PATENT SPECIFICATION

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798,070

THE PATENT OFFICE LONDON

Date of Application and filing Complete Specification: Feb. 15, 1956.

No. 4791/56.

Complete Specification Published: July 16, 1958.

Index at acceptance:—Classes 1(2), A1C1; and 55(2), D14.

International Classification:—C01b. C10b.

COMPLETE SPECIFICATION

Removal of other Acid Gases from Mixtures containing Carbon Dioxide

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, 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 an improved method for the removal of hydrogen cyanide and/or hydrogen sulphide from gaseous mixtures containing carbon dioxide.

It is often desired to remove acid gases such as those named above from gas mixtures which contain carbon dioxide, so as to enable the production of substantially pure carbon dioxide or carbonates, and several procedures are known for accomplishing this purpose. In some of these the mixture of acidic gases is brought into intimate contact with water or an alkaline liquid and one of the gases is preferentially liberated from the resulting solution by controlled heating or by a chemical reaction which releases one but not the other dissolved gas. One such procedure is described and claimed in British Patent Specification No. 444,327.

Other prior procedures, especially for the recovery of hydrogen sulphide from its mixtures with carbon dioxide, have commonly employed a brief wash or spray of aqueous ammonia to absorb the hydrogen sulphide preferentially from the gas stream being treated. Variations of that procedure are described in British Patent Specification Nos. 520,327, 695,214, 711,008 and 772,905.

It is an object of this invention to provide a method whereby hydrogen cyanide and/or hydrogen sulphide may be removed preferentially from a gas stream containing carbon dioxide.

According to the present invention a method for effecting at least partial removal of hydrogen cyanide and/or hydrogen sulphide from carbon dioxide-containing gas mixtures in which these are the principal acidic constituents comprises bringing a stream of such a gas mixture into contact with a relatively slowly moving stream of an alkaline liquid comprising diethanolamine, trisodium phosphate, sodium hydroxide or a mixture of sodium hydroxide and sodium cyanide, and maintaining said contact only for a period of less than 0.05 second.

When the period of contact exceeds 0.05 second, absorption is not sufficiently selective to give the desired separation of the acidic constituents of the gas.

The gas-liquid contact may be obtained in any way as long as the recognized principles of efficient gas absorption are observed. Thus, the gas may be fed through a cylinder down whose walls is flowing a film of the alkaline liquid, or the gas may be blown upward through a sieve plate which is kept wet with the alkaline liquid, or the alkaline liquid may be fed axially to the throat of a venturi tube while the gas is supplied to the same point about the periphery of the liquid stream. In these and other ways of effecting the gas-liquid contact, the velocity of the gas mixture must be such that, in the apparatus employed, there will be not over 0.05 second contact between the rapidly moving gas and the more slowly moving liquid. In some absorbers, there may be intermittent contact between the acid gases and alkaline absorbent. The aggregate contact time should be not over 0.05 second.

In a preferred method the alkaline liquid is an aqueous solution containing sodium hydroxide, and the contact time is controlled within the range from 0.02 to 0.04 second.

The operating temperature of the process is any temperature above the freezing point of the alkaline liquid but temperatures much

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above atmospheric favour a disproportionately high absorption of carbon dioxide even at the short contact times employed in the present process and should be avoided. It is preferred to operate at or near room temperature.

The follow Table I illustrates the effect of gas-liquid contact time on the separation ratio when hydrogen sulphide is being absorbed in aqueous sodium hydroxide from a mixture of hydrogen sulphide, carbon dioxide and air. The gas and a liquid film of sodium hydroxide solution flowed concurrently at known rates down a tube of measured length and diameter. The exit gas was analyzed, as was the alkaline solution. In all cases the gas flow was 20 litres per minute, and the feed gas was 90 per cent air and 5 per cent each of hydrogen sulphide and carbon dioxide and was at one atmosphere pressure.

In all tables herein the term "separation ratio" refers to the ratio of the mol percentages of the gases absorbed.

TABLE I

Absorption Tube		Sodium Hydroxide Solution		Gas contact time, seconds	Per cent of acid gases absorbed		Separation Ratio, H_2S/CO_2
Internal Diameter, mm	Length, inches	Normality	Flow, ml. per minute		H_2S	CO_2	
10	48	1.0	189	0.29	85.6	17.0	5.04
5	48	1.0	189	0.072	95.8	17.5	5.47
5	24	1.0	185	0.036	95.5	11.9	8.02
5	12	1.0	187	0.018	91.0	7.9	11.5
3.7	24	10.0	10.7	0.020	94.0	4.4	20
3.7	24	8.0	9.7	0.020	90.8	4.6	20
3.7	24	8.0	8.3	0.020	89.7	4.2	21

Using the same gas mixture, flowing upward through a sieve tray against a film of sodium hydroxide solution, and with contact times below 0.05 seconds, separation ratios were obtained in the same range, indicating that about 8 times as much hydrogen sulphide as carbon dioxide was absorbed.

