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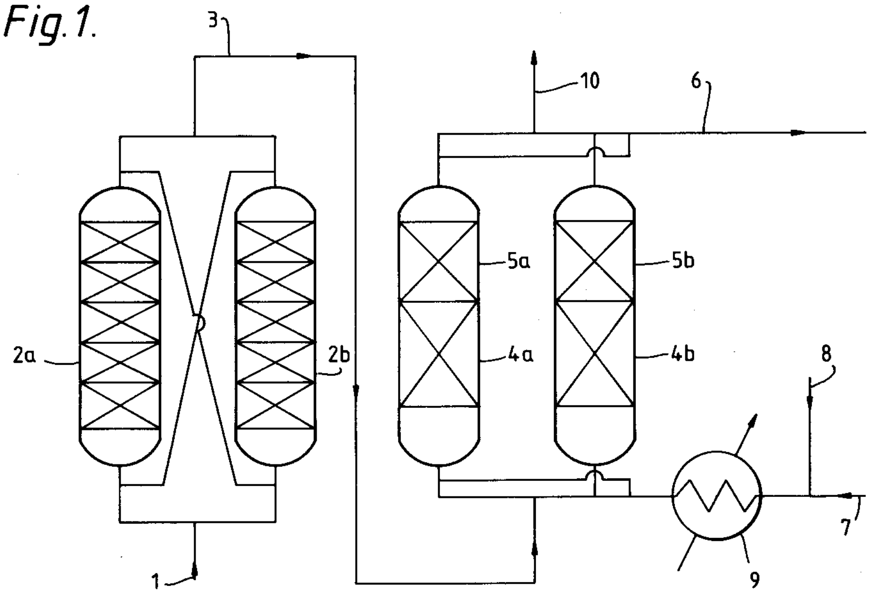
(54) Sulphur removal process.

(57) Elemental sulphur is removed from streams of gaseous, or preferably liquid, organic materials, particularly hydrocarbons, by contact with an absorbent material comprising metallic copper. Reactive contaminants, such as hydrogen sulphide or carbonyl sulphide, are preferably absorbed from the stream by contact with zinc oxide and/or copper oxide prior to contact with the metallic copper absorbent.

Fig.1.



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This invention relates to a process for the removal of elemental sulphur from organic compounds.

Elemental sulphur is soluble, and is often present as a contaminant, in organic liquids such as carbon tetrachloride and hydrocarbons such as benzene and petroleum. Also organic polysulphides are often present in such liquids and these readily decompose to give elemental sulphur dissolved in the liquid. Elemental sulphur can also result from the reaction of sulphur compounds such as hydrogen sulphide with oxidising agents. Furthermore elemental sulphur has an appreciable volatility and may be present in gaseous hydrocarbon streams. It has been found that such elemental sulphur is reactive with metals and can cause severe corrosion problems in pumps and other equipment which are used to handle the organic compounds: of particular concern is the corrosion of submerged automobile fuel injection pumps which may occur if the automobile fuel contains elemental sulphur.

The removal of reactive sulphur compounds, such as hydrogen sulphide and carbonyl sulphide, from gaseous or liquid streams is well known. Elemental sulphur, however, is significantly more difficult to remove than reactive sulphur compounds and existing sulphur removal processes are largely ineffective in the removal of elemental sulphur.

It has now been found that an active form of metallic copper, as produced through the reduction of a reducible copper compound, can be used to remove elemental sulphur from streams of gaseous or liquid organic compounds, particularly elemental sulphur dissolved in liquid hydrocarbon streams.

Accordingly the present invention provides a process for decreasing the content of elemental sulphur of a stream of gaseous or liquid organic material contaminated with elemental sulphur comprising contacting the stream with a sorbent containing metallic copper as an active constituent.

The process of the present invention is preferably conducted under conditions of temperature and pressure such that the organic stream is in the liquid state. Preferably the process is effected at a temperature below 300 ° C, particularly below 150 ° C, and at pressures up to to 100 bar abs. Organic liquids suitable for treatment by the present invention include hydrocarbon streams such as petroleum, kerosene, liquefied petroleum gas (LPG), natural gas liquid (NGL), aromatic liquid hydrocarbons, and liquefied natural gas (LNG).

The initial concentration of the elemental sulphur is usually from 1 to 200 ppm, and typically from 1 to 50 ppm, by weight.

