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PREPARATION OF GUANIDINE NITRATE

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The present invention relates to the preparation of guanidine salts and more particularly to a new and improved method of preparing guanidine nitrate.

It has been known for many years that guanidine salts may be produced by fusing an anhydrous mixture of appropriate ammonium and cyanamide salts, this preparative method being illustrated by the preparation of guanidine nitrate from calcium cyanamide and ammonium nitrate according to the overall equation:

$$CaCN_2+3NH_4NO_3\rightarrow NH_2C(NH)—NH_2.HNO_3+2NH_3+Ca(NO_3)_2$$

The process illustrated by the above equation requires excessively high temperatures in order to effect the fusion of the ammonium nitrate, and because of the explosive character of mixtures containing ammonium nitrate and carbonaceous materials, the anhydrous fusion procedure is hazardous to carry out. In 1939, British Patent 507,498 proposed a similar method wherein the fusion of the ammonium nitrate at more moderate temperatures was accomplished by the addition of water to the ammonium salt. A somewhat related method is described in U. S. Patent 2,109,934. By the use of water in accordance with these modified procedures, it was expected that the reaction temperature could be reduced to about 100–125° C. It was found, however, that the presence of water in the reaction mixture promoted the formation of various reaction by-products including dicyandiamide, melamine and also certain insoluble and infusible impurities which may have been formed from one or more of the hydrolytic by-products. Of these by-products, dicyandiamide may be converted to guanidine nitrate by treatment with an excess of ammonium nitrate but this transformation is not effected below about 160° C. (Compare Blair and Brahams, Ind. and Eng. Chem., 23, 1124 (1939).) Accordingly, in order to reduce the amount of dicyandiamide in the reaction product, it is necessary to carry out the above wet fusion process at a temperature of about 160° C. or above, under which conditions pressure equipment capable of withstanding 200–225 lbs. pressure per square inch is required.

Although the wet fusion procedure described above represents an improvement over the earlier anhydrous fusion technique, in certain respects, the more recent of these procedures is not entirely satisfactory particularly for large scale manufacture. In the first place, under the high temperature conditions required to convert the

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dicyandiamide by-product to guanidine nitrate, the reaction mixture has been found to be corrosive to most metals, even including 18–8 stainless steel. In the second place, the process requires the use of pressure equipment and this fact, coupled with the corrosive character of the reaction mixture, renders the process inherently hazardous. In the third place, even though dicyandiamide may be eliminated from the reaction products by carrying out the reaction at 160° C., the high temperature employed tends to increase the amount of insoluble and infusible by-products formed in the presence of water. It is therefore apparent that the wet cyanamide fusion procedure is characterized by several serious disadvantages and limitations.

Broadly speaking, the object of the present invention is to provide an improved process for the production of guanidine nitrate, the improved procedure being so designed as to obviate the disadvantages of the methods heretofore employed.

A more particular object is the provision of a guanidine nitrate process that may be carried out at ordinary atmospheric pressure in thin walled vessels.

A further object is a process of the character described which permits the production of guanidine nitrate under conditions such that the reaction mixture is not corrosive to stainless steel equipment.

Still another object is to provide a process capable of producing guanidine nitrate that is free from dicyandiamide, melamine and from insoluble and infusible impurities.

A further object is to provide a process that enables the direct conversion of crude nitrolime to guanidine nitrate in yields of at least 90% or better, calculated on the basis of the cyanamide content of the nitrolime.

Other objects and advantages will be apparent as the invention is hereinafter more fully described.

The foregoing objects may be attained in accordance with the present invention by effecting the fusion of the ammonium salt and the cyanamide salt in the presence of sufficient urea to reduce the melting point of the reaction mixture at all times to below about 120° C. By this procedure, the reaction between the added cyanamide salt and the ammonium salt may be carried out under reasonably anhydrous conditions at a temperature within the range of about 110 to about 135° C.

The process of the present invention as briefly

outlined above is characterized by several important advantages. In the first place, the undesirable hydrolytic by-products formed in the wet fusion procedure of the prior art are not produced under the essentially anhydrous conditions prevailing in the process of the present invention. In the second place, the absence of appreciable quantities of water in the reaction mixture obviates the necessity for using an autoclave during the fusion operation, ordinary thin walled vessels being satisfactory. In the third place, the reaction mixture of the present process is practically non-corrosive to stainless steel equipment within the relatively moderate temperature range (110–135° C.) employed during the fusion operation. Other advantages of the process will be apparent as the invention is described more fully.

