

AS: 87.295

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES
E. S. D.

Radicación : 02014503 00000004 Folios: 3
Fecha (ORD): 2004-02-18 15:54:19
Trámite : 002 PATENTES D / REGISTRO/ 534 PETICION
Dependencia: 2000 DIVISION DE NUEVAS CREACIONES

REF.: Expediente No. 02 014.503 solicitud de Patente a nombre de
INTEVEP, S.A.
Titulada: MÉTODO PARA RETIRAR H₂S Y CO₂ DE CORRIENTES DE
CRUDO Y GAS

RAMIRO CASTRO DUQUE, vecino de Bogotá, portador de la tarjeta profesional No. 1003 del Consejo Superior de la Judicatura, obrando como apoderado de la Sociedad INTEVEP, S.A., según lo acredita el documento de poder presentado en la Secretaría General, de acuerdo con el Artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina, me permito solicitar que se examine si la invención contenida en la solicitud en referencia es patentable.

De acuerdo con lo anterior, me permito anexar los recibos oficiales de caja Nos. 03-79,322 y 04-353 por valor de \$353.000.

Señor Superintendente,



RAMIRO CASTRO DUQUE
C.C. No. 170.322 de Bogotá
Código 340
T.P. No.1003 del C.S.J.
Cra 7 No. 16-56 Piso 9

Febrero 17, 2004
CHP/MEV/hsr.

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SUPERINDUSTRIA Y COMERCIO

Radicacion : 02014503 00000004 Folios: 3

Fecha (MM): 2004-02-18 16:54:19

Tramite : 002 PATENTES D REGISTRO/ 536 PETICION

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 3 - 79,322

FECHA : OCTUBRE 29 DE 2003

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO POPULAR	030-00110-6	16391115	29/10/2003	30,070,000.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	30005-01-01 SOLICITUDES	05 EXAMEN DE PATENTABILIDAD DE INVEN	335,000.00
		TOTAL :	\$ 335,000.00

SON: TRESCIENTOS TREINTA Y CINCO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL ASUNTO No.

NIT : 800176089-2

CERTIFICACION DE EXCEDENTE : 04 - 333
FECHA : ENERO 5 DE 2004

79
75
3
SUPERINTENDENCIA Y COMERCIO
Radicacion : 0203-583-00000004 Folios: 3
Fecha (AMD): 2004-01-10 15:54:39
Tramite : 002 PATENTES D 1 REGISTRO/ 538 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

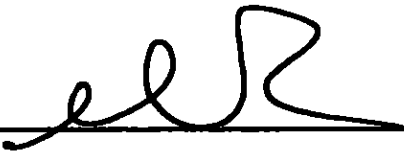
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO POPULAR	050-00110-6	12688054	05/01/2004	29,049,000.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-09	OTROS SERVICIOS DE PROPIEDAD I	
		99 OTROS SERVICIOS ADMINISTRATIVOS	18,000.00
		TOTAL I	18,000.

SON: DIEZ Y OCHO MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

ESTA CERTIFICACION DE EXCEDENTE DE PAGO SOLO PODRA SER UTILIZADA
COMO PARTE DE LA CANCELACION DE UNA TARIFA VIGENTE Y NO PODRA SER
SUSTITUIDA POR NINGUN RECIBO.

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 02-14503

EL EXTRACTO DE LA PRESENTE SOLICITUD DE PATENTE DE INVENCION FUE PUBLICADO

EN LA GACETA DE PROPIEDAD INDUSTRIAL No 536, DE FECHA 30 DE ENERO DE 2004, EL

TERMINO HABIL SEÑALADO POR LA LEY EXPIRA EL 28 DE ABRIL DE 2004.

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI

NO **X**

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**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D. C., 11 de Noviembre de 2005

Doctor

RAMIRO CASTRO DUQUE

Representante INTEVEP S. A.

ASUNTO

Radicación No.	02-14503
Trámite	002
Evento	001
Actuación	430
Oficio	10825
Folios	032

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica

1) Documentos estudiados:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 7 a 17 de la solicitud en estudio.
- b) Para el presente estudio se tendrán en cuenta los dibujos comprendidos en el folio 20 de la solicitud en estudio.
- c) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 4 reivindicaciones en el folio 74 de la solicitud en estudio.
- d) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 20 de febrero de 2002 y en el momento de la radicación si se reclama prioridad de la primera solicitud presentada en Estados Unidos US 791178.

2) Objeto de la Invención

- a) Las reivindicaciones 1 a 4 de la solicitud en estudio se refieren a un método para retirar por lo menos un contaminante seleccionado a partir del grupo que consiste de H₂S y CO₂ de corrientes de hidrocarburos, que comprende los pasos de: proporcionar una corriente de hidrocarburos que contiene dicho por lo menos un contaminante; y colocar nanopartículas que contienen metal en dicha corriente, dichas nanopartículas que contienen metal que se seleccionan a partir del grupo que consiste de óxidos de metal, hidróxidos de metal y sus combinaciones, por lo cual dichas nanopartículas adsorben dicho por lo menos un contaminante de dicha corriente.

- b) El anterior procedimiento busca minimizar la presencia de contaminantes en ciertas corrientes fluidas.
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 10 G 25/06

3) Claridad de la Solicitud

- a) El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina de Naciones establece

"La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"

La descripción no está correctamente redactada, toda vez que se emplean unidades que no corresponden al Sistema Internacional de Unidades. Además, los dibujos no están hechos según las normas del dibujo técnico. Estos dos puntos deben corregirse en un nuevo capítulo completo y una nueva tanda de figuras.

4) Determinación del Estado de la Técnica

El artículo 16 de la Decisión 486 de la Comisión establece:

"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 10 G 25/06 y las más cercanas a ellas, se encontró que antes del 23 de febrero de 2001 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con corras de retirar contaminantes del corrientes de hidrocarburos.

De acuerdo con lo establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

Nº	Documento	Título	Fecha de Publicación
D1	US 2618586	Process for desulfurizing petroleum products in the liquid phase.	1952.11.18
D2	EP 0 332 324	Desulphurization	1989.09.13
D3	EP 0 254 781	Method of removing sulfur from a hydrocarbon feed stream	1988.02.03

5) Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

“Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial”.

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

a) Evaluación del Nivel Inventivo

El art. 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

“Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica”.

Desde hace ya varias décadas, es muy conocido el empleo de ciertos compuestos que adsorben otros compuestos contaminantes tales como los que contienen azufre. El documento D1 (US 2618586) así lo revela. De la misma forma, dichas técnicas se convirtieron en algo normal en la industria, tal como lo muestran D2 (EP 0 332 324) y D3 (EP 0 254 781). Los tres documentos coinciden con la solicitud colombiana en la técnica a emplear y en los compuestos a emplear. La diferencia radica en el tamaño de la partícula, toda vez que las anterioridades no hablan explícitamente de nanopartículas. Sin embargo, un técnico medio sabe que la velocidad del proceso radica en el área superficial de la partícula. La ventaja en emplear partículas pequeñas radica en que para la misma cantidad de compuestos adsorbentes la velocidad del proceso es mayor en compuestos que tenga mayor área superficial, lográndose esto con partículas lo más pequeñas posibles. Si se compara el documento D2 con la presente solicitud se encontrará que las áreas superficiales coinciden completamente.

Por todo lo anterior, y a la luz de los documentos citados como anterioridades, la presente solicitud carecería de la altura inventiva necesaria para que se le conceda el privilegio solicitado.

b) Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D2	US 2618586	1 - 4	Nivel inventivo
D2	EP 0 332 324	1 - 4	Nivel inventivo
D2	EP 0 254 781	1 - 4	Nivel inventivo

6) Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única N° 10 de 2001


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en la lista, de fecha

17 JUL 2003

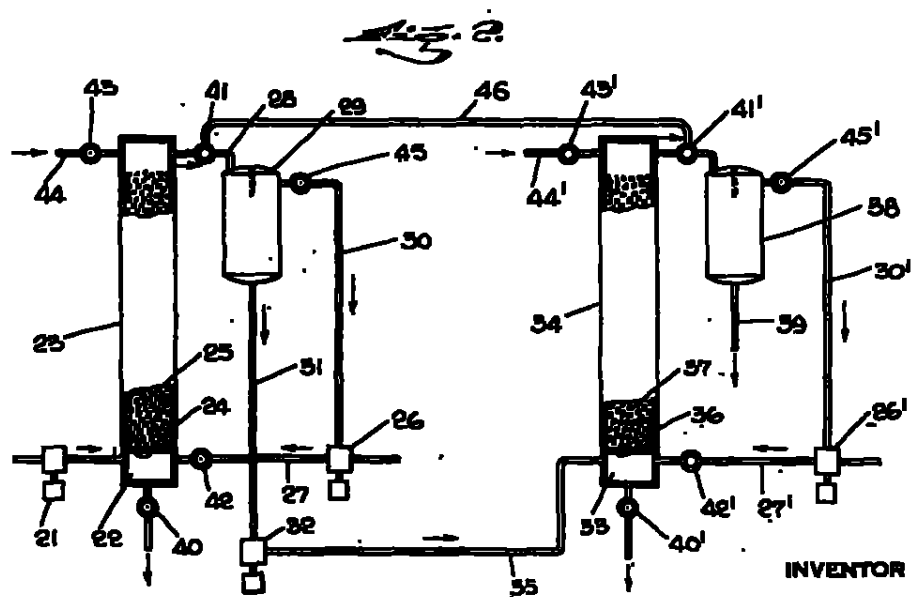
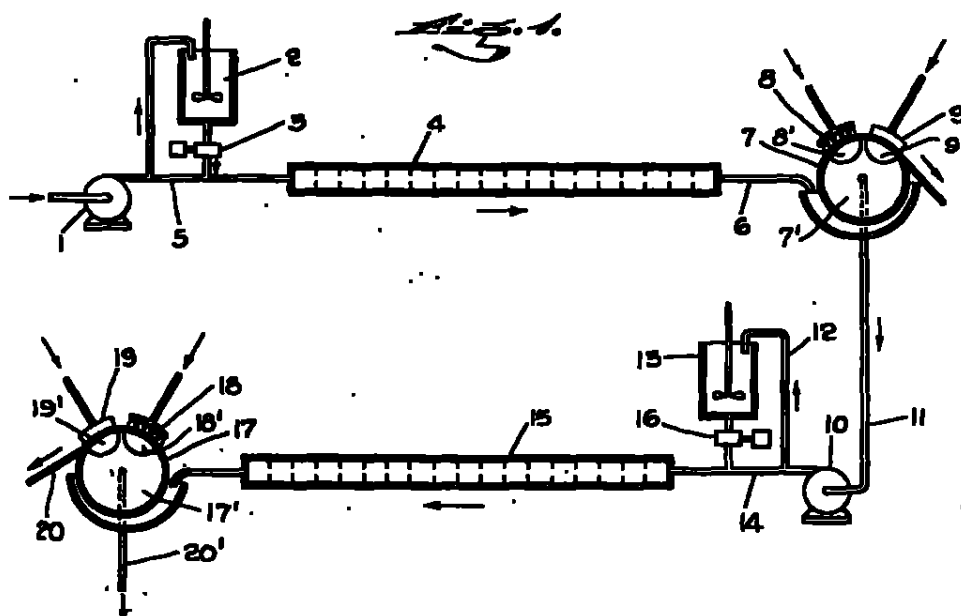
Concepto Técnico N°	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
1803	202003	

