

PATENT SPECIFICATION

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(54) GAS PURIFICATION

(71) We, TOYO ENGINEERING CORPORATION, a Body Corporate organised and existing under the laws of Japan of 2-5 3-chome, Kasumigaseki, Chiyoda-ku, Tokyo, Japan, 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:—

The invention relates to an industrial process for the purification of gas from petroleum refinery or petrochemical operations, such as cracked gas, fuel gas or waste gas, by the removal of hydrogen sulphide and/or carbon dioxide, alkali-soluble oily organic materials, and any other acids present. The invention is extremely advantageous from the point of view of the efficient utilization of alkali scrubbing solution and the repression of the dissolution of the alkali-soluble oily organic materials. Such alkali-soluble oily organic materials are generally formed by petroleum cracking, and comprise non-hydrocarbon components containing acid radicals such as alkyl mercaptans and aryl mercaptans, phenols and thiophenols, and naphthenic acid.

The process of the invention comprises scrubbing the gas with caustic alkali solution under conditions such that in at least one scrubbing stage an acid salt is produced and in at least one other scrubbing stage a normal salt is produced, such stages being connected in series so that the solution is passed from the normal salt-producing stages to the acid salt-producing stage(s) and the gas is passed from the acid salt-producing stage(s) to the normal salt-producing stage(s).

Among normal salts principally produced are those of the formulae Na_2S , K_2S , Na_2CO_3 and $\text{1K}_2\text{CO}_3$. Among acid salts principally produced are those of the formulae NaSH , KSH , NaHCO_3 , and KHCO_3 . Each scrubbing stage or zone may be divided into two or more sections. Each zone and section is generally provided with means for mixing and circulating the scrubbing solutions so that the amounts of circulating alkali scrubbing solution in each

are controllable at predetermined alkali levels. The molar ratio of acid salts to residual alkali in the section of the acid salt-producing zone furthest from the normal salt-producing zone is preferably larger than 4:1. The molar ratio of acid salts to residual alkali in the section of the normal salt-producing zone furthest from the acid salt-producing zone is preferably smaller than 1:1. It follows from the series connection of the zones and sections that the concentration of alkali decreases stepwise from section to section in the direction of the acid salt-production. The acid salt solution may satisfactorily be used as digestion liquor in pulp manufacture and in the flotation of ores so that off-shore and other dumping causing environmental pollution, can be avoided.

Since the alkali scrubbing solution reacts with acid gases ultimately to form a large proportion of acid salts, and since the formation of acid salts requires only one mol of alkali for each mol of hydrogen sulphide or carbon monoxide, the consumption of alkali is only one half that required where normal salts are formed in the waste scrubbing solution. This leads to more efficient use of the alkali scrubbing solution.

The invention is based upon the discovery that the alkali component of the scrubbing solution absorbs and combines with acid gases until the major part is converted to hydro-sulphide and acid salts, thus absorbing twice as much acid gas as a system wherein the alkali is converted to normal salts. Since alkali-soluble oily organic materials are not significantly soluble in an acid salts solution, the dissolution of such materials is prevented thereby avoiding pollution and contamination of an otherwise useful inorganic acid salt solution.

The invention is illustrated by the accompanying drawings of which Figures 1 and 2 each show apparatus for the purification of gas comprising a number of separate gas scrubbing zones. In Figure 1 the zones are vertically disposed; gas to be purified travels upward, and alkali scrubbing solution travels

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downward. In Figure 2 the scrubbing zones are horizontally disposed; and gas to be purified and alkali scrubbing solution travel in countercurrent.

