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COMPLETE SPECIFICATION

Process for the Removal of Hydrogen Cyanide from Coke-oven Gas

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, a German Company, of Homberg/Niederrhein, 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:—

The invention relates to a process for the removal of hydrogen cyanide from coke-oven gas or from a concentrate of the gaseous impurities in coke-oven gas.

Gaseous mixtures which contain substantial amounts of hydrogen sulphide are increasingly produced in the purification of coke-oven gas. These gases are generally treated to convert the hydrogen sulphide into sulphur or sulphuric acid. In addition to carbon dioxide proportions of 1%—20% by volume of hydrocyanic acid constitute a further chief constituent of these gases which is burnt in the conversions referred to, without being of any use. Apart from its corrosive action, hydrocyanic acid is a disturbing factor due to the fact that one of its products of combustion, namely nitric oxide, causes considerable difficulties.

It is known to remove the hydrogen cyanide from such gases by scrubbing with water and to isolate it in the pure state. In doing so, aqueous hydrocyanic acid solutions of approximately 2 wt. % concentration are produced from which the hydrogen cyanide is separated by fractional distillation.

According to the invention, a process for the removal of hydrogen cyanide from coke-oven gas or from a concentrate of the gaseous impurities of coke-oven gas comprises scrubbing the gas with a liquid scrubbing medium containing a saturated aliphatic ketone, a saturated aliphatic aldehyde or an epoxide, the scrubbing medium having a pH above 7 or in the range 2—5, preferably 3—4. Even with low concentrations of hydrogen cyanide of less than 5 vol. % in the gas, hydrogen cyanide concentrations of approximately 8 wt. % can be obtained in the scrubbing medium.

When an acid scrubbing medium is used its pH can be maintained in the range 2—5 by the addition of small amounts of a dilute acid. The hydrogen cyanide may be separated from such a scrubbing medium by distillation. When the scrubbing medium used has a slightly alkaline reaction, which is preferably imparted to the scrubbing medium by small amounts of dilute aqueous alkali metal hydroxide or aqueous alkali metal carbonate, the absorption of hydrogen cyanide is increased. The hydrogen cyanide absorbed as such may be separated by distillation from such a scrubbing medium after acidification.

Suitable saturated aliphatic ketones are those containing not more than 10 carbon atoms in the molecule such as acetone, methyl ethyl ketone, methyl propyl ketone and diethyl ketone, suitable saturated aliphatic aldehydes include paraformaldehyde and propionaldehyde, and a suitable epoxide is, for example, ethylene oxide maintained under pressure in the liquid phase. The scrubbing medium may comprise two or more of the members of the group consisting of said ketones, aldehydes and epoxides.

The scrubbing medium preferably contains an ionized salt of hydrocyanic acid, particularly when it is desired to recover the hydrogen cyanide as the cyanhydrin.

The ionized salt of hydrocyanic acid is advantageously introduced into the scrubbing medium as an aqueous solution of an alkali metal cyanide. The ionized salt may however, sometimes be formed *in situ* by using a scrubbing medium containing an aqueous solution of an alkali metal hydroxide or alkali metal carbonate. Frequently, however the formation of the ionized salt *in situ* is, presumably due to the acidic substances other than hydrogen cyanide in the gas, impeded or reduced to such a degree that either the formation of cyanhydrin is suppressed, or the cyanhydrin yield is insufficient and the cyanhydrin is contaminated by the products of side reactions and is thus of little use.

The preferred scrubbing medium is acetone. The process of the invention is hereinafter described in greater detail with the use, by way of example, of acetone as the scrubbing medium.

In all cases where the reaction of hydrogen cyanide was started with acetone which contained only an aqueous alkali metal hydroxide or alkali metal carbonate, the highest obtainable yield of acetone cyanhydrin was 66 wt. % relative to the hydrocyanic acid used. However, with acetone to which an alkali metal cyanide had been added, a practically complete conversion of the hydrogen cyanide into cyanhydrin was achieved even from gases the hydrogen cyanide content of which did not exceed 10 grams per normal cubic metre of hydrogen sulphide-containing gas mixture. The acetone cyanhydrin thus obtained may be separated from the reaction mixture by fractionation after acidification and is practically free from impurities. Thus upon acidification and vacuum distillation, there frequently remains less than 1% of a dark oily residue relative to the pure acetone cyanhydrin withdrawn.

