PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in and relating to the Purification of Gases

We, NORMAN BOOTH and LESLIE JOHN JOLLEY, both of the Fuel Research Station, River Way, Blackwall Lane, East Greenwich, S.E.10, in the County of London, and both British subjects, do hereby declare the nature of this invention to be as follows:—

This invention relates to the purification of gases or mixtures of gases, and in particular coal gas, by the removal of organic sulphur compounds.

It is often desirable to reduce the organic sulphur content of gases to a low figure. For example, in the synthesis of methane or higher hydrocarbons from coal gas or water gas, amounts of sulphur greater than about 0.1 grain/100 cu. ft. may cause excessive poisoning of the synthesis catalyst.

In accordance with our invention we pass the gas or mixture of gases containing organic sulphur impurities through a heated tube containing iron deposited on a support by the thermal decomposition of iron carbonyl.

We find that the organic sulphur is largely converted to hydrogen sulphide, which can be absorbed in the usual manner.

Suitable supports for the iron are porcelain rings, porous pot, glass beads or copper gauze.

The tube containing the finely divided iron may be maintained for example at a temperatures between 300 and 600°C. and preferably at a temperature above 450°C.

If desired the gas may first be treated in any manner known to remove a substantial proportion of the organic sulphur, such as by scrubbing with gas oil, or by passing it over an absorbent such as active charcoal.

In particular, when it is desired to reduce the sulphur content to a very low figure, and it is found that some of the organic sulphur compounds are resistant to hydrogenation by the iron catalyst described, the gas may first be treated in any known manner to remove these other compounds.

By the use of complementary processes in this way the final sulphur content of the gas may be reduced to 0.05 grain or less/100 cu. ft.

As examples of the manner in which the invention can be used the following experimental results are quoted:

(a) Coal gas free from hydrogen sulphide but containing 20.2 grains of organic sulphur per 100 cu. ft. was passed at a space velocity of 400 vols./vol./hour over iron at 500°C. The iron was prepared by passing water gas containing iron carbonyl through a tube containing a bed of porcelain rings positioned by copper gauze and maintained at 400—450°C. The hydrogen sulphide formed was absorbed by iron oxide at atmospheric temperature. The sulphur content of the effluent gas was 0.8 grain per 100 cu. ft.

(b) Coal gas free from hydrogen sulphide but containing 20.2 grains of organic sulphur per 100 cu. ft was scrubbed with gas oil at a rate of 4 gals./100 cu. ft./hour and the organic sulphur thereby reduced to 11.9 grain/100 cu. ft. The scrubbed gas was then treated as described in (a) and the sulphur content of the effluent gas was less than 0.05 grain/100 cu. ft.

It will be understood that although our invention has been described with particular reference to the preparation of purified gas for use in the synthesis of methane or higher hydrocarbons, it is equally applicable to the desulphurisation of town's gas and in other cases where it is desired to reduce the organic sulphur content of gases or mixture of gases.

Dated this 9th day of July, 1941.

NORMAN BOOTH,
LESLIE JOHN JOLLEY.

[*Price* 1/-]

COMPLETE SPECIFICATION

Improvements in and relating to the Purification of Gases

We, NORMAN BOOTH and LESLIE JOHN JOLLEY, both of the Fuel Research Station, River Way, Blackwall Lane, East Greenwich, S.E.10, in the County of London, and both British subjects, 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:—

This invention relates to the removal of organic sulphur compounds from gases or mixtures of gases containing a sufficiency of hydrogen, and in particular from coal gas, coke oven gas or water gas. By "sufficiency" we mean that sufficient hydrogen is present to combine with the sulphur to form hydrogen sulphide.

It is already known to convert organic sulphur present in coal gas into hydrogen sulphide by passing it through a tube containing a catalyst such as iron at high temperature; according to a prior proposal the temperature could be kept down to about 400—450°C. by heating the gas itself before its passage over the catalyst to a temperature at least 80 per cent of the temperature of the tube.

We have found that of a number of different forms of iron, that obtained by thermal decomposition of iron carbonyl is the only one which, for use as a catalyst in the removal of organic sulphur from gases, combines the advantages of high conversion, high space velocity and long life. In accordance with our invention therefore we pass the gas or mixture of gases containing organic sulphur impurities through a heated tube containing iron deposited on a support by the thermal decomposition of iron carbonyl; we have found that the temperature should be at least 450°C. and may be as much higher as practical considerations will allow. The hydrogen sulphide formed is absorbed in any usual manner.

