PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

No. 33,276, A.D. 1930.

Improvements in Desulphurisation of Gases.

I, James Yate Johnson, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany), to be as follows:—

It has already been proposed to desulphurise gases containing hydrogen sulphide, such as the gases from the distillation of coal and to recover the sulphur, by passing the gases, together with the amount of air or oxygen requisite for the oxidation of the hydrogen sulphide into sulphur over catalysts, especially active carbon. The oxidation to sulphur is attended with a considerable evolution of heat, which leads to a great increase in the temperature of the catalyst. It has further been proposed to carry out this process at such high temperatures that the sulphur is obtained in a molten condition. Difficulties however then arise owing to the fact that the molten sulphur, which is highly viscous immediately above its melting point, does not run off sufficiently fast, and clogs up the entire contact chamber, so that the resistance to the passage of the gas increases very considerably Moreover, the molten sulphur is far more difficult to recover from the active carbon than that which is deposited at temperatures below the melting point of sulphur. Although by working at still higher temperatures, readily fluid sulphur can be obtained continuously, this proposal has failed to lead to any practicable process owing to the accurate regulation of temperature required. On the contrary it has always been found that notwithstanding suitable cooling, the process becomes impracticable when the gases contain a considerable proportion of sulphur, such as about 15 grams per cubic metre of the gas.

My foreign correspondents have now found that the said process can be applied, without difficulty, even to gases containing more than 7 grams of sulphur per cubic metre (such as the waste gases from destructive hydrogenation processes and from the cracking and destructive distillation of sulphur-bearing organic substances) if the hydrogen sulphide content of the gases to be exposed to the catalyst, be first decreased by the addition of gases which are free from or low in sulphur. The amount of diluent gases added is such that the sulphur content of the gaseous mixture does not exceed about 7 grams of sulphur per cubic metre. A portion of the gas which has been freed from sulphur in the process itself may preferably be employed as the diluent, but other gases, free from or low in sulphur, such as industrial waste gases, hydrogen, nitrogen or carbon dioxide, may also be employed with advantage.

The oxidation of the hydrogen sulphide can be facilitated in any known or suitable manner by the presence of basic substances. In particular a small proportion of basic nitrogen compounds which may be solid or volatile, as for example ammonia, or ammonium carbonate constitutes a suitable addition either to the gases or the contact mass. Use may also be made of other basic substances such as sodium bicarbonate.

In the desulphurisation of gases which contain substances that are injurious to the catalyst such as benzene hydrocarbons, it is often beneficial to subject the gases before hand to a preliminary purification, for example with sulphuric acid or other suitable absorbents so as to remove the said injurious constituents.

The following example will further illustrate the nature of this invention which however is not restricted thereto.

Example.

1000 cubic metres of a waste gas obtained in the cracking of sulphur-bearing oils, and containing 25 grams of sulphur per cubic metre, are treated with an addition of 2600 cubic metres of hydrogen or nitrogen, so that the sulphur content of the resulting mixture amounts to 7 grams per cubic metre. The mixture is then treated with the amount of air needed to oxidise the hydrogen sulphide at room temperature or slightly higher temperatures for example at 30° Centigrade, and with 0.1 gram of ammonia per cubic metre, and is passed through a layer of

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active carbon, in which the oxidation of the hydrogen sulphide to sulphur takes place. A portion of the sulphur-free gas issuing from the apparatus is cooled and is then mixed, in the said proportion, with further incoming quantities of the initial material to be desulphurised.

Dated this 5th day of November, 1930.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C. 2,
Agents.

PROVISIONAL SPECIFICATION.

No. 38,889, A.D. 1930.

Improvements in the Desulphurisation of Gases.

