

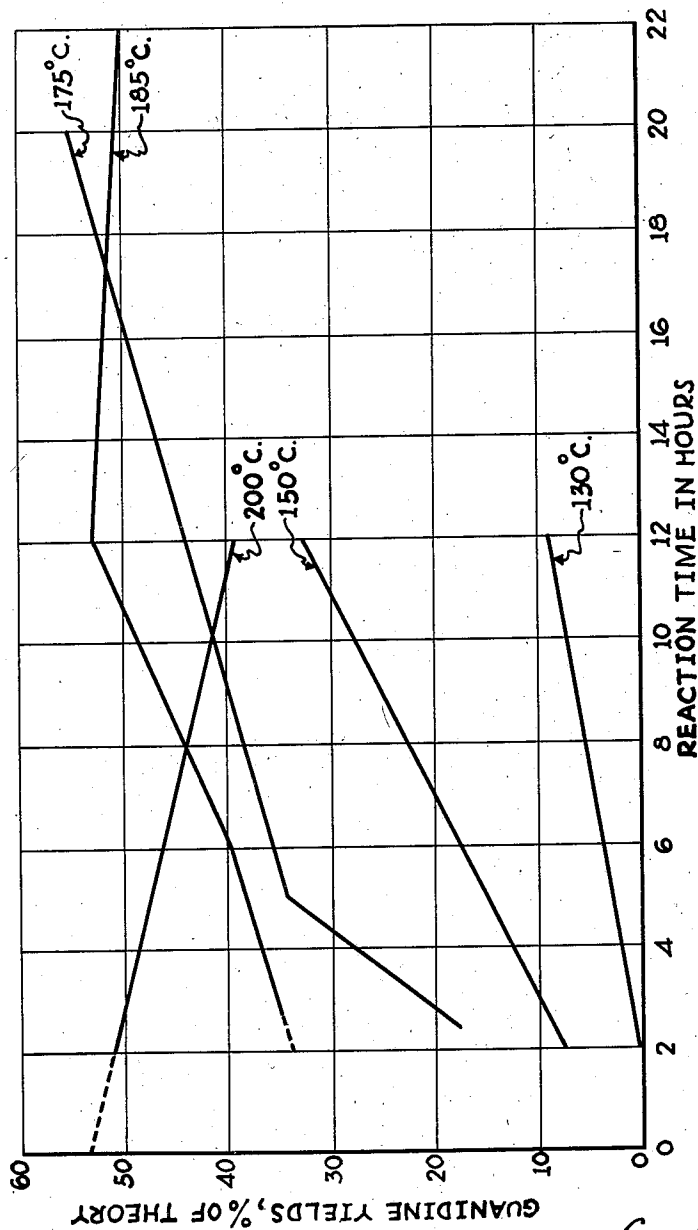
April 26, 1949.

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2,468,067

PREPARATION OF GUANIDINE NITRATE

Filed Jan. 31, 1948



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Patented Apr. 26, 1949

2,468,067

# UNITED STATES PATENT OFFICE

2,468,067

## PREPARATION OF GUANIDINE NITRATE

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Application January 31, 1948, Serial No. 5,562  
In Great Britain July 15, 1947

9 Claims. (Cl. 260—564)

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The present invention relates to an improved process for the manufacture of guanidine nitrate and has reference more particularly to its manufacture from ammonium thiocyanate.

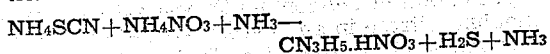
It has been known that guanidine nitrate can be prepared by the conversion of ammonium thiocyanate at elevated temperatures to guanidine thiocyanate which is reacted in solution with a compound bearing the nitrate anion to form guanidine nitrate. This procedure is limited theoretically to at best a 50 per cent yield of guanidine nitrite based on the weight of ammonium thiocyanate employed because two mols of ammonium thiocyanate are required to produce one mol of guanidine thiocyanate. As a further development it was attempted to react ammonium thiocyanate directly with a nitrate salt in molten admixture therewith whereby a theoretical yield of 100 per cent of guanidine nitrate on the said basis of the weight of ammonium thiocyanate employed might be expected. Such procedure was discovered to involve a severe explosion hazard and therefore was not further developed.