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Nov. 18, 1952

F. J. HENDEL
PROCESS FOR DESULFURIZING PETROLEUM
PRODUCTS IN THE LIQUID PHASE
Filed Nov. 3, 1952

2,618,586



INVENTOR

Frank J. Hendel

B6
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Patented Nov. 18, 1952

2,618,586

UNITED STATES PATENT OFFICE

2,618,586

PROCESS FOR DESULFURIZING PETROLEUM PRODUCTS IN THE LIQUID PHASE

Frank J. Hendel, Newark, N. J., assignor to Wigan-Abbott Corporation, Plainfield, N. J., a corporation of New Jersey

Application November 2, 1950, Serial No. 193,912

1-Claims. (Cl. 199-30)

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This invention relates to desulfurizing of petroleum products and, particularly, to new and improved procedures for desulfurizing petroleum products by treating such products in the liquid phase and at low temperatures with agents which remove the sulfur containing compounds without substantial chemical change.

Various procedures are known for desulfurizing petroleum products by chemical reactions which break down the sulfur containing compounds and remove the sulfur either in the form of a gas, such as hydrogen sulfide, or in the form of an insoluble metal sulfide. While these procedures are reasonably effective in removing the sulfur, they are generally costly and cumbersome to carry out commercially. Furthermore, the hydrocarbon residues left after chemical removal of the sulfur from the sulfur containing compounds remain in the petroleum product and, in some instances, the presence of these residues is objectionable.

I have now discovered that the desulfurizing of petroleum products can be carried out in an efficient and practical way, while avoiding the disadvantages inherent in chemical desulfurization above mentioned, by treatment of petroleum products in the liquid phase and at low temperatures with materials which adsorb the sulfur containing compounds. My new process actually comprises two adsorption steps which will be referred to as a primary adsorption step and a secondary adsorption or decolorization step, and which can be carried out in an efficient and practical way in either continuous or semi-continuous or batchwise operation of the process as more fully hereinafter described.

In the primary adsorption step, a liquid petroleum product having a bad odor due to the presence of sulfur containing compounds is brought into intimate and extended contact with a body of a heavy metal oxide having an affinity for the sulfur containing compounds, said metal oxide being in the form of a fine powder, porous pellets or other particles, such as oxide coated particles of an inert carrier, to provide a large adsorbent surface. The adsorption is carried out at a temperature within the range of about -20° to 200° F. and below the temperature at which the particular liquid being treated will react chemically with the metal oxide to form a metal sulfide. In general, light petroleum fractions, such as naphtha, gasolines and kerosene are treated at about room temperature or below, whereas heavier fractions and sulfur containing crudes are treated at somewhat higher temperatures.

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Various heavy metal oxides of the type previously employed in chemical or catalytic desulfurization procedures can be employed in my primary adsorption step, but those which have been found to be most satisfactory are the oxides of nickel, tungsten, molybdenum, manganese and lead, and mixtures thereof. It should be noted; in this connection, that the surprising adsorbent properties of the metal oxides in my process, in contrast to the chemical reaction to form metal sulfides in prior desulfurization procedures, is apparently due to the low temperature which I employ.

The sulfur bearing petroleum liquid can be contacted with the metal oxide in various ways, the important thing being to provide a contact or retention period sufficiently long to permit the sulfur containing compounds to be adsorbed on the metal oxide. In general, a minimum contact time of from two to five minutes for light petroleum fractions to about ten to fifteen minutes for heavy fractions and crudes will be adequate, but it will be understood that the optimum contact time will vary considerably depending on the viscosity of the petroleum liquid, the amount of mixing or agitation that is provided and the nature and amount of sulfur compounds to be removed.

The amount of metal oxide to employ also varies with different petroleum liquids depending upon the particular metal oxide employed and the nature and amount of sulfur containing compounds to be removed. For most purposes, however, about one part by (metric) weight of metal oxide to five parts by (metric) volume of petroleum liquid, i. e., one kilogram to five liters, will produce satisfactory results.

In treating small amounts of petroleum liquid, a mixture of the petroleum liquid and metal oxide can be placed in a suitable vessel, thoroughly agitated for the required contact period, and then filtered to separate the metal oxide and adsorbed sulfur compounds from the desulfurized petroleum liquid. When treating large amounts of petroleum liquid on a commercial scale, the desulfurization is more efficiently carried out continuously by passing both the petroleum liquid and the adsorbent through a suitable mixer, such as the orifice mixer hereinafter described, or semi-continuously by passing the petroleum liquid through a stationary body or column of adsorbent.

Although the continuous and semi-continuous adsorption procedures can be used interchangeably, the continuous adsorption is particularly

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suited for the treatment of viscous and/or high sulfur containing petroleum liquids while the semi-continuous adsorption is particularly suited for the treatment of low viscosity and/or low sulfur containing liquids.

In any of the contact or adsorption procedures above mentioned, a small amount of the adsorbent is dissolved or suspended in the petroleum liquid imparting a dark color to the liquid even in instances where the starting liquid was substantially water-white. A portion of the sulfur containing compounds, generally not more than about 10% of the amount present in the initial liquid is adsorbed or agglomerated around the suspended particles of adsorbent forming big colloidal aggregates or micelles. Although these micelles are relatively stable, they will, upon standing for several days, break down to precipitate the metal oxide and liberate part of the bound sulfur compounds. It is, therefore, advisable to follow the primary adsorption step promptly with a secondary adsorption or decolorization step.

The decolorization step can be carried out, either batchwise, continuously, or semi-continuously as previously described for the primary adsorption step using as adsorbent a decolorizing agent, such as bentonite clay, diatomaceous earth, fuller's earth, alumina, or even an excess of the heavy metal oxide used in the primary adsorption step. Thorough mixing is also essential in the decolorizing step although the contact time is generally shorter than in the primary adsorption step.

If desired, the primary adsorption step and decolorization step can be carried out concurrently by employing as adsorbent a mixture of a heavy metal oxide and a decolorizing agent, or as above mentioned, by employing an excess of the heavy metal oxide.

Both the metal oxide used in the primary adsorption and the bentonite clay or other adsorbent used in the decolorization can readily be regenerated by washing with water at a temperature not exceeding 100° C. and then blowing with steam. The water merely removes the petroleum liquid which remains in the body of adsorbent while the steam treatment removes the adsorbed sulfur compounds either by distilling them, or melting and washing them away.

It is preferable when steam blowing the metal oxide to simultaneously feed some air or oxygen to prevent the adsorbed sulfur compounds from reacting with the metal oxide to form the metal sulfide. With this simple precaution, however, the metal oxide can be regenerated and reused in the process more or less indefinitely.

The simple regeneration of the bentonite clay or other decolorizing agent leaves behind the metal oxide, and when the amount of metal oxide after a number of regenerations begins to impair the efficiency of the adsorbent, the metal oxide can be removed by washing the adsorbent with dilute acid. With the periodic acid treatments, the bentonite clay or other adsorbent can be reused indefinitely.

The following example will serve to demonstrate how my new adsorption process for the desulfurization of petroleum liquids is carried out, but it is to be understood that this example is given by way of illustration and not by way of limitation.

Example

A heavy sulfur free naphtha with a boiling range 180°-195° C. was contaminated with amyl

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mercaptan and 2.57% of thiofene. Hence, the sulfur content by weight was:

	Percent by weight
Mercaptan S	1.39
Thiofene S	1.00
Total	2.39

50 cc. of that liquid was shaken vigorously for ten minutes with 10 grams of black nickel oxide that was in the form of a fine powder. After filtering the liquid was of a dark color but the odor was sweet. The sulfur content dropped to 0.36% by lamp method. Hence, the sulfur reduction was 85%.

By shaking this filtrate with 7 grams of bentonite clay and filtering it again a water-white product was achieved. The sulfur content was further reduced; the product did not lose either its water-white color or the sweet odor even after standing for a long period.

The procedures involved and apparatus employed in commercial application of my invention will best be understood from a consideration of the accompanying drawing, in which various parts of the apparatus are designated by suitable reference characters in each of the views, and in which:

Fig. 1 is a schematic view, diagrammatically illustrating procedures and apparatus for the continuous operation of my process, and

Fig. 2 is a view similar to Fig. 1, but showing procedures and apparatus for the semi-continuous operation of my process.

In Fig. 1 of the drawing, I have diagrammatically illustrated an apparatus for the continuous desulfurization of petroleum liquids such, for example, as high sulfur Santa Fe Springs crude oil. The starting crude oil is fed to the system by the pump 1, a portion being by-passed to an agitator mixer 2, where it is mixed with powdered nickel oxide, and the resulting sludge is fed by pump 3 to an orifice mixer 4. The major portion of the crude oil feed passes directly to this orifice mixer through the pipe 5. The primary adsorption step takes place within the orifice mixer 4 and the mixture of oil and nickel oxide-sulfur compound adsorbate leaving the orifice mixer is carried by the pipe 6 to a drum filter 7 having a main collecting chamber 7' which separates the desulfurized oil from the adsorbate. As the drum rotates, the saturated adsorbent is carried beneath a water spray 8 and the washings are withdrawn through a second collecting chamber 8'. Further rotation of the drum carries the saturated adsorbent past a steam discharge 9 and a third collecting chamber 9' where the adsorbed sulfur compounds are removed to regenerate the nickel oxide; the regenerated oxide being scraped from the drum in the usual way and collected for reuse in the process. In the operation of the drum filter, the separate filtrations can be effected either by applying pressure externally of the drum, or by applying a vacuum to the chambers 7', 8' and/or 9'.

