PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Process for the Purification of Gases

We, METALLGESELLSCHAFT AKTIENGESELLSCHAFT, of 14, Reuterweg, Frankfurt-on-the-Main, Germany, a body corporate organised under the Laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for purifying, by washing, gases accumulating during the refining or conversion of fuels, and in particular, to the washing of such gases with an organic water-soluble absorbent containing nitrogen and oxygen such as an N-alkylated pyrrolidone or piperidone.

Pyrrolidones and piperidones are lactams of the γ- and δ-amino acids derived from butyric acid, valeric acid and caproic acid. Since these substances are cyclic acid amides, they are neutral and therefore act as physically dissolving absorbents. These substances are characterised by having a distinctly selective absorptive power for hydrogen sulphide and organic sulphur compounds before absorbing carbon dioxide and hydrocarbons. Since these substances are water-soluble, they will also absorb any water vapour contained in the gases treated thereby.

It has been proposed to use such substances in the purification of gases in such a manner that all impurities, such as hydrogen sulphide organic sulphur compounds, carbon dioxide, light gasoline ranging from C_6 and higher, and water vapour are jointly washed out from the gases to be purified. Further, these impurities can be individually recovered from the desorbate or desorbing agent resulting from the regeneration of the charged absorbent.

However, in order effectively to utilise the high selectivity of these substances with respect to acid gaseous compounds, the gas-washing processes utilising these substances as absorbents are preferably carried out in several stages. In the first stage, hydrogen sulphides and organic sulphur compounds are washed out from the gases. In one or several of the subsequent stages, carbon dioxide and hydrocarbons are washed out either separately or jointly.

The carbon dioxide can be recovered in a manner known *per se* by utilising washing solutions having an alkaline effect and the hydrocarbons by means of an oil-washing or by adsorption using active carbon. However, the carbon dioxide can also be washed out in a similar known manner by means of methanol or of an organic polar washing agent or detergent such as, for instance, acetone, either together with the hydrocarbons or separately therefrom.

In many applications the hydrogen sulphide and the organic sulphur compounds as well as the carbon dioxide are washed out with N-alkylated pyrroliodnes or piperidones in two completely separated stages, each stage being provided with its own regenerating apparatus and washing agent circulation.

As is usually done with physically dissolving substances, the regeneration of these absorbents is accomplished by expanding and then subsequently heating and stripping the absorbent with steam.

It is an object of the present invention to provide a novel and improved process for purifying gases such as those resulting during the refining or conversion of fuels by washing out various impurities including hydrogen sulphide, organic sulphur compounds, carbon dioxide, hydrocarbons and water vapour under pressure by using as an absorbent N-alkylated pyrrolidones or piperidones which may also contain 1 to 2 C-atoms in side chains.

According to the present invention there is provided a process for purifying gases by removing therefrom impurities including hydrogen sulphide, organic sulphur compounds, carbon dioxide, hydrocarbons and water vapour, wherein the gases are washed with an absorbent comprising an N-alkylated pyrrolidone and/or piperidone and 1 to 50% by volume of a low-boiling polar organic water-soluble substance.

Thus in the process of the present invention a low-boiling organic, polar, water-soluble substance such as methanol, ethanol or acetone, is added to the N-alkylated pyrrolidone or piperidone in quantities ranging from 1 to 50% by volume and preferably from 5 to 20% by volume. It has been discovered that the addition of such a substance to the absorbent results in considerable advantages in both the charging and the regeneration of the absorbent. During the absorption process, during which the absorbent is being charged with the impurities, the removal of the impurities by the absorbent is greatly facilitated since the addition of the water-soluble substance decreases the viscosity of the absorbent and also the temperature necessary for the thermal regeneration of the absorbent. As a result, a great volume of steam is formed which acts as a propellant.