A primary object of the present invention is the provision of an improved process for the manufacture of guanidine nitrate in a single step from ammonium thiocyanate.

A further object of the invention is the provision of a process for the preparation of guanidine nitrate in improved yields and under conditions whereby the hazard of explosion is avoided.

The invention has four further objects such other improvements and such other operative advantages or results as may be found to obtain in the processes or apparatus hereinafter described or claimed.

Briefly stated, the present invention comprehends the reacting of ammonium thiocyanate and ammonium nitrate in solution in ammonia at temperatures at least above 120° C. It is preferable to employ in the reaction anhydrous ammonia in order to avoid the possibility of any decomposition of ammonium thiocyanate in the presence of water at temperatures employed for the reaction. The temperature range employable in the reaction is from 120° C. to about 210° C. above which temperature an undesirable amount of decomposition of the product occurs. The process is believed to follow the following equation:



It has been found that the danger of explosion does not arise at the temperatures employed for the reaction. This is believed to be made possible by the blanket of ammonia which remains in the system during the progress of the reaction as is indicated by the equation. As can further be seen from the above equation, the employment

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of ammonium thiocyanate and ammonium nitrate together in a one-stage reaction provides a theoretical yield from the ammonium thiocyanate employed of 100 per cent of guanidine nitrate. The hydrogen sulfide produced by the reaction, however, is necessarily retained in the reaction phase because, owing to the volatility of the employed reactants, the reaction must be carried out in a closed vessel and is subject to the autogenic pressure developed by the said reactants. It may, therefore, be found preferable to incorporate a further improvement which constitutes the elimination of hydrogen sulfide from the reaction mass. This may be done in several ways within the scope of the present invention. One method which can be employed comprises halting the reaction after it has proceeded to a predetermined degree, separating the hydrogen sulfide and ammonia from the guanidine nitrate by hereinafter described means, separating the ammonia from the hydrogen sulfide, and returning the ammonia to the reaction mass for further production of guanidine nitrate. Another expedient within the scope of the invention contemplates the employment of an excess of ammonium nitrate whereby produced hydrogen sulfide is oxidized to elemental sulfur which, being insoluble in the reaction melt, is thereby removed from the environment of reaction.

The time of reaction may vary widely depending upon the ratio of reactants employed and especially the selected temperature, and optimum reaction times for a particular set of conditions may be anywhere from two to about twenty-four hours. At longer reaction times and higher temperatures, decompositions occur which affect adversely the residual ammonium thiocyanate and also the yield of guanidine nitrate, as it appears that at such higher temperatures some reaction occurs between guanidine nitrate and the hydrogen sulfide developed thus producing free guanidine which appears to be unstable at the higher reaction temperatures. Although the described excess of employed ammonium nitrate effects the elimination of hydrogen sulfide as foresaid, presence of the excess at elevated temperatures does affect deleteriously the yield of guanidine nitrate because at such elevated temperatures guanidine nitrate also appears to be attacked by the ammonium nitrate. Therefore, when this latter expedient is employed for the removal of hydrogen sulfide, it is desirable to carry out the reaction at the lower temperatures within the range employed in the invention.

The relationship of guanidine yield to reaction time at various temperatures is set forth in the drawing.

It is of particular importance to the feasibility of the described procedure for the manufacture of guanidine nitrate that both ammonium thiocyanate and ammonium nitrate are readily soluble

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in ammonia and form therewith the well known Diver's solutions, whereas guanidine nitrate is much less soluble in ammonia at ordinary temperatures and is therefore readily crystallizable from the reaction mass. The affinity of the constituents of the Diver's solution furthermore increases the critical temperature of the employed ammonia and therefore makes possible the carrying out of the reaction in equipment suitable only for moderate pressures.

