641559

AUSTRALIA
Patents Act 1990

PATENT REQUEST: STANDARD PATENT AND NOTICE OF ENTITLEMENT

I/We, being the person(s) identified below as the Applicant, request the grant of a patent to the person(s) identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

Applicant and Nominated Person:

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Invention Title:

METHOD OF ELIMINATING THE ARSENIC FROM A GAS BY PASSING IT OVER A COPPER SULPHIDE AND CARRIER BASED COMPOUND.

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BASIC CONVENTION APPLICATION(S) DETAILS

Application Number	Country	Country Code	Date of Application
90/13598	FR		30th October 1990

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I,

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being the applicant in respect of this Application state the following:-

The person(s) nominated for the grant of the patent:

The nominated person is the assignee of the actual inventors.

The person(s) nominated for the grant of the patent:

The applicant and nominated person is the basic applicant.

The basic application(s) listed above is/are the first application(s) made in a Convention country in respect of the invention.

INSTITUT FRANCAIS DU PETROLE

29th October 1991

GRIFFITH HACK & CO.

Patent Attorneys for and
on behalf of the applicant.

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METHOD OF ELIMINATING THE ARSENIC FROM A GAS BY PASSING IT OVER A COPPER SULPHIDE AND CARRIER BASED COMPOUND

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(56) Prior Art Documents
US 4094777
US 4962662
AU 86837/91

(57) Claim

1. A method of eliminating arsenic from a gaseous charge characterised in that the charge is contacted with a solid recovery mass constituted by a carrier and at least one copper sulphide compound in which the copper sulphide content on the carrier is comprised between 2% and 65% by weight (expressed as copper), at a working temperature between -50 and +200°C with a V.V.H. (volume of charge by volume of recovery mass per hour) of between 500 and 50,000 h^{-1} for the gaseous charges.

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ORIGINAL

COMPLETE SPECIFICATION

STANDARD PATENT

Invention Title:

METHOD OF ELIMINATING THE ARSENIC FROM A GAS BY PASSING IT OVER A COPPER SULPHIDE AND CARRIER BASED COMPOUND.

The following statement is a full description of this invention, including the best method of performing it known to me:-

The present invention relates to a method of eliminating arsenic, in the presence or in the absence of mercury, from a gaseous charge. The method is characterised by the use of a recovery compound comprising a carrier and a copper sulphide compound.

It is known that natural gas and the associated condensates may contain numerous metallic compounds such as arsenic and mercury as traces, generally present in elementary form (Hg for example), in hydride form (AsH_3 for example) or for instance also in organometallic form (AsR_3 and HgR'_2 in which at least one of the three R radicals is a hydrocarbonated function and at least one of the two R' radicals is a hydrocarbonated function, R and/or R' possibly being a hydrogen atom). The elimination of both types of metallic compounds is important to ensuring the satisfactory functioning (1) of catalysts downstream of the recovery unit which are contaminated by these compounds and (2) of heat exchangers which are sensitive to the presence of mercury.

It has been discovered that a recovery compound, the copper sulphide carried, which is well known to eliminate mercury in gaseous and liquid phases is

also very effective in eliminating arsenic in the gaseous phase.

It is known that the oxides of iron, cobalt, nickel, lead, copper and molybdenum and the sulphides or iron, cobalt and nickel are more or less effective in the de-arsenification of hydrocarbonated fluids (see for example patents US-A-4 003 829, US-A-4 601 998 and US-A-4 849 577 of the Applicants).

Copper salts such as sulphate, chloride, bromide, fluoride, iodide, nitrate, acetate and formate are likewise known from the patent US-A-2 781 297 for their aptitude to recover arsenic from liquids such as liquid petroleum fractions. The working conditions under pressure are 0.35 to 70 bars ($0.35.10^5$ to 70.10^5 Pa) and in terms of temperature: 20°C to 260°C, the recovery compound containing 0.1 to 20% and preferably 1 to 10% by weight of copper.

Patent application WO 90/10684 likewise describes a method of eliminating arsenic and mercury from liquid petroleum fractions. The method comprises a first stage consisting of bringing the fraction to be

treated in contact with a first compound for the recovery of arsenic having catalytic properties and then in causing the said fraction to circulate over a second recovery compound which is based on copper sulphide.

The first compound retains a major part of the arsenic and activates the remaining arsenic compounds, the second compound retains the activated arsenic and the mercury.