The desulfurized oil is drawn from the main collecting chamber 7' by the pump 10 through the pipe 11 and fed to a decolorizing system generally similar to the primary adsorption system above described. The pump 10 feeds a portion of the oil through pipe 12 to an agitator mixer 13, where it is combined with an adsorbent such as bentonite clay, and the remainder of the oil passes through the pipe 14 directly to an orifice mixer 15. The pump 16 feeds the oil-adsorbent

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sludge to the orifice mixer 15 where it is thoroughly mixed with the main portion of the desulfurized oil and the resulting mixture is discharged to a drum filter 17, similar to the filter 7. The decolorized oil is drawn into the main vacuum chamber 17' and the clay is then regenerated as it passes between water sprays 18 and vacuum chamber 18' and then between steam discharge 19 and vacuum chamber 19', the regenerated clay being scraped from the drum in the usual way, as indicated at 20. The desulfurized and decolorized oil is discharged from the main vacuum chamber 17' through the pipe 20'.

It will be understood that, in the apparatus above described, the capacity in continuous operation depends upon the size, i. e., diameter and length, of the orifice mixers and the retention time that is required to remove sulfur compounds from a particular starting material. The optimum retention time can be attained by appropriate regulation of the rates at which the starting oil, heavy metal oxide, and decolorizing agent are fed through the apparatus.

In Fig. 2 of the drawing, a modified form of desulfurizing apparatus is shown which is adapted for the semi-continuous or columnwise treatment of sulfur bearing petroleum liquids. The petroleum liquid, such for example as kerosene, is fed by the pump 21 to a chamber 22 at the lower end of a column or tower 23. The chamber 22 is separated by a perforated wall 24 from the adsorption chamber 25, which is packed with particled adsorbent, such as porous pellets of nickel oxide.

In order to create good mixing of the kerosene around the surfaces of the nickel oxide, a refinery gas is delivered from a suitable source of supply from a compressor 26 through pipe 27 to the chamber 22. This gas bubbles through the liquid and the nickel oxide in tower 23 and, then together with the liquid, leaves the top of the tower through pipe 28 and passes into a separating vessel 29. In the vessel 29, the gas is separated from the liquid and this gas or lighter vapors is delivered back to the tower 23 by the pipe 30 which leads to the compressor 26. The liquid in the vessel 29 is pumped through pipe 31 by pump 32 and delivered to a chamber 33 in the bottom of another column or tower 34 through pipe 35. A perforated plate 36 separates the chamber 33 from an adsorption chamber 37 in the tower 34 and the adsorption chamber is packed with particles or pellets of an adsorbent, such as bentonite clay.

Here again, refinery gas from a source of supply, which may be common to the source supplying the compressor 26, is fed by compressor 26' to the chamber 33 through pipe 37'. The gas entering the chamber 33 bubbles up through the liquid and the pellets and around the pellets in the tower 37 and the liquid and gas are discharged into a separator 38, similar to the separator 29, the gas and vapors discharging from separator 38 through pipe 39'; whereas the desulfurized and decolorized product is discharged through pipe 39.

From the foregoing, it will be apparent that a single compressor can be utilized to supply gas to the towers 23 and 34 by simply joining the pipes 26 and 26' and the pipes 27 and 27' respectively.

In connection with the method as disclosed in Fig. 2, whenever the nickel oxide and the bentonite clay require regeneration, this can be cared for by providing the valve control drains 40, 40' and which control the discharges from

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chambers 22, 33 and employing valves 41 and 42 in pipes 28, 27 and corresponding valves 41', 42' controlling tower 34, and further employing valves 43, 43' which control pipes 44, 44' and, further, by incorporating valves 45, 45' in the pipes 30, 30' adjacent separators 29 and 38. The valves 41, 41' are preferably three-way valves to provide means for establishing direct communication from the top of tower 23 to the top of tower 34 through pipe 40. (For use in the water wash hereinafter described.)

In regenerating the columns, the feed of oil by the pump 21 is stopped, the valves 41, 42; 41', 42' are closed and the valves 40, 40' are opened to permit the oil to drain from the two towers. The valve 40 is then closed, valves 41, 41' are adjusted to permit passage of fluid through the pipe 40 and water is pumped through the system by the pump 21, displaced oil and wash water passing out through the valve 40' at the bottom of the tower 34. When the oil has been completely displaced, the pump 21 is stopped, the valves 41, 41' are again closed and valve 40 is then opened. After the water has drained from the towers 23 and 34, the valves 43, 43' are opened to permit the charging of steam to the columns through the pipes 44, 44'. The steam removes the sulfur containing compounds from the adsorbents and carries them from the towers through the discharge valves 45, 45'. Air or oxygen is preferably admitted with the steam to prevent any reaction of the sulfur compounds with the heavy metal adsorbent, particularly in column 23. When all of the sulfur containing compounds have been removed by the steam treatment, the columns of adsorbent material are ready for use in the desulfurization of additional petroleum liquid.

The semi-continuous desulfurizing treatment, as shown in Fig. 2 of the drawing, is particularly suitable for use in treating petroleum liquids which have a relatively small amount of sulfur containing material to be removed. With material of this type, the adsorption process can continue for a relatively long period of time before the columns of adsorbent become saturated and desulfurizing efficiency begins to fall off. Even in instances where regeneration would have to be carried out quite frequently, the ease of regeneration with an apparatus, such as that shown in Fig. 2, reduces to a minimum the time and expense of the regeneration step. The apparatus set up of the type and kind shown in Fig. 1 has the advantage, of course, of effecting regeneration of the adsorbent continuously as it is separated from the treated petroleum liquid on the drum filter. This type of apparatus, therefore, provides a true continuous desulfurizing operation.

Modifications in the foregoing procedures will occur to those skilled in the art and to the extent that such modifications are embraced in the following claims, it is to be understood that they constitute part of my invention.

I claim:

1. The process for removing sulfur containing compounds from a petroleum liquid, that comprises contacting the petroleum liquid with an adsorbent material selected from the class consisting of oxides of nickel, tungsten, molybdenum and manganese, and mixtures thereof, at a temperature within the range of about -20° to 200° F. and below the temperature at which the liquid being treated will react with the metal oxide to form a metal sulfide, and separating the metal

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oxide and adsorbed sulfur compounds from the desulfurized petroleum liquid.

2. The process for removing sulfur containing compounds from a petroleum liquid, that comprises intimately contacting a sulfur bearing petroleum liquid with an adsorbent material, comprising a substance selected from the class consisting of oxides of nickel, tungsten, molybdenum, and manganese, and mixtures thereof, by passing the petroleum liquid through a column packed with particled adsorbent material, recovering the effluent stream of desulfurized petroleum liquid, continuing the flow of sulfur bearing petroleum liquid through the column of adsorbent until the adsorbent is substantially saturated with sulfur compounds, then temporarily discontinuing the feed of sulfur bearing petroleum liquid and regenerating the adsorbent by washing with water at a temperature below 100° C. to remove residual petroleum liquid, and then treating with steam to remove the adsorbed sulfur compounds.

3. The process as defined in claim 2, wherein the intimate contacting of petroleum liquid and adsorbent in the column is facilitated by continuously feeding to the column a stream of refinery gas.

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㉔ **Desulphurisation.**

㉕ Low temperature desulphurisation process using a bed of zinc oxide-containing absorbent in which the water content within the bed is temporarily increased, thereby increasing the sulphur absorption capacity of the absorbent.

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Desulphurisation

This invention relates to desulphurisation and in particular to the removal of sulphur compounds such as hydrogen sulphide from a gaseous or liquid feedstock stream, particularly hydrocarbon feedstock streams such as natural gas. Such hydrocarbon feedstock streams often contain substantial amounts of sulphur compounds, for example, where the hydrocarbon is gaseous, in an excess of 50 ppm by volume expressed as equivalent hydrogen sulphide.

Desulphurisation of a gaseous or liquid feedstock stream can be effected by passing the feedstock stream through a suitable absorbent such as zinc oxide in the form of a bed or beds of granules or pellets, wherein the absorbent combines with that sulphur present so as to form a sulphided absorbent, for example zinc sulphide in the case of a zinc oxide absorbent.

While such beds of absorbent enable a product stream of low sulphur content, typically below 10 ppm, to be obtained, breakthrough of the sulphur compounds into the product stream generally occurs long before all of the absorbent is fully sulphided.

Premature breakthrough is particularly noticeable where the absorption temperature is low.

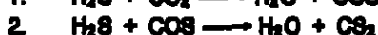
Although absorbents having a high surface area, typically above 20, and particularly in the range 50 to 200, m².g⁻¹ are of particular use for low temperature desulphurisation of gaseous or liquid feedstock streams, e.g. at temperatures between -10 and 200°C, they are still susceptible to the problem of premature breakthrough.

By the term breakthrough we mean that the sulphur content of the product stream is at a level that is unacceptable to the user. This level will of course depend on the use to which the product stream is to be put.

By the term absorption capacity, when used with reference to a sulphur absorbent, we mean the amount of sulphur retained by the absorbent before breakthrough occurs.

By the term regeneration, when used with reference to a sulphur absorbent, we mean the increasing of the absorption capacity of a sulphur absorbent without removal of sulphur from the absorbent.

It has been proposed in GB-A-1568703 to adjust the water vapour content of a synthesis gas stream, i.e. a gas stream containing hydrogen and carbon oxides, to 0.5 to 5% by volume prior to desulphurisation with a zinc oxide bed. In this reference the desulphurisation is preferably effected at temperatures above 200°C. The object of incorporation of water vapour in the gas stream used in the process of that reference was to suppress the formation of sulphur compounds such as carbonyl sulphide and carbon disulphide which are less readily removed than hydrogen sulphide from gas streams. Such compounds presumably result from the reactions:



These reactions are reversible and so the formation of carbonyl sulphide and carbon disulphide is suppressed by the incorporation of water in the gas stream. The equilibrium constants for reaction (1) above are given for various temperatures at pages 203 and 306 of Catalyst Handbook, 2nd Edition, edited by M V Twigg, published by Wolfe Publishing Ltd. At equilibrium, the extent of reaction (1) reduces with temperature, and at low temperatures the extent of reaction is negligible. Furthermore, the rates of reaction for reactions (1) and (2) are believed to be also very small at low temperatures and so carbonyl sulphide and carbon disulphide formation is unlikely to be a problem when effecting desulphurisation of carbon dioxide-containing feedstock streams at low temperatures.

It has been further proposed in EP-A-279116 that the continued presence of a controlled amount of water in the feedstock stream, particularly a gaseous feedstock stream, such that the relative humidity of the water in the feedstock stream is above 30%, has the effect of increasing the absorption capacity of zinc oxide containing absorbent beds when operating at low temperatures.

