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PRODUCTION OF HYDROGEN CYANIDE

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This invention relates to the recovery of hydrogen cyanide as such or in the form of compounds thereof, from reaction gases containing hydrogen cyanide in admixture with ammonia or water vapor, or with ammonia and water vapor.

In the literature there are a number of processes describing the production of hydrogen cyanide from gaseous mixtures containing nitrogen, hydrogen and carbon either with or without the addition of oxygen or air and either in the presence or absence of a catalyst. Among these processes are those involving (1) the reaction of nitrogen and methane; (2) the reaction of ammonia with a volatile hydrocarbon; (3) the reaction of nitrogen, methane and oxygen; (4) the reaction of ammonia, a volatile hydrocarbon and oxygen; (5) the reaction of carbon monoxide and ammonia and (6) the reaction of an oxide of nitrogen and a volatile hydrocarbon. In all of these reactions the gaseous mixtures are heated to temperatures of from about 600° to 1250° C. in any one of a number of ways such as, for example, by an electrical discharge, or by preheating the reaction gases, or by passing the gases over heated contact material, or by supplying the heat directly from some outside source.

The foregoing reactions each produces hot effluent hydrogen cyanide reaction gases containing a nitrogenous compound or nitrogen itself, hydrogen, some unreacted hydrocarbon, and also either ammonia or water vapor (if ammonia or an oxygen containing gas is employed). For recovering the hydrogen cyanide in these processes, it has heretofore been suggested that the hot effluent gases be reacted with alkali to form cyanide salts, either directly or after cooling by contact of the gases with heat exchange surfaces, next scrubbing with dilute sulphuric acid to fix ammonia in the form of its sulphate and finally, recovering the hydrogen cyanide in an aqueous solution.

Experimentation with the foregoing processes has led to the discovery that a larger quantity of hydrogen cyanide is initially produced in the hot reaction gases than is ultimately recovered. This loss in potential yield has been determined as resulting from decomposition or polymerization of the cyanide, or both through (1) contact with hot surfaces, or (2) contact with cold water employed in cooling and absorbing the hydrogen cyanide gases, or (3) contact with either water or solutions of hydrogen cyanide condensed on the cold surfaces of conventional heat exchange equipment, or (4) becaue of polymerization in the water solutions which are not sufficiently acidic.

An ultimate object of the instant invention is to provide increased yields of hydrogen cyanide and maximum recovery of ammonia from hot effluent hydrogen cyanide gaseous products of any kind, as coke oven gases and especially those of the character hereinbefore described. Another object is to provide a process by which hydrogen cyanide reaction gases may be cooled to a temperature between 400° C. and about the temperature of the surrounding atmosphere, whereby optimum reaction conditions for the hydrogen cyanide are possible without at the same time causing or permitting the decomposition and loss of any appreciable amount of the hydrogen cyanide in the reaction gases to occur.

In one embodiment a specific object is to recover hydrogen cyanide as such instead of in the form of sodium cyanide or other converted form without sacrificing any of the initial yield of hydrogen cyanide in the hot effluent reaction gases. Other specific objects are to produce maximum possible yields of various hydrogen cyanide derivatives and to accomplish maximum recovery of ammonia from the effluent reaction gases when the same is present.

In its preferred specific embodiment, the invention involves rapidly cooling a hydrogen cyanide-containing hot gas mixture of the character hereinbefore defined to a temperature at least as low as 400° C. by directly contacting the gas mixture, substantially immediately upon its emergence from the reaction zone or production source, with a relatively cool or cold aqueous solution of a boric acid-polyhydroxy complex which is of acidic character and collecting the hydrogen cyanide either by dissolution in a stabilizing solution or by chemically reacting the same with a suitable reagent.

Contact between the quenching solution and the hot gas mixture may be brought about in any suitable way or by any desired apparatus, as for example, by scrubbing or by spraying the quenching solution into a stream of the gas or by both procedures.

By varying the quench solution volume or its temperature or both, several different results may be attained. Firstly, the gas mixture may be cooled to 400° C. or somewhat below such temperature whereupon the hydrogen cyanide is recovered by conventional means as by reacting the hot gas with alkali. Secondly, the gases may be cooled down to room temperature in contact with the quench solution whereby the hydrogen cyanide is dissolved therein and the ammonia (if present) is completely absorbed by reaction with the complex. Thirdly, the gaseous mixture may be cooled to an intermediate temperature with the result that the ammonia is selectively absorbed and after which the hydrogen cyanide gas is taken up in any desired manner.

In commercial operations, regardless of the variation of the process employed, a portion or all of the quenching solution is withdrawn from the quenching zone and if hot is cooled for example by contacting it with cooling surfaces as in a conventional heat exchanger and is then recycled for further quenching. If the hydrogen cyanide has been dissolved in the quenching solution it may be recovered by distillation. If both ammonia and hydrogen cyanide are present, they may be recovered separately and in substantially pure form by selectively stripping the solution in accordance with the procedure described in the copending application, Serial Number 83,132 now Patent No. 2,590,146.

Boric acid-polyhydroxy complexes of the nature contemplated by the present invention are described in many published articles. Of the earlier articles there may be mentioned:

1. J. Boeseken et al., Rec. trav. chim. 30, 392–406, Chem. Abstracts 6, 623. The conductivity (due to acidity) of boric acid is described as being increased by reaction with glycerol, pentaerythritol, pyrocatechol, and pyrogallol.

2. J. Boeseken et al., Rec. trav. chim. 34, 96–113, Chem. Abstracts 9, 1766. Conductivity increases are reported for reaction products with erythritol, mannitol, dulcitol, sorbitol, and $CNO_2(CH_2OH)_3$.

3. J. Boeseken, Rec. trav. chim. 40, 553–67, Chem. Abstracts 16, 906. Conductivity increases by a number of compounds are described and here it is stated that the mutual increase in the electrical conductivity by mixing polyalcohols, polyphenols, HO acids, ketonic acids, etc. with H_3BO_3 is due to the formation of complex acids stronger than the components.

The complexes preferred in the operation of the process of the instant invention are the boric acid-pentaerythritol complex and the boric acid-glycerol complex.

When ammonia is present in the gases treated and is to be absorbed in the stabilizing solution, such solution should be more strongly acidic in order that the minimum acidity required for effecting stabilization will be maintained until a satisfactorily large quantity of hydrogen cyanide has been taken up. Stabilization ordinarily will be effected up to the point where the pH value reaches about 6.8 as the absorption process progresses.

As stated, the present invention is applicable to hydrogen cyanide reaction gas mixtures resulting from any of the known processes hereinbefore enumerated and includes gases produced from hydrocarbons which may