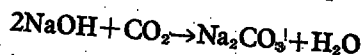
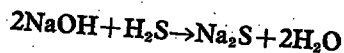
5 As shown in Figures 1 and 2, the apparatus is divided into an acid salt-producing zone consisting of Section A and Section B, and a normal salt-producing zone consisting of Section C and Section D. Section D is the final purification section for the gas to be treated, while Section C is a preliminary normal salt-producing section through which the gasses are passed prior to entry into the final purification section. Solution containing normal salts is conducted from the normal salt-producing zone to an acid salt-producing zone for reaction with acid to be treated within Section B of the acid salt-producing zone so that the major amount of alkali in the alkali scrubbing solution is converted to acid salts. On reaching Section A, the acid salt-containing alkali scrubbing solution is subjected to further reaction with acid gases contained in the crude gas stream to form acid salts thereby substantially completing the reaction of the alkali content of the scrubbing solution. Each of the scrubbing Sections A, B, C and D consists of similar components distinguished by indices III, II, I respectively in the first three cases: a gas-liquid contact area 6 and a scrubbing solution reservoir 7. The gas-liquid contact area 6 is filled with Raschig rings and perforated plates in order to increase the contact time to effect reaction between the alkali solution and the gas stream. The reservoir 7 is serially interconnected via lines 10, and the gas-liquid contact sections are serially connected via lines 9. The solution circulation system for each section serves to control the amount of circulating alkali scrubbing solution within the apparatus and consists of circulation pumps 3 connected via outlet lines 2 from the reservoirs 7 and inlet lines 4. By means of the circulation system which allows circulation of the alkali scrubbing solution from the reservoir 7 to the gas-liquid contact area 6 of each section, the contacting efficiency of the alkali solution with the gas stream and the absorption reaction between the alkali scrubbing solution and the acid gases are promoted.

Crude gas containing acid components is supplied to the scrubbing system via inlet feed pipe 9 to Section A of the acid salt-producing zone where part of the acid reacts with scrubbing solution to produce an acid salt solution. The partially purified gas from Section A is conducted via the line 9' to Section B where it is scrubbed by the scrubbing solution. Thence gas is passed to Section C, which is the preliminary normal salts solution producing zone, which has a stronger absorbtivity for the acid gases than the solution of Sections A and B. In Section C the gas is stripped of the major portion of acid

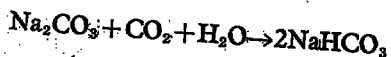
contained therein to produce normal salts and a small amount of acid salts. Subsequently the gas stream containing a small amount of acid gases is transferred from Section C to Section D via the line 9'' where the gas is purified to final condition by scrubbing with fresh alkali scrubbing solution containing normal salts produced in Section D. Fresh alkali scrubbing solution is supplied via the lines 1 and 2, the circulation pump 3 and the inlet line 4. Make-up alkali solution in the amount required to maintain the effective alkali concentration at predetermined levels is supplied to Sections B and C through the circulation systems via the lines 1'' and 1'.

The substantially acid gas free scrubbed gas produced in Section D passes out through line 11 to a rinse vessel 12 where it is washed with water to remove residual traces of alkali scrubbing solution. The purified gas from rinse vessel 12 is carried out of the system through a line 13 while rinse solution is removed through a line 14.

Different reactions predominate in the normal salt-producing zone and in the acid salt-producing zone as the gases countercurrently contact the scrubbing solution. In the normal salt-producing zone, alkali primarily reacts with the acid gas components of the gas to be treated as shown in the following equations:



In the acid salt-producing zone, the acid components of the gas to be treated react with the normal salts to produce acid salts in accordance with the following:



Thus, the alkali scrubbing solution which is partially neutralized in Section D is sequentially transferred to Sections C and B to sequentially contact gases having higher acid gas concentration and react therewith producing normal salts and acid salts. The gases from Section A are conducted to Section B wherein the crude gas having the highest concentration of acid gases meets with scrubbing solution having the lowest alkali concentration. Though the acids salts solution in Section B contains normal salts as well, the acid salts in Section B form the major part of the dissolved salts content thereof. The solution in Section B, containing predominantly acid salts, is transferred to Section A where it encounters crude gas containing the highest concentration of acid gases. In Section A the major part of the normal salts content is consumed and the scrubbing solution becomes acidified. The acidified salts solution, sub-

stantially free of alkali soluble organic oily components is removed from acid salts solution reservoir 7''' via the line 8 for recovery and use.

- 5 The following Examples further illustrate advantages of carrying out a process according to the invention; all parts and % being by weight unless otherwise stated.

Example 1.

- 10 In order to investigate the influences of acid salt concentrations (including acid salts generated by the hydrolysis of normal salts) produced by the reaction of acid gases with alkali scrubbing solution, the following experiment was conducted:

- 15 Raschig rings of about 13 mm in length, fabricated by cutting glass tubing having an inner diameter of 5 mm are filled for a length of about 700 mm into a glass tube having an inner diameter of 70 to 71 mm and a length of 1500 mm to form the gas-liquid contact zone. A 480 ml scrubbing liquid reservoir is connected to the lower end of the glass tube and to a spray nozzle mounted in the upper part of the gas-liquid contact zone via a circulation pump having a capacity of 8 litres per minute to form a circulation mechanism. Lower and upper parts of the gas-liquid contact zone are respectively provided with inlet and outlet means for the gas to be scrubbed.

