brought into contact with the solvent N-Methyl-Caprolactam in conventional substance transfer equipment for fast reactions such as the Venturi column absorber or the stream or bubble column absorber. Before its entry into the abovementioned substance transfer equipment, SO₂ is mixed with the crude gas in a stoichiometric amount in accordance with the reaction equation:

\[ \text{SO}_2 + 2 \text{H}_2\text{S} \rightarrow 3 \text{S} + \text{H}_2\text{O} \quad (1) \]

However, it is also possible to add the required SO₂ amount to the NMC in an additional absorption device so that the NMC with the premixed SO₂ is introduced into the H₂S absorption equipment. NMC is an excellent solvent for...
SO₂ and H₂S gases. It was found at the same time that NMC catalyses reaction (1).

As a result of the catalytic effect of NMC, which is based on the ring structure of the compound and the lactam group contained in it, no induction period occurs as in the case of other organic and inorganic solvents so that no additional catalyst is required. Consequent to this extremely short contact sides are required for the substance transfer in the case of stoichiometric dosages and breaches by H₂S and/or SO₂ do not occur.

The reaction system is suited to guarantee residual contents of H₂S and SO₂ of a few ppm. Coarse grained crystalline sulphur is created during the reaction which allows itself to be completely separated from the solvent through sedimentation alone for direct contact times under technical conditions of less than or equal to 2 minutes.

Due to the good settling capacity of sulphur, high turbulence in the absorption system using Venturi or stream washers is essential so that a premature precipitation is avoided, which otherwise leads to blockages in the absorber due to the sulphur deposited.

The separation of the sulphur from NMC is carried out preferably at a temperature level of 130 °C because the liquid sulphur has a low viscosity at this temperature, a density differential between the NMC and sulphur that is sufficient for gravitational separation occurs and reaction water formed as per equation (1) can be removed from the system through a simple pressure regulation. A water content of NMC over 15 wt-% is to be avoided because
otherwise the sulphur formed is present in colloidal form in the NMC which can only be separated with great difficulty from the NMC.

Example of Execution

The invention will be explained in detail in the following example:

During the deacidification and conditioning of a substantially inert crude oil escort gas by means of a physical absorption process, a waste gas is developed with the following parameters:

Quantity of gas: \(10\,000\ \text{m}^3\text{i.N./h}\)

Gas pressure: \(0.2\ \text{MPa(a)}\)

Temperature: \(30\ \text{oC}\)

Composition (mol. proportions)

\[
\begin{align*}
\text{H}_2\text{S} & : 0.05 \\
\text{N}_2 & : 0.03 \\
\text{C}_2\text{O}_2 & : 0.68 \\
\text{CH}_4 & : 0.15 \\
\text{C}_2\text{H}_6 & : 0.03 \\
\text{C}_3\text{H}_8 & : 0.03 \\
\text{C}_4\text{H}_{10} & : 0.02 \\
\text{C}_5 & : 0.01
\end{align*}
\]
Due to the low H₂S content and the concentration of higher hydrocarbons, this gas cannot be processed in conventional Claus plants. Incineration is also ruled out due to inadmissible SO₂ emissions.

The technological connections of the process for the removal of the H₂S from the abovementioned waste gas are shown in Figure 1.

The crude gas enters the Venturi washer 1 through the crude gas pipe. Via pipe 2 SO₂ from a SO₂ tank (3) is fed into the crude gas at the rate of 715.3 kg/h through a quantity control. 15 m³/h NMC is fed into the Venturi washer as an absorption and reaction medium through pipe 4. In the liquid phase, a suspension of coarse crystalline sulphur in NMC is present at the outlet of the Venturi washer. The suspension is separated from the gas phase by means of the cyclone separator (5). At the end the desulphurated gas is used as a heating gas in other processes.

The NMC with the sulphur content is suctioned out of the sump of the cyclone separator by means of a pump (6) and by using a storage control. The liquid bypass (7) in the cyclone separator prevents a premature precipitation of the sulphur in the sump of the separator.

The NMC is fed into the combination gravity separator/sulphur melter (9) through a heat exchanger (8). Here a temperature of 130 °C is set through serpentine steam heating. In the sump of the container (9) liquid sulphur is collected at the rate of 1073 kg/h. From the central area the NMC is slid into the heat exchanger (8); it gives off a large proportion of its sensible heat to the NMC sulphur suspension and gets into the Venturi washer.
again through the cooler (10). The reaction water is removed from the system in the form of water vapour via the pressure regulator and after condensation is present as waste water in a cooler (11).

The liquid sulphur developed can be sold as a product in the form of liquid sulphur or flake sulphur.
List of reference symbols used

1. Venturi washer
2. Pipe
3. SO₂ tank
4. Pipe
5. Cyclone separator
6. Pump
7. Liquid bypass
8. Heat exchanger
9. Gravitational separator / Sulphur melter
10. Cooler
11. Cooler
CLAIMS
The claims defining the invention are as follows:

1. Process for the removal of hydrogen sulphide from technical and natural gases is characterised by the fact that the gas containing hydrogen sulphide together with a stoichiometric amount of sulphur dioxide and the solvent N-Methyl-Caprolactam (NMC) are fed into an absorption instrument where coarse, crystalline sulphur, which can be separated easily from the NMC through gravitational separation, is created in the solvent as a result of the reaction of the $\text{H}_2\text{S}$ with the $\text{SO}_2$.

2. Process as per Claim 1 characterised by the separation of sulphur from the solvent N-Methyl-Caprolactam being carried out in the temperature range of 120 - 130 °C and thus leading to the production of liquid sulphur.

3. Process as per Claims 1 and 2 characterised by the reaction water created as a result of the sulphur separation from the solvent N-Methyl-Caprolactam in the temperature range of 130 °C through depressurisation being removed from the system in the form of water vapour.

4. Process as per Claim 1 characterised by the NMC being enriched, before entry into the absorption equipment, with the required quantity of $\text{SO}_2$ in an additional absorber.

5. Process for the removal of hydrogen sulphide from technical and natural gases substantially as disclosed herein in conjunction with figure 1.

DATED this 6th day of FEBRUARY, 1989
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