However, in a number of applications, the continued presence of water is not desirable and consequently the option of continuously adding water to improve the sulphur absorption capacity of the absorbent is not acceptable. For instance, when in contact with substantial quantities of water at relatively low temperatures, methane may give rise to the formation of methane hydrates, which are prone to cause blockages and operating difficulties; therefore it is not desirable to generate a low temperature methane-containing stream which also contains a high level of water on a continuous basis.

We have found that the absorption capacity of certain zinc oxide containing absorbents can be usefully increased if the proportion of water in the feedstock or other fluid stream passing or otherwise making contact with the absorbent is temporarily increased. Thus a bed of zinc oxide-containing absorbent may be regenerated by such treatment and the useful life of the absorbent extended.

Accordingly the present invention provides a process for the removal of hydrogen sulphide from a substantially water-free hydrogen sulphide-containing feedstock stream comprising passing the feedstock stream, at a temperature between -10 and 350°C through a bed of zinc oxide-containing absorbent particles thereby forming a hydrogen sulphide-depleted product stream characterised in that, in order to increase the absorption capacity of the particles for hydrogen sulphide, after a period of use for absorption of hydrogen sulphide from the feedstock stream, the particles are contacted with a water-containing fluid so as to temporarily increase the water content within the fluid space of the bed for a period of time until the particles absorb such an amount of water that the particles increase in weight by an amount in the range 0.5 to 20%.

Although a slight increase in the absorption capacity of the absorbent particle may be seen after the absorbent particles have absorbed smaller amounts of water, significant increases are only obtained if the particles absorb at least 0.5% by weight of water. However, the amount of water employed is preferably such as to increase the weight of the particulate sulphided absorbent by between 1.5 to 10%, and particularly between 2 to 8%. The amount of water required depends to some extent on the surface area of the absorbent: thus more water is required for high surface area absorbents than with low surface area absorbents. It is preferred that the amount of water employed is such that the absorbent absorbs at least 0.2 mg, and preferably at least 0.5 mg, of water per m^2 of absorbent surface area.

The treatment of the particles by temporarily increasing the water content within the fluid space of the bed constitutes regeneration of the absorbent.

The bed of zinc oxide-containing absorbent particles may be subjected to the regeneration whilst absorbing sulphur compounds from the feedstock stream if the resultant increase in water content of the product stream is acceptable. Alternatively, and in some cases preferably, the bed is regenerated whilst the bed is not absorbing sulphur compounds from the feedstock stream. Thus in a continuous process for the generation of a product stream, two or more beds of absorbent may be provided and, while one or more beds are removing sulphur compounds from the feedstock stream, one or more other beds are subjected to regeneration.

The regeneration may be effected by the continuous flow of a water-containing fluid, i.e. either a gas or liquid, through the absorbent bed, or the holding of such a water-containing fluid within the bed for the required period.

The water-containing fluid used to effect the regeneration may be any water-containing fluid stream which does not adversely affect the desulphurisation properties of the absorbent. In some cases it may be possible to employ a feedstock stream to which water has been added as the water-containing fluid: in this case, of course, absorption of the sulphur compounds will continue during contact of the water-containing stream with the bed of absorbent, so the absorbent should be regenerated sufficiently before breakthrough of sulphur compounds into the product stream occurs.

Alternatively the water-containing fluid used to effect regeneration may be part of the product stream to which water has been added. After use for regeneration, the part stream may be returned to the remainder of the product stream. Where the presence of water in the product stream is not acceptable, the part stream may be dried, for example by the use of a molecular sieve, before return to the remainder of the product stream, or the whole of the product stream may be dried after return of the part stream. Indeed, since the absorption of hydrogen sulphide by zinc oxide produces water, it may in some cases be necessary to dry the product stream before further use. In this case it is convenient that a part of the product stream is taken before the drier, water is added, and the water-laden part product stream is used as the water-containing fluid for regeneration. After use for regeneration, this water-laden part product stream is returned to the remainder of the product stream and then the whole of the product stream is passed through the drier, e.g. a molecular sieve.

Where the regeneration is effected by means of a water-containing gas, it is preferred that the water-containing gas is passed through the bed of absorbent continuously during the regeneration stage.

Where such a water-containing gas is to be used to effect the regeneration, provision may be made for heating the gas prior to addition of the water, so that the quantity of water held as vapour per quantity of gas is increased, thereby accelerating the rate at which the increase in absorption capacity of the absorbent is achieved. The water-containing gas preferably has a relative humidity, at the regeneration temperature, of at least 25%, preferably at least 50%, and most particularly at least 75%. Where the absorbent comprises substantially only zinc oxide, the water-containing gas preferably is substantially free from carbon dioxide in order to avoid the formation of zinc carbonate which has an absorption capability for sulphur compounds inferior to that of zinc oxide.

Where the presence of liquid water in the absorbent bed and/or in the water-containing gas from the absorbent bed, is not desirable, then provision may be made for heating the water-containing gas, and/or

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the vessel in which the absorbent is held, so that the water-containing gas as it both enters and leaves the bed is free of liquid water.

In one application of the invention the desulphurisation stage is operated in combination with a drying stage employing a molecular sieve drier which is regenerated by passage of a heated fluid stream therethrough to effect desorption of the water removed during the drying stage. In such a process, in some cases it may be possible to employ the water-containing fluid leaving the molecular sieve during the regeneration thereof as the water-containing fluid used to effect regeneration of the zinc oxide containing absorbent.

Where the regeneration of the zinc oxide containing particles is effected with a water-containing liquid, it is preferred that an appropriate amount of water-containing liquid is charged to the bed, (and an excess of such liquid may be employed), the bed held in that state until the absorbent has absorbed the requisite amount of water, and then the bed is freed of liquid water by passage of a dry gas or liquid stream therethrough. The amount of such a water-containing liquid, which is preferably water substantially free from any other materials, is preferably sufficient to fill the pores of the absorbent.

Where a water-containing liquid is used to effect the regeneration provision maybe made for heating the water-containing liquid, and/or the vessel in which the absorbent is held, thereby accelerating the rate at which the increase in absorption capacity of the absorbent is achieved.

Contacting the water-containing fluid with the absorbent for the required length of time enables the absorbent to absorb the required amount of water for regeneration. Once regenerated the absorbent may again be used to remove sulphur compounds from the feedstock stream. However the initial contact of the feedstock stream with the absorbent after regeneration of the absorbent will tend to strip-off that water which has been absorbed by the absorbent. The water which has been stripped-off will be carried through the bed of absorbent to emerge in the product stream. The water content in the product stream will therefore initially increase, and then drop back as the amount of water which is stripped-off diminishes.

Where the initial increase in the water content of the product stream can be tolerated, for instance where the product stream would in any event be dried, this may not present a problem. However in some cases an initial increase in the water content of the product stream, after regeneration of the absorbent may be a problem. In such cases the absorbent may be dried before the feedstock stream is reintroduced to the bed. The drying of the absorbent may be achieved in a number of ways, for example by passage of a dry inert stream through the bed, or by passage of a fluid stream that is subsequently to be used as the water-containing fluid for regenerating another bed of absorbent.

The time interval required before the regeneration will depend on the rate at which the absorbent becomes sulphided, e.g. upon the nature and proportions of the absorbable sulphur compounds in the feedstock stream, the space velocity at which the feedstock stream is fed through the bed, on the nature of the feedstock stream, the temperature at which the absorption takes place, and the acceptable level of sulphur compounds in the effluent product stream.

The particulate absorbent material preferably comprises at least 80%, especially at least 80%, by weight of zinc oxide, calculated on the constituents of the absorbent material non-volatile at 800 °C. As used in the process the zinc oxide may be, at least initially, wholly or partly hydrated or in the form of a salt of a weak acid, e.g. a carbonate.

The absorbent is preferably particulate in form, particularly in the form of porous agglomerates, as may be made, for example, by mixing a finely divided zinc oxide composition with a cement binder and a little water, insufficient to give a slurry, and then granulated or extruded. In order to aid access of the feedstock stream into the particulate absorbent, the latter may be provided in the form of extruded pellets having a plurality of through passages.

It is believed that the absorption efficiency and hence the life of a particulate zinc oxide-containing absorbent depends on the rate of diffusion of that sulphur which has been absorbed by the zinc oxide present on the surface of the absorbent, away from the surface of the absorbent. As the rate of adsorption of sulphur compounds at low absorption temperatures is controlled by the exposed zinc oxide surface area, it is preferable when operating at absorption temperatures below 120 °C, preferably below 80 °C, and particularly below 50 °C, to employ a particulate zinc oxide-containing absorbent having a high pore volume, above 0.2 cm³.g⁻¹, and high surface area, above 50 m².g⁻¹, preferably in the range 70 to 200 m².g⁻¹. With a particulate zinc oxide-containing absorbent having a lower pore volume and a surface area of the order of 25 to 30 m².g⁻¹ the increase in absorption capacity by the temporarily rise in the water content of the fluid space is not nearly so significant and so the useful life of such a low surface area absorbent at low absorption temperatures is relatively low. Thus large volumes of low surface area absorbent would be needed in order to avoid premature breakthrough of the sulphur compounds into the product stream. However, by using a zinc oxide-containing absorbent of pore volume above, for example, 0.25 cm³.g⁻¹ and

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surface area above, for example, $70 \text{ m}^2.\text{g}^{-1}$, the volume of absorbent required can be markedly reduced, e.g. to about one third of that required with a low surface area absorbent. The particulate zinc oxide-containing absorbents employed thus preferably have a surface area above $70 \text{ m}^2.\text{g}^{-1}$ and a pore volume above $0.25 \text{ cm}^3.\text{g}^{-1}$.

5 Preferred particulate absorbents for the process at low absorption temperatures have a hydrogen sulphide absorption capacity of at least 20%, especially at least 25%, of the theoretical maximum, at a temperature of 25°C , as determined in a standard test in which a dry mixture of hydrogen sulphide (2000 ppm by volume), carbon dioxide (4% by volume), and methane (balance) is passed through a bed of the particulate absorbent at atmospheric pressure and a space velocity of 700 h^{-1} using a bed of circular cross
10 section having a length to diameter ratio of 5.

A particularly suitable particulate zinc oxide containing absorbent is that sold by Imperial Chemical Industries plc as "Catalyst 78-1". This absorbent is in the form of granules typically having a surface area of the order of $80 \text{ m}^2.\text{g}^{-1}$ and a pore volume of about $0.3 \text{ cm}^3.\text{g}^{-1}$, and an adsorption capacity of about 27% of theoretical when measured by the above procedure.

15 Alternatively the particulate absorbent may comprise agglomerates of particles of an intimate mixture of oxides, hydroxides, carbonates and/or basic carbonates of copper, and zinc and/or at least one element such as aluminium as described in EP-A-243052.