The present invention relates to a method of eliminating arsenic from a gaseous charge constituted particularly by a natural gas and/or a natural gas condensate in the gaseous phase, a method in which the charge is contacted with a solid recovery mass or ~~circulates over~~ compound constituted by a carrier and at least one copper sulphide compound.

Of course, all the synthetic methods known to a man skilled in the art for the preparation of a compound containing at least copper sulphide and a mineral carrier can be used for the present invention. By way of example, mention may be made of the recovery compounds prepared in US-A-4 094 777 and the patent US-A-4 902 662 of the Applicants.

The patent US-A-4 094 777 describes a method of preparing a recovery compound comprising the incorporation of a copper compound into a mineral carrier followed by sulphuration at a temperature below 300°C.

Sulphuration by the method described in this patent is carried out by means of a gaseous agent, for example hydrogen sulphide, or a solution of a mineral sulphide in the water or in an organic solvent, for example an aqueous solution of sodium sulphide, potassium sulphide or ammonium sulphide.

The patent US-A-4 902 662 describes a method of preparing a recovery mass comprising the incorporation of a copper compound into a mineral carrier followed by sulphuration at a temperature which is normally below 250°C.

Sulphuration by the method described in this patent is carried out by means of an organic polysulphide of the general formula $R_1-S_{(n)}-R_2$ in which n represents a whole number from 2 to 20, R_1 represents a hydrogen atom or an organic radical containing 1 to 150 carbon atoms, chosen from the group consisting of the saturated or unsaturated linear or ramified alkyl radicals, or those of the

naphthene type, the aryl radicals, the alkyl aryl and the aryl alkyl radicals, and R_2 represents an organic radical identical to or different from R_1 containing 1 to 150 carbon atoms chosen from the group of organic radicals defined for R_1.

According to another preferred embodiment, the method of preparing the solid recovery mass comprises the following stages:

a) incorporation of at least one copper compound other than a sulphide, into a solid mineral carrier or dispersant,

b) calcination on the hypothesis that the said compound is not copper oxide, of the product obtained in stage (a) in order to convert at least partly the copper compound or compounds which it contains into copper oxide (CuO and/or Cu_2O),

c) bringing the product obtained which contains copper oxide into contact with the elementary sulphur which is possibly at least partially dissolved in the organic solvent,

d) a heat treatment of the product obtained in stage (c) in a non-oxidising atmosphere, accompanied by gas scavenging, at a temperature and taking sufficient time to allow formation of sulphide of the metal or metals present and particularly in order to combine at least 50% of the copper in the form of copper

sulphide Cu_xS_y in which x and y are each a whole number from 1 to 10.

The solid mineral dispersants or carriers which may be used for the mass comprising copper sulphide are normally chosen from the group comprising carbon, activated carbon, coke, silica, silicon carbide, silica gel, the synthetic or natural silicates, the clays, the diatomaceous earths, the fuller's earths, kaolin, bauxite, the refractory inorganic oxides such as for example alumina, titanium oxide, zirconia, magnesia, the alumina silicas, the magnesia silicas and zirconia silicas, the boron oxide-alumina mixtures, aluminates, silico-aluminates, crystalline, synthetic or natural zeolitic alumino-silicates, for example the mordenites, faujasites, offretites, erionites, ferrierites, zeolites ZSM5 and ZSM11, mazzites, and cements, such as for example those of the Secar^R type, produced by the Society LAFARGE.

Preferably, a carrier is used which is chosen from the group comprising carbon, activated carbon, coke and even more advantageously silica, the aluminas, silica-aluminas, silicates, aluminates and the silico-aluminates (zeolitic for example). Alumina is the preferred carrier.

When the arsenic recovery masses are intended for use in the processing of charges containing condensible hydrocarbons (for example C_4 or higher than C_4) at a temperature situated in a temperature range in which recovery takes place, it has been found that masses having a mean pore diameter at least equal to 100 Angstroms (10^{-8}m) have enhanced stability.

The conditions under which masses or compounds (or carriers intended to produce these masses) are obtained which have a mean pore diameter of at least 100 Angstroms (10^{-8}m) are sufficiently well known to a man skilled in the art that they do not need to be repeated here with in the scope of the present invention (see for example US-A-4 094 777).