- 20 Into this scrubbing apparatus were charged 5 and 10% aqueous solution of sodium hydroxide prepared by mixing 10% aqueous sodium hydroxide solution with different

quantities of alkali metal acid salts (from 7 to 20% sodium hydrogen sulphide). The gas to be scrubbed (the acid gas source) was a hydrocarbon gas containing (50% by volume) of hydrogen sulphide or of a mixture of hydrogen sulphide and carbon dioxide. The influence of the alkali acid metal salts produced on the course of the absorption of the acid gases by the alkali solution was investigated by stepwise experiments using an emulsion of cadmium carbonate as a hydrogen sulphide detecting solution. The experiments were carried out as follows: 20 kg of the 5 to 10% sodium hydroxide solution containing 0, 7, 14, or 21% of sodium hydrogen sulphide as the alkali metal acid salt are charged into the circulation system of the gas scrubbing apparatus. The circulation volume of the solution is controlled at 8 litres per minute and the hydrocarbon gas (a cracked gas product) containing hydrogen sulphide or a mixture of hydrogen sulphide with carbon dioxide is charged into the scrubbing apparatus through the gas inlet at the flow rate of 0.5 litres per minute. A 50 ml hydrogen sulphide detecting bottle containing cadmium carbonate emulsion (white) is connected to the upper part of the scrubbing column. The measurement of the period required for the colour conversion of the detection solution to yellow by the introduction of a part of the exhaust gas reveals the influence of the alkali metal acid salts on the absorption reaction. The results obtained are shown in the following Table 1.

TABLE 1

Run	NaOH (%)	NaSH (%)	Effective NaOH (%)	H ₂ S 0.5 l/min.	H ₂ S, CO ₂ 0.5 l/min.
1	5.01	0	5.01	184 min	186 min
2	5.02	7.03	5.02	189	184
3	5.02	14.05	5.02	186	180
4	5.03	21.00	5.03	185	178
5	10.02	0	10.02	389	385
6	10.01	7.01	10.01	380	379
7	10.02	14.07	10.02	385	382
8	10.02	21.10	10.02	383	380

The molar ratio of hydrogen sulphide to carbon dioxide in the gas mixture was about 4:1 and the molar concentration of total acid gases was about 50% based on the total gas composition.

These results prove that the absorptivity of the alkali scrubbing solution for acid gases is not as dependent upon the normal salt and acid salt content of the scrubbing solution, but is substantially proportionate only to the alkali content of the scrubbing solution. The alkali content of the scrubbing solution is the sum of the quantity added to the scrubbing solution and the quantity produced by the hydrolysis of normal salts. The total concentration of alkali from these two sources is the effective alkali concentration.

Example 2.

In order to investigate the behaviour of oily alkali-soluble organic materials present in small quantities in cracked gas, fuel gas, and waste gases of petroleum plants, the following experiments were conducted:

An alkali scrubbing solution which had been used to scrub the gaseous cracked product of LPG, was neutralized by over saturation with a gas containing hydrogen sulphide. Then oily alkali-soluble organic materials were separated. The separated oily materials

were mixed with 10% aqueous sodium hydroxide solution until the aqueous solution was saturated with the oily materials and a white suspension had formed. After standing, excess oily materials separated leaving an alkali solution of the alkali-soluble organic material. About 2.0 kg of this solution was charged into the laboratory scrubbing apparatus and treated as in Example 1, under operating conditions of Example 1, with the gas mixture used in Example 1. Samples of 120 g each arbitrarily withdrawn from the solution reservoir at the lower part of the scrubbing column. After being left standing, the separated oily components are isolated and their volume is determined. The alkali consumption (percent) is measured, and the effective alkali concentration per 100 g of the sample liquid is determined. The amount of organic oily component is determined as follows:

The sample is mixed with an excess of about 50% sulphuric acid for neutralization and 20g of sodium sulphate are added. By the dissolution of the sodium sulphate and the increases of the sample density the sample solution is salted out and mixed with benzene as a solvent. The oily organic material is recovered and measured. The results of this experiment are shown in Table 2.