Suitable supports for the iron are porcelain rings, porous pots, glass beads or copper gauze.

When the activity of the iron falls below the desired value, reactivation can be effected by heating it in an oxidisng gas, e.g. in a current of air and then treating it with a reducing gas, such as hydrogen, water gas or coal gas, also at high temperature. The suitable temperature for both the oxidising and reducing treatments is that at which the iron is used as a catalyst, i.e. 450°C. or upwards.

If desired the gas may first be treated in any manner known to remove a substantial proportion of the organic sulphur, such as by scrubbing with gas oil, or by passing it over an absorbent such as active charcoal.

In particular, when it is desired to reduce the sulphur content to a very low figure, and it is found that some of the organic sulphur compounds are resistant to hydrogenation by the iron catalyst described, the gas may first be treated in any manner known to remove these other compounds.

By the use of complementary processes in this way the final sulphur content of the gas may be reduced to 0.02 grain or less/100 cu. ft.

The invention lends itself well to the treatment of coal gas or water gas to be used in the synthesis of methane or higher hydrocarbons, when amounts of sulphur greater than about 0.1 grain/100 cu. ft. may cause excessive poisoning of the synthesis catalyst. Notwithstanding this low figure, in the process according to the invention a space velocity up to about 1000 vols./vol./hour can be used, while for the simple desulphurization of town's gas where a reduction to about 1 grain/100 cu. ft. suffices a substantially higher space velocity can be used.

The active life of the catalyst for purification of synthesis gases, i.e. the period during which it will, when used in conjunction with an oil scrubbing process, reduce the organic sulphur content of the coal gas to less than 0.1 grain per 100 cu. ft., is 10—15 days at a space velocity of 1000 vols./vol./hour. After this its activity diminishes slowly with time, but if reactivated as described above it retains its activity for a further period of 10—15 days, and the reactivation process may be repeated indefinitely as necessary. If it is not necessary for the organic sulphur content of the gas to be reduced to as low a figure as 0.1 grain per 100 cu. ft., the active life of the catalyst before reactivation is necessary is corespondingly longer.

As examples of the manner in which the invention can be carried out the following experimental results are quoted:

(a) Coal gas free from hydrogen sulphide but containing 20.2 grains of organic sulphur per 100 cu. ft. was passed at a space velocity of 400 vols./vol./hour over iron at 500°C. The iron was prepared by passing water gas

containing iron carbonyl through a tube containing a bed of porcelain rings positioned by copper gauze and maintained at 400—450°C. The hydrogen sulphide formed was absorbed by iron oxide at atmospheric temperature. The sulphur content of the effluent gas was 0.8 grain per 100 cu. ft.

(b) Coal gas free from hydrogen sulphide but containing 20.2 grains of organic sulphur per 100 cu. ft. was scrubbed with gas oil at the rate of 4 gals./100 cu. ft. and the organic sulphur thereby reduced to 11.9 grains per 100 cu. ft. The scrubbed gas was then passed at a space velocity of 1000 vols./vol./hour over iron prepared as described in (a), at 500°C. After removal of the hydrogen sulphide formed the organic sulphur content of the effluent gas was less than 0.5 grain per 100 cu. ft., and remained below this figure for a period of 10 days, after which it increased slowly. The catalyst was restored to its original activity by passing a slow stream of air over it at 500°C., at a space velocity of 3500 for 2 hours and then reducing with hydrogen at 500° C. at a space velocity of 3500 for 1 hour. The catalyst thus reactivated continued to reduce the organic sulphur content of oil-scrubbed coal gas in the conditions described above to less than 0.05 grain per 100 cu. ft. for a further period of 15 days without any falling-off in activity.

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 reducing the organic sulphur content of gases or mixtures of gases containing a sufficiency of hydrogen, which comprises the steps of passing the gas or mixture through a tube heated to 450° C. or above and containing iron which has been deposited on a support by the thermal decomposition of iron carbonyl, and then absorbing the hydrogen sulphide formed in the first mentioned step.

2. A process according to claim 1 in which the iron is reactivated from time to time by heating it in an oxidising gas and then treating it with a reducing gas, also at high teamperature.

3. A process according to either preceding claim in which the gas or mixture is previously treated by another process for the reduction of organic sulphur con tent, as by scrubbing with gas oil or by passage over an absorbent such as active charcoal.

4. A process for reducing the organic sulphur content of coal gas substantially as set forth in either of the examples particularly described herein.

Dated the 9th day of July, 1942.

H. K. WARR-LANGTON,
Agent for the Applicants.

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