The preferred carriers generally have a specific surface area of approx. 20 to 300 $m^2 \times g^{-1}$, these values not being limitative.

The incorporation of a copper compound other than a sulphide into a solid mineral dispersant or carrier may be carried out by any method known to a man skilled in the art, for example by mixture with a copper compound or by impregnation by means of a solution of a copper compound. The copper compounds which are normally used are compounds which are

easily transformable to copper oxide at relatively low temperatures.

As an example of a copper compound, it is possible without limitation to cite: copper oxides, copper hydroxide $Cu(OH)_2$, the basic copper salts, particularly the carbonates to the formulae $CuCO_3$, $Cu(OH)_2$ and $2CuCO_3$, $Cu(OH)_2$, the organic salts and complexes of copper such as the salts or carboxylic acids, for example the formiates, acetates, tartrates, citrates, benzoate, oxalates, malonates, succinates, glycolates, lactates and acetylacetonate and copper nitrate.

Normally, it is preferred to introduce the copper compound by impregnation of the carrier with an aqueous or organic solution of a copper compound and preferably by means of an aqueous solution of a copper compound. Advantageously, an aqueous solution of copper nitrate is used.

Possibly, a small proportion of a soluble silver compound may be introduced into the carrier. The quantity of silver introduced into the carrier expressed by weight of silver in relation to the carrier normally represents 0 to 5% by weight. Other metals may likewise be present, for example iron.

The quantity of copper sulphide on the carrier is comprised between 2 and 65% (expressed by weight of copper) and is preferably 5 to 80% and more preferably 6 to 40%.

The recovery masses thus obtained are used according to the present invention in order to purify gaseous charges containing arsenic. The arsenic is for the most part found in the form of arsine AsH_3 and organometallic arsenic compounds may be present.

The range of temperature in which the recovery compounds are effective is normally comprised between approx. -50°C and +200°C. The recovery of arsenic and mercury if it is present may be carried out at atmospheric pressure or at a lower or more elevated pressure, the total pressure being as much as 10 MPa for example. Under these conditions, the charge to be treated is gaseous. The V.V.H. (volume of charge per volume of recovery mass and per hour) for gaseous charges is normally approx. 500 to 50,000 h^{-1}, but preferably the working V.V.H. is approx. 2000 to 20,000 h^{-1} and advantageously approx. 4000 to 15,000 h^{-1}.

The gaseous fluids treated by means of recovery masses according to the invention may for example

contain between 1 nanogram and 0.3 grams arsenic and 10 nanograms to 2 grams or more of mercury per cubic metre. The gases treated are more often hydrocarbons or mixtures of hydrocarbons such as for example natural gases containing a major proportion of methane and a lesser proportion of C_2 and/or higher hydrocarbons and arsenic and mercury.

Thus it is possible to treat a natural gas and/or a natural gas condensate in the gaseous phase.

The natural gases for the most part contain methane but also they may contain ethane and propane. The C_4 fractions (butenes) and C_5 + fractions (pentiene, hexane...) associated with the natural gas are generally referred to as "natural gas condensates". The compounds which are higher than butanes are liquid at normal temperature and pressure.

The working conditions are precisely chosen to be within the indicated ranges of pressure and temperature values in order to obtain a gaseous fraction and possibly a liquid fraction but only the gaseous fraction will be treated according to the invention.

The gases treated often contain other gaseous substances such as CO_2, water, H_2S, in variable quantities.

The treated gas may also be hydrogen or other gases containing an arsine charge (electronics manufacture for example); it may also be air on condition that the working temperature and/or pressure conditions are such that contact with the gas does not cause oxidation of the absorption mass or of an excessive portion of the said mass. It is likewise possible to envisage the processing of mixtures containing a plurality of the compounds or gases mentioned hereinabove.

Any apparatuses known to a man skilled in the art and currently used for the purification of gaseous fluids may be employed. The recovery masses are used in the form of a fixed bed through which the charge passes.

The apparatus for arsenic elimination may for instance consist of a single reactor or at least two reactors in parallel but preferably at least two reactors will be used in series.

