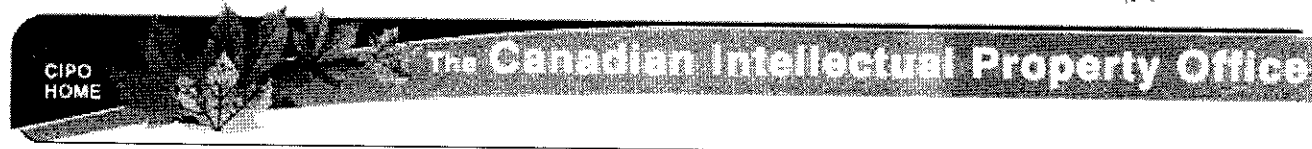




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(54) SULPHUR REMOVING PROCESS

(54) PROCEDE A ENLEVER LE SOUFRE

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My invention relates to the removal of sulfur from gases. It has particular reference to the purification of gas mixtures containing CO and H by the removal of the sulfur combined with organic radicals which are admixed to these gases, and it is an object of my invention to provide means, whereby this purification is rendered easier and more effective than similar purification processes hitherto in use.

As is well known to those skilled in the art, the removal of all the sulfur, including that combined with organic radicals, from gas mixtures containing CO and H has hitherto been effected either by catalytical decomposition of the organic sulfur compounds at a temperature above normal followed by extraction of the hydrogen sulfide formed by this decomposition, or by directly combining these compounds with gas purification masses capable of absorbing sulfur at a temperature above normal.

Either way of operating the purification involves drawbacks of its own. While it is true that the catalytic purification is a continuous operation not requiring the addition of chemicals other than those designed to extract the hydrogen sulfide, it is impossible to thus effect in a single operation the complete removal of the sulfur including the last traces and to obtain gases of a purity such as is required for instance for the catalytic hydrogenation of carbon monoxide. On the other hand the direct extraction of the sulfur by chemical combination at an elevated temperature, while allowing the removal of all the sulfur excepting only insignificant traces,

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requires a corresponding consumption of purification chemicals for each gram of sulfur extracted and in addition the necessity of regenerating these chemicals.

According to the present invention I effect the purification of gas mixtures containing CO and H in two stages, in the first of which the bulk of the organic sulfur compounds is decomposed in a manner well known per se by catalytic reaction at an elevated temperature. I thereafter prefer extracting the hydrogen sulfide formed in the reaction and then fix completely the whole of the remaining sulfur at an elevated temperature by means of chemicals which absorb sulfur.

I thus succeed in radically removing the sulfur from gas mixtures containing CO and H without their composition suffering any other change. By thus combining the two greatly differing modes of purification I further obtain a purification process which offers quite a number of advantages as compared with each of these processes.

The catalytic purification which forms the first stage of my process is no more required to remove the last traces of sulfur and I am therefore enabled to operate in this stage at high gas velocities, so that the main quantity of the sulfur can be extracted quickly. Furthermore I need not fear that under the influence of a catalytic action of the walls of the apparatus, such as the heat exchanger, organic sulfur compounds might be regenerated from CO and H<sub>2</sub>S when the gases leaving the apparatus cool down, and I am therefore at liberty to transfer to the entering gas and to thus recover without any drawback the palpable heat of the gas treated in the first stage.

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Furthermore, since it is not necessary that the decomposition be carried out in a quantitative manner, the gas may still carry along a small percentage of hydrogen sulfide. It is therefore possible to insert the catalytic decomposition in the normal process of removal of the hydrogen sulfide at a point where the main proportion of hydrogen sulfide has already been extracted. Therefore a separate extraction of hydrogen sulfide cannot only be dispensed with at the end of the catalytic purification stage, but I also recover, during the normal purification process by chemical combination with iron oxide or the like, that part of the sulfur which was originally present in the gas mixture in combination with organic radicals.

As regards the second stage of the process, the combined process according to this invention also offers a number of advantages. Since, if the first stage is operated in a correct manner, 90% or more of the sulfur may be removed, the consumption of chemical purification mass in the second stage will be low. Apart therefrom I have found that this mass is now enabled to retain the last traces of sulfur in a far more perfect manner than if the first stage of the process were omitted. I have for instance found that when using purification masses consisting of a mixture of an iron oxide and an alkali carbonate, the efficiency of the mass up to the point where the first traces of sulfur appear in the gas escaping from the mass is the greater the lower the initial concentration of the gas.