In carrying out the process according to the present invention, ammonium thiocyanate and at least an equimolar proportion of ammonium nitrate are dissolved in ammonia of a weight equal to about one-half the total weight of the employed salts. The salts dissolve completely. The solution is thereafter placed in an autoclave and heated to a temperature above 120° C. for a selected reaction time. At the completion of the reaction the charge is allowed to cool, is removed from the autoclave, and guanidine nitrate is crystallized therefrom. The charge can be poured out into a mixture of ice and water whereupon guanidine nitrate crystallizes as a thin crystal mush that is readily separable by filtration from the solution. The solution is then evaporated for the removal of hydrogen sulfide and ammonia. The ammonia is separated from the hydrogen sulfide and is returned to a further admixture of salts in the autoclave. Residual ammonium thiocyanate and ammonium nitrate and unprecipitated guanidine nitrate are liberated by evaporation of the filtrate and are thereafter returned to the autoclave for further production of guanidine nitrate.

Both batchwise and continuous process steps can be employed, within the scope of the present invention, for the elimination of hydrogen sulfide from the reaction melt thereby to procure improved yields of guanidine nitrate. In batchwise operation, the employed reaction vessel is vented after the reaction has progressed until a substantial quantity of hydrogen sulfide has accumulated, and ammonia and hydrogen sulfide are permitted to escape. Anhydrous ammonia is injected into the reaction melt so as to sweep through the melt and carry out of the vessel hydrogen sulfide while at the same time maintaining a protective blanket of ammonia in the reaction vessel. Advantageously the reaction mass need not be cooled more than the cooling that would be effected by the permitted expansion and the introduction of the unheated ammonia. The introduction of ammonia into the reaction mass is continued until the effluent gases from the vessel contain only a trace of hydrogen sulfide. The reaction vessel is then closed and reaction is continued until the reactant salts have been consumed. The ammonia and hydrogen sulfide in the effluent gases are separated and the ammonia is returned for employment as hereinbefore described.

The reaction of the present invention can also be performed in a continuous manner with provision made for elimination of hydrogen sulfide. Ammonium thiocyanate and ammonium nitrate are dissolved in anhydrous ammonia in the prescribed proportions and the resultant solution is thereafter pumped under pressure through a pipe still or heated coil that is maintained at the selected reaction temperature. The coil is made sufficiently long that a definite proportion of the complete reaction to guanidine nitrate occurs with each pass therethrough. The resultant admixture is continuously discharged from the pipe

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still into a flash chamber under a lower pressure than that which is maintained in the pipe still. Gaseous ammonia and hydrogen sulfide are permitted to escape from the flash chamber and further quantities of ammonia are injected through the reaction mass so as to maintain that protective blanket of ammonia which prevents explosions. Ammonia is passed through the reaction mass until the effluent gases contain little or no hydrogen sulfide. Guanidine nitrate, unreacted salts and ammonia from which the hydrogen sulfide has been substantially removed are continuously recycled to the pipe still and are pumped therein in admixture with added fresh reactants. The chamber may advantageously be divided into two or more compartments so that the reaction mixture in one of these can be treated with ammonia gas for removal of hydrogen sulfide while the reaction mixture, in another from which hydrogen sulfide has been removed is being recycled to the pipe still. Guanidine nitrate is withdrawn from the chamber at an average rate equivalent to the rate of its continuous production, and is crystallized as hereinbefore described.

The ammonia and hydrogen sulfide comprising the effluent gases from the chamber are continuously separated. They can be separated by several known methods, for example, by passing them through an iron oxide box. The hydrogen sulfide-free ammonia, if moisture-bearing, can then be dried by passing the same through a desiccator containing for example activated alumina, and is then recycled to the reaction mixture for solution of further quantities of the reactant salts.

The following specific examples are presented to illustrate specific instances in the practice of the invention and are not intended to limit its scope:

#### Example 1

Eight parts by weight of ammonium nitrate and 7.6 parts by weight of ammonium thiocyanate were together placed in an open vessel and cooled to below room temperature. Gaseous ammonia was passed through the mixture of salts and was condensed thereby forming a Diver's solution of the salts. Between 8 to 9 parts by weight of ammonia was condensed in the solution. All of the salts were dissolved in the formed liquid ammonia. The resultant solution was then placed in an autoclave which was immediately sealed. The mixture in the autoclave was raised to a reaction temperature of 120° C. The reaction was continued at the said temperature for two hours and a maximum pressure of 130 pounds per square inch was exhibited. Upon analysis of the reaction product no guanidine nitrate was produced thus proving that the temperature of 120° C. is too low to effect reaction between the ammonium nitrate and ammonium thiocyanate when it is in solution in ammonia.