I, James Yate Johnson, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany), to be as follows:—

It has already been proposed to desulphurise gases containing hydrogen sulphide, as for example coal distillation gases, by leading the gases together with an amount of air or oxygen sufficient to oxidise the hydrogen sulphide to sulphur, and preferably in the presence of small amounts of ammonia over active carbon. In the case of gases having a high content of hydrogen sulphide, as for example those containing about 15 grams of sulphur per cubic metre, the process can no longer be carried out successfully on an industrial scale. In the desulphurisation by means of active carbon, the speed of reaction is largely dependent on the relative moisture content of the gases to be desulphurised. The relative humidity of the gases should as a rule be at least 15 to 20 per cent, in order successfully to carry through the purification. However, in the case of gases having a high content of hydrogen sulphide, such a reduction of the relative moisture content of the gases takes place by reason of the reaction heat that the catalytic reaction only proceeds very slowly and finally comes to a standstill. By reason of this fact it is practically impossible completely to desulphurise gases containing more than from 7 to 8 grams of sulphur per cubic metre in a single operation in an economical manner.

My foreign correspondents have now found that gases having a high content of hydrogen sulphide, corresponding to at least 8 grams of sulphur per cubic metre, especially low temperature carbonisation gases, waste gases from the destructive hydrogenation of coals, tars, mineral oils and the like, or cracking gases are desulphurised in a very simple manner by the catalytic oxidation of the hydrogen sulphide to sulphur by means of active carbon, by carrying out the usual desulphurisation with air or oxygen, if desired with the addition of ammonia, in stages. The gas to be desulphurised is freed from a part of the hydrogen sulphide in the first stage, cooled, if necessary moistened, and then led over active carbon again. It is preferable to proceed so that the fraction of hydrogen sulphide oxidised in the first stage is considerably greater than those in the later stages of the purifying process.

It is usually advantageous to add the amount of air necessary for the oxidation likewise in appropriately measured portions before the single stages. The whole amount of air or oxygen may, however, be added to the gases to be desulphurised before the first stage, because a retardation of the reaction takes place by reason of the increase in temperature effected by the high content of hydrogen sulphide and therefore only a part of the oxygen is used up. The hot gases leaving the catalytic chamber are then cooled and if necessary moistened. They are then led over the active carbon in the subsequent stages with a considerably higher relative humidity than when leaving the first stage, whereby the unused oxygen still contained in the gases effects the further desulphurisation.

In the case of gases having a hydrogen sulphide content of from about 15 to 20 grams per cubic metre, a complete purification from hydrogen sulphide may be effected in this manner even by two stages, while in the case of gases having still higher hydrogen sulphide contents the process is preferably carried out in three or more stages.

When exhausted, the laden active carbon is regenerated by the extraction of the sulphur with a suitable solvent. By desulphurising in stages according to the present invention, the active carbon in the last stage is less affected and is therefore still active when the active carbon in the first stage is already exhausted and must be regenerated. After regenerating the active carbon of the first stage, the gas stream is therefore preferably passed in the reverse direction through the container so that the crude gas first comes into contact with partially laden active carbon.

The following Example will further illustrate the nature of this invention but the invention is not restricted to this Example.

EXAMPLE.

200 cubic metres of a cracking gas rich in hydrogen sulphide and containing 15 grams of sulphur per cubic metre are passed per hour through two iron containers each of 1 square metre cross section and each charged with 1 cubic metre of active carbon. Before entry into the first container the crude gas which is at a temperature of from 25° to 30° Centigrade, has added to it air in an amount of 4 cubic metres per hour. When the gas leaves the first container it only contains 5 grams of sulphur per cubic metre and has become heated to from 75° to 80° Centigrade by the heat of reaction. It is cooled to about 30° Centigrade in an interposed cooler and at the same time saturated with water vapour by rinsing with water. It then passes into the second container containing active carbon, 2 cubic metres of air and 29 litres of ammonia gas being added per hour at the same time. When leaving the second container the gas is practically free from hydrogen sulphide. After about 5 days the active carbon in the first container is exhausted. It is extracted with ammonium sulphide solution and steamed, and is then ready for further use.

Dated this 24th day of December, 1930.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C. 2,
Agents.

COMPLETE SPECIFICATION.

Improvements in the Desulphurisation of Gases.

