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PATENT SPECIFICATION

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3695

COMPLETE SPECIFICATION.

Process for Desulphurising Gases.

We, STUDIEN- UND VERWERTUNGS-GESELLSCHAFT MIT BESCHRANKTER HAFTUNG, of Mülheim-Ruhr, Germany, a Company organised and existing under the laws of the German State, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

For the purpose of removing all the sulphur compounds—including those of organic origin—from gases containing carbon monoxide and hydrogen it has been proposed not only to decompose the organic sulphur compounds catalytically with the assistance of heat followed by the removal of the sulphuretted hydrogen formed, but also to effect the direct removal thereof by means of bodies which absorb sulphur while at a high temperature.

An example of the first method is disclosed by Specification No. 391,660 according to which the organic sulphur is converted into sulphuretted hydrogen by passage over a ferrous sulphide catalyst at a temperature which may be between 700°—900° F., followed by the removal of the hydrogen sulphide by contact with a suitable absorbent, such, for example, as "Lux Mass" or "Alpha Lux" without reduction of temperature. Similarly, an example of the second method is contained in the Specification No. 452,417 according to which, for the removal of sulphur compounds from gases containing carbon monoxide and hydrogen, alkali carbonates are employed to the extent of at least 10% in intimate admixture with reactive oxides or hydroxides of iron at temperatures lying between 150° C. and 300° C. but maintained so low that the purifying mixture at no time produces subordinate reactions of carbon monoxide.

Both methods have their particular disadvantages. It is true that the catalytic purification is continuous and does not require the use of chemicals other than those necessary for removing the sulphuretted hydrogen. It is, however, known that the last traces of sulphur cannot possibly be completely removed in this way in a single operation so as to obtain gases purified to the extent required for example, for the catalytic hydrogenation of carbon monoxide. Further, although the direct removal of the sulphur by chemical combination under heat enables all the sulphur to be removed, except for negligible traces, it involves for each gramme of sulphur absorbed a corresponding consumption of the absorbent material and the necessity for regeneration.

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According to the present invention purification is carried out in two stages, in the first of which the bulk of the organic sulphur compounds is decomposed catalytically at high temperatures above 300° C. whereupon the sulphuretted hydrogen formed is removed at reduced temperature, after which in the second stage the residual sulphur compounds are completely taken up by contacting the gas, at elevated temperatures below 300° C., with sulphur absorbing masses which have the capacity for absorbing not only the remaining hydrogen sulphide produced during the catalytic decomposition of the organic sulphur compounds, but also the organic sulphur still present in the gas. In this manner gases containing carbon monoxide and hydrogen can be completely desulphurised without the composition of the gases being altered. At the same time the combined use of the two entirely different methods of purification enables the total purification to be carried out in a manner that is far more advantageous in many respects than in the case of one of the two methods alone.

The catalytic purification employed as the first stage is not expected to effect the—for it difficult—removal of the last traces of sulphur. Consequently in the first place it is possible to operate at high velocities and thus rapidly to transform the bulk. Secondly there is no longer any need to take into consideration that under the influence of the walls of the apparatus which have a catalytic action—such as the walls of heat exchangers—during cooling of the effluent gases a more or less complete reversion from carbon monoxide and sulphuretted hydrogen to the form of organic sulphur compounds

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takes place. Hence in this case the sensible heat of the effluent gases can without disadvantage be transferred to the incoming gas in heat exchangers and so recovered.

The first stage catalytic decomposition of the organic sulphur compounds can be introduced into the course of the normal removal of the hydrogen sulphide. The usual removal of the hydrogen sulphide with a dry purifying composition is effected in known manner by the use of a number of dry purifiers which are traversed in succession by the gases from which the hydrogen sulphide is to be removed. The first stage catalytic removal of the organic sulphur compounds is advantageously introduced into the course of the removal of the hydrogen sulphide at a point where already the main quantity of the hydrogen sulphide has been removed from the gases. The hydrogen sulphide produced during the catalytic decomposition of the main quantity of the organic sulphur compounds is thereby also removed by means of the dry purifying composition during a subsequent removal of hydrogen sulphide, that is to say, without any necessity for apparatus specially for the removal of the hydrogen sulphide. Furthermore during the normal sulphur purification, for example, by means of ferric oxide, the sulphur which originally was present in the gases in organic combination is in this way recovered.

The combined process according to the invention is also advantageous to the hot purification forming the second stage for the removal of organic sulphur compounds. Since given suitable precautions 90% and over of the organic sulphur compounds can be decomposed in the first stage of the removal of organic sulphur compounds the consumption of purifying material in the second stage is small. Moreover, it has been found that the last traces of sulphur are far more effectively retained by the hot purification mass than when the first stage of the removal of organic sulphur compounds is omitted. Thus, for example, it has been found that with the use of masses composed of iron oxides or hydroxides, for example, ferric oxide, and alkali metal carbonate for the hot-purification or second stage, the capacity of the purifying mass for taking up the last traces of sulphur is in inverse proportion to the original concentration of the sulphur. The practical effect of the combined action of the two stages for the removal of organic sulphur compounds is therefore greater than the merely additive effect of the two stages separately.

Certain gases, such as coke-oven gas, cannot be completely desulphurised by means of only one of the stages owing to the special nature of the compounds present in the gases. On the one hand the catalytic purification is impaired by heavy hydrocarbons. On the other hand the hot purification—by means for example, of the aforesaid purification masses—can be carried out only at such low temperatures as have no effect on certain particularly stubborn sulphur compounds, such as thiophene, as by the use of temperatures high enough to effect the decomposition, for example, of thiophene, the carbon monoxide is reduced to methane, whereby the gases to be cleaned would suffer an undesirable change of composition.