The N-alkylated, preferably N-methylated, pyrrolidones and piperidones are miscible with water. Additions of water of less than 10% will improve the selectivity of the pyrrolidones and piperidones for sulphur compounds but will not increase the viscosity which will increase to a maximum regardless of further increases in the water content. Thus, limits are defined for a decrease in the temperature of absorption which, in turn, increases the absorptive power of physically dissolving absorbents.

The addition of low-boiling organic polar substances, particularly methanol, ethanol and acetone, allows for a considerable decrease in the viscosity of the absorbent without impairing in any way its absorptive power. This considerably increases the speed at which the impurities are removed from the gases even in the case of low washing temperatures such as lower than 0° C. The operation of the process at low washing temperatures, for example between 0° C. and the ambient temperature, means that when physically dissolving absorbents are used in order to obtain a predetermined purity in the end product, smaller quantities of absorbents can be used. As a result, the dimensions of the apparatus with respect to the absorption stage, the regeneration stage and the heat exchangers can be decreased but the resulting smaller apparatus will still be sufficient for carrying out the process.

This improvement in the exchange of impurities from the gases to the absorbent also favourably affects the regeneration of the charged absorbent, particularly if this regeneration is achieved through expansion.

In thermal regeneration, wherein the charged absorbent is heated and blown out with steam, the addition of methanol, ethanol or acetone to the absorbent lowers the boiling point thereof. In the sump of the column of the regeneration tower, the temperature is 100° C to 110° C. Temperatures which are capable of impairing the qualities of the absorbent are not reached. The vapours of the added substances, i.e. methanol, ethanol or acetone, act as a stripping vapour, so that the heat requirement for the thermal regeneration is considerably reduced since the regeneration column can be heated with relatively inexpensive waste heat, such as, for instance, with low-pressure steam.

During the regeneration process, a large proportion of the added substance is evaporated. The methanol, ethanol or acetone together with the desorbing agent pass out through the head of the regeneration column, whereas the N-alkylated pyrrolidone or piperidone remains in the sump of the column. The present process provides for the recovery of this added substance from the desorbate through condensation and adding this recovered substance to the cooled sump product of the regeneration tower prior to recirculation of the same into the head of the washing column. As a result, the same proportion selected for the absorbent is re-established for each washing step.

The dissolving power of the absorbent with respect to hydrocarbons is increased through the addition of methanol, ethanol or acetone to the N-methylated pyrrolidones or piperidones. As a result, the light gasolines ranging from C_5 to approximately C_8, if they are at all present in the crude gas, are also dissolved when the hydrogen sulphide and the organic sulphur compounds are washed out.

This simultaneous absorption of hydrocarbons may be carried out subsequently to the washing out of carbon dioxide, particularly in those cases where there is no previous washing step for sulphur compounds. The washing-out of the corban dioxide is preferably carried out at the lower temperature and using a larger quantity of absorbent. During the regeneration process these hydrocarbons are contained as a concentrate in a zone located in approximately the central portion of the regeneration tower. This concentrate may be tapped as a side product from a lateral outlet and be passed into a countercurrent washer. In the washer the added substances are washed out from the hydrocarbons by water. The aqueous additional substance is then rectified in a distilling column and then recirculated with the absorbent together with the recovered additional substance.

The present process is particularly suited for purifying gases occurring during low temperature carbonisation, the coking or gasification of solid fuels, as natural gases, or during the thermal catalytic or oxidising cracking of petroleum fractions

In order to enable the invention to be more readily understood, reference will now be made to the accompanying drawing, which illustrates diagrammatically and by way of example an embodiment thereof, and which is a flow diagram schematically illustrating the process of this invention.

With reference to the drawing, the apparatus for carrying out the present invention comprises an absorption tower 1, a regeneration tower 2, a countercurrent washer 3, and a rectification column 4. The absorption tower 1 and the regeneration tower 2 both consist of substance-exchange columns known *per se* and provided with trays.

The gas which is to be purified is introduced into the lower end of the absorption tower 1 through a conduit 5, and the treated gas is discharged from the head of the absorption tower 1 through an outlet conduit 6.