Water-free gaseous feedstocks that may be treated are those that are less than 10%, and especially less than 1%, saturated with water.

20 Alternatively, the process of the present invention may be used to treat liquid substantially water-free feedstock streams wherein the amount of water (if any) in the feedstock stream is insufficient to fill the pores of the absorbent.

The feedstock stream typically contains hydrocarbons up to those containing six carbon atoms. Usually it will contain, in addition to methane, and one or more of ethane, propane, propene, butanes, and butenes.

25 The invention is also of utility with other feedstocks, for example air, naphtha, carbon dioxide, or the product of fractionating a gas mixture produced by cracking or hydrocracking a normally liquid hydrocarbon feedstock, or the gaseous by-product of a zeolite-catalysed conversion of a feedstock such as methanol to gasoline.

30 The composition of the raw gas, where the latter is a natural or oilfield associated gas, expressed by volume, is typically:

ethane	2 to 20 %
propane plus propene	1 to 10 %
butanes plus butenes	0.5 to 5 %
higher hydrocarbons	0.2 to 2 %
carbon dioxide	0 to 20 %
nitrogen	0 to 20 %
water	up to saturation
methane	balance.

35 When such natural or oilfield associated gas streams contain substantial amounts of water, i.e. the stream is above 10% saturated, a drying stage is normally employed to reduce the amount of water present prior to sulphur removal. The dried stream is then desulphurised. The use of the present invention in the desulphurisation of such streams enables the absorption capacity of the absorbent to be increased without reintroducing significant amounts of water into the stream.

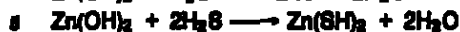
In addition to hydrogen sulphide, other sulphur containing compounds that are initially present in the feedstock stream may be removed by the process of the present invention. Examples of such compounds include carbonyl sulphide, carbon disulphide, methyl, ethyl or other mercaptans, diethyl sulphide and other
40 alkyl sulphides up to C_{18} , and/or tetrahydrothiophene. The total initial concentration of sulphur compounds, expressed as sulphur equivalent hydrogen sulphide, is typically in the range 1 to 1000 ppm by volume of the feedstock when the latter is in the gaseous phase. The absorption stage can be conducted so that a substantial proportion, e.g. over 75% by volume of the sulphur content of the feedstock stream can be removed. Typically the sulphur compounds content of the product stream is under 10, for example under 5,
45 ppm by volume, expressed as above, but this is a matter of design, depending on the user's requirements.

Without wishing to be limited it is thought that a possible explanation of the increase in absorption capacity of a bed of particulate zinc oxide-containing absorbent, resulting from the temporary increase in the amount of water in the fluid space of the bed, is that the reaction mechanism for the absorption of

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hydrogen sulphide by zinc oxide, particularly at low temperatures, may involve the hydration of the zinc oxide surface, indicated in a simplistic form by the following equations



in preference to the reaction



which is the prevalent mechanism at high temperatures and which proceeds only slowly at low temperatures. The surface hydrated zinc oxide provides mobile hydroxy or SH (bisulphide) groups that allow the movement of sulphur away from the sulphur saturated exterior thereby generating new sulphur deficient absorbent on the surface.

The invention is illustrated by the following examples. In these examples about 80 ml of the absorbent in the form of granules were charged to a tube of internal diameter 2.54 cm to form a vertical bed of length 12 cm.

The sulphur absorption capacity of the bed of absorbent was tested, in an absorption stage, by passing a test gas substantially at atmospheric pressure, down through the bed maintained at about 20° C at a rate of 700 ml/min, (i.e. space velocity 700 hr⁻¹).

The test gas was "dry" methane (which contained about 120 ppm by volume of water) in admixture with about 1% by volume of hydrogen sulphide.

The hydrogen sulphide content of the test gas leaving the bed of absorbent was monitored and breakthrough was deemed to have occurred when the hydrogen sulphide content of the test gas exit the bed of absorbent reached about 2 ppm by volume.

The absorbent was then regenerated as described in the individual examples.

After regeneration, the flow of test gas was resumed and the time taken for breakthrough to reoccur was measured.

At the conclusion of each experiment the absorbent was discharged in six equal parts A to F, (A = top; F = bottom) which were analysed so that the distribution of sulphur down the depth of the bed could be determined.

Example 1

This example shows the effect on the absorption capacity of an absorbent with repeated regeneration using a water-containing gas.

The absorbent employed was granules of size approximately 3 to 5 mm of ICI "Catalyst 75-1".

The water-containing gas used to regenerate the absorbent, in a regeneration stage, was "wet" hydrogen sulphide-free methane, obtained by saturating the "dry" methane with water at 20° C. The "wet" methane was passed down through the bed of absorbent at about 20° C and substantially at atmospheric pressure at a space velocity of 700 hr⁻¹.

As a comparative experiment, a similar bed of absorbent was regenerated by passing "dry" hydrogen sulphide-free methane substantially at atmospheric pressure, down through the bed of absorbent maintained at about 20° C at a space velocity of 700 hr⁻¹.

The absorbent regenerated according to the present invention was then subjected to a succession of absorption and regeneration stages.

The results are shown in the following table in which an absorption stage and the regeneration stage immediately following are termed a "cycle"; T_{STB} is the time to breakthrough from the start of the absorption stage; and T_{REG} is the duration of the regeneration stage.

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Cycle	"Dry" regeneration gas		"Wet" regeneration gas	
	T _{brn} (hours)	T _{reg} (hours)	T _{brn} (hours)	T _{reg} (hours)
First	5.9	22.5	6.4	21.5
Second	0.2	-	1.9	24
Third	-	-	1.0	23
Fourth	-	-	1.0	>8.5*
Fifth	-	-	0.5	24
Sixth	-	-	0.4	-
Total	6.1	22.5	11.2	>99

* Precise time not known, but less than 10 hours.

The difference between the breakthrough time for the first cycle of the comparative experiment (5.9 hr) compared with that of the present invention (6.4 hr) probably reflects differences in the precise amount of absorbent employed and/or minor variations in the hydrogen sulphide content of the test gas.

The following table shows the sulphur content down the beds of absorbent on termination of the experiment after the second cycle ("dry" gas) and sixth cycle ("wet" gas). The sulphur content down a bed of absorbent after the first cycle, i.e. without further sulphur absorption occurring, is included for additional comparison.

Bed Portion	Sulphur content (% w/w)		
	Regenerated		Non - Regenerated
	"Dry" Gas	"Wet" Gas	
A	10.3	16.1	7.9
B	10.5	17.2	8.1
C	9.9	15.8	7.9
D	7.8	12.2	5.9
E	4.1	7.0	2.0
F	1.1	2.2	0.3
Average	7.3	12.1	5.4

It is seen that the successive "regeneration" stages enabled the useful life of the absorbent to be increased by about 84%, and thereby retaining an additional 66% more sulphur.

Example 2

In this example the application of the invention to a zinc oxide absorbent used for desulphurising damp carbon dioxide-containing gas (wherein the absorbent becomes carbonated during use), is illustrated, by repeating the procedure of Example 1 using a "carbonated" absorbent.

The "carbonated" absorbent was obtained by enclosing a sample of the fresh absorbent as employed in Example 1, with solid carbon dioxide, and water, which were in proportions of 10:1 on a weight basis in an autoclave, allowing the temperature to rise to ambient, and maintaining at ambient temperature for 48 hours. This "carbonated" absorbent was then dried for 18 hours at 110°C before use. As in Example 1, the regeneration of the absorbent was effected using the "wet" hydrogen sulphide-free methane, and in a

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comparative experiment with the "dry" hydrogen sulphide-free methane. The results are shown in the following table:

Cycle	"Dry" regeneration gas		"Wet" regeneration gas	
	T _{arr} (minutes)	T _{reg} (hours)	T _{arr} (minutes)	T _{reg} (hours)
First	21	23	25	24
Second	7	-	53	>8.5*
Third	-	-	60	21.5
Fourth	-	-	67	19.5
Fifth	-	-	50	23
Sixth	-	-	56	21.5
Seventh	-	-	55	-
Total	28	23	365	>118

* Precise time not known, but less than 19 hours.

As in Example 1, the difference between the time to breakthrough for the first cycle for the comparative experiment (21 minutes) compared with that of the present invention (25 minutes) probably reflects differences in the precise amount of absorbent employed and/or minor variations in the hydrogen sulphide content of the test gas.

After the second cycle ("dry" gas) and sixth cycle ("wet" gas), the sulphur content of the absorbent down the bed was as follows:

Bed Portion	Sulphur content (% w-w)	
	"Dry" regeneration gas	"Wet" regeneration gas
A	0.9	12.8
B	1.1	11.5
C	1.0	9.4
D	0.8	7.1
E	0.6	4.3
F	0.4	1.3
Average	0.8	7.8

It is seen, that by comparing the results of this example with those of Example 1, that the "carbonated" zinc oxide absorbent has a much inferior sulphur absorption capability to that of the uncarbonated zinc oxide absorbent used in Example 1, but the successive regeneration stages with "wet" gas enabled the useful life of the "carbonated" zinc oxide absorbent to be increased dramatically.

Example 3

In this example the effect is shown of incorporating a drying stage after the regeneration stage of the cycle.

The procedure of Example 1 was repeated, but using only a single regeneration stage using the "wet" hydrogen sulphide-free methane.

After the regeneration stage, the absorbent was dried by passing "dry" hydrogen sulphide-free

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methane down through the bed of absorbent.

During the regeneration and drying stages, the weight of the absorbent was monitored in order to determine the degree of "water pickup". The "water pickup" is a measure of that water retained by the bed of absorbent and is the weight of water in the bed of absorbent after contact with the water-containing fluid, and immediately before a subsequent drying stage, divided by the total weight of absorbent and sulphur in the bed at the start of the regeneration stage.

The results are shown in the following table and indicate that the effects of the regeneration are apparent after the absorbent has been dried.