I, James Yate Johnson, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

It has already been proposed to desulphurise gases containing hydrogen sulphide, such as the gases from the distillation of coal and to recover the sulphur, by passing the gases, together with the amount of air or oxygen requisite for the oxidation of the hydrogen sulphide into sulphur over catalysts, especially active carbon, preferably in the presence of small amounts of ammonia. The oxidation to sulphur is attended with a considerable evolution of heat, which leads to a great increase in the temperature of the catalyst. It has further been proposed to carry out this process at such high temperatures that the sulphur is obtained in a molten condition. Difficulties, however, then arise owing to the fact that the molten sulphur, which contains varying proportions of the very viscous amorphous sulphur modification above its melting point, does not run off sufficiently fast, and clogs up the entire contact chamber, so that the resistance to the passage of the gas increases very considerably. Moreover, the molten sulphur is far more difficult to recover from the active carbon than that which is deposited at temperatures below the melting point of sulphur. Although by working at still higher temperatures, readily fluid sulphur can be obtained continuously, this proposal has failed to lead to any practicable process owing to the accurate regulation of temperature required. On the contrary it has always been found that notwithstanding suitable cooling, the process becomes impracticable when the gases contain a considerable proportion of sulphur, such as about 15 grams per cubic metre of the gas.

In the desulphurisation by means of active carbon, the speed of reaction is largely dependent on the relative moisture content of the gases to be desulphurised. The relative humidity of the gases should as a rule be at least 15 to 20 per cent, in order successfully to carry through the purification. However, in the case of gases having a high content of hydrogen sulphide, such a reduction of the relative moisture content of the gases takes place by reason of the reaction heat that the catalytic reaction only proceeds very slowly and finally comes to a standstill. By reason of this fact it is practically impossible completely to desulphurise gases containing more than from 7 to 8 grams of sulphur per cubic metre in a single operation in an economical manner.

My foreign correspondents have now found that the said process can be applied, without difficulty, even to gases containing more than 7 grams of sulphur per cubic metre (such as the waste gases from destructive hydrogenation processes and from the cracking and destructive distillation of sulphur-bearing organic substances) by first producing from the said gases gases containing not more than 7 grams of sulphur and then catalytically desulphurising the latter in a known manner.

This result may be obtained in different ways. Thus, the process may be successfully carried out if the hydrogen sulphide content of the gases to be exposed to the catalyst, be first decreased by the addition of gases which are free from or low in sulphur. The amount of diluent gases added is such that the sulphur content of the gaseous mixture does not exceed about 7 grams of sulphur per cubic metre. A portion of the gas which has been freed from sulphur in the process itself may preferably be employed as the diluent, but other gases, free from or low in sulphur, such as industrial waste gases, hydrogen, nitrogen or carbon dioxide, may also be employed with advantage.

Another modification of the process according to the present invention consists in carrying out the usual desulphurisation with air or oxygen, if desired with the addition of ammonia, in stages. The gas to be desulphurised is freed from a part of the hydrogen sulphide in the first stage cooled, if necessary moistened, and then led over active carbon again. It is preferable to proceed so that the fraction of hydrogen sulphide oxidised in the first stage is considerably greater than those in the later stages of the purifying process.

It is usually advantageous to add the amount of air necessary for the oxidation likewise in appropriately measured portions before the single stages. The whole amount of air or oxygen may, however, be added to the gases to be disulphurised before the first stage, because a retardation of the reaction takes place by reason of the increase in temperature effected by the high content of hydrogen sulphide and therefore only a part of the oxygen is used up. The hot gases leaving the catalytic chamber are then cooled and if necessary moistened. They are then led over the active carbon in the subsequent stages with a considerably higher relative humidity than when leaving the first stage, whereby the unused oxygen still contained in the gases effects the further desulphurisation.

In the case of gases having a hydrogen sulphide content of from about 15 to 20 grams per cubic metre, a complete purification from hydrogen sulphide may be effected in this manner even by two stages, while in the case of gases having still higher hydrogen sulphide contents the process is preferably carried out in three or more stages.