An absorbent containing, for example, 80% by volume of N-methylpyrrolidone and 20% by volume of methanol is introduced into the upper end of the absorption tower 1 by a distributor or spray nozzles through a conduit 7 which leads from the regenerator tower 2. The absorbent flows downwardly through the packing in the absorption tower 1 and comes into contact with the gas flowing upwardly therethrough in countercurrent relation therewith. The absorbent charged with impurities during this countercurrent contact with the gas is discharged from the bottom of the absorption tower 1 through a conduit 8 and flows through an expansion valve 9 into an expansion vessel 10. The gases liberated in the expansion vessel 10 through the decrease of pressure therein are compressed by a compressor 11 and returned to the absorption tower 1 through conduit 12.

The partly expanded absorbent is discharged from the expansion vessel 10 through a conduit 13 and then passed through a heat exchanger 14 and an expansion valve 15 to be introduced into approximately the central portion of the regeneration tower 2. The regeneration tower 2 is provided at its lower end with a steam coil 16 to function as a heating unit in a manner known *per se*.

The substances absorbed from the gas, together with the methanol, are evaporated in the regeneration tower 2 and escape from the head thereof through a conduit 17 leading to a condenser 18, in which the methanol and water vapour are condensed. A separator 19 is connected in series with the condenser 18 and the gaseous desorbate escapes from the separator 19 through a conduit 20 for further utilisation. The condensate consisting substantially of methanol and water returns from the separator 19 through a conduit 21 as reflux into the head of the regeneration column 2.

Pure N-methylpyrrolidone is tapped from the sump of the regeneration column 2 through a conduit 22 and returned into the head of the absorption tower 1 by a pump 23 through the heat exchanger 14 and a cooler 24. The methanol recovered during the regeneration is again admixed to the N-methylpyrrolidone at a suitable point in the conduit 7.

After the absorbent has absorbed hydrocarbons such as light gasoline from the gas which is to be purified, the hydrocarbons are concentrated in a zone in the upper central portion of the regeneration tower 2 and are tapped from that zone as a fraction containing methanol through a side outlet 25. The mixture of methanol and gasoline is passed into the countercurrent washer 3 within which it is washed with water introduced through a conduit 26. The hydrocarbons are then removed through the outlet conduit 27 while the aqueous methanol is removed through a conduit 28 and passed through a heater 29 into the rectification column 4. Water is tapped from the bottom of the rectification column through a conduit 30.

In the head of the rectification column 4, the methanol is vaporised and removed through a conduit 31 to be condensed in a cooler 32. A portion of the condensed methanol is returned as a reflux flow into the head of the rectification column 4 through a conduit 33. However, the major portion of the methanol is passed through a conduit 34 to a pump 35 from which it is pumped through a conduit 36 into the conduit 7 to be again admixed with the N-methylpyrrolidone.

In the event that the gas which is to be purified is free of hydrocarbons, the pure methanol can be tapped as a side product from the regeneration tower 2 through conduit 25 and directly into the conduit 36. Under these circumstances the countercurrent washer 3 and the rectification column 4 can be eliminated.

When the methanol from the conduit 36 is admixed to the N-methylpyrrolidone in conduit 7, the initial concentration of the absorbent is re-established and the absorbent is then recirculated through the absorption tower 1.

In order further to describe the process of the present invention and to assist in the comprehension thereof, the following specific example is presented for illustrative purposes only:

EXAMPLE

This example demonstrates the application of the present process to the purification of a gas obtained from the gasification of carbon by means of steam and oxygen under pressure. The cooled gas from which tars have been removed has the following composition:

H_2S	- -	1% by volume
CO_2	- -	29% by volume
CO	- -	20% by volume
H_2	- -	40% by volume
CH_4	- -	10% by volume

In addition, the gas contains in vaporous form small quantities of carbon oxysulphide and mercaptans as well as the hydrocarbons which have not been condensed during the cooling, such as light gasoline in a quantity of approximately 5 g./Nm^3. The gas is under a pressure of 25 atmospheres absolute.