Various alkaline liquids were used as absorbents in a series of tests carried out in a venturi absorber. The liquid and gas were mixed at the throat of the venturi tube and the two phases were separated at once in a cyclone chamber. The gas was in contact with the alkaline absorbent for, at most, about 0.02 to 0.04 seconds. Details of these runs on H_2S—CO_2—air and HCN—CO_2—air are given in Table II.

TABLE II

Absorbent		Flow		Gas				Per cent of acid gases absorbed		Separation Ratio
				Composition		Flow, gm. mols per hour				
Kind	Molar Concentration	ml/min.	Gram mols per hour	H_2S Mol %	CO_2 Mol %	H_2S	CO_2	H_2S	CO_2	H_2S/CO_2
Sodium Hydroxide	1 M	100	6.0	5.2	5.2	2.83	2.77	79.3	4.02	19.7
" "	1 M	161	9.7	5.3	5.3	2.83	2.88	90.9	6.0	15.1
Diethanolamine	0.25 M	98	1.47	5.4	5.2	2.92	2.78	15.1	1.13	13.4
"	0.25 M	200	3.0	5.6	5.3	3.0	2.86	45.9	2.19	21.0
"	0.25 M	200	3.0	5.3	5.3	2.86	2.83	52.6	2.08	25.3
"	1.0 M	197	11.8	5.4	5.4	2.94	2.91	75.7	4.61	16.4
"	4.0 M	71.4	17.1	5.2	5.2	2.79	2.82	55.7	4.79	11.6
"	4.0 M	224	53.8	5.6	5.4	3.04	2.92	83.6	7.30	11.4
"	4.0 M	126	30.2	4.3	4.5	2.88	3.05	64.3	4.04	15.9
Trisodium phosphate	0.5 M	223	6.7	5.4	5.4	2.94	2.92	74.0	6.48	11.4
Sodium Hydroxide	1 M	70	4.2	5	5	2.68	2.68	70	3.7	18.1
" "	1 M	100	6.0	5	5	2.68	2.68	88	5.6	15.7
" "	1 M	100	6.0	5	5	2.68	2.68	86	4.8	17.9
" "	1 M	150	9.0	5	5	2.68	2.68	89	6.9	12.9
" "	1 M	170	10.2	5	5	2.68	2.68	93	7.8	11.9
Sodium hydroxide and Sodium cyanide	1.57M 6.6 M	100	9.4 39.6	5	4	2.39	1.95	66	1.5	44.0
Sodium hydroxide and Sodium cyanide	0.125 M 10.2 M	300	2.25 184.0	5	5	2.22	2.25	52	about 1.0	about 52

It is seen that, with a sacrifice in the degree of absorption, there may be obtained an extract which is substantially free from carbon dioxide.

The invention is not limited to the simple types of gas mixtures which have been shown in the examples, as it is effective in the separation of more complex mixtures containing carbon dioxide and hydrogen cyanide and/or hydrogen sulphide. Among such mixtures commonly encountered are flue gases, coke oven gases, and many gaseous mixtures produced in chemical synthesis such as the gases obtained by burning hydrocarbons and ammonia to form hydrogen cyanide.

What we claim is:—

1. A method for effecting at least partial removal of hydrogen cyanide and/or hydrogen sulphide from carbon dioxide-containing gas mixtures in which said gases are the principal acidic constituents which method comprises bringing a stream of such a gas mixture into contact with a relatively slowly moving stream of an alkaline liquid comprising diethanolamine, trisodium phosphate, sodium hydroxide or a mixture of sodium hydroxide and sodium cyanide, and maintaining said contact only for a period of less than 0.05 second.

2. The method claimed in claim 1, wherein the alkaline liquid is an aqueous solution containing sodium hydroxide, and the contact time is controlled within the range from 0.02 to 0.04 second.

3. A method for effecting at least partial removal of hydrogen cyanide and/or hydrogen sulphide from carbon dioxide—containing gas mixtures substantially as described with reference to the specific examples hereinbefore set forth.

4. Gas when purified by the method claimed in any one of the preceding claims.

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Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1958.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.