Thus the technical effect obtained by the combination of the two stages is far superior to a purely additive effect of the two individual stages.

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Instead of carrying the second stage through with a mixture of iron oxide and alkali carbonate I may also pass the gas first in contact with an alkali carbonate in order to decompose the organic sulfur compounds, which may still be present, whereupon the hydrogen sulfide formed in the reaction is fixed by passing it in contact with iron oxide or the like.

There are a number of gas mixtures including for instance coke oven gas, which it is impossible to completely free from sulfur by one or the other of the two operations separately, this being due to the special nature of the compounds contained therein. The catalytic purification is hindered partly by the presence of heavy hydrocarbons. On the other hand the chemical purification at a high temperature, for instance by means of a mixture of chemicals such as mentioned above, can be carried through only at so low a temperature that some particularly resistive sulfur compounds, such as for instance thiophen, will not be decomposed.

According to the present process it is possible to quantitatively free from sulfur also gases of the kind here mentioned, including coke oven gas, by operating the first stage at so high a temperature that the more resistive sulfur compounds are converted into other organic or inorganic compounds which can subsequently be extracted in one of the two processes of sulfur fixation.

In order to extract the sulfur in the second stage any well known purification masses, including for instance finely divided metals, may be used, but I have found it particularly advantageous to operate this stage with purification masses which are capable of binding and removing all the sulfur at

comparatively low temperatures. I have found that masses containing, besides an iron oxide, also a comparatively large percentage of an alkali carbonate allow extracting also the last traces of sulfur at temperatures ranging between 150 and 300°C. On the other hand the catalytic decomposition in the first stage always requires operation at a temperature above 300°C.

I am thus also enabled to heat up the gases about to enter the second stage with the aid of the hot gases resulting in the first stage, and I am therefore in a position to keep the heat losses, at least in the first stage, low by heat exchange between the entering and the escaping gases of reaction. As pointed out in the foregoing, this is possible without any disadvantage owing to the purification in two stages.

If the process is operated in combination with a subsequent catalytic hydrogenation of the carbon monoxide I can also utilize in the second stage spent hydrogenation catalysts for binding and retaining the last traces of sulfur, since here it is only a question of small quantities.

It is also possible to first pass the gas in the second stage in contact with a special purification mass, consisting for instance of an iron oxide and soda, at a raised temperature and to extract the last traces of sulfur with the aid of spent hydrogenation catalysts, it being even possible to carry this operation through in the hydrogenation apparatus proper. Such a utilization of the hydrogenation catalysts is possible for instance without any disadvantage if they are subsequently regenerated by dissolving them in nitric acid and reprecipitating them, the sulfur being recovered as sulfate in the regeneration liquor.

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Alternatively it is also possible to employ chemical purification masses, after they have taken up a sufficient percentage of sulfur, as decomposition catalysts at higher temperature.

I may therefore proceed with particular advantage in such manner that a body of purification mass is first used for extracting the last traces of the sulfur still remaining in the gas mixture, whereupon the same body of purification mass is inserted in the corresponding phase of the first stage of the process to be there saturated with sulfur, the temperature being at first held substantially constant for instance at  $300^{\circ}\text{C}$ , whereupon the same body serves as decomposition catalyst at a temperature which is preferably raised for instance to  $400^{\circ}\text{C}$ . It could not be foreseen that the same mass would be capable of such double use.

In practising my invention I may for instance proceed as follows:

Example 1: Crude watergas is first freed from all but the last traces of hydrogen sulfide by passing it in contact with about two thirds of the quantity of an iron oxide required for the complete extraction of all the hydrogen sulfide. The partly purified gas is now heated up in a heat exchanger by means of the heat emitted by watergas leaving the catalytic purification apparatus and is thereafter heated to  $400^{\circ}\text{C}$  in a separate heater, whereupon it is treated with a decomposition catalyst which may consist for instance of sulfurised iron turnings or steel wool or of a mixture of one part by weight cobalt sulfide and two parts molybdenum oxide, or of nickel metal precipitated on a ceramic carrier. The gas thereafter flows through the heat ex-

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changer and is cooled to room temperature in a cooler, whereupon it is passed in contact with the remaining third of the dry purification mass for the removal of the hydrogen sulfide. The gas is now heated up to 250°C by the heat of the waste gases from the gas heater and is passed at this temperature across a granulated purification mass being a mixture of two parts of a mass containing iron oxide (Lux mass) and one part soda. The watergas thus treated, while being otherwise unchanged, does not contain any traces of sulfur which might be ascertained by the usual analytical means.