The process of the present invention is conveniently effected by slowly adding the nitrolime or any other convenient source of cyanamide salt to a fused mixture of ammonium salt and urea, maintained at about 110–135° C., preferably at 120° C. Thermo-regulation is necessary during the addition of the nitrolime, inasmuch as the reaction is exothermic. With proper temperature control and with slow addition of the cyanamide salt, the formation of by-products, especially dicyandiamide, is greatly minimized, if not entirely prevented.

After the addition of the cyanamide salt to the ammonium salt-urea mixture is completed, the temperature of the reaction mixture is maintained at about 120° C., preferably until the total reaction time is about two hours. The reaction mixture is then diluted with sufficient water to dissolve and retain in solution any unreacted ammonium salt remaining in the mixture. Thereafter any lime present in the mixture (when the cyanamide salt consists of calcium cyanamide) may be precipitated in the form of the insoluble carbonate, and then separated from the hot solution. The hot solution is then cooled to crystallize the guanidine salt. If desired, the mother liquors remaining after the separation of the guanidine salt may be evaporated to dryness and the recovered mixture of salts and urea may then be recycled in the process after fortification with additional quantities of ammonium salt.

As pointed out above, in the process of the present invention, liquefaction of the ammonium salt is accomplished at moderate temperatures by carrying it out in the presence of sufficient urea materially to depress the fusion temperature of the mixture. The proportion of urea employed may obviously be varied within very wide limits. However, the lower limit is that necessary to reduce the fusion temperature of the ammonium salt-urea mixture to below 120° C. Where the ammonium salt consists of ammonium nitrate, the urea content of the mixture should not be permitted to fall materially below about 15% of the weight of the ammonium salt employed. To ensure a reasonable safety factor, it is preferable to use more than 15% urea, for example 25% or even larger proportions. The maximum ratio of urea to ammonium salt is determined largely by convenience in handling the reaction mixture which of course becomes progressively bulky as the urea content increases. Using mixtures containing from about 15% to about 45% urea, yields approaching the theoretical, calculated on the basis of the calcium cyanamide content of the crude nitrolime have been obtained. Where larger amounts of urea are employed, the effect of dilution of the reaction mixture generally renders it desirable to increase the amount of ammonium nitrate employed per unit weight of nitrolime used, in order to achieve a satisfactory yield.

The ammonium nitrate-urea mixture employed in accordance with the present invention, although not necessarily completely free of water, should not contain a large proportion of water inasmuch as the presence of a few per cent of water causes a rather marked diminution of yield to about 85–87% of the theoretical. For this reason it is preferable (but not essential) to employ a "substantially anhydrous" mixture of ammonium nitrate and urea, this term being understood to mean not more than 0.5% moisture.

It is significant that dicydiamide is not present in the reaction product, by qualitative tests, if the heating time following completion of the initial reaction is reduced to one hour or if the total time of addition and heating does not exceed about 2 hours. Furthermore, the use of an excess ammonium nitrate (for example, 100% excess) over that theoretically required permits the addition of the nitrolime to be made at a fairly rapid rate. The reaction mixture will attack 18–8 stainless steel at a temperature above about 140° C. but at lesser temperatures within the range of 110 to about 135° C., stainless steel remains unaffected.

In order more clearly to disclose the nature of the present invention a specific example illustrating the production of guanidine nitrate will hereinafter be described in considerable detail. It should be clearly understood, however, that this is done solely by way of example and is not intended to restrict the scope of the appended claims.

Example

Crude lime nitrogen (40.0 g., 63.3% $CaCN_2$=0.317 mole) was added over a twenty minute period to a fused mixture containing 180 g. (2.25 moles) of ammonium nitrate and not less than 30 g. of urea (0.5 mole). It is important that this urea content not drop below 15% of the urea-ammonium nitrate mixture during subsequent cycles in order that the mixture-melting point be maintained below about 120° C.