10	Cycle Stage	Total time (hours) from start of Cycle Stage	Water Pickup (% w/w)
	Regeneration	0	0
		18.5	8.5
15		19.5	8.6
		21.5	8.9
		22	-
		22.5	8.9
20	Drying	0	8.9
		1	5.8
		3	-
		4	-
		17.5	1.5
25		19	1.3
		21	-
		22	1.2
30			Time to Breakthrough (minutes)
	First Cycle		349
	Second Cycle		102

35	Bed Portion	Sulphur Content (% w/w)
40	A	12.5
	B	12.7
	C	11.8
	D	9.0
45	E	5.5
	F	2.1
	Average	8.9

Example 4

In this example the effect is shown of regenerating the absorbent with a water-containing liquid. The absorbent was a sample of the fresh absorbent granules as used in Example 1. The absorption stages were as conducted in the previous examples. The first absorption stage was terminated on breakthrough, after 4.4 hours. The regeneration stage was then effected by adding sufficient liquid water to the bed of absorbent so

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as to fill the pores of the absorbent with water. The bed of absorbent was then left at ambient temperature, without flow of gas or liquid therethrough, for 16 hours. The bed of absorbent was then dried out for 22 hours to a constant weight by passing "dry" hydrogen sulphide-free methane down through the bed at a temperature of about 20° C and at atmospheric pressure.

A second cycle was then started, and when breakthrough reoccurred after 1.4 hours, the bed was again regenerated and dried in the same manner as described above.

Flow of the test gas (i.e. "dry" methane in admixture with hydrogen sulphide) was again recommenced and the experiment was terminated on subsequent breakthrough.

The total time during which the bed of absorbent was absorbing sulphur from the test gas, without breakthrough occurring, was 7.3 hours and the sulphur content of the absorbent down the bed, on termination of the experiment, was as follows:

Bed Portion	Sulphur Content (% w/w)
A	18.1
B	18.1
C	14.4
D	11.4
E	8.4
F	1.8
Average	11.0

Example 5

This example shows the effect of different regeneration times.

The absorbent employed was a sample of the fresh granules as employed in Example 1.

Nitrogen saturated with water at ambient temperature was used as the water-containing gas used in the regeneration stage. The regeneration stages were conducted at ambient temperature, in a manner similar to that of Example 1.

In some cases a drying stage was conducted after the regeneration stage. The drying stage comprised passing dry nitrogen down through the bed of absorbent at about ambient temperature, and atmospheric pressure, for 16 hours prior to recommencing passage of the test gas through the bed of absorbent.

The results are shown in the following tables.

In some cases the absorbent was subjected to more than one cycle, comprising an absorption stage and a regeneration stage. At least one drying stage was included in the multiple cycle cases.

Thus in experiment 5f the absorbent was subjected to in turn an initial absorption stage; an initial regeneration stage of 2 hours duration; a second absorption stage; a second regeneration stage of 4 hours duration; a third absorption stage; a third regeneration stage of 8 hours duration; a drying stage; a fourth absorption stage; a fourth regeneration stage of 8 hours duration; a second drying stage; and a fifth, and final, absorption stage.

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	Regeneration		Bed portion sulphur content (% w/w)					
	Number	Time (h)	A	B	C	D	E	F
5a	1	0.50*	10.7	11.1	10.4	8.2	4.5	1.3
5b	1	1.17*	11.4	12.0	11.2	8.8	4.1	1.0
5c	1	2*	11.9	12.2	11.9	10.4	7.0	3.5
5d	1	4*	12.0	12.2	11.2	8.8	4.8	1.2
5e	1	8*	12.4	12.8	12.0	9.8	8.0	1.9
5f	4	2 4 8* 8*	17.7	17.2	16.5	12.2	7.4	2.8
5g	3	2* 4* 8*	14.1	13.8	13.0	10.7	6.9	2.5

* Dried after regeneration

	Total Time To Breakthrough (h)	Water Pickup (% w/w)
5a	6.95	0.63
5b	6.15	0.90
5c	5.00	1.52
5d	5.18	2.83
5e	5.30	4.33
5f	7.32	-
5g	6.95	-

The "Water Pickup" is as previously defined.

The "Total Time To Breakthrough (h)" is the total time that the bed of absorbent was removing sulphur from the test gas, without breakthrough occurring. Variations in the concentration of hydrogen sulphide in the test gas during the experiments are reflected in the breakthrough times in some instances being less than that of the "dry" gas regenerated absorbent of Example 1. However the absorption capacity of the absorbent has in all instances been increased to above that of the "dry" gas regenerated absorbent of Example 1.

The concentration profile of absorbed sulphur down the bed shows a relatively sharp trailing edge, plus a small tail in the bottom third of the bed. It is the tail that determines when breakthrough occurs. However improvement in the absorption capacity can be seen by comparing the top half to two thirds of each absorbent bed.

Example 8

In this example the effect is shown of regeneration by a water-containing gas at a temperature higher than 20° C.

The absorbent employed was a sample of fresh granules as employed in Example 1.

The absorption stage was as conducted in Example 1.

Regeneration was performed by passing air, heated to 70° C and thereafter saturated with water, down through the bed of absorbent for 2.3 hours.

After regeneration, the bed of absorbent was dried to constant weight and allowed to cool to the absorption temperature before flow of the test gas was recommenced.

The total time during which the bed of absorbent was absorbing sulphur from the test gas, without breakthrough occurring, was 5.7 hours and the sulphur content of the absorbent down the bed, on termination of the experiment, was as follows:

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Bed Portion	Sulphur Content (% w/w)
A	13.4
B	13.4
C	12.1
D	8.4
E	5.3
F	1.0
Average	8.9

Thus a bed of zinc oxide-containing absorbent after one regeneration using a gas stream saturated at 70° C can retain about 22% more sulphur than the "dry" gas regenerated absorbent of Example 1.

Example 7

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In this example the effect of regeneration by a water-containing liquid at higher temperatures is shown. The absorbent employed was a sample of fresh granules as employed in Example 1. The absorption stage was as conducted in Example 1. The regeneration was conducted in a similar manner to that of Example 4. Sufficient liquid water, at 70° C, was added to the bed of absorbent so as to fill the pores of the absorbent with water. The bed of absorbent was then left at 70° C, without flow of gas or liquid therethrough, for 4 hours. The bed of absorbent was then dried out for 132 hours to a constant weight by passing "dry" nitrogen through the bed. Most of the water was in fact lost in the first 24 hours of the drying stage. The bed of absorbent was allowed to cool to the initial absorption temperature, whereupon flow of the test gas was again recommenced and the experiment was terminated on subsequent breakthrough. The total time during which the bed of absorbent was absorbing sulphur from the test gas, without breakthrough occurring, was 7.1 hours and the sulphur content of the absorbent down the bed, on termination of the experiment, was as follows:

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Bed Portion	Sulphur Content (% w/w)
A	13.9
B	14.1
C	13.0
D	10.1
E	5.9
F	1.0
Average	9.7

Thus a bed of zinc oxide-containing absorbent after one regeneration using a water-containing liquid can retain about 33% more sulphur than the "dry" gas regenerated absorbent of Example 1.

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Example 8

In this example the effect is shown of regenerating the absorbent using a water-containing gas stream, having a relative humidity of 50%. The absorbent employed was a sample of fresh granules as employed in Example 1. The absorption stage was as conducted in Example 1.

Regeneration was performed by using hydrogen sulphide-free methane, in admixture with sufficient water so as to be 50% saturated with water at 20 °C. The "semi-wet" methane was passed down the bed of absorbent at about 20 °C and atmospheric pressure at a space velocity twice that previously used, i.e. 1400 hr⁻¹, for 104 hours. Thus the same amount of water was contacted each hour as when fully saturated methane is employed at a space velocity of 700 hr⁻¹.

A drying stage was then performed after the regeneration stage, wherein "dry" hydrogen sulphide-free methane was passed down the bed for 100 hours at the a space velocity of 700 hr⁻¹.

10	Bed Portion	Sulphur Content (% w/w)
	A	11.2
	B	11.7
15	C	11.1
	D	8.9
	E	5.5
	F	1.8
20	Average	8.3

Thus a bed of zinc oxide-containing absorbent after one degeneration using a gas half saturated with water can retain about 14% more sulphur than the "dry" gas regenerated absorbent of Example 1.

Claims

1. A process for the removal of hydrogen sulphide from a substantially water-free hydrogen sulphide-containing feedstock stream comprising passing the feedstock stream, at a temperature between -10 and 350 °C through a bed of zinc oxide-containing absorbent particles thereby forming a hydrogen sulphide-depleted product stream characterised in that, in order to increase the absorption capacity of the particles for hydrogen sulphide, after a period of use for absorption of hydrogen sulphide from the feedstock stream, the particles are contacted with a water-containing fluid so as to temporarily increase the water content within the fluid space of the bed for a period of time until the particles absorb such an amount of water that the particles increase in weight by an amount in the range 0.5 to 20%.
2. A process according to claim 1 wherein the absorbent absorbs water, and thereby increases in weight by at least 0.2 mg per m² of absorbent surface area.
3. A process according to claim 1 or claim 2 wherein the water content within the fluid space is temporarily increased whilst the absorbent is not absorbing hydrogen sulphide from the feedstock stream.
4. A process according to claim 3 wherein two or more beds of absorbent are provided and while a bed of absorbent removes hydrogen sulphide from the feedstock stream, the water content within the fluid space of another bed is temporarily increased.
5. A process according to any one of claims 1 to 4 wherein the water-containing fluid is continually passed through the bed during the period of time in which the water content in the fluid space of the bed is temporarily increased.
6. A process according to any one of claims 1 to 4 wherein the water-containing fluid is held within the bed during the period of time in which the water content in the fluid space of the bed is temporarily increased.
7. A process according to claim 5 wherein the water-containing fluid is a feedstock stream to which water is added during the period of time in which the water content in the fluid space of the bed is temporarily increased.
8. A process according to any one of claims 1 to 6 wherein the water-containing fluid comprises part of the product stream to which water has been added.
9. A process according to either claim 7 or claim 8 wherein after contacting the water-containing fluid with the bed so as to temporarily increase the water content within the fluid space of the bed, the water-containing fluid is combined with the product stream.

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10. A process according to claim 9 wherein after contacting the water-containing fluid with the bed so as to temporarily increase the water content within the fluid space of the bed, the water-containing fluid stream is dried before combining with the product stream.

11. A process according to claim 9 wherein the product stream is dried after combining the water-containing fluid with the product stream.

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Method of removing sulfur from a hydrocarbon feedstream.

Sulfur is removed from a hydrocarbon feedstream to a catalytic reformer by contacting the feedstream with a sulfur sorbent comprising a metal component containing a metal selected from Group I-A or Group II-A of the Periodic Table supported on a porous refractory inorganic oxide support.

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METHOD OF REMOVING SULFUR FROM A HYDROCARBON FEEDSTREAM

This invention relates to a method of removing sulfur compounds from the hydrocarbon feedstreams to a catalytic reformer.

Catalytic reforming processes play an integral role in upgrading naphtha feedstocks to high octane gasoline blend stocks. These processes have become more important in recent years because of the increase in demand for low-lead and unleaded gasoline.