Example 2: A mixture of equal parts watergas and coke oven gas is passed first through moist suspended iron oxide, thereafter through a heat exchanger, through a heater, at 450°C through a decomposition catalyst consisting of a spent mixture of Lux mass and soda which has absorbed sulfur, again through the heat exchanger, through a cooler, through another body of Lux mass for the removal of hydrogen sulfide, through a gas heater supplied with the waste gases from the first heater, thereafter at 230°C through another body of Lux mass and soda and finally through a spent hydrogenation catalyst in order to be freed from the .5 grams residual sulfur contained in 100 cubicmetres of the gas.

This treatment leads to a complete desulfuration of the gas. It requires only minimum quantities of fresh chemical purification mass and of heating gas, and the bulk of the sulfur bound to organic radicals is deposited in the dry purification mass in utilisable form. Obviously this mode of proceeding is particularly advantageous.



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Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

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## I CLAIM:-

1. The multistage process of removing sulfur in organic combination from a gas mixture containing CO and H<sub>2</sub> which comprises decomposing, in the first stage of the process, part of the organic sulfur compounds at a temperature above normal by catalytic action, and passing, in the second stage, the partly desulfurized gas mixture at a temperature above normal in contact with a substance capable of binding the residual sulfur by chemical reaction.

2. The multistage process of removing sulfur in organic combination from a gas mixture containing CO and H<sub>2</sub> which comprises decomposing, in the first stage of the process, part of the organic sulfur compounds at a temperature above normal by catalytic action, removing the hydrogen sulfide formed in this stage and passing, in the second stage, the partly desulfurized gas mixture at a temperature above normal in contact with a substance capable of binding the residual sulfur by chemical reaction.

3. The multistage process of removing sulfur in organic combination from a gas mixture containing CO and H<sub>2</sub> which comprises decomposing, in the first stage of the process, part of the organic sulfur compounds at a temperature above normal by catalytic action, and passing, in the second stage, the partly desulfurized gas mixture at a temperature above normal in contact with an iron oxide.

4. The multistage process of removing sulfur in organic combination from a gas mixture containing CO and H<sub>2</sub> which comprises decomposing, in the first stage of the process, part of the organic sulfur compounds at a temperature above normal by catalytic action, and passing, in the second stage, the partly desulfurized gas mixture at a temperature above normal in contact with a mixture of an iron oxide and an alkali carbonate.

5. The multistage process of removing sulfur in organic combination from a gas mixture containing CO and H<sub>2</sub> which comprises decomposing, in the first stage of the process, part of the organic sulfur compounds at a temperature above normal by catalytic action, and passing, in the second stage, the partly desulfurized gas mixture at a temperature above normal in contact with an alkali carbonate and thereafter with an iron oxide.

6. The multistage process of removing sulfur in organic combination from a gas mixture containing CO and H<sub>2</sub> which comprises decomposing, in the first stage of the process, part of the organic sulfur compounds at a temperature above normal by catalytic action, and passing, in the second stage, the partly desulfurized gas mixture at a temperature above normal in contact with a spent hydrogenation catalyst.

7. The multistage process of removing sulfur in organic combination from a gas mixture containing CO and H<sub>2</sub> which comprises decomposing, in the first stage of the process, part of the organic sulfur compounds at a temperature above normal by catalytic action, and passing, in the second stage, the partly desulfurized gas mixture at a temperature above normal in contact with a mixture of an iron oxide and an alkali carbonate and thereafter with a spent hydrogenation catalyst.

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8. The multistage process of removing sulfur in organic combination from a gas mixture containing CO and H<sub>2</sub> which comprises decomposing, in the first stage of the process, part of the organic sulfur compounds at a temperature above normal by catalytic action, and passing, in the second stage, the partly desulfurized gas mixture at a temperature above normal in contact with a substance capable of binding the residual sulfur by chemical reaction, as catalyst being employed in the first stage a substance, which has already served in the second stage to bind sulfur by chemical reaction.

*Otto Kuelen*

Oberhausen, Germany, October 21, 1955.