Conventional sorbents, such as those based on zinc oxide, which are used for the removal of reactive sulphur compounds, are ineffective at removing elemental sulphur. It has now been found that metallic copper can be used as the active constituent in a sorbent which is effective to sorb elemental sulphur from an organic gaseous or liquid stream: during the sorption process the metallic copper is converted into copper sulphide. Generally, the higher the copper content of the sorbent the more elemental sulphur can be removed before replenishment of the sorbent is required. Consequently, it is preferred that the sorbent has a copper content of at least 30% by weight (expressed as the percentage of the copper (II) oxide present in the loss free sorbent after ignition of the sorbent at 900 ° C), and more usually from 50% to 90% by weight. The ability of the sorbent to sorb elemental sulphur is also effected by the accessibility of the copper metal by the elemental sulphur. Generally, a high copper metal surface area sorbent is more efficient at sorbing sulphur than a sorbent of comparable copper content but lower copper metal surface area. Particularly efficient sorbents are those having copper metal surface areas in excess of 20 $m^2.g^{-1}$, and especially those having copper metal surface areas in the range 20-40 $m^2.g^{-1}$. Sorbents having greater copper metal surface areas, eg in an excess of 50 $m^2.g^{-1}$, may also be used. A high copper metal surface area sorbent may be formed by the reduction of a copper compound, e.g. the oxide, carbonate, or nitrate, with a suitable reducing agent. Suitable reducing agents include hydrogen, a compound decomposable to hydrogen in the presence of the sorbent, carbon monoxide, and mixtures of carbon monoxide and hydrogen. The conditions under which the reduction of the copper compound is conducted may be similar to those be employed in the preparation of a copper based methanol synthesis catalyst from the oxidic precursor to such a catalyst. The temperature at which the sorbent is reduced is will depend to some extent on the nature of the reducing agent: typically the temperature will be in the range 90 to 250 ° C, and is usually in the range 150 to 200 ° C.

Conveniently, the sorbent may prepared in the form of particulates similar in size to those conventionally used for the removal of reactive sulphur compounds, such as described in US patents US-4871710, US-4996181 and US-4983367. The sorbent may be disposed in a single bed or more usually in a plurality of serially and/or concurrently arranged beds. Typically, the flow of organic liquid through each bed would be at a rate sufficient to give a liquid hourly space velocity (LHSV) from 1 to 20 hr^{-1}, and more usually from 1 to 10 hr^{-1}.

Usually, the organic streams to be treated will contain other contaminants in addition to elemental sulphur. These other contaminants may include hydrogen sulphide, carbonyl sulphide, organic sulphur compounds, arsenides, and heavy metals such as mercury. The metallic copper sorbent may be used to remove these contaminants in addition to the elemental sulphur. It is preferred, however, to remove these contaminants from the organic stream by conventional means, e.g. a sorbent comprising zinc oxide and/or copper oxide, prior to contacting the metallic copper sorbent, thereby minimising the amount required of the metallic copper sorbent. Some of the byproducts, e.g. water and carbon dioxide, of the reactions between the contaminants and the conventional sorbents may subsequently react with the metallic copper sorbent, thereby reducing the effectiveness of the metallic copper sorbent to remove elemental sulphur from the organic liquid. It may thus thus also be preferred to remove these reaction byproducts prior to contacting the metallic copper sorbent.

The present invention is further illustrated by reference to the accompanying figure.

Figure 1 is a schematic diagram of an elemental sulphur removal process of the present invention.

Figure 1 shows an organic liquid feed stream **(1)** contacting one of two interchangeable contaminant removal reactors **(2a, 2b)**. The valving necessary to isolate each reactor and to direct the liquid stream between successive units has been omitted for clarity. Reactors **(2a, 2b)** are used to remove at least some of the reactive contaminants such as hydrogen sulphide, carbonyl sulphide as listed above and may contain a sorbent such as zinc and/or copper oxide. As a result of the reaction ocurring in beds **(2a, 2b)**, the stream **(3)** is freed of the aforesaid reactive contaminants but may contain by-products such as water and carbon dioxide. Stream **(3)** is then passed through one of two beds **(4a, 4b)** effective to sorb at least some of the byproducts produced in beds **(2a, 2b)** from the stream **(3)**. The byproduct-free stream then flows directly into the respective metallic copper sorbent bed **(5a, 5b)** wherein the dissolved elemental sulphur is removed to produce a desulphurised product stream **(6)**. The metallic copper sorbent is usually formed in situ by reduction of a precursor comprising a reducible copper compound. Reduction of the precursor may be accomplished by passing a hydrogen stream **(8)** which has been diluted with an inert stream **(7)** and heated in a heat exchanger **(9)** to a suitable reduction temperature through the bed of precursor and thereafter venting the effluent gas stream **(10)**.

In some cases it may be desirable to provide for regeneration of the metallic copper sorbent. This may be achieved by re-reducing the spent metallic copper sorbent with a stream of hydrogen: typically the reduction may be effected using a hydrogen stream at 200-300 ° C. The copper sulphide formed by reaction of the copper with the elemental sulphur is converted back to copper metal with the concurrent formation of hydrogen sulphide. The hydrogen sulphide may be scrubbed from the hydrogen stream and then fed to a sulphur recovery plant, eg a Claus plant.

The invention is further illustrated by the following examples.

