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PRODUCTION OF ALKALI METAL CYANATES

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This invention relates to a method of preparing alkali metal cyanates.

It is well known that the most common method for preparing cyanates involves oxidation of the corresponding alkali cyanides with lead oxide. This oxidation is usually carried out by melting the cyanide and then gradually incorporating lead oxide into the molten mass, the cyanide reacting with the oxide to produce the alkali cyanate and molten lead; the molten lead may be withdrawn as it is produced. It will be evident that this process possesses important disadvantages. In the first place, relatively expensive lead oxide must be employed. In the second place, it is necessary to remove and handle molten lead during the course of this process; this operation requires the employment of considerable care and the use of special equipment designed to protect workmen from the dangers incidental to the handling of a hot molten metallic product. In the third place, small amounts of lead inevitably are present in the final product. As a result of these disadvantages the above method is not particularly practical from a commercial standpoint. Attempts to provide more commercially practical processes for the preparation of cyanates have not succeeded in improving substantially over the above-described method from the standpoint of simplicity and economy of operation.

Oxidation of alkali metal cyanides with oxygen-containing gases yields the corresponding carbonates; although it has generally been assumed that the cyanates were intermediate oxidation products, it has not been possible to control the extent of this oxidation so as to produce cyanates on a commercial scale. As a result, oxidation of cyanides with oxygen-containing gases has up to the present been of academic interest only in so far as the production of cyanates has been concerned.

It is an object of this invention to provide a simple and inexpensive method for the manufacture of alkali metal cyanates.

It is a more specific object of this invention to provide a method for the controlled oxidation of alkali cyanides to the corresponding cyanates by treatment with oxygen-containing gases.

We have made the surprising discovery that alkali metal cyanates may be manufactured in a simple and economical manner by contacting a molten alkali metal cyanide with an oxygen-containing gas under controlled conditions serving to prevent or substantially minimize oxidation of the cyanate thus produced. We have found that in order to obtain alkali metal cyanates in commercial quantities by this method, it is important that the temperature at which the oxidation is carried out should be below about 700° C. Moreover, high concentrations of oxygen in contact with the cyanide should be avoided; therefore, air or an oxygen-containing gas containing not more than about 25% oxygen is most advantageously employed, and the oxidation is carried out in a manner such that an excess of the oxygen-containing gas will not collect in the cyanide melt. Furthermore, oxidation of the cyanide should not be carried to completion, but should be terminated while the reaction mass still contains appreciable quantities of the cyanide; attempts to carry the oxidation to completion, we have found, result in the substantial conversion of the cyanate product to carbonate. We prefer to carry out the oxidation in vessels constructed of Monel metal, since this alloy appears to catalyze the reaction, thus reducing the reaction time, and is not subject to corrosion. By carrying out oxidation of the cyanide in accordance with these controlled conditions, alkali metal cyanates may be obtained in a comparatively pure state and in excellent yields. Since our invention preferably involves the employment of air as one of the reactants, it is obvious that our method is much more economical than methods such as those employing lead oxide as one of the reactants. Moreover, our invention is extremely simple to operate.

In carrying out our invention a suitable quantity of an alkali metal cyanide is first introduced into a reaction vessel and heated until molten. The temperature to which the cyanide is heated should be sufficiently high to form a completely fluid mass; the particular temperature employed may, however, vary with the cyanide to be treated. Thus, when potassium cyanide is to be oxidized, an initial temperature in the neighborhood of 650° C. is preferable, whereas if sodium cyanide is to be treated, a temperature in the neighborhood of 600° C. is more suitable. The temperature of the melt during oxidation should in all cases be below about 700° C. in order to achieve the desired results. The reaction vessel in which the oxidation is carried out is preferably constructed of Monel metal, i. e. the alloy containing about 68% to 70% nickel, about 28% copper, and small amounts of iron, silicon and manganese, since we have found that vessels constructed of this material not only resist corrosion by the cyanide and cyanate, but also catalyze oxidation of the cyanide to cyanate. It is to be understood, however, that it is not intended to limit our in-

vention to oxidation of the cyanides in Monel equipment, since other metallic equipment capable of resisting substanital corrosion when in contact with the molten cyanide or cyanate and which does not facilitate the formation of the alkali carbonate may be employed.

After the cyanide has been melted and the temperature of the melt adjusted to the desired point below about 700° C., the molten mass may be thoroughly agitated and contacted with air or other oxygen-containing gas, whereby the cyanide is oxidized to cyanate; since considerable heat is evolved during the oxidation, care should be taken that the temperature does not rise above about 700° C. by reason thereof. As hereinabove stated, high concentrations of oxygen in contact with the cyanide should be avoided; hence, we prefer to employ as the oxidizing medium air or an oxygen-containing gas containing not more than about 25% oxygen. Furthermore, an excess of oxygen should not be permitted to build up in the molten cyanide. We have found that in some cases, particularly in small-scale installations, the presence of an excess of oxygen in contact with the cyanide may be avoided and the oxidation most suitably carried out by vigorously stirring the molten mass in a vessel open to the atmosphere so as to form a vortex in the center thereof, whereby air is sucked into the vortex in amounts sufficient to accomplish the desired oxidation. However, in large-scale operations it is ordinarily preferable to bubble air through the molten mass under agitation at a comparatively slow rate in order to furnish the cyanide with sufficient oxygen to accomplish the desired oxidation. We have found that when approximately 50% or more of the cyanide is oxidized, it is usually preferable to lower the temperature of the melt somewhat and then to complete the oxidation at these lower temperatures; when treating potassium cyanide it is most advantageous to drop the temperature to between about 570° and about 625° C., whereas in the oxidation of sodium cyanide a temperature between about 550° and about 600° C. is most suitable.