#### Example 2

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 and heated for a period of 2.7 hours at a reaction temperature of 175° C. exhibited a maximum pressure of 198 pounds per square inch. A 19 per cent yield of guanidine nitrate was obtained. 67.6 per cent of the charge of ammonium thiocyanate was recovered as residual ammonium thiocyanate.

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*Example 3*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was heated for a period of 21.5 hours at a temperature of 175° C. and developed a pressure of 245 pounds per square inch. A yield of 57.6 per cent of theory of guanidine nitrate was obtained. 24.2 per cent of the weight of the charged ammonium thiocyanate was recovered.

*Example 4*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was heated in said autoclave for a period of 5 hours at a temperature of 185° C. and developed a maximum pressure of 238 pounds per square inch. A yield of 37.3 per cent of the theoretical yield of guanidine nitrate was obtained.

*Example 5*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was heated for a period of 12 hours at a temperature of 175° C. and exhibited a pressure of 208 pounds per square inch. A yield of 42.7 per cent of theory of guanidine nitrate was obtained. 43.2 per cent of the charged weight of ammonium thiocyanate was recovered for reprocessing.

*Example 6*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was charged to an autoclave and heated for a period of 12 hours at a temperature of 185° C. exhibited a maximum pressure of 250 pounds per square inch. A yield of 52.9 per cent of theoretical of guanidine nitrate was obtained. 30.8 per cent of the weight of charged ammonium thiocyanate was recovered.

*Example 7*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was charged to an autoclave and heated for a period of 24 hours at a temperature of 185° C. A maximum pressure of 268 pounds per square inch was exhibited. A yield of 49.2 per cent of guanidine nitrate was obtained. 22.4 per cent of the charged weight of ammonium thiocyanate was recovered.

*Example 8*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was charged to an autoclave and heated therein for a period of 2 hours at a temperature of 200° C. and to a maximum temperature of 202° C. A maximum pressure of 275 pounds per square inch was exhibited. A 50.2 per cent yield of guanidine nitrate was obtained. 26.1 per cent of the weight of ammonium was recovered.

*Example 9*

Sixteen parts by weight of ammonium nitrate and 7.6 parts by weight of ammonium thiocyanate were dissolved in 8 to 9 parts by weight of ammonia in the manner described in Example 1 except, as noted, the ammonium nitrate is considerably in excess of equimolar proportion. The solution was charged into an auto-

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clave and heated for a period of 12 hours at a temperature of 175° C. 28 per cent by weight of the sulfur introduced in combined form into the reaction mass was found as elemental sulfur in the reaction product. A yield of 45.1 per cent of guanidine nitrate was obtained. 19.5 per cent of the weight of the ammonium thiocyanate charged was recovered.

*Example 10*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was charged to an autoclave and heated therein for a period of 2 hours at a temperature of 130° C. wherein the temperature did not vary more than  $\pm 2^\circ$  from 130°. The maximum pressure was 245 lbs. per square inch. A yield of 0.07 per cent by weight of theoretical of guanidine nitrate was obtained.

*Example 11*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was charged to an autoclave and heated for a period of 12 hours at a temperature of 130° C. The maximum pressure was 230 lbs. per square inch. A yield of 9.0 per cent of theoretical of guanidine nitrate was obtained.

*Example 12*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was charged to an autoclave and heated therein for a period of 2 hours at a temperature of 150° C. A maximum pressure of 245 lbs. per square inch was exhibited. A yield of 7.6 per cent of theoretical of guanidine nitrate was obtained.

*Example 13*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was charged to an autoclave and heated therein for a period of 12 hours at a temperature of 150° C. with a maximum temperature of 152° C. The maximum pressure was 230 lbs. per square inch. A yield of 32.7 per cent by weight of theoretical of guanidine nitrate was obtained.