TABLE 2.

Sample Liquor No.	1	2	3	4	5	6
Alkali consumption (%)	0.0	31.2	48.4	71.5	84.6	94.6
Soluble oily component (c.c.)	5.40	3.75	2.75	0.90	0.05	Trace
Effective alkali (g.)	10.07	6.89	5.25	2.82	1.51	0.50

The results obtained reveal that the solubility of the alkali-soluble oily organic materials in the alkali solution is proportionate to the effective alkali concentration within the range of alkali consumption of 50 to 60%, but when the absorption reaction with acid gases progresses beyond this point and the alkali consumption ratio is increased, then the organic oily component becomes disproportionately insoluble in the alkali solution. This indicates that there is a significant decrease in solubility of the alkali-soluble organic materials as the rate of alkali consumption increases to from 75 to 90%. Alkali consumption of 94.6% as shown in Table 2 only dissolves trace amounts of the oily materials. It is thought that a part of the soluble organic oily components dissolved in the alkali solution may be in the form of alkali salts, but that another part may be dissolved in the alkali solution due to a physiochemical phenomenon.

However it is evident that the solubility of the oily organic materials dissolved in the alkali solution is not proportionate to the effective alkali concentration but significantly diminishes by a factor which is related to the increase in the concentration of the acid salts above a certain limit.

Example 3.

This Example is a practical application based upon the results of Examples 1 and 2. Samples weighing 2.0 kg of the alkali solutions having the composition shown in Table 3 were prepared and introduced into the scrubbing apparatus employed in Examples 1 and 2. Gas mixture as in Example 1 was introduced at a feeding rate of 0.5 litres per minute into the lower part of the scrubbing column as in Example 2. After the absorption reaction had progressed to the condition of sample liquor number 6 of Table 2, the alkali consumption

- rate due to the formation of acid salts and the quantity of soluble organic component separated from the alkali solution were measured. At the same time the quantities of other salts of the formulae: NaSH, Na₂S, Na₂CO₃ (including NaHCO₃), Na₂SO₃, and Na₂S₂O₃; and of the soluble organic materials dissolved in the alkali solution were determined by chemical analysis. The results are in Tables 4 and 5.

10

TABLE 3

Solution No.	Alkali Soln.	Alkali Soln.	Alkali Soln.
	No. 1	No. 2	No. 3
20% NaOH soln. (g.)	1,000	1,000	1,000
20% NaSH soln. * (g.)	0	700	560
NaHCO ₃ (99.8%) (g.)	0	0	42.2
Alkali-soluble organic component ** (c.c.)	20	20	20
Total Liquid volume	2,000	2,000	2,000

Note: * This 20% NaSH solution was prepared from NaSH purified by the alcohol purification process.

** The alkali soluble organic component was the same as in Example 2.

TABLE 4

Run No.	1	2	3	4
Components of acid gas	H ₂ S	H ₂ S	H ₂ S, CO ₂	H ₂ S, CO ₂
Alkali soln.	No. 1	No. 2	No. 1	No. 3
Separated org. component (c.c.)	20.80	20.10	20.05	20.00
Alkali consumption (%)	94.2	95.4	96.2	96.8

TABLE 5

Composition	Run No.			
	1	2	3	4
NaSH (%)	11.00	16.65	9.14	13.32
Na ₂ S (%)	1.05	1.17	0.56	0.66
Na ₂ CO ₃ (%)	0.03	0.04	3.26	5.41
Na ₂ SO ₃ (%)	0.35	0.34	0.27	0.47
Na ₂ S ₂ O ₃ (%)	0.17	0.12	0.15	0.20
Organic oils	trace	trace	trace	trace