It has been found to be of advantage to remove, by scrubbing with dilute sulphuric acid, the substantial amounts of ammonia which, due to operating difficulties in the coke-oven plant, may be present in the coke-oven gas from which hydrogen cyanide is to be removed. It is also of advantage to prevent oxygen from entering the starting gas. 1%—2% by volume of oxygen and less than 0.5 grams of NH_3 per normal cubic metre of gas mixture generally do not disturb the reaction between the hydrogen cyanide and acetone.

It is also advantageous to use a ketone to which an ionized salt of hydrocyanic acid has been added where it is desired to produce hydrogen cyanide in the pure state, as the absorption of hydrogen cyanide is thereby substantially increased. In this case, the hydrogen cyanide is removed from the reaction mixture by fractional distillation without prior acidification.

Dissolution or conversion of the hydrogen cyanide from the gas may also be carried out under elevated pressure. Such elevated pressure is advantageously the pressure employed in the pressure purification of the coke-oven gas.

The scrubbing is advantageously effected at a temperature in the range 5°—20° C., a temperature which may readily be maintained by cooling with a stream of water.

The process according to the invention permits the production in a single, simple apparatus and directly from acetone and the crude gas, of pure hydrogen cyanide or acetone cyanhydrin, whilst at the same time removing hydrogen cyanide from the gas and so facilitating the subsequent treatment of the hydrogen sulphide contained in the gas.

Occasionally it is found that, through some disturbance in the operation of the coking plant (particularly in the saturator), no acetone cyanhydrin is formed in spite of the fact that the acetone contains aqueous alkali metal cyanide. Upon acidification and distillation, free hydrogen cyanide and acetone distil over and no acetone cyanhydrin is present in the residue. In such case, the ditillate should be condensed and passed into acetone containing an ionized salt of hydrocyanic acid (preferably introduced into the acetone as an aqueous alkali metal cyanide) and the evolution of heat will indicate the formation of acetone cyanhydrin which can then be separated by acidification and subsequent fractionation of the product. Should this step fail to yield the cyanhydrin, the acetone which should be alkaline and which will be alkaline if the salt was introduced as alkali metal cyanide, should be distilled in its alkaline state and the distillate condensed and introduced into acetone containing an aqueous alkali metal cyanide. It has been found that the formation of acetone cyanhydrin always then occurs.

These occasional failures to form cyanhydrin when the gas is first contacted with the acetone containing the ionized salt of hydrocyanic acid is probably due to the presence in the gas of alkaline or acidic substances other than ammonia, hydrogen sulphide and carbon dioxide, which substances suppress the reaction between acetone and hydrogen cyanide.

When gaseous mixtures saturated with steam were used, no detrimental effect in the dissolution of the hydrogen cyanide in, or in the reaction of the hydrogen cyanide with, the acetone could be observed. The rectification of the acetone cyanhydrin can, however, be effected in a simpler manner by limiting the water content of the gas, for example, by drying the gas over calcium or by cooling the gas to a sufficiently low temperature. Low temperature cooling of the starting gas may advantageously be combined, with heat-exchange, with the low temperature cooling of the tail gas for separation of entrained acetone. The amount of circulating acetone is thereby substantially reduced.

If sufficiently soluble in water, ketone discharged (corresponding to the partial pressure of the ketone) entrained in the tail gas which is free from hydrogen cyanide, may, for example, be recovered by scrubbing with water, dehydrated by fractional distillation, and recycled to the process. Similarly, the decomposition of the cyanhydrin into ketone and hydrogen cyanide which occurs to a small extent during the vacuum distillation, may be nullified by recycling the ketone and the hydrogen cyanide to the gas scrubbing stage.

The removal of hydrogen cyanide by scrubbing, the isolation thereof, and/or its conversion into cyanhydrin may, therefore, advantageously be carried out as a fully continuous process which includes the recycling of all unconverted reactants.

The continuous scrubbing-out, or the reaction of the hydrogen cyanide with ketones, may be effected in counterflow in a scrubbing tower, as, for example, in a packed tower, or in a tower provided with trays, or in scrubbing or wash bottles, in all cases in one or more stages.

The invention is illustrated by the following examples.

EXAMPLE 1

The hydrogen sulphide concentrate obtained by the scrubbing of a coke-oven gas with potash under pressure in accordance with the Koppers process, contained approximately 70 vol. % of H_2S, 7 vol. % of HCN, and 13 vol. % of CO_2. In addition, the concentrate contained 1.2 vol. % of O_2 and 5.4 vol. % of N_2. The amount of NH_3 present in the gas was 0.23 grams per normal cubic metre.