*Example 14*

A solution of ammonium thiocyanate and ammonium nitrate in ammonia prepared in a manner identical to that described in Example 1 was charged to an autoclave and heated therein for a period of 12 hours at a temperature of 200° C. and a maximum temperature of 202° C. The maximum pressure reached was 450 lbs. per square inch. A yield of 39.6 per cent of theoretical of guanidine nitrate was obtained.

The production of guanidine nitrate in accordance with the present invention is shown graphically in the accompanying drawing which shows five curves at the temperatures of 130° C., 150° C., 175° C., 185° C. and 200° C. As mentioned above a test was made at 210° C. but it was found that at the high temperature there was an undesirable amount of decomposition of guanidine nitrate taking place. The curve for 185° C. shows that after the reaction has continued for more than 12 hours decomposition or secondary reactions take place to cut down the production of guanidine nitrate. The curve for 200° C. shows that the production of guanidine nitrate is falling off be-

fore the reaction products have been held in the autoclave for 2 hours.

A temperature of 200° C. is particularly well adapted for continuous operation because the time of holding the reaction products in the reaction zone can be varied by the rate of circulation of the reaction products through a heating coil. Thereby the capacity of the apparatus may be increased while securing only the primary reaction products. The curves, however, show that at temperatures above 120° C., and particularly at temperatures above 150° C., a substantial amount of guanidine nitrate is produced if the reaction products are held at the various temperatures for a sufficient time.

All of the above examples were carried out in a batch process in a heavy metal autoclave. This autoclave had a comparatively large heat radiating surface so that it was difficult to get the temperature stabilized for periods shorter than 2 hours. This difficulty could be readily overcome if the process is carried out in a continuous heating coil.

The present application is a continuation-in-part of my application Serial No. 642,133 filed January 18, 1946, now abandoned.

The invention as hereinabove set forth is embodied in particular form and manner but may be variously embodied within the scope of the claims hereinafter made.

I claim:

1. A process for the manufacture of guanidine nitrate comprising: dissolving ammonium thiocyanate and at least an equimolar weight of ammonium nitrate in ammonia; heating the so-formed solution in an enclosed vessel at a reactive temperature between 130° C. and 210° C. for a period between 20 hours and several minutes to effect reaction therebetween; and recovering guanidine nitrate from the reaction product.

2. A process for the manufacture of guanidine nitrate comprising: dissolving ammonium thiocyanate and at least an equimolar weight of ammonium nitrate in sufficient ammonia to form a protective blanket in the reaction vessel to avoid explosions during heating; heating the so-formed solution in an enclosed vessel at a reactive temperature between 130° C. and 210° C. for a period between 20 hours and several minutes to effect reaction therebetween; and recovering guanidine nitrate from the reaction product.

3. A process for the manufacture of guanidine nitrate comprising: dissolving ammonium thiocyanate and at least an equimolar weight of ammonium nitrate in anhydrous ammonia; heating the so-formed solution in an enclosed vessel at a temperature of about 175° to 185° C. and effecting reaction therebetween; and recovering guanidine nitrate from the reaction product.

4. A process for the manufacture of guanidine nitrate comprising: dissolving ammonium thiocyanate and at least an equimolar weight of ammonium nitrate in anhydrous ammonia; heating the so-formed solution in an enclosed vessel at a temperature of about 175° to 185° C. for a period between two to twenty-four hours and thereby effecting reaction therebetween; and recovering guanidine nitrate from the reaction product.

5. A process for the manufacture of guanidine nitrate comprising: dissolving ammonium thiocyanate and ammonium nitrate in molar excess

of the former in anhydrous ammonia; heating the so-formed solution in an enclosed vessel at a temperature of about 175° to 185° C. for about eight to twelve hours and effecting reaction therebetween whereby guanidine nitrate is formed and adventitiously formed hydrogen sulfide is oxidized by the said excess of ammonium nitrate; and recovering guanidine nitrate from the reaction product.

6. A process for the manufacture of guanidine nitrate comprising: dissolving ammonium thiocyanate and at least an equimolar weight of ammonium nitrate in anhydrous ammonia; heating the so-formed solution