5 The alkali scrubbing solution, initially con-
 taining definite quantities of acid salts and
 alkali soluble organic materials was tested with
 petroleum hydrocarbon gas from a cracking
 reactor, which gas contained acid gases such
 as hydrogen sulphide and carbon dioxide as
 well as traceable amounts of alkali-soluble
 oily organic materials. According to Tables
 4 and 5, it is clear that the production of
 10 acid salts does not depend as much on the
 acid salts previously present in the scrubbing
 solution or on the acid salts and normal salts
 produced by the absorption reaction, and that
 the acid gas absorption reaction develops
 15 until the alkali consumption exceeds 90%.
 Furthermore, it is confirmed that the total
 or more than total of the previously added
 alkali-soluble organic components is separated
 from the scrubbing solution as the concen-
 20 tration of acid salts increases and the alkali

consumption ratio exceeds 90%. Thus, an
 alkali scrubbing solution is utilizable for the
 purification of hydrocarbon gases containing
 acid gases, not withstanding the formation
 of neutral salts therein, until the major por-
 tion of the alkali is converted to acid salts.
 This mode of gas scrubbing utilizes a small
 amount of alkali reduces dumping of alkali
 waste material having a high concentration
 of unreacted alkali and alkali soluble oily
 organic materials. A useful solution principally
 composed of acid salts can be recovered
 directly from the alkali scrubbing process.

A fresh gas stream having the composition
 shown in Table 6 is introduced into the scrub-
 35 bing system illustrated in Figure 1 through
 the line 9. At the same time an alkali scrub-
 bing solution containing about 15% sodium
 hydroxide is supplied to the system through
 the line 1.

TABLE 6 (mol %)

H ₂	14.55	C ₃	12.74
CO	0.08	C ₄	4.74
CO ₂	0.03	C ₅	2.13
H ₂ S	0.11	C ₆₊	2.05
C ₁	28.75	H ₂ O	0.72
C ₂	34.10	Soluble organic oily material	trace

Table 7 shows the results obtained by one
 scrubbing procedure until 70% of the alkali
 had been consumed, and by another until
 45 91% of the alkali had been consumed. The

crude acid containing gas used for this experi-
 ment was the hydrocarbon effluent from a
 cracking reactor.

TABLE 7

Alkali Consumption (%)	Scrubbing Solution Recovered by this Treating Process	
	70	91
NaOH (%)	0	0
Na ₂ S (%)	6.30	1.83
NaSH (%)	5.25	10.47
Na ₂ CO ₃ (%)	2.32	0.68
NaHCO ₃ (%)	2.46	4.90
Na ₂ SO ₃ (%)	0.68	1.30
Na ₂ S ₂ O ₃ (%)	0.25	0.49
dissolved oily component (c.c.)	0.15	trace

Example 4.

The apparatus illustrated in Figure 2 was supplied with spent scrubbing solution having an alkali consumption ratio of 35.9%. The

cracked gas which was used was the same as that in Example 3 and shown in Table 6. Table 8 indicates the analytical composition of the acid salts solution which was recovered.

TABLE 8

Alkali consumption	93%	NaHCO ₃	5.14%
NaSH	11.45%	Na ₂ SO ₃	1.08%
Na ₂ S	1.43%	Na ₂ S ₂ O ₃	0.25%
Na ₂ CO ₃	0.45%	Soluble oily components	trace

WHAT WE CLAIM IS:—

1. A process for the purification of a gas from petroleum refinery or petrochemical operations by the removal of hydrogen sulphide and/or carbon dioxide, alkali-soluble oily organic materials, and any other acids present which comprises scrubbing the gas with a caustic alkali solution under conditions such that in at least one scrubbing stage an acid salt is produced and in at least one other scrubbing stage a normal salt is produced, such stages being connected in series so that the solution is passed from the normal salt-producing stage(s) to the acid salt-producing stage(s) and the gas is passed from

the acid salt-producing stage(s) to the normal salt-producing stage(s).

2. A process according to claim 1 in which the acid salt-producing stage is divided into at least two separate sections.

3. A process according to claim 1 or claim 2 in which the normal salt-producing stage is divided into at least two separate sections.

4. A process for the purification of a gas substantially as described with reference to Figure 1 or Figure 2 of the drawings.

5. A gas purified by a process according to any of the preceding claims.

6. A salt solution produced by a process according to any of the preceding claims.

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WHAT WE CLAIM IS:—

1. A process for the purification of a gas from petroleum refinery or petrochemical operations by the removal of hydrogen sulphide and/or carbon dioxide, alkali-soluble oily organic materials, and any other acids present which comprises scrubbing the gas with a caustic alkali solution under conditions such that in at least one scrubbing stage an acid salt is produced and in at least one other scrubbing stage a normal salt is produced, such stages being connected in series so that the solution is passed from the normal salt-producing stage(s) to the acid salt-producing stage(s) and the gas is passed from

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