Before the gas concentrate was passed through a scrubbing bottle, containing 600 cc. of acetone and 6 cc. of 1N.H_2SO_4, the NH_3 was substantially retained together with approximately 2 grams of HCN in two tubes each of which contained ten balls by scrubbing the gas thoroughly with 100 cc. of 1N.H_2SO_4, the water vapour being largely retained in a $CaCl_2$. tower. The initial temperature was +15° C.

Quantity of gas passed through, normal cubic metres	HCN dissolved in acetone, wt. %	Temperature in the acetone
0.5	4.8	+10° C.
1.0	10.0	+ 6° C.
2.2	10.1	+ 5° C.

Equilibrium in the acetone solution was, therefore, already established after one normal cubic metre of the gas had been passed through. 400 grams of the acetone solution were subjected to fractional distillation, and 39 grams of anhydrous hydrogen cyanide were obtained.

400 grams of acetone solution containing 10.2 wt. % of HCN were taken from a parallel run and distilled off on a water bath, the distillate being condensed and introduced with cooling (+15° C.) into a mixture of 100 cc. of acetone and 4.5 cc. 1N.KCN solution. After completion of the distillation, 6 cc. of 1N.H_2SO_4 were added to the contents of the receiver, and the mixture was once more distilled off on a water bath. The residue was rectified in a vacuum in a small column. 110 grams of product containing 98.8 wt. % of acetone cyanhydrin was obtained.

EXAMPLE 2

A gas concentrate of the same composition as that used in Example 1, was passed through two scrubbing bottles each of which contained 500 cc. of acetone plus 4.5 cc. of 1N.NaOH, the sulphuric acid scrubbing and the $CaCl_2$ tower being, however, omitted. The temperature of the acetone was maintained at +15° C. After one normal cubic metre of gas had been passed through, the contents of the scrubbing bottles were combined, acidified with 12 cc. of 1N.H_2SO_4, distilled on a water bath, and the residue rectified *in vacuo*. 158 grams of product was obtained containing 96.2 wt. % of acetone cyanhydrin. The quantity of HCN present in the tail gas rose during the run to 27 grams per cubic metre.

EXAMPLE 3

The method of Example 2 was repeated with the sole difference that 4.5 cc. of N/1.KCN solution instead of NaOH were added to the acetone present in each scrubbing bottle. 245 grams of product containing 98.5 wt. % of acetone cyanhydrin was obtained. The tail gas contained less than 1 gram of NCH per cubic metre.

EXAMPLE 4

When the method used in Example 2 was applied to a gas which contained 0.8 grams of NH_3 per cubic metre but which was otherwise of substantially the same composition and employing a sulphuric acid wash and drying in a $CaCl_2$ tower, only 45 grams of product containing 81.5 wt. % of acetone cyanhydrin was produced from 1 normal cubic metre of gas. The product was of a deep yellow colour. The sulphuric acid had retained or absorbed approximately 1.5 grams of HCN.

EXAMPLE 5

Using the same conditions as those used in Example 4, but adding KCN instead of NaOH to the acetone in the wash bottles, 238 grams of a product containing 98.4 wt. % of acetone cyanhydrin was obtained. In this case also, the sulphuric acid had retained or absorbed 1.5 grams of HCN. The tail gas contained less than 1 gram of HCN per cubic metre.

EXAMPLE 6

During a 125 hour run, 200 litres of a hydrogen sulphide concentrate of substantially the same composition as that used in Example 4 were passed per hour through two series-connected scrubbing bottles containing 1.5 litres and 0.5 litres of acetone respectively, the gas having previously been passed through 2.5 litres of 1N. sulphuric acid as scrubbing medium and through a $CaCl_2$ tower. A total of 18 cc. of 1N.KCN solution had been added to the acetone. At a reaction temperature of 15° C. which was maintained by cooling with fresh water, the density in the first scrubbbing bottle increased steadily. As soon as a density of 0.870 had been reached, one-half of the contents of the first scrubbing bottle was withdrawn and replaced by fresh acetone to which the above proportion of KCN had been added. At intervals, acetone escaping due to evaporation, was continuously replaced by fresh acetone, omitting, however, the addition of KCN. The withdrawn reaction mixture was acidified with dilute sulphuric acid and distilled off on a water bath. The residue remaining from this distillation was subjected to vacuum rectification. The tail gas was passed through a reflux condenser which was maintained at a temperature of −5° C., and subsequently scrubbed with water, the acetone being this completely removed therefrom. The aqueous acetone thus obtained was dehydrated in an efficient column. The acetone recovered from the scrubbing with water and as well as from the reaction mixture was, according to yield and requirements, returned to the gas-scrubbing process, any loss being replaced by fresh acetone.

