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METHOD OF MAKING CYANOHYDRINS

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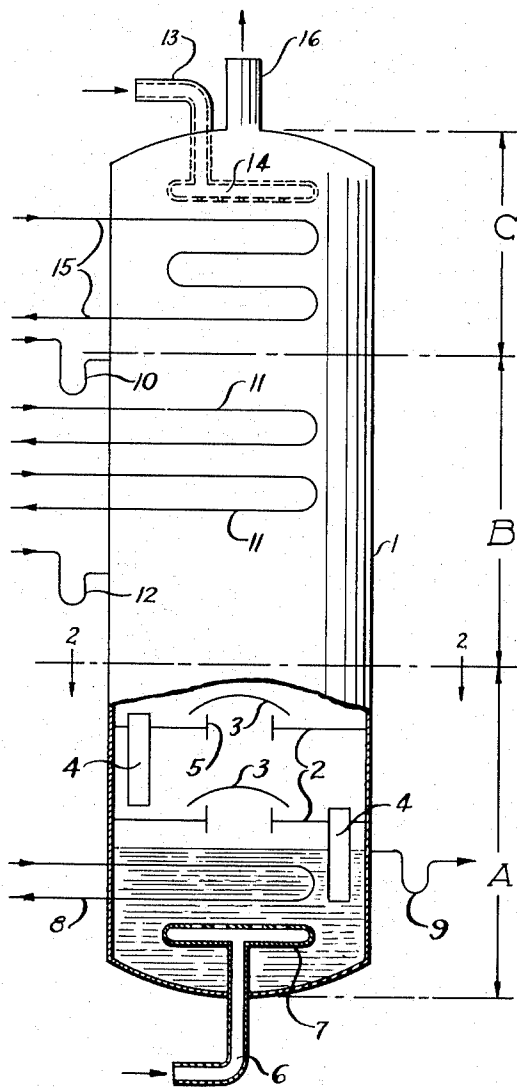


FIG. 1

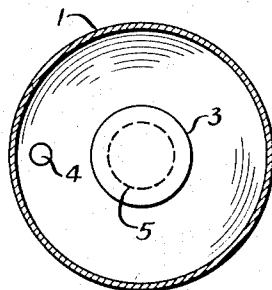


FIG. 2

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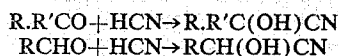
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10 Claims. (Cl. 260—465.6)

The present invention is directed to the production of cyanohydrins and more particularly to a continuous method having high efficiency.

It is well known that aldehydes and ketones react with hydrocyanic acid to form cyanohydrins according to the following equations.



wherein R and R' are hydrocarbon radicals.

The reaction is one that comes to an equilibrium and even if exact combining weights of reactants are used, there is also present in the final mixture some uncombined HCN and uncombined aldehyde or ketone. The ratio of uncombined reactant differs for the various aldehydes or ketones. It varies also with the amount of water present and with the temperature.

The rate of reaction of the HCN with the carbonyl compound is accelerated by the presence of small amounts of alkali. Under such conditions the equilibrium is reached very quickly. Conversely, the reactions, both of combination and dissociation, are slowed down and may be stopped altogether by the addition of small amounts of acidic substances.

For example, in the prior art acetone cyanohydrin has been manufactured by taking 96% liquid hydrocyanic acid, cooling, adding a small amount of alkali or sodium cyanide solution in water and then adding acetone under agitation with cooling. When the acetone has all been added, the mixture was agitated for a while at the low temperature and then acidified with dilute aqueous hydrochloric acid. After this it was allowed to warm up to room temperature and the free acetone and HCN removed by blowing with air or by heating under vacuum. Because of the acid condition, dissociation of the cyanohydrin did not occur. The yield was less than about 45%. In order to get superior raw material yield, it was necessary to recover the free reactants, separately, and re-use them in the process, which was a relatively costly operation; even then the overall yield was far from theoretical.

The preparation of liquid HCN is expensive. If sodium cyanide and acid are used, raw material costs are high. If HCN is made from natural gas and ammonia, for example, by the method of Andrussov, described in U. S. Patent No. 1,934,838, raw material and production costs are low, but recovery of liquid HCN from the dilute gas adds a substantial item of expense. In any case, the preparation, storage and handling of liquid HCN is hazardous and requires an expensive refrigeration system.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in prior methods, it being among the objects of the present invention to provide a simple and safe method adaptable for continuous operation of forming cyanohydrins using hydrocyanic acid gas.