When exhausted, the laden active carbon is regenerated by the extraction of the sulphur with a suitable solvent. By desulphurising in stages according to the present invention, the active carbon in the last stage is less affected and is therefore still active when the active carbon in the first stage is already exhausted and must be regenerated. After regenerating the active carbon of the first stage, the gas stream is therefore preferably passed in the reverse direction through the container so that the crude gas first comes into contact with partially laden active carbon.

The oxidation of the hydrogen sulphide can be facilitated in any known or suitable manner by the presence of basic substances. In particular a small proportion of basic nitrogen compounds which may be solid or volatile, as for example ammonia or ammonium carbonate constitutes a suitable addition either to the gases or to the contact mass. Use may also be made of other basic substances such as sodium bicarbonate either to the gases or the contact mass.

In the desulphurisation of gases which contain substances that are injurious to the catalyst, such as benzene hydrocarbons, it is often beneficial to subject the gases before hand to a preliminary purification, for example with sulphuric acid or other suitable absorbents so as to remove the said injurious constituents.

The following Examples will further illustrate how this invention may be carried out in practice, but the invention is not restricted to these Examples.

Example 1.

1000 cubic metres of a waste gas obtained in the cracking of sulphur-bearing oils, and containing 25 grams of sulphur per cubic metre, are mixed with 2600 cubic metres of hydrogen or nitrogen, so that the sulphur content of the resulting mixture amounts to 7 grams per cubic metre. The mixture is then treated with about 18 to 20 litres of air per cubic metre of gas mixture, which amount is needed to oxidise the hydrogen sulphide at room temperature or slightly higher temperatures for example at 30° Centigrade, and with 0.1 gram of ammonia per cubic metre, and is passed through a layer of active carbon, obtained by activating brown coal by means of steam in which the oxidation of the hydrogen sulphide to sulphur takes place. A portion of the sulphur-free gas issuing from the apparatus is cooled and is then mixed, in the said proportion, with further incoming quantities of the initial material to be desulphurised.

EXAMPLE 2.

200 cubic metres of a cracking gas rich in hydrogen sulphide and containing 15 grams of sulphur per cubic metre are passed per hour through two iron containers each of 1 square metre cross section and each charged with 1 cubic metre of active carbon obtained by activating brown coal by means of steam. Before entry into the first container the crude gas which is at a temperature of from 25° to 30° Centigrade, has added to it air in an amount of 4 cubic metres per hour. When the gas leaves the first container it only contains 5 grams of sulphur per cubic metre and has become heated to from 75° to 80° Centigrade by the heat of reaction. It is cooled to about 30° Centigrade in an interposed cooler and at the same time saturated with water vapour by rinsing with water. It then passes into the second container containing active carbon, 2 cubic metres of air and 29 litres of ammonia gas being added per hour at the same time. When leaving the second container the gas is practically free from hydrogen sulphide. After about 5 days the active carbon in the first container is exhausted. It is extracted with ammonium sulphide solution and steamed, and is then ready for further use.

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

1. A process for the desulphurisation of gases containing more than 7 grams of sulphur per cubic metre by means of active carbon which consists in first producing from the said gases gases containing not more than 7 grams of sulphur and then catalytically desulphurising the latter in a known manner.

2. A specific method of carrying out the process as claimed in claim 1 which consists in first decreasing the hydrogen sulphide content of the gases to be exposed to the catalyst to not more than 7 grams of sulphur per cubic metre by the addition of gases which are free from or low in sulphur.

3. A specific method of carrying out the process as claimed in claim 1 which consists in carrying out the usual desulphurisation in stages while employing for the last stage gases containing not more than 7 grams of sulphur.

4. The process for the desulphurisation of gases containing more than 7 grams of sulphur per cubic metre by means of active carbon substantially as described in each of the foregoing Examples.

5. Gases when desulphurised in accordance with the preceding claiming clauses.

Dated this 3rd day of September, 1931.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C. 2,
Agents.

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