5.875 kilograms of a product containing 98.4 wt. % of acetone cyanhydrin was obtained from 25 normal cubic metres of gas containing 85 grams of hydrogen cyanide per normal cubic metre. 75.8 grams of hydrogen cyanide had been retained during the sulphuric acid scrubbing.

Upon carrying out the process on a large scale, the sulphuric acid used can be returned to the saturator and thus be completely utilized together with the hydrogen cyanide absorbed therein. The absorption of hydrogen cyanide by the sulphuric acid used in the scrubbing process can, however, be prevented to a substantial extent by increasing the temperature.

EXAMPLE 7

Before being charged to the potash pressure-scrubbing process, a crude coke-oven gas which had been compressed to 8.4 atmospheres gauge and which was free from benzene, was passed through a pressure scrubbing-bottle which contained methyl ethyl ketone. 12 cc. of 1N.KCN solution per litre had been added to the methyl ethyl ketone. In a subsequent pressure column, the coke-oven gas was freed from entrained methyl ethyl ketone by sprinkling with water. Prior to the scrubbing, the proportion of hydrogen cyanide present in the coke-oven gas was 62 grams per 100 normal cubic metres. The gas left the pressure scrubbing bottle with a content of 4 grams of hydrogen cyanide per 100 normal cubic metres. The scrubbing medium was acidified with $1N.H_2SO_4$ distilled on a water-bath and the residue rectified *in vacuo*. 160 grams of a product containing 97.6 wt. % cyanhydrin of methyl ethyl ketone was obtained from 100 normal cubic metres of coke-oven gas with continuous replacement of the methyl ethyl ketone which had been lost through evaporation at a scrubbing temperature of 20° C.

WHAT WE CLAIM IS:—

1. A process for the removal of hydrogen cyanide from coke-oven gas or from a concentrate of the gaseous impurities of coke-oven gas, which comprises scrubbing the gas with a liquid scrubbing medium containing a saturated aliphatic ketone, a saturated aliphatic aldehyde or an epoxide, the scrubbing medium having a pH above 7 or in the range 2—5.

2. A process according to Claim 1, in which the scrubbing medium employed has a pH in the range 2—5, the scrubbing medium being subsequently distilled to separate absorbed hydrogen cyanide.

3. A process according to Claim 1, in which when the scrubbing medium has a pH above 7, the alkaline reaction being imparted by the presence of an aqueous solution of an alkali metal hydroxide or an alkali metal carbonate.

4. A process according to Claim 1 or Claim 3, in which the scrubbing medium employed has a pH above 7, and, after absorption of hydrogen cyanide from the gas, the scrubbing medium is subjected to distillation to separate absorbed hydrogen cyanide.

5. A process according to Claim 1, in which the scrubbing medium contains an ionized salt of hydrocyanic acid.

6. A process according to Claim 5, in which the reaction mixture is acidified and fractionated to separate cyanhydrin.

7. A process according to Claim 6, in which the ionized salt is an alkali metal cyanide.

8. A process according to any one of the preceding claims, in which the scrubbing is effected at a temperature in the range 5°—20° C.

9. A process according to any one of the preceding claims, in which the scrubbing medium contains a saturated aliphatic ketone having not more than 10 carbon atoms in the molecule.

10. A process according to Claim 9, in which the ketone is acetone.

11. A process according to any one of Claims 1 to 8, in which the scrubbing medium comprises a mixture of two or more of the members of the group consisting of saturated aliphatic ketones containing not more than 10 carbon atoms in the molecule saturated aliphatic aldehydes, and epoxides.

12. A process according to any one of the

preceding claims, in which the ammonia content of the hydrogen cyanide-containing gas is maintained at or reduced to less than 0.5 grams per normal cubic metre before contact with the scrubbing medium.

13. A process according to any one of the preceding claims, in which the hydrogen cyanide-containing gas is subjected to drying before contact with the scrubbing medium.

14. A process for the removal of hydrogen cyanide coke-oven gas, which comprises absorbing the hydrogen cyanide in acetone substantially as hereinbefore described.

15. A process for the removal of hydrogen cyanide from coke-oven gas, substantially as hereinbefore described with reference to Example 1.

16. A process for the production of a cyanhydrin from hydrogen cyanide contained in coke-oven gas, substantially as hereinbefore described with reference to any one of the Examples 2 to 7.

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