The sulphur compounds including hydrogent sulphide are first to be washed out from the gas.

An initial quantity of 1000 Nm^3. of this gas is treated with 2.8 m^3. of an absorbent, which consists of 85% by volume of N-methylpyrrolidone and 15% by volume of methanol, in the apparatus shown in the drawing. The washing temperature in the absorption column 1 is maintained at —10° C. by means of the cooler 24.

The purified gas having a residual sulphur content of 1 mg./Nm^3. is discharged from the absorption tower 1 through the conduit 6. The charged absorbent is conducted from the absorption tower into the expansion vessel 10. At a decrease in pressure of about 5 atmospheres absolute there escape from the expansion vessel 10 equally absorbed quantities of methane, hydrogen and carbon monoxide as well as small quantities of hydrogen sulphide and carbon dioxide. This expanded gas is raised to the pressure within the absorption tower 1 by means of the compressor 11 and returned into the absorption tower through the conduit 12.

The remaining portion of the partly expanded absorbent is then passed through the conduit 13 wherein it is expanded in the valve 15 and introduced at atmospheric pressure into the regeneration tower 2. The heating coil 16, which is connected to a suitable source of steam, maintains the sump of the regeneration tower 2 at a temperature of approximately 110° C. The temperature in the head of the tower 2 is about 75° C. As a result, a substantial portion of the methanol is contained in the absorbent which is discharged from the head of the tower through the conduit 17 into the cooler 18. The methanol is completely returned as a reflux flow through the conduit 21 into the head of the tower 2.

The sulphur compounds and a small portion of the carbon dioxide totalling approximately 62 Nm^3. are removed through the conduit 20 from the separator 19, the sulphur concentration of this desorption gas being about 16.4% and being sufficient for further treatment.

After washing out the sulphur compounds, a second step of this process is conducted in order to wash out the carbon dioxide.

The apparatus for achieving this corresponds to that illustrated in the drawing with only the quantity and composition of the absorbent as well as the temperature in the absorption tower being different.

In order to wash out the remaining 25% of carbon dioxide down to a residual concentration of 0.6%, 13.2 m^3. of an absorbent containing 70% of N-methylpyrrolidone and 30% of methanol is used in the absorption tower which has a temperature of —5° C.

Thus it can be seen that the present invention provides an improved process for the purification of gases by washing, particularly those gases obtained during the refining or conversion of fuels. The increased efficiency of the absorbent used in the washing of the gases enables a decrease in the size of the apparatus necessary to carry out this process as well as a decrease in the quantity of absorbent required.

WHAT WE CLAIM IS:—

1). A process for purifying gases by removing therefrom impurities including hydrogen sulphide, organic sulphur compounds, carbon dioxide, hydrocarbons and water vapour, wherein the gases are washed with an absorbent comprising an N-alkylated pyrrolidone and/or piperidone and 1 to 50% by volume of a low-boiling polar organic water-soluble substance.

2). A process as claimed in Claim 1, wherein said substance is methanol, ethanol or acetone.

3). A process as claimed in Claim 1 or 2, wherein said substance is added to the N-alkylated pyrrolidone or piperidone in stages to wash out during each stage the impurities in the gases.

4). A process as claimed in any preceding Claim, wherein said absorbent comprises 5 to 20% by volume of methanol, ethanol or acetone.

5). A process as claimed in any preceding Claim, wherein the gases to be purified are passed through an absorbing tower in countercurrent to the absorbent and wherein the absorbent is thermally regenerated, including evaporating the added substance, condensing the added substance to recover the same and adding the recovered substance to the remainder of the absorbent prior to passing the absorbent into the absorbing tower.

6). A process as claimed in Claim 5, wherein during the thermal regeneration, a side product is tapped consisting of the hydrocarbons removed from the gases and a portion of the added substance, the side product being washed with water to remove the hydrocarbons therefrom, and wherein the added substance and water are rectified to remove the water therefrom, the substance being added to the absorbent prior to passing the absorbent through the absorbing tower.