In typical modern reforming processes, the naphtha feed is passed over a promoted noble metal catalyst at a temperature in the range of 315°C to 595°C, a pressure in the range of from 1 atmosphere to 70 atmospheres, a liquid hourly space velocity (LHSV) in the range of .1 to 10, and a hydrogen to hydrocarbon mole ratio in the range of 1 to 10. Variations in these conditions will depend in large measure upon the type of feed processed and the desired product octane level.

It is generally recognized that the sulfur content of the feedstock must be minimized to prevent poisoning of the reforming catalyst. Preferably, the feed will contain less than 2 to 5 parts per million by weight (ppm) of sulfur, since the presence of sulfur in the feed decreases both the activity and the selectivity of the catalyst. Certain reforming catalysts are extremely sulfur sensitive, and sulfur levels in the feed of even less than 1 ppm can severely deactivate these catalysts.

Sulfur sorbents can remove nearly all of the sulfur present in the feed at the high temperatures used in reforming. One sulfur sorbent that is used at low temperatures is a metal or metal compound, such as copper, which is supported on a porous refractory inorganic oxide support or on a carbon support. An example of such a sorbent is disclosed in U.S. Patent No. 4,204,947. That sorbent is copper supported on alumina. Other similar sorbents are disclosed in U.S. Patent Nos. 2,583,484 and 4,224,181. Copper on alumina works well as a sorbent for H₂S or mercaptan type sulfur, but copper sorbents tend to be less effective at higher temperatures, removing less sulfur as the temperature goes above 300°C. Furthermore, copper sorbents do not work on some types of sulfur which can be present in the reforming feed, such as thiophenic sulfur. Also, copper is costly.

Various promoter metals have been used in conjunction with copper. For example, U.S. Patent No. 4,008,174 discloses copper and chromium on a carbon support. The chromium aids in regeneration of the sorbent.

The present invention is a novel method of removing sulfur from hydrocarbon feedstreams by using a metal component containing a metal selected from Group I-A or Group II-A of the Periodic Table supported on a porous refractory inorganic oxide support. Preferred metal components include sodium, potassium, calcium and barium. Preferred refractory inorganic oxide supports include alumina, silica, boria, titania, zirconia, aluminosilicates, aluminophosphates, and mixtures of two or more thereof.

One preferred method of making these sulfur sorbents is by impregnating a preformed porous refractory inorganic oxide support with an aqueous solution of a metal salt, where the metal is selected from Groups I-A or II-A of the Periodic Table, and drying and calcining the resulting material.

An alternative method is by peptizing a refractory inorganic oxide support, thereby forming a plastic mass, mulling the mass with a compound containing a Group I-A or Group II-A metal, then extruding the mass, and drying and calcining it.

For a better understanding of the invention, reference will now be made, by way of example, to the accompanying drawing which is a plot of the average catalyst temperature of an exemplary material required to maintain the target refractive index of the C₆+ liquid product of 1.4300, which corresponds to about 47 wt% aromatics in the feed.

A refinery produces naphtha fractions having substantial amounts of sulfur in the form of organic sulfides, such as thiophenes and mercaptans. Sometimes the sulfur level is higher than 100 ppm in the untreated naphtha fraction. These feeds with very high sulfur levels can be contacted with hydroprocessing catalysts to convert the sulfur compounds to H₂S. If the remaining sulfur level is too high, then the high sulfur level can cause the reforming catalyst to rapidly lose both activity and selectivity when used for reforming. Prudent operation demands that heavily sulfur contaminated feeds be further treated before contacting sulfur sensitive catalysts.

Preferred supports for the sulfur sorbent include alumina, silica, titania, zirconia, boria, and the like, and mixtures thereof. Clays can also be used as supports. Particular clays of interest include the fibrous magnesium silicate clays, for example, attapulgite, halloysite, palygorskite and sepiolite. The support can be premade by any method known in the art.

The surface area of the finished sulfur sorbent is in large part due to the support chosen. It is believed that the active sulfur sorbents of this invention can have nitrogen surface areas in the range of between 20 and 300 m²/g.

Since the sulfur sorbents of this invention can be used for removing sulfur from feedstreams for reforming units, one typical feedstock will be low molecular weight hydrocarbons which are in the vapor phase at reforming conditions. In particular, the feedstock will normally comprise alkanes and naphthenic compounds having between about five and twelve carbon atoms. Hydrogen may also be present, such as the recycle hydrogen stream of a reforming unit. Because vapors diffuse rapidly into the pores of the support material, the precise size and pore distributions are not thought to be critical in a sulfur sorbent for use in this application.

The metal components of the sulfur sorbents in this invention can be Group I-A or Group II-A metal containing compounds. The preferred metal components are sodium, potassium, calcium, and barium. The metal components are not in general present as the reduced metal. Instead, they are usually present in the form of a salt, oxide, hydroxide, nitrate, or other compound. It is the metal in the compound, in any form, that is the metal component of the sorbent of this invention. The sulfur sorbents of this invention can be made by impregnation of a preformed refractory inorganic oxide support with a metal component, or by commulling the metal component with the inorganic oxide support.

Preferred metal compounds include sodium chloride, sodium nitrate, sodium hydroxide, sodium carbonate, sodium oxalate, potassium chloride, potassium nitrate, potassium carbonate, potassium oxalate, potassium hydroxide, barium chloride, barium nitrate, barium carbonate, barium oxalate, barium hydroxide, calcium chloride, calcium nitrate, calcium carbonate, calcium oxalate, calcium hydroxide, and the like.

A preformed inorganic support can be impregnated with Group I-A or Group II-A metals by standard techniques. It may be necessary to impregnate the support several times to achieve the desired amount of metal component on the inorganic support. Various metal compounds can be dissolved to form aqueous solutions useful for this impregnation. The preferred compounds for impregnation are the more soluble compounds. To be useful for impregnation, a compound should have a solubility of at least 0.1 mole per liter of water.

Another method of making the sulfur sorbents of this invention is by mulling the powdered inorganic support material, which may be prepeptized or mixed in the presence of a peptizing agent, together with a compound containing a Group I-A or Group II-A metal. Preferred peptizing agents are mineral acids, such as nitric acid. For example, peptized alumina powder could be mixed with a metal component, such as potassium carbonate. The resulting mass is then extruded, dried and calcined to form the final sulfur sorbent.

The choice of the appropriate compound to use during fabrication of the sulfur sorbent is primarily dictated by the solubility of the salt. For example, in impregnation, very soluble salts are desired such as nitrates, but in mulling, relatively insoluble salts such as carbonates are preferred.

If sulfur is present that is not in the form of H₂S, it is preferred that the sulfur sorbent of this invention include being commingled with or preferably preceded by small amounts of platinum or palladium, either on the sorbent or on a suitable support. Between 0.01 weight percent and 0.5 weight percent platinum or palladium may be added. In the presence of added hydrogen, the added metals catalyze the conversion thiophenic and other organic type sulfur compounds that may exist in the feedstream into easily sorbed sulfur compounds. If the platinum or palladium is on the sorbent particles themselves, it may also reduce coking of the feed on the sorbent particles. When thiophenic and other organic sulfur compounds contact platinum and palladium, hydrogen sulfide is formed, which is readily removed by the sulfur sorbent.

The sorbent of this invention is used to remove sulfur from feedstocks containing sulfur levels as high as several percent to levels as low as 1 ppm (part per million) and lower. Typically, the sorbent and reforming catalyst are contained in separate vessels. The vessel containing the sulfur sorbent is typically placed upstream of the vessel containing the reforming catalyst. The feedstock may be heated to as high as the reforming reaction temperature or to a lower temperature before it contacts the sulfur sorbent; from ambient temperature to as high as 1000°F (540°C) and higher.

The sorbent can be placed in the same reaction vessel as the reforming catalyst. If the sorbent is given the proper porosity and shape it can be inter-mixed with the reforming catalyst, in the same bed. As any residual organic sulfur is converted by the reforming catalyst to H₂S, the sorbent removes it, preventing harm to subsequent beds, and prolonging operational life of the system because the sorbent functions well at reforming temperatures.

The sorbent can safely contact the amounts of water normally found in reforming feedstreams. The feedstreams do not have to be as extraordinarily dry as they would if they were contacting the reduced, metallic form of alkali metals or alkaline earth metals and if this reduced, metallic form were required. Group I-A and Group II-A metals can form hydroxides or oxides in a water-containing stream. However, the water level in the hydrogen recycle stream should be kept low, preferably to less than 100 ppm, and more preferably to less than 50 ppm.

This sorbent can be used in combination with other sorbents. For instance, in one embodiment, the hydrocarbon feedstock is contacted with a hydrotreating catalyst to convert organic sulfur compounds in the feedstock, then the feedstock is contacted with a sorbent, such as zinc oxide or copper oxide, supported on a clay base, then the feedstock is contacted with the sorbent of the present invention.

In the following non-limitative examples, the preformed gamma alumina base used was a commercially available 1/16th inch (1.6 mm) extrudate, with a H₂O pore volume of approximately .7 cc/gm and a N₂ surface area of approximately 200 m²/gm. It was calcined at 1250°F (677°C). It was made by peptizing a pseudoboehmite alumina of crystal size in the range of approximately 33 to 40 Angstroms as determined by X-ray diffraction (XRD) with an aqueous solution of a mineral acid, mixing it until it reached an extrudable state, then extruding, drying and calcining the resulting material.

Example I

This example shows a sulfur sorbent of this invention. The sorbent was prepared by taking 100 gm of pre-extruded alumina and impregnating it with 25.9 gm KNO₃ in 78 ml H₂O, by pore fill impregnation. The sorbent was dried for 18 hours at 250°F (121°C) and then calcined for 2 hours at 1100°F (593°C). .12 ml of a solution of .083 gm Pt/ml, where the form of Pt was H₂PtCl₆, in distilled water was then impregnated onto the support. It was dried for 48 hours at 250°F (121°C) and calcined for 2 hours at 500°F (260°C). This composition of matter will be identified as A.

Example II

This example shows another sulfur sorbent of this invention. 200 grams of pre-extruded alumina were impregnated with .22 ml of .083 gm Pt/ml, where the form of Pt was H₂PtCl₆, in 184 ml H₂O, under 30 inches (76.2 cm) of vacuum. The extrudate was then impregnated with 57.43 grams of potassium nitrate in 184 ml of water. The extrudate was dried at 250°F (121°C) overnight and then calcined for 2 hours at 1100°F (593°C). This composition of matter will be identified as B.