It is also among the objects of the present invention to utilize a cheap source of HCN which is dilute, and obtain a full recovery of cyanohydrins by the use thereof.

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In practicing the present invention there is provided a continuous system consisting of a set of three zones in vertical arrangement and usually contained in a single tower provided with sets of bubble caps throughout the length thereof. In the lowermost zone, the cyanohydrin is recovered and at the same time any excess of HCN, aldehyde or ketone is removed therefrom. The intermediate zone constitutes the zone of reaction, wherein gaseous HCN is reacted with a ketone or aldehyde with cooling to prevent volatilization of the reactants. The uncombined HCN passes into the uppermost zone where it meets a stream of cold water containing alkali, causing the HCN to be absorbed as alkali metal cyanide and the residual gases are allowed to flow out of the top of the tower.

The invention allows the use of dilute HCN gas such as an 8% mixture obtained in the process referred to above without concentration and without conversion to liquid HCN. In order to avoid the reaction of the cyanohydrin with ammonia, I remove the free ammonia which is present in the HCN gas in unreacted form. This is very easily done by scrubbing with sulfuric acid whereby a valuable by-product, sulfate of ammonia, is obtained.

In the accompanying drawing constituting a part hereof and in which like reference characters indicate like parts,

Fig. 1 is a front elevational view diagrammatic in character, showing a tower with suitable equipment for practicing the present invention, some parts being shown in section, and

Fig. 2 is a horizontal cross-sectional view taken along line 2—2 of Fig. 1.

The apparatus consists of a vertical tower, one usually circular in cross-section and having a series of horizontal plates 2 spaced apart and extending for practically the entire height of the tower. Each of the plates is provided with a bubble cap 3, an overflow pipe 4 and a dam 5 whereby a body of liquid is held on each of the plates. The showing is diagrammatic and this type of bubble cap tower is well known.

Through the bottom of tower 1 extends a pipe 6 for the entrance of HCN gas, the pipe terminating in a head 7 having a series of openings at the upper face thereof to divide the gas into fine streams. Heating coils 8 are provided below the liquid level in zone A and a trap 9 is provided to maintain a constant level of liquid with overflow of product as it is formed.

At the top of zone B there is an inlet 10 for the reactant which is an aldehyde or a ketone. A series of coils 11 are provided between the plates of the zone for the purpose of providing cooling means to absorb the heat of the reaction. At the bottom of zone B is a duct 12 for the entrance of an acid for the purpose of neutralizing the alkali in the reacted mass.

The uppermost zone C has a pipe 13 entering the top thereof, terminating in a head 14 having a series of openings in the lower face thereof for spraying water into the top of the tower. Cooling coils 15 are provided in zone C and at the top thereof is an outlet 16 for waste gas.

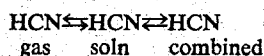
In the operation of the process, a solution of alkali is introduced through pipe 13 into zone C, which is cooled moderately and usually below ordinary room temperatures by cooling coils 15. The carbonyl compound is introduced at 10, dissolving in the solution which passes downwardly over successive plates where it meets and contacts with the HCN gas passing upwardly. A reaction takes place forming the cyanohydrin and the heat of reaction is removed by cooling coils 11. The reaction mixture then passes out of zone B and into zone A, there being added thereto sufficient amount of an acid introduced through inlet 12, to render the mixture acid and thus prevent hydrolysis of the cyanohydrin.

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The product accumulates in the bottom of zone A and overflows through exit 9. The temperature is maintained at above the boiling point of the carbonyl used by heating coils 8.

In zone A, free carbonyl compound and free HCN are removed from the aqueous solution of cyanohydrin without dissociation of the cyanohydrin which is stabilized by the acid conditions. This is accomplished by the sweeping action of the inert gas, the temperature being high enough to prevent the absorption of HCN.

In zone B, HCN is absorbed from the dilute gas and dissolved in the water present. The cooling helps the absorption and the absorbed HCN reacts with the carbonyl compound to form the cyanohydrin. As a result of this removal of HCN from solution by reaction, more HCN is dissolved and so HCN is rapidly and continuously removed from the dilute gas stream. This may be represented by the series of equilibria shown below:



The net effect is displacement to the right. The cooling also removes any heat generated by the reaction. In addition, there is condensation or absorption of the carbonyl compound vaporized by the passage of gas through warm zone A.

Zone C serves to catch small amounts of HCN that may have been carried out of zone B by the inert gas. This is accomplished by the scrubbing action of cold water containing small amounts of alkali. This alkali serves a double purpose; it absorbs HCN from the gas and it serves as catalyst in zone B to promote the formation of cyanohydrin. If the carbonyl compound is somewhat volatile it also will be scrubbed out by the cold water.

The following is a specific example of the operation of the present invention:

By means of heating coil 8 the temperature in zone A is maintained at about 80° C. By cooling coils 11, the temperature in zone B is maintained at 25°-30° C. In zone C by cooling coils 15, a temperature of 1° to 4° C. is maintained.

There is introduced through pipe 6 a dilute HCN containing about 8% thereof in a mixture of various gases and free from ammonia. Through pipe 13 there is introduced a 40% aqueous solution of sodium hydroxide having a pH of 8.5 to 9.0. Acetone is introduced at 10 in an amount which is equimolecular with respect to the HCN. The reaction therebetween takes place and the cooling by coils 11 is adjusted so as to maintain the desired temperature therein.

At 12 there is introduced a 50% aqueous acetic acid in an amount sufficient to give a pH of about 3.0. The pH may be tested by any suitable means, such as paper, impregnated with methyl red or by any other suitable color method. In order to check on the equimolecular proportions of acetone and HCN, provision is made at the upper part of zone A to withdraw a sample from time to time. The sample is analyzed and the flow of acetone or HCN, or both, are adjusted to give the desired proportions.

In the present invention a number of aldehydes and ketones may be used, such compounds being liquid at room temperatures and having from 1 to 5 carbon atoms. The compounds have a boiling point not over about 100° C. and are water soluble and distillable in steam. Among the ketones which may be used are methyl ethyl ketone, diethyl ketone, and methyl propyl ketone. Among the aldehydes used are acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde and crotonaldehyde.

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Considerable variation in the details may be made within the scope of the invention. For instance, the temperature in the three zones may vary substantially, depending upon various factors and the temperature in zone A may range from about 65° to 100° C. In zone B the temperature may vary between about 25° and 60° C. In zone C the temperature may vary from 0° to about 20° C. Similarly the pH in the several zones may vary within relatively wide limits. In zone A the pH may range from 2.0 to 5.0 and in zones B and C, the pH may vary from 7.5 to 9.0.

Various acids may be used for bringing the pH to the acid side, it being important that the acid be non-volatile under the conditions used and non-reactive with respect to the constituents. Among such acids are sulfuric, oxalic and phosphoric. The concentration of the HCN gas may vary within wide limits, and although usually the HCN content is from 5% to 10%, it may vary from 2% and up to 60%.

I claim:

1. A continuous method of making cyanohydrins which comprises passing a gas containing HCN upwardly through successive zones of reaction, introducing aqueous alkali solution into the uppermost zone and causing the same to flow downwards, introducing into the intermediate zone a liquid carbonyl substance taken from the class consisting of aldehydes and ketones, and introducing into the lowermost zone an acid sufficient in amount to provide a pH less than 7.

2. A method according to claim 1 in which the temperature in the lowest zone is sufficiently high to prevent absorption of HCN in the liquid therein.

3. A method according to claim 1 in which said uppermost zone is at a moderate temperature and said intermediate zone is cooled to absorb heat of reaction.

4. A method according to claim 1 in which the temperature in the lowest zone is sufficiently high to prevent absorption of HCN in the liquid therein to cause volatilization of said carbonyl substance.

5. A method according to claim 1 in which in said uppermost zone free HCN is fixed by said alkali in the form of alkali metal cyanide.

6. A method according to claim 1 in which in said intermediate zone HCN gas is dissolved in the solution and is reacted with said carbonyl substance.

7. A method according to claim 1 in which the amount of HCN in said gas is not over 10%.

8. A method according to claim 1 in which the HCN is freed from ammonia before being introduced into said zones.

9. A method according to claim 1 in which said zones are vertically arranged in a tower.

10. A method according to claim 1 in which said zones are vertically arranged in a tower and each zone consists of a plurality of sections holding liquid through which said gas passes.

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