PATENT SPECIFICATION

COMPLETE SPECIFICATION

Production of Cyanogen

We, E. I. Du Pont de Nemours and Co., a corporation organised and existing under the laws of the State of Delaware, United States of America, located
5 at Wilmington, Delaware, United States of America, and Burritt Samuel Lacy, Lewiston Heights, Harlan Avery Bond, 3025, Macklem Avenue, and Wilbie Scott Hine Gardener, 8449, West Rivershore
10 Drive, all of Niagara Falls, New York, County of Niagara, United States of America, all citizens of the United States of America, do hereby declare the nature of this invention and in what manner the
15 same is to be performed, to be particularly described and ascertained in and by the following statement: —

This invention relates to the production of cyanogen and more particularly to a
20 method for producing cyanogen from hydrogen and cyanide and chlorine or cyanogen chloride.

Cyanogen is a colourless gas of high stability which is useful for a variety of
25 chemical syntheses and other chemical operations and as a lethal agent, for example, in fumigation. Heretofore cyanogen has not been manufactured in large quantities nor used to the extent im-
30 plied by its useful properties, no doubt because of the unsatisfactory and relatively expensive character of known methods for making this compound. Cyanogen was discovered in 1815 by Gay-
35 Lussac, who prepared it by thermal decomposition of mercuric cyanide. Proposed improvements since that date have similarly involved methods such as decomposition of heavy metal cyanides by
40 heating at high temperatures or in aqueous media from copper sulphate and alkali cyanides. Cyanogen also has been made by decomposition of organic nitrogen-containing compounds, for example
45 by heating oxamide. Such methods are expensive, inefficient and unsatisfactory for economical large scale production of a chemical product.

According to the present invention we
50 provide a process for the production of cyanogen which comprises reacting hydrocyanic acid with chlorine or with cyanogen chloride in the vapour phase at an

elevated temperature. Advantageously the reaction is carried out by passing the 55 reaction mixture over a surface active material at an elevated temperature between 200° C. and 1000° C.

When hydrocyanic acid is reacted in this way with chlorine, cyanogen can be 60 produced practically quantitatively without appreciable formation of polymers or other undesired by-products.

$$2HCN + Cl_2 \rightarrow (CN)_2 + 2HCl$$
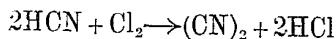
The reaction may be carried out simply 65 by mixing hydrogen cyanide and chlorine in the stoichiometrical proportions as indicated by the above equation and passing the mixture through a suitable reaction chamber at an elevated temperature 70 which, for example, may vary from about 200 to 1000° C.

The reaction temperature must be sufficiently high to cause the formation of cyanogen at a satisfacorily high rate. 75 For this purpose the minimum temperature required will vary, depending upon space velocity and the characteristics of the reaction chamber employed. For example, we have found that when the 80 reaction chamber is an empty glass or quartz tube having smooth sidewalls, it is generally necesesary to maintain a reaction temperature not lower than 600° to 700° C. in order to obtain conversion 85 of the hydrogen cyanide to cyanogen at economically high rates. On the other hand if the reaction chamber is packed with a surface active material, the minimum temperature will be lowered con- 90 siderably. Various known surface active materials may be used, or the reaction chamber may be packed with any inert solid material which will provide a larger area of surface. In general however, 95 the greater the surface activity of the packing material, the lower will be the minimum required reaction temperature. For example when the reaction chamber is packed with a good grade of activated 100 carbon, the reaction occurs at appreciable rates at temperatures as low as 200—300° C. We therefore generally prefer to use a surface active packing material such as

[*Price* 1/-]

activated carbon, silica gel and the like and operate at reaction temperatures of from 200—300° C. and higher.

The necessary reaction temperature
5 will depend on the space velocity, i.e., the ratio of the volume measured at normal temperature and pressure of reaction mixture passing through the reaction space in unit time to the volume of the
10 reaction space. Thus a low reaction temperature requires a comparatively low space velocity, while higher temperatures accelerate the reaction, and permit the employment of high space velocity. For
15 example with an empty reaction space at a temperature between 700° C. and 750° C., the space velocity (for isothermal reaction) should preferably not exceed 50 S.V.H. (space velocity using an hour as
20 the unit of time). On the other hand at temperatures of approximately 850° C., the permissible space velocity may be as high as 1500 S.V.H. Similarly with some activated carbon catalysts at a
25 temperature of approximately 300° C., a space velocity of 15 S.V.H. or less should be used, while at temperatures of 650° C. or higher a space velocity of 1500 S.V.H. is suitable.
30 Under the preferred operating conditions as above described, practically complete conversion of hydrogen cyanide to cyanogen is obtained. However, the invention is not restricted to those con-
35 ditions, as cyanogen begins to form at lower temperatures. For example, with the activated carbon catalyst, more or less cyanogen may be formed at temperatures as low as 100° C., and with no catalyst
40 at temperatures of 450° C., or lower, at sufficiently low space velocities. Under such conditions, the reaction product may be a mixture of cyanogen and cyanogen chloride.
45 Instead of reacting the hydrogen cyanide with chlorine it may be reacted with cyanogen chloride, when reaction occurs in accordance with the equation

$$HCN + CNCl \longrightarrow (CN)_2 + HCl$$
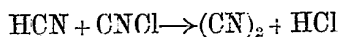
50 In carrying out this reaction, reaction conditions similar to those described above for reaction with chlorine may be utilised with equally good results.

Thus, the formation of cyanogen by
55 our process may be considered as occurring in two stages:

(1) $HCN + Cl_2 \longrightarrow CNCl + HCl$
(2) $HCN + CNCl \longrightarrow (CN)_2 + HCl$
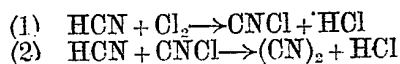
By reacting two moles of HCN with
60 one mole of chlorine, the two stages may occurr concurrently. If desired the first stage reaction (1) may be carried out under such conditions that little or no cyanogen formation occurs by reaction
65 (2) and the resulting cyanogen chloride (with or without first separating the by-product HCl) may be converted to cyanogen by reaction (2). We have found that the two reactions tend to occur at different
70 temperatures, reaction (1) usually being complete at temperatures where reaction (2) is incomplete. Under certain conditions of space velocity, especially in the presence of a catalyst (for example as de-
75 scribed by Sernagiotto, Giorn. Chim. Ind. Appl. 3: 153, 1921; Chem. Abs. 15: 2593) reaction (1) is complete below the minimum temperature required to initiate reaction (2). For example at a
80 reaction temperature of 100° to 200° C. and an S.V.H. of 500, in the presence of a surface active catalyst such as activated carbon, reaction (1) goes to completion to convert HCN to cyanogen chloride with
85 practically no cyanogen formation. Under the same conditions, except at a temperature of 400—500° C., reaction (2) is initiated. In the absence of a catalyst, the initiation temperatures are higher for
90 both reactions and generally both reactions occur concurrently. It is thus possible, by selection of reaction conditions, to produce either a mixture of cyanogen chloride and cyanogen or to
95 produce either product substantially uncontaminated by the other.

It should be understood that the above described reaction temperatures are for isothermal reaction in the reacting gases.
100 If for practical reasons an essentially adiabatic reaction (i.e. in a thermally insulated reactor) is desired, then, since the reactions are highly exothermic, the gases are fed to the reactor at tempera-
105 tures suitably below the desired final reaction temperature and yet high enough to initiate the reaction at a satisfactorily high velocity. The appropriate initial temperature of the incoming gases thus
110 will depend on the space velocity, rate of radiation or other cooling in the reactor, etc. and may be calculated for the particular conditions which are employed. Generally we prefer to preheat the re-
115 actants to a temperature several hundred degrees below the desired maximum offgas temperature and operate at a space velocity of 100 to 1500 S.V.H. For example, if the maximum offgas tempera-
120 ture desired is between 600° and 1000° C., the reactants may suitably be pretreated to a temperature between 100° C. and 500° C.

We find it advantageous to dilute the
125 mixture of reactants with partially cooled offgas from the reaction chamber, thus re-

cycling part of the product. The purpose of this is primarily to prevent the final offgas temperature reached in adiabatic second stage reaction from being unduly high; yet it is desirable that the reactant mixture should be warm (140° C.) on entering the reactor, in order that the rise in temperature due to the first stage reaction shall make the gas mixture hot enough to initiate the second stage reaction at a high rate. However, even if the reactant gases are brought at room temperature (e.g. 30° C.) into the adiabatic reactor, the first stage reaction will nevertheless initiate itself at a fair rate; and if too high a proportion of recycled gas has not been added as diluent, the gas, as a result of the first stage reaction, will still be hot enough to initiate the second stage reaction at a fair rate. In other words, the preheating is advantageous under certain conditions, but is not essential. In cooling the final offgas, instead of reducing its temperature directly from 880° C. to say 100° C. or less by a conventional water-cooled tubular cooler, it may first be instantaneously " chilled " from 880° C. to, say, 250° C. by mixing with recirculated offgas at 100° C., and then the mixture at 250° C. (after by-passing from it the 0.5 $(CN)_2 + 1.0$ HCl desired as hot diluent for the initial reactant mixture) is cooled from 250° C. to say 100° C. or less in a conventional cooler.

In a preferred mode of operation which is described in the way of example, we may react hydrogen cyanide with chlorine in the presence of activated carbon in an adiabatic reactor. The reactant mixture, in the proportions of 1.0 mole chlorine gas at room temperature added to about 2.1 moles hydrogen cyanide vapour at 100° C. (i.e. 5%, or in general say about 1 to 10%, in excess of the stoichiometrical 2.0 moles of hydrogen cyanide corresponding to complete reaction of the chlorine) is diluted with about half its volume of recycled offgas (that is with about 0.5 mole $(CN)_2 + 1.0$ mole HCl), which has been partially cooled to about 250° C.; this results in the total mixture entering the reactor at about 140° C. (though this last temperature may be varied widely). The flow rates used depend of course on the reaction temperatures employed, as well as on the activity of the catalyst, but good results are obtainable at an S.V.H. of 500 (or even considerably higher), corresponding for the above-given total mixture to an S.T.Y. of about 380; S.T.Y. denotes the space-time yield in lbs. cyanogen produced by the reaction per 24 hours per cu. ft. of catalyst.

Under the above conditions, the first stage of the process, that is the reaction $Cl_2 + HCN \rightarrow ClCN + HCl$, is initiated and goes on with great rapidity, as the mixture at 140° enters, and traverses the inlet portion of, the catalyst bed of activated carbon; and the temperature reached adiabetically as a result of this exothermic reaction is in the neighbourhood of 500°. When—and even somewhat before—this last temperature is reached, however, the second step of the process, i.e. $CNCl + HCN \rightarrow (CN)_2 + HCl$, also is initiated at a good rate; and this second step, if carried on strictly adiabatically, results in the offgas from it, consisting of 1.0 mole $(CN)_2 + 2.0$ moles HCl (plus the original recycled 0.5 mole $(CN)_2 + 1.0$ mole HCl, plus the few percent. of excess HCN) leaving the catalyst bed at a temperature of around 880° C. (The latter temperature does no harm to the reactants or to the catalyst, though actually it may be considerably reduced by thermal conduction through the insulation of the reactor; practically it makes little difference whether the final temperature is 700° or 880°).

The offgas is then cooled, and passed through a water scrubber, which removes hydrogen chloride as a concentrated solution, together with a minute fraction of the total cyanogen. The cyanogen issuing from the top of the scrubber, after drying, is substantially pure, except for a slight amount of hydrocyanic acid resulting from the small excess of the latter used in the reactant mixture, from which it is readily purified by rectification. The hydrochloric acid solution produced in the scrubber may be further treated by conventional means to remove its very small content of dissolved hydrogen cyanide and cyanogen and forms a usable by-product.

The above example is merely illustrative as to temperatures, rates, and the like. Thus if the operation is carried on in an isothermal reactor, there will be no point in adding any recycled gas as diluent for the reactant mixture, and the whole operation may be carried on at a temperature of for example 500—700°; or the first stage reaction may be carried on at say 30°—200° and the second stage at 400—700°. Moreover the proportion of diluent recycled offgas added to the reactant mixture, and its temperature, may if desired be varied quite widely from the values given in the example.

In a preferred method for practising our invention without the use of a catalyst or packing material, the reactant gases, diluted with about twice their volume of recycled hot offgas, and the

whole at a temperature of around 500—600° C., are passed through a large empty reaction space at a space velocity of 100 S.V.H. During the course of the reaction, the temperature (without allowing for thermal losses) will rise to 900—1000° C. The offgas is then treated in the same general way as described above. Although the invention is not restricted to any particular proportions of hydrogen cyanide and chlorine or cyanogen chloride passed into the reaction space, we usually prefer to use close to the stoichiometric proportions, i.e. slightly more than 2 moles of hydrogen cyanide to one mole of chlorine, or slightly more than one mole of hydrogen cyanide to one mole of cyanogen chloride, in order to ensure a considerable reaction velocity even near the end of the reaction, and consequently an essentially complete absence of chlorine in the offgas.

While as explained above, there is a minimum temperature at which complete conversion to cyanogen occurs and which depends upon surface conditions within the reactor and space velocity, there is no theoretical upper limit to the permissible reaction temperature except the decomposition temperature of cyanogen, which thermally is very stable. We have, for example, satisfactorily operated the above-described reactions at temperatures as high as 950° C. without causing appreciable formation of polymers or other undesired by-products. Under such conditions we have obtained substantially quantitative yields of cyanogen.

Operating without the use of a surface active material, that is, in an empty reaction space having quartz sidewalls, we have obtained quantitative conversion of HCN to cyanogen at reaction temperatures of from 670° to 950° C. With different grades of activated carbon we have obtained quantitative yields of cyanogen in our process at reaction temperatures of from 170° C. to 600° C. and higher, depending on the space velocity. With broken silicon shards of 8-mesh size, we have obtained quantitative yield of cyanogen at reaction temperature of about 700° C. It is understood that there is no harm in permitting the temperature to rise to 900° C. or even higher, even though the reaction is carried out in the presence of a surface active material such as activated carbon which permits the reaction to occur at a lower temperature.

Our process is simple and easy to carry out in practice. When a surface active catalyst such as activated carbon or other reactor packing is used, the process may be operated for indefinite periods of time with no decrease in yield or rate of production. There is no substantial deposition of solids or reaction by-products on the catalyst or packing material and catalyst regeneration is unnecessary. Likewise, when no catalyst or packing is used, the reactor remains clean over indefinite periods. No desirable by-products are formed in any appreciable quantity and a pure product is obtained which may be recovered from the reaction mixture without substantial loss and with a minimum of purification operations.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of cyanogen which comprises reacting hydrochloric acid with chlorine or with cyanogen chloride in the vapour phases at an elevated temperature.

2. A process according to claim 1, in which the reaction is carried out by passing the reaction mixture over a surface active material at a temperature between 200° C. and 1000° C.

3. A process according to claim 2 in which the surface active material is active carbon.

4. A process according to any of the preceding claims in which the hydrocyanic acid is reacted with chlorine substantially in the molar ratio of 2:1.

5. A continuous process according to claim 4, in which the gaseous reaction mixture is treated by passing it through a thermally insulated reaction space containing an activated carbon catalyst at a temperature between 600° C. and 1000° C.

6. A process according to claim 5 in which the gaseous reaction mixture is delivered to the reaction space at a temperature between 100° and 500° C.

7. A process according to claim 5 or claim 6 in which the mixture of reactants is diluted with part of the gases leaving the reaction space.

8. A process according to any of claim 1 to 2 in which hydrocyanic acid is reacted with a substantially equivalent amount of cyanogen chloride.

9. A process for the production of cyanogen, substantially as hereinbefore described.

10. Cyanogen, whenever obtained by a process according to any of the preceding claims.

Dated the 17th day of December, 1943.
J. W. RIDSDALE,
Solicitor for the Applicants.