The present process enables gases such as coke-oven gas to be quantitatively desulphurised without an undesired reduction of the carbon monoxide taking place by employing in the first stage such a high temperature that the resistant organic sulphur compounds are converted into other organic or inorganic sulphur compounds which are afterwards held back in the second stage of the process.

For the purpose of keeping back the sulphur in the second stage any suitable known absorbents of sulphur, such as finely divided metals, may be used. It is, however, necessary to use purifying materials which have the capacity of completely removing the sulphur, even at relatively low temperatures. Thus, the absorbent materials referred to are effective for extracting the last traces of sulphur, even at temperatures of 150—300° C.; on the other hand temperatures of above 300° C. are needed throughout for the catalytic decomposition in the first stage.

At the same time the possibility is afforded of heating the gases prior to the second stage by means of the effluent heating gases from the heating operation preceding the first stage. The heat losses can at the same time be kept low at least in the first stage by heat exchange between the incoming and the effluent reaction gases, an arrangement which, as mentioned, can be carried out without disadvantage in two stages, owing to the purification.

If the process is carried out in connection with a subsequent catalytic hydrogenation of the carbon monoxide by the use, for example, of finely divided cobalt as the catalyst, it is also possible to use spent hydrogenation catalysts in the second stage for keeping back the last traces of sulphur, as only small quantities are involved. In the second stage the gas can be first passed through an absorbent material such, for example, as ferric oxide and soda—at an elevated temperature below 300° C., and the last traces of sulphur removed with a spent hydrogenation catalyst, which may be left in the hydrogenation apparatus. Such use of hydrogenation catalysts is possible without disadvantage for example when they are regenerated for their specific purpose by dissolving in nitric acid and then again precipitating, the sulphur passing as sulphate into the regeneration liquor.

Conversely, spent purification masses of the second stage can—so far as they have absorbed sufficient sulphur—be afterwards employed at a higher temperature as catalysts in the first stage of the decomposition of organic sulphur compounds. Consequently desulphurisation according to the invention can be carried out with great advantage by first using one and the same purification mass for removing the last traces of the residual sulphur, by decomposing the residual organic sulphur compounds and at the same time absorbing the hydrogen sulphide produced as well as any that is still present in the gas, and finally employing it as a decomposition catalyst at a temperature which has been raised advantageously to, for example, 400° C. This double applicability could not have been foreseen.

EXAMPLE 1.

Crude water gas is first freed from sulphuretted hydrogen, except for small traces, by dry purification, the water gas being brought into contact with two-thirds of the amount of absorbent (ferric oxide) needed for the complete removal of sulphuretted hydrogen. It is then heated in a heat exchanger by the water gas coming from the catalytic purification and is raised to a temperature of 400° C. in a gas heater. Thereupon it is treated with a decomposition catalyst, which may consist, for example, of sulphurised metal turnings or steel wool or of a mixture of 1 part of cobalt sulphide and 2 parts of molybdenum oxide or of nickel deposited on a ceramic carrier. The gas is then again passed through the heat exchanger and reduced to room temperature in a cooler. Thereupon it is treated with the remaining one-third of the dry-purifying agent for the purpose of removing the sulphuretted hydrogen. The gas is next heated to 250° C. by the exhaust gases from the gas heater, and is passed at that temperature through a granulated hot-purifying mixture of 2 parts of "Luxmasse" and 1 part of soda. On issuing therefrom sulphur is no longer detectable by the ordinary analytical methods in the water gas, the composition of which otherwise remains unchanged.

EXAMPLE 2.

A mixture of equal parts of water gas and coke-oven gas is submitted to the following:—The mixture is first freed, by the wet method, from sulphuretted hydrogen by the use of ferric oxide in suspension; it is then passed through a heat exchanger and through a heater; then subjected to the action of a decomposition catalyst at 450° C., which consists of a spent sulphuretted hot purifying mixture of "Luxmasse" and soda; the mixture is then passed through the heat exchanger and then through a cooler, after which it is purified by the dry method for the removal of the sulphuretted hydrogen by means of "Luxmasse"; thereupon the mixture passes through a gas heater fed with the heating gases discharged from the first heater, after which it is treated at 230° C. with the hot purifying mixture as in Example 1 and finally with a spent hydrogenation catalyst, for example, finely divided cobalt having a content of 0.5 gm. of residual sulphur per 100 cubic meters. These operations result in the complete desulphurisation of the gas, requiring only the minimum quantity of fresh hot-purifying material and heating gas, and at the same time changes the bulk of the organically combined sulphur into a form that is utilisable in the dry purification. It will be seen that this process produces a particularly advantageous total effect.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for removing in two stages the organically combined sulphur from gases containing carbon monoxide and hydrogen, characterised in that the first stage consists in passing the gas at elevated temperatures above 300° C. over catalysts for the catalytic decomposition of the bulk of the organic sulphur compounds, followed by the removal at reduced temperature of the sulphuretted hydrogen formed and in that the second stage consists in the removal of the residual sulphur by contacting the gas with sulphur absorbing masses at elevated temperatures below 300° C.

2. A process according to claim 1, characterised in that mixtures of carbonates of the alkali metals and of oxides or hydroxides of iron are employed for removing the residual sulphur in the second stage.

3. A process according to claims 1 and

2, characterised in that spent, sufficiently sulphuretted masses that have been used in carrying out the second stage are employed in the first stage of the process as decomposition catalysts.

Dated this 30th day of October, 1935.

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