Example 1

In this example two absorbent beds were employed in series. The first bed was 300 g of granules of an absorbent comprising a high surface area zinc oxide and a cement binder, while the second bed was produced by reducing in situ 300g of granules formed from mixture of high surface area copper and zinc oxides and a cement binder. The mixture contained 55% by weight of copper oxide. The reduction was effected by means of a stream of hydrogen at a temperature of 180 ° C. It is estimated, from measurements performed on another sample of the mixture, that after reduction, the copper surface area of the second bed was 20 $m^2.g^{-1}$.

A liquid gasoline stream containing about 400-500 ppm by weight of total sulphur of which about 20 ppm by weight was elemental sulphur, was passed through at 20 ° C at an average rate of approximately 500 ml/h through the series of beds and the elemental sulphur content of the effluent was monitored at intervals. The experiment was terminated when the elemental sulphur content of the effluent reached 5 ppm by weight which ocurred after 87 days. The cumulative flow and effluent elemental sulphur content at various times were as set out in Table 1.

The spent copper/zinc oxide bed was then analysed and found to have a sulphur content of about 7.2% by weight. On examination by XRD it was found that cupric sulphide was present in the bed, but there was no cuprous sulphide, copper sulphate, or zinc sulphide. The absence of zinc sulphide in the spent copper/zinc oxide bed indicates that reactive sulphur compounds, such as hydrogen sulphide, present in the gasoline were absorbed by the first zinc oxide bed. The presence of cupric sulphide, rather than cuprous sulphide, in the spent copper/zinc oxide bed indicates that the copper could be regenerated by reduction with hydrogen since cupric sulphide is easier to reduce to metallic copper than cuprous sulphide.

Table 1

Time (days)	Cumulative flow (1)	effluent sulphur (ppm)
1	10.5	0
11	116.7	0.2
21	223.2	0.2
31	341.3	0.7
41	486.0	1.0
51	628.4	1.3
61	765.4	2.5
73	905.0	1.6
79	974.0	nm
81	nm	2.8
87	nm	5.0
nm = not measured		

Example 2

One concern was that the metallic copper sorbent would react with, or decompose, methyl cyclopentadiene manganese tricarbonyl (MMT) which is often employed as an octane number improver in gasoline. In order to examine this, a series of three catalyst beds, viz a sample of the zinc oxide absorbent granules of the first bed of Example 1, a sample of the spent, ie sulphided, absorbent granules of the second bed of Example 1, and a sample of the fresh copper oxide/zinc oxide absorbent granules of the second bed of Example 1, were charged to a glass reactor. The air in the reactor was displaced by nitrogen and the apparatus wrapped in aluminium foil to shield it from light (which effects decomposition of MMT). Hydrogen at 180 ° C was then passed through the series of beds to effect reduction of the copper compounds to metallic copper. The reactor was then filled with a mixture of xylene (70% by weight) and heptane (30% by weight). A solution containing 540 ppm by weight of MMT dissolved in the aforesaid xylene/heptane mixture was then passed through the series of beds at atmospheric pressure and at 22-25 ° C for 48 hours at a liquid hourly space velocity of 2 h^{-1}. Analysis of the solution before and after passage through the beds failed to reveal any change in the manganese content. The reactor was then flushed with fresh solvent, purged with nitrogen. The absorbents were then dried at 110 ° C and analysed for the presence of manganese. No manganese was detected in the zinc oxide sample while the reduced sulphided copper containing adsorbents contained about 300-500 ppm by weight of manganese. Since manganese is a possible contaminant of the cement employed as the granule binder, it is likely that this found manganese resulted from that contamination in view of the lack of detected change in the manganese content of the solution during passage through the beds. If all the MMT had been decomposed and absorbed by the absorbents, the average manganese content of the absorbent beds after the experiment would have been about 3% by weight.

Claims

1. A process for decreasing the content of elemental sulphur of a stream of gaseous or liquid organic material contaminated with elemental sulphur comprising contacting the stream with a sorbent containing metallic copper as an active constituent.

2. A process according to claim 1 wherein the organic material is a liquid having the elemental sulphur dissolved therein.

3. A process according to claim 1 or claim 2 wherein the sorbent has a copper content of at least 30% by weight (expressed as the percentage of the copper (II) oxide present in the loss free sorbent after ignition of the sorbent at 900 ° C).

4. A process according to any one of claims 1 to 3 wherein the sorbent has a copper metal surface area in excess of 20 $m^2.g^{-1}$.

5. A process according to any one of claims 1 to 4 wherein the organic stream contains one or more reactive sulphur compounds in addition to elemental sulphur and these reactive sulphur compounds are removed by passage of the stream through a bed of a zinc oxide and/or copper oxide sorbent prior to contact with the metallic copper sorbent.

6. A process according to claim 5 wherein byproducts formed by the reaction of reactive sulphur compounds with the copper and/or zinc oxide sorbent are removed prior to contacting the stream with the metallic copper sorbent.

7. A process according to any one of claims 1 to 6 wherein the metallic copper sorbent is regenerated after a period of time in use by reducing the spent metallic copper sorbent with a stream of hydrogen.

8. A process according to claim 7 wherein the reduction is effected at 90-250 ° C.

Fig.1.