The addition (which was carried out in a stirred vessel of capacity twice that required to hold the reaction mixture) was followed by a heating period such that the total reaction time was two hours. The temperature was maintained throughout at about 120° C., although this was somewhat difficult during the addition stage since the initial reaction is slightly endothermic. Thermoregulation was therefore employed in order to maintain the temperature at about 120° C.

At the end of this time the reaction was diluted with about 100 cc. water, the calcium precipitated with carbon dioxide and ammonium carbonate (42 g., 0.35 mole) and the mixture was filtered at about 95° C. to remove the carbonaceous sludge. This precipitate was washed with about 110 cc. water, the wash water being used as diluent for a successive run. The hot solution was cooled to about 25° C. to crystallize the guanidine nitrate, which was removed and dried.

The final filtrate was analyzed for ammonium nitrate, and then evaporated by a single pass through a stainless steel column jacketed at about 142° C., using boiling isoamyl acetate for this purpose, the internal pressure being maintained at about 10 mm. The ammonium nitrate-urea-

guanidine nitrate solution was collected in a receiver (which served as the reaction vessel for a successive run) containing the fortifying ammonium nitrate, and maintained at about 120° C. For simplification purposes, the solution was not allowed to solidify before the subsequent run.

The average overall yield of guanidine nitrate for an entire series of runs was 92% of the theoretical. There was no tendency for this to decline, the final runs showing a slightly higher percentage conversion. The product showed an average purity of 90%, the remainder being largely ammonium nitrate. The thiourea formed was destroyed during the evaporation of the recycled residue at 140° C. at such a rate that the maximum amount (11 g. in 200 cc. filtrate) did not reach saturation value, and only small amounts, not more than 1.5%, appeared in the product. The thiourea may be destroyed on standing in the ammoniacal solution of the reaction at 100° C., which provides a convenient method for its removal, should this be found desirable. Dicyandiamide was not detected in the product, nor was there any trace of insoluble matter present.

It will be apparent to those skilled in the art that many variations in proportions, reactants and conditions may be made in the procedure described in the foregoing example. Thus other ammonium salts may be substituted for the nitrate employed in the illustrative example, where it is desired to produce other guanidine salts. It will also be apparent that cyanamide salts other than the calcium salt may be used if desired, the procedure being modified where necessary or desirable to take care of such changes. All such variations and modifications are to be understood as included within the scope of the appended claims.

I claim:

1. In the production of guanidine nitrate by the fusion of ammonium nitrate with a cyanamide salt, the improvement which comprises effecting the fusion under substantially anhydrous conditions in the presence of urea in an amount substantially 15 to 45% by weight of the ammonium nitrate to provide a reaction mixture which is liquid at a temperature below 120° C.

2. A method of producing substantially pure guanidine nitrate which comprises mixing ammonium nitrate with at least substantially 15% by weight of urea to form a mixture which becomes liquid at a temperature not exceeding 120° C., heating the mixture to a temperature between substantially 110 and 135° C., adding calcium cyanamide to said mixture while maintaining the temperature within said limits to form guanidine nitrate, adding water to form an aqueous solution, converting lime in the solution to an insoluble carbonate, removing the insoluble carbonate and cooling the solution to a temperature between 0 and 30° C. to precipitate substantially pure guanidine nitrate.

3. A method of producing guanidine nitrate which comprises providing an anhydrous mixture comprising from about 55% to about 85% ammonium nitrate and from about 15% to about 45% urea, fusing said mixture by heating the same to a temperature between about 115° C. and about 140° C., slowly adding calcium cyanamide to said fused mixture while maintaining the temperature of the resulting reaction mixture at about 115° C. to about 135° C., continuing the heating of said reaction mixture after the addition of said calcium cyanamide for a total heating period not exceeding about two hours, diluting the resulting crude product with water in a sufficient amount to dissolve and to retain in solution during subsequent purification a substantial portion of any unreacted ammonium nitrate present in the crude material, treating the resulting solution with ammonium carbonate in an amount sufficient to precipitate substantially all of the calcium contained therein in the form of the carbonate, separating the calcium carbonate from the hot solution, cooling the hot solution to about 0° C. to about 30° C. to crystallize guanidine nitrate therefrom and separating the crystallized guanidine nitrate from the cooled supernatant liquid.

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