Example III

This example shows the manufacture of a monometallic reforming catalyst. 50 grams of pre-extruded alumina was impregnated under 30 inches (76.2 cm) of vacuum with 1.6 ml of an aqueous solution of H₂PtCl₆ of concentration .083 gm Pt/ml in 30 ml of H₂O. The impregnated alumina was allowed to stand for 2 hours and then dried at 250°F (121°C) overnight and then calcined for 2 hours at 950°F (510°C) in air. The catalyst produced can be used for reforming. This composition of matter will be identified as C.

Example IV

1000 gm of an L zeolite of crystal size between 1000 and 2000 Angstroms was mixed with 10 liters of .3 molar Ba(NO₃)₂ solution. The zeolite and solution were placed into 2 bottles. Lids were placed on the bottles and they were shaken. They were then placed into a preheated oven at 80°C for 3 hours. Then the contents were filtered and washed with 2 liters distilled water. The solids were dried for 18 hours at 250°F (121°C) and calcined for 18 hours at 1100°F (593°C) in air.

752.4 gm of smaller than 14 mesh powder made as above was impregnated with a solution of Pt(NH₃)₄(NO₃)₂ to 8 wt % Pt, in 752.4 ml of aqueous solution. This was then dried for 18 hours at 250°F (121°C), rescreened to < 14 mesh, and calcined for 2 hours at 500°F (260°C) in air. This composition of matter will be identified as D.

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Example V

This example was a standard reforming run using a sulfur-sensitive reforming catalyst except that (1) there was no sulfur sorber; and (2) 1 ppm sulfur was added to the feed after 480 hours. The catalyst in this example was D. The results before and after sulfur addition are shown in the following table. After 600 hours, control of temperature to maintain the required aromatics content was no longer possible due to rapid catalyst deactivation. After 670 hours, the addition of sulfur to the feed was discontinued, and clean feed was used. No recovery of activity was observed during 50 hours of clean feed operation. In addition, the feed was withdrawn at 720 hours, and the catalyst was stripped with sulfur-free hydrogen gas for 72 hours at 830°F (499°C). Only a small gain in activity was observed.

Run time, Hrs.	For 50 wt% Aromatics In Liquid, Temperature °F(°C)		C ₅ + Yield LV%
200	862	(461)	84.5
400	866	(463)	85.4
480	868	(464)	84.8
550	882	(472)	86.1
600	908	(487)	86.2

Example VI

This example was run as shown in Example V, except that .5 ppm mercaptan-type sulfur was added to the feed from 270 hours to 360 hours on stream, and again from 455 hours to 505 hours on stream. After 450 hours, control of temperature to maintain the required aromatics content was no longer possible due to rapid catalyst deactivation. The results are shown below:

Run time, Hrs.	For 50 wt% Aromatics In Liquid, Temperature °F(°C)		C ₅ + Yield LV%
200	862	(461)	84.2
300	864	(462)	85.0
350	876	(469)	85.6
400	887	(475)	85.6
450	896	(480)	85.5
500	904	(484)	85.8

Example VII

Deionized water was added to 0.23 ml of a solution containing 0.093 gm Pt/ml, the Pt as H₂PtCl₆. The water was added until the total volume of the solution was 170 ml. This mixture was used to vacuum impregnate 200 gm of a preformed alumina extrudate. The impregnated extrudate was then allowed to stand for 2 hours at room temperature, and was then dried for 18 hours at 250°F (121°C).

Next, 284.8 gm of Ca(NO₃)₂·4H₂O was mixed into 100 ml hot deionized water, and stirred until clear. The solution was then evaporated, cooled, and the volume adjusted to 170 ml. This solution was then used to impregnate the extrudate under vacuum. The extrudate then sat for 2 hours at room temperature, and was then dried at 250°F (121°C) overnight.

Finally, the material was calcined at 1100°F (593°C) in flowing air.

This material will be designated E.

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Example VIII

To 3.2 ml of a solution of 0.093 gm Pt/ml, the Pt as H_2PtCl_6 , was added deionized water until the total solution volume reached 80 ml. This solution was then used to impregnate 100 gms of a preformed alumina extrudate under vacuum. The extrudate was allowed to sit for 2 hours at room temperature and was then dried for 16 hours at 250°F (121°C). Finally, it was calcined for 2 hours in flowing air at 950°F (510°C).

This material will be designated F.

Example IX

To 1100 gm of an L zeolite was added 11 litres of an aqueous solution of 0.3 molar Ba as $Ba(NO_3)_2$. This mixture was placed in polypropylene bottles, the lids were closed, and the bottles were placed in a preheated 178°F (80°C).

After 4 hours, the contents of the bottles were poured off into filters and the solids collected. The filter solids were reslurried in fresh deionized water and refiltered to a total of 10 times.

The solids were then dried at 250°F (121°C) over a weekend, and calcined for 16 hours at 1100°F (593°C) in flowing air.

863.1 gm of the material was then screened to below 14 mesh. 0.6% Pt was added to the solids in a pore fill impregnation, using $Pt(NH_3)_4(NO_3)_2$ as the Pt source, and 680.5 ml of total solution. The material was allowed to sit at room temperature for 2 hours and was then dried at 250°F (121°C) for 16 hours.

Finally, the material was treated at 500°F (260°C) hours in flowing air.

This material will be designated G.

Example X

This example shows the process of this invention. In a fixed bed tubular reactor, 25 cc of material F at 24 to 80 mesh was layered over 25 cc of material E at 24 to 80 mesh. This material was layered over 100 cc of material G, also at 24 to 80 mesh.

A naphtha feedstock of API gravity 87.0, boiling range as determined by D-86 distillation of start, 160°F (71°C); 5% Pt. 167 (75); 10% Pt. 169 (76); 20% Pt. 171 (77); 30% Pt. 173 (78); 40% Pt. 175 (79); 50% Pt. 177 (81); 60% Pt. 180 (82); 70% Pt. 183 (84); 80% Pt. 190 (88); 90% Pt. 208 (98); 95% Pt. 208 (98); and end Pt. 254°F (123°C), and molecular type as determined by GC of 59.8 LV% paraffins, 36.8 LV% naphthenes, and 3.8 LV% aromatics, was fed over the catalyst at a LHSV relative to the reforming catalyst, N, at a pressure of 150 psig (10 bar) and an H_2/HC ratio of 2. Organic sulfur as thiophene was doped into the feed and fed at a 1 to 2.5 ppm S level, based on feed.

Figure 1 is a plot of the catalyst average temperature of the material G required to maintain the target refractive index of the C_6+ liquid product of 1.4300, which corresponds to about 47 wt% aromatics in the liquid.

The Pt containing material F in front of the sorbent material E serves to convert the thiophenic sulfur to H_2S , a form readily sorbed by the material.

Note that the reforming catalyst G was not deactivated by the sulfur to any measurable extent. Sulfur analyses on various layers of the catalysts after the completion of the run showed 440 and 370 ppm of sulfur on the Pt containing thiophene conversion catalyst F, 127% S and 1250 ppm S on the sorbent E, and 40, 24, and 18 ppm S on the reforming catalyst G.

Claims

1. A method of removing sulfur from a hydrocarbon feedstream, which comprises contacting said hydrocarbon feedstream with a sulfur sorbent comprising a metal component containing a metal selected from Group I-A or Group II-A of the Periodic Table supported on a porous refractory inorganic oxide support.

2. A method according to Claim 1, wherein said metal component contains sodium, potassium, barium or calcium.

3. A method according to Claim 1 or 2, wherein said porous refractory inorganic oxide support is alumina, silica, zirconia, titania, boron, or a mixture of two or more thereof.

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4. A method according to Claim 1 or 2, wherein said porous refractory inorganic oxide support is a clay selected from attapulgite, halloysite, palygorskite, and sepiolite.

5. A method according to Claim 1, 2, 3 or 4, wherein the hydrocarbon feedstream is contacted with a platinum or palladium conversion catalyst in addition to the sulfur sorbent, the location of the conversion catalyst being separate from or the same as the sulfur sorbent.

6. A method according to Claim 5, wherein the contacting of the hydrocarbon feedstream by the conversion catalyst precedes the contacting with the sulfur sorbent.

7. A method according to Claim 5, wherein the conversion catalyst and sulfur sorbent are used in the same reaction zone.

8. A method according to Claim 7, wherein the conversion catalyst and sulfur sorbent are inter-mixed.

9. A method according to any preceding claim, wherein the sulfur sorbent is prepared by:

(a) impregnating a preformed porous refractory inorganic oxide support with a solution comprising a solvent and a metal component containing a Group I-A or Group II-A metal of the Periodic Table; and

(b) drying and calcining the resulting impregnated material.

10. A method according to Claim 9, wherein said solution is an aqueous solution.

11. A method according to Claim 9 or 10, wherein said metal component has a solubility in water of at least 0.1 mole per liter of water.

12. A method according to any one of Claims 1 to 8, wherein the sulfur sorbent is prepared by:

(a) contacting the porous refractory inorganic oxide support and metal component to form an extrudable mass;

(b) mulling the extrudable mass;

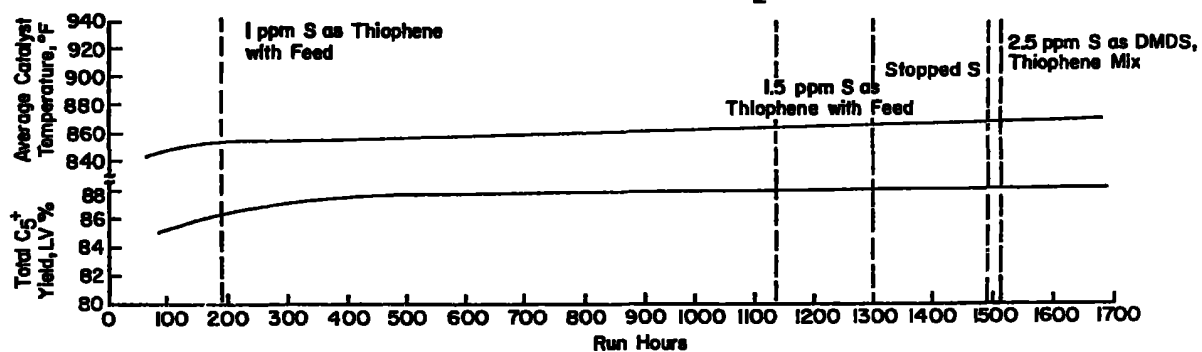
(c) extruding the extrudable mass to form extrudates; and

(d) drying and calcining the extrudates to form the required sulfur sorbent.

SULFUR PROTECTION WITH Ca SORBENT - THIOPHENE

150 psig, 1.5 LHSV on G, 2.0 H₂/HC,

1.4300 R.I.



0 254 781

HT