7). A process for purifying gases, substantially as hereinbefore described with reference to the accompanying drawing and/or the foregoing Example.

THIEMANN, SON & CO.,
Chartered Patent Agents,
Prestige House, 14 to 18, Holborn,
London, E.C.1,
Agents for the Applicants.

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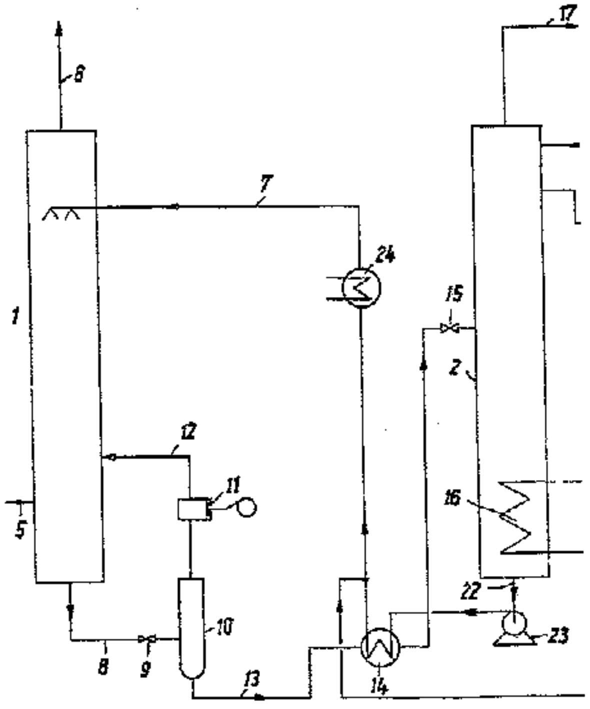
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938392 COMPLETE SPECIFICATION

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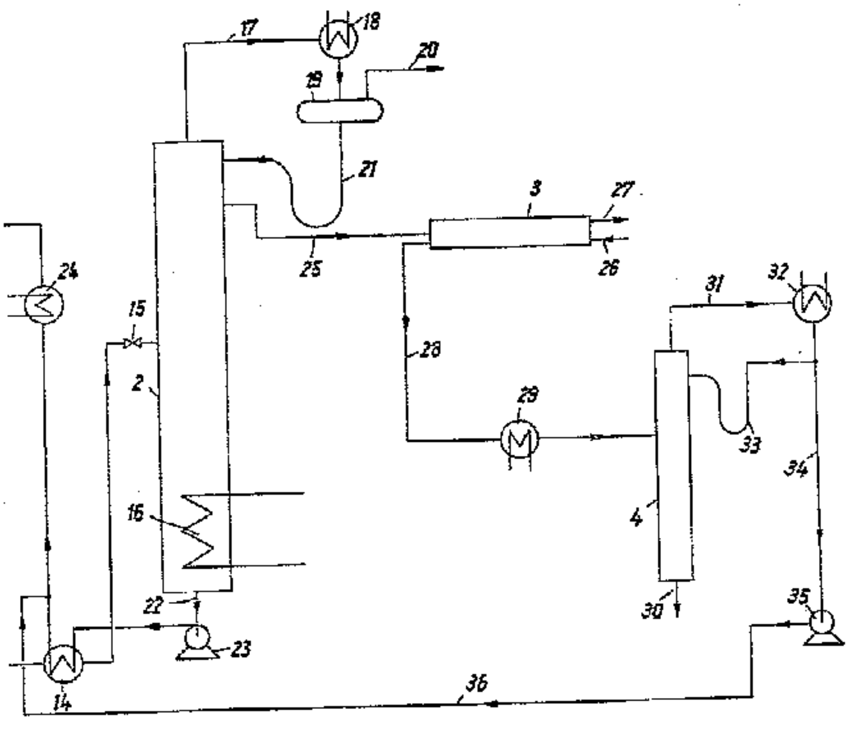

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