If one considers the case of three reactors A, B, C, in series, the procedure is preferably as follows:

when the first reactor A ha reached a recovery efficiency which will no longer be more than for example 90% or 70% of its initial efficiency, that will be the time to commence regeneration or replacement of the recovery mass contained in A. During the time needed for this regeneration or replacement stage, the fluid will pass into the reactors B and C; after the regeneration or replacement of A, the fluid will pass into B and C and then into A; B will then be regenerated or replaced when its efficiency is no longer more than for example 90% or 70% of its initial efficiency; throughout this time, the fluid will pass over to C and A. After the regeneration or replacement of B the fluid will pass into C, A and then B. Then C will be regenerated or replaced, and so on.

The following example illustrates the invention without limiting its scope.

EXAMPLE

1 kg of balls of autoclaved alumina of 170 $m^2 x g^{-1}$ of specific surface area and with a pore volume of 1.2 $cm^3 \times g^{-1}$ is impregnated with 1.2 l of an aqueous solution containing 370 g trihydrated copper nitrate $Cu(NO_3)_2, 3H_2O$.

The alumina balls thus impregnated are dried and calcined for 7 hours at 400°C in a current of air at a V.V.H. of 5000 h^{-1}. So-called base balls are obtained for the next stage in the experiment. The balls thus obtained are impregnated in a coating apparatus, by means of 1 l containing 0.52 l water and 0.48 l of a 20% by weight aqueous solution of ammonium sulphide. The excess sulphur is eliminated by drying in an oven at 200°C for 10 hours in a nitrogen current (V.V.H. 5000 h^{-1}).

The mass A obtained contains copper sulphide in a quantity of 15% in relation to the weight of the mass. X-ray defraction analysis indicates that all the copper is in the form of copper sulphide. Chemical analysis shows that the atomic ratio of Cu:S is equal to 1.0.

The arsenic recovery mass obtained has been tested under the following conditions. The apparatus consists of a tubular metal reactor of which the arsenic fixing inactivity has been monitored. 100 ml of the recovery mass to be tested are introduced into this reactor and a current of natural gas containing arsenic is passed through at a temperature of 60°C and at a pressure of 35 bars (3.5 MPa). The bed of recovery mass was separated into five zones of 12 g.

The zone referred to as "zone 1" was the first to contact the charge containing the arsenic.

The percentage volumetric composition of the natural gas to be purified is 84% CH_4, 0.6% hydrocarbons containing 5 carbon atoms and more in their molecule, the balance consisting of a mixture of N_2, CO_2, C_2H_4, C_3H_8 and C_4H_{10}. The quantity of arsenic in the gas at the entrance to the reactor is 1607×10^{-4} g per hour.

The quantity of arsenic remaining in the gas after purification is evaluated by establishing a difference between the quantity of arsenic in the charge (known) and the total quantity of arsenic detected in the recovery mass after test by X-ray fluorescent measurement.

The efficiency of the recovery masses is defined by the equation

$$E\% = 100 - \frac{\text{(weight of arsenic at the entrance)} - \text{(weight of arsenic in the mass)} \times 100}{\text{(weight of arsenic at the entrance)}}$$

The results show that the mass obtained by the method according to the present invention have a very high degree of efficiency in the recovery of arsenic.

Zone 1	(ppm As)	9651	
Zone 2	(ppm As)	3666	
Zone 3	(ppm As)	35	(detection limit)
Zone 4	(ppm As)	<30	
Zone 5	(ppm As)	<30	
Total	(ppm As)	13.352	
Total	(g As)	0.1602	
Duration of test	(h)	1000	
Total As at intake	(g)	0.1607	
E %		> 99.7	

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of eliminating arsenic from a gaseous charge characterised in that the charge is contacted with a solid recovery mass constituted by a carrier and at least one copper sulphide compound in which the copper sulphide content on the carrier is comprised between 2% and 65% by weight (expressed as copper), at a working temperature between -50 and +200°C with a V.V.H. (volume of charge by volume of recovery mass per hour) of between 500 and 50,000 h^{-1} for the gaseous charges.

2. A method according to Claim 1, characterised in that the gaseous charge also contains mercury.

3. A method according to Claim 1 or Claim 2 in which working is carried out in a fixed bed.

4. A method according to any one of the preceding Claims, characterised in that the gaseous charge is a natural gas, a natural gas condensate in the gaseous phase or a mixture of both.

5. A method according to any one of the preceding Claims, characterised in that the said gaseous charge contains 10^{-9} to 0.3 g arsenic per cubic metre of gas to be treated.

DATED THIS 26TH DAY OF JULY 1993
INSTITUT FRANCAIS DU PETROLE
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