UNITED STATES PATENT OFFICE.

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RECOVERING AS AN AMMONIUM SALT THE NITROGEN OF THE HYDROCYANIC ACID IN CRUDE COAL-GAS.

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No Drawing. Application filed July 30, 1914. Serial No. 854,173.

To all whom it may concern:

Be it known that I, EDWARD VICTOR EVANS, a subject of the King of Great Britain, residing in London, England, have invented certain new and useful Improvements in Recovering as an Ammonium Salt the Nitrogen of the Hydrocyanic Acid in Crude Coal-Gas, of which the following is a specification.

A known process for disposing of the hydrocyanic acid present in crude coal gas consists in absorbing the hydrocyanic acid in the form of ammonium sulfocyanid and then treating the latter so as to convert the cyanogen nitrogen into ammonia which may be worked up with the ammonia present as such in the crude gas.

Among methods of treating the ammonium sulfocyanid for the object in question, heating it with sulfuric acid has been mentioned. No directions for obtaining ammonia in this manner have been given, however, either in this connection or in any other save in the scientific investigation hereinafter cited. It is known that some of the nitrogen in a sulfocyanid is converted into ammonia when the salt is hydrolyzed, while some of the carbon becomes carbon oxysulfid or carbon dioxid.

The chemical change is generally represented by the equation:—

$$NH_4SCN+H_2O=COS+2NH_3,$$

and Klason in 1887 investigated the reaction from the point of view of the conditions under which it must occur in order that the yield of carbon oxysulfid may be a maximum.

I have found that these conditions are not such as are suitable for the maximum yield of ammonia, which latter is obtained, of course, in the form of a salt of the acid used for hydrolysis.

Temperature is the most important condition for my purpose. With regard to this factor Klason merely states that the effect of temperature on his reaction is only to increase its velocity as the temperature is raised. I have found that the temperature plays a much more important part than Klason supposed, if the reaction is considered from the point of view of production of ammonia. By operating at a temperature considerably higher than that suitable for maximum yield of carbon oxysulfid, the production of bodies containing nitrogen of the type of thiocarbamic acid, which, as may be gathered from Klason's statement, are inevitably formed as products of the reaction, may be substantially avoided and a yield of ammonia obtained which is comparable with that represented by the foregoing equation. This was not to be foreseen, since Klason has stated that these nitrogenous compounds resist the attack of even strong acids at the temperature of the water bath.

According to the present invention, therefore, the ammonium sulfocyanid made from the hydrocyanic acid in crude coal gas is hydrolyzed by an acid, preferably sulfuric acid, at a temperature not lower than 50° C., and under conditions of concentration and proportion by mass suitable for obtaining the maximum yield of ammonia in the form of an ammonium salt.

The best temperature can only be ascertained by experiment when it has been decided what is to be the proportion of ammonium sulfocyanid to acid, and what is to be the degree of dilution of the mixture undergoing reaction. These conditions vary with the nature of the coal carbonized to produce the coal gas, the mode of carbonization and the particular process adopted for absorbing the hydrocyanic acid in the form of ammonium sulfocyanid, in short with the practice of gas works or coke oven installation where the invention is applied.

The invention is primarily intended for gas-works or coke oven works where ammonia is used for making ammonium sulfate; for here it is convenient to use sulfuric acid for the hydrolysis and owing to the fact that excess of acid must be used for obtaining the best yield of ammonia, the liquor produced by the hydrolysis is a suitable liquor for feeding the saturator of the ammonium sulfate plant, from which the yield is increased by the sulfate produced by the hydrolysis. In such works the temperature of reaction should be between 80° C. and 110° C., since this is best for the conditions likely to prevail when ordinary gas coals are used, namely:—

(1) An extraction of some 95 per cent. of the cyanogen in the crude gas in the form of a solution of ammonium sulfocyanid of

20–30 per cent. strength, (2) the use of sulfuric acid of 70–80 per cent. strength for the ammonium sulfate saturator; (3) such a proportion of ammonia in the gas that if the acid in the saturator is to be equivalent to both this ammonia in a given volume of the gas and that equivalent to the ammonium sulfocyanid produced from the cyanogen in that volume, the volume of acid (of the above strength) used to hydrolyze the sulfocyanid should bear the ratio to the volume of ammonium sulfocyanid solution (of the above strength) of about 1.5:1. Thus, with an ammonium sulfocyanid solution of 30 per cent. strength the following procedure may be expected to give some 96–99 per cent. of the theoretical yield of ammonia as calculated from the foregoing equation, and this ammonia will be contained in an acid liquor suitable for the saturator of the ammonium sulfate plant, that is to say, the liquor after the hydrolysis reaction will contain so much free acid that when saturated with the gases evolved in the ammonia stills a copious quantity of ammonuim sulfate crystals is produced.

Sulfuric acid of 70 per cent. strength is maintained at a temperature of 80°–90° C. in a vessel provided with a stirrer. Into the vessel is run slowly the solution of ammonium sulfocyanid the rate of flow being adjusted to avoid violent escape of gas and care being taken that the proportion by volume of the total quantity of sulfocyanid solution to that of the acid is 1:1.5. The stirrer is worked vigorously throughout the operation and the temperature of the liquid is maintained at 80°–90° C., by a steam jacket or otherwise.

Since there are so many variable conditions affecting the process, it is practically impossible to set forth the best procedure for all conditions. The following experimental work, however, may be prescribed for those wishing to ascertain the best conditions for the particular strength of sulfocyanid solution or sulfuric acid which is to be used.

Assuming that a test made on the lines of the foregoing example with the sulfocyanid solution and sulfuric acid at disposal fails to give a satisfactory yield of ammonia (say about 96 per cent.), the nitrogen escaping hydrolysis may be found either in the form of a precipitate in the vessel or may have escaped as a gas during the reaction. The first observation to be made in this case is whether or not there is a precipitate in the reaction vessel or considerable dilution with water of the liquor of the reaction vessel produces a precipitate. In either event the temperature of the reaction should be increased until that is found which insures the absence of a precipitate; another method of avoiding a precipitate is to increase the relative volume or strength of acid employed for hydrolysis, an increase of relative volume being more effective than an increase of strength. The temperature to be maintained should be only slightly above (say 5 or 10° C.) that at which precipitation is avoided. If, on the other hand, the elevation of temperature does not procure the high yield of ammonia required, or the temperature is elevated to such a point that the reaction becomes difficult to manage owing to proximity to the boiling point of the mixture, and there remains an inefficient yield of ammonia, it is an indication that the quantity of nitrogenous gases lost by volatilization is considerable. To overcome this a larger relative volume of acid, or acid of higher concentration should be used. It is obvious that a lower concentration of sulfocyanid solution would effect the same result. To exemplify this, if an inefficient yield is obtained by hydrolysis, and no precipitate is formed, it is generally an indication that the temperature maintained during the reaction is too high. If on reducing the temperature, a precipitate occurs before the efficient yield of ammonia is attained, then the volume or strength of the acid must be increased, or the sulfocyanid solution diluted.

The precipitate herein mentioned should not be confused with a small quantity of sulfur which is sometimes produced (especially with concentrated acids) as the result of the reducing action of sulfureted hydrogen. Its nature has not been fully investigated, but it is considered to be a mixture of persulfocyanic acid and certain sulfided compounds of thiocarbamic acid.

Having thus described my invention and the best means I know of carrying the same into practical effect, I claim:—

1. A process for recovering in the form of an ammonium salt the nitrogen of the hydrocyanic acid in crude coal gas, which process consists in first converting the hydrocyanic acid into ammonium sulfocyanid and then heating the ammonium sulfocyanid at a temperature above 50° C. with such a proportion of water and acid that no appreciable precipitate is produced in the liquor and that no appreciable volatile nitrogenous products escape.

2. A process for recovering in the form of an ammonium salt the nitrogen of the hydrocyanic acid in crude coal gas which process consists in first converting the hydrocyanic acid into ammonium sulfocyanid and then heating the ammonium sulfocyanid at a temperature above 50° C. with such a proportion of water and sulfuric acid that no appreciable precipitate is produced in the liquor and that no appreciable volatile nitrogenous products escape.

3. A process for recovering in the form

of an ammonium salt the nitrogen of the hydrocyanic acid in crude coal gas, which process consists in first converting the hydrocyanic acid into ammonium sulfocyanid and then heating the ammonium sulfocyanid at a temperature above 50° C. with water and with sulfuric acid equivalent in quantity to the ammonium sulfate which will be produced from the ammonium sulfocyanid by this heating and to the ammonia in the volume of gas from which the sulfocyanid has been made, and finally introducing the liquor thus produced into the saturator of the apparatus in which the ammoniacal liquor produced from the said gas is distilled.

4. A process for recovering in the form of an ammonium salt the nitrogen of the hydrocyanic acid in crude coal gas, which process consists in first converting the hydrocyanic acid into ammonium sulfocyanid solution of 20–30 per cent. strength and then heating this solution at 80–110° C. with one and a half times its volume of sulfuric acid of 70–80 per cent. strength.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

EDWARD VICTOR EVANS.

Witnesses:
JOSEPH MILLARD,
W. J. SKERTEN.