The time required for carrying out oxidation of the cyanide may vary, depending upon the particular cyanide being oxidized, the temperature employed, the oxygen content of the gas, and the material of which the reaction vessel is constructed. When employing Monel equipment it will be found that the desired degree of oxidation may be achieved in from four to ten hours, whereas with other equipment the time may be somewhat longer. Oxidation of the cyanide should not be carried to completion, but should be terminated while there is still an appreciable cyanide content in the melt. We have found that it is preferable to discontinue the oxidation when the cyanide content of the melt has been reduced to between about 2% and about 3%. Continuance of the oxidation substantially beyond this point ordinarily results in considerable oxidation of the cyanate product to carbonate with consequent loss of product.

When oxidation of the cyanide has reached the desired point, agitation of the melt may be discontinued and the molten mass may be removed from the reaction vessel and permitted to solidify. It will be found that this mass may contain anywhere from 80% to 95% cyanate, the particular amount depending chiefly upon the purity of the cyanide treated, the balance of the mass being the corresponding alkali carbonate and unreacted cyanide. The cyanate may be recovered from this mass in any suitable manner such as by crystallization from alcohol. We prefer, however, to recover the cyanate by dissolving the reaction mass in a hot aqueous medium containing at least one-half mol of a strong alkali per liter of solution and then cooling the solution to cause the cyanate to crystallize therefrom; this process is disclosed and claimed in the co-pending application of Hans R. Neumark Serial No. 390,909, filed April 29, 1941.

The following example is illustrative of the process of our invention. Amounts are given in parts by weight.

Example 1.—1,840 parts of potassium cyanide were introduced into a Monel kettle and the cyanide then heated to a temperature of 650° C., whereby a completely fluid molten mass was formed. This mass was then rapidly agitated with a Monel agitator, air being slowly bubbled through the mass during the agitation thereof. When analysis of the melt indicated that about 50% of the cyanide had been oxidized, the temperature was permitted to drop to about 570° C. and agitation continued at this temperature until analysis of the melt showed that the cyanide content had been reduced to between about 2% and about 3%. At this point agitation and flow of air through the mass was discontinued, and the melt was removed from the vessel and permitted to solidify. A product containing 86% potassium cyanate and only 11% potassium carbonate was obtained.

From the above description it will be evident that our invention provides a simple and highly effective method for the production of cyanates from alkali metal cyanides. Since this method obviates the economic and technical difficulties inherent in prior processes for the production of cyanates, it will be of great interest to those engaged in the production of such products.

Since certain changes may be made in carrying out the above method without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. The method for the production of alkali metal cyanates which comprises oxidizing a molten alkali metal cyanide by contact with an oxygen-containing gas at a temperature below about 700° C., and terminating oxidation of the cyanide when the reaction mass has a cyanide content of not less than about 2%.

2. A method for the production of alkali metal cyanates which comprises oxidizing a molten alkali metal cyanide by contact with an oxygen-containing gas containing not more than about 25% oxygen at a temperature below about 700° C., and terminating oxidation of the cyanide when the reaction mass has a cyanide content of not less than about 2%.

3. A method for the production of alkali metal cyanates which comprises oxidizing a molten alkali metal cyanide by contact with air at a temperature below about 700° C., and terminating oxidation of the cyanide when the reaction mass has a cyanide content of not less than about 2%.

4. A method for the production of alkali metal cyanates which comprises melting an alkali metal cyanide in a Monel metal vessel, rapidly agitating the melt in contact with air at a temperature below about 700° C., whereby the cyanide is oxidized to cyanate, lowering the temperature when more

than 50% of the cyanide has been thus oxidized, discontinuing agitation and permitting the melt to solidify when the cyanide content thereof is between about 2% and about 3%, and recovering the alkali metal cyanate from the solidified mass.

5. A process for the production of potassium cyanate which comprises heating potassium cyanide in a Monel metal vessel to a temperature of about 650° C., rapidly agitating the melt in contact with air, whereby the cyanide is oxidized to cyanate, lowering the temperature to between about 570° and about 625° C. when more than 50% of the cyanide has been thus oxidized, discontinuing agitation and permitting the melt to solidify when the cyanide content thereof is between about 2% and about 3%, and recovering potassium cyanate from the reaction mass.

6. A process for the production of sodium cyanate which comprises heating sodium cyanide in a Monel metal vessel to a temperature of about 600° C., rapidly agitating the melt in contact with air, whereby the cyanide is oxidized to cyanate, lowering the temperature to between about 550° and about 600° C. when more than 50% of the cyanide has been thus oxidized, discontinuing agitation and permitting the melt to solidify when the cyanide content thereof is between about 2% and about 3%, and recovering sodium cyanate from the reaction mass.

7. In the oxidation of alkali metal cyanides to the corresponding cyanates, the improvements which comprise contacting a molten alkali metal cyanide with an oxygen-containing gas and terminating the oxidation while the reaction mass still contains an appreciable quantity of the cyanide, the temperature of the reaction mass during the entire oxidation being maintained below about 700° C.

8. A method for the production of alkali metal cyanates which comprises melting an alkali metal cyanide in a Monel metal vessel, rapidly agitating the melt in contact with air at a temperature below about 700° C., whereby the cyanide is oxidized to cyanate, and terminating the oxidation while the reaction mass still contains an appreciable quantity of the cyanide.

9. A process for the production of potassium cyanide which comprises heating potassium cyanide in a Monel metal vessel at a temperature not exceeding 700° C. while contacting the potassium cyanide with an oxidizing gas to oxidize the cyanide to cyanate, and terminating the oxidation while the reaction mass still contains an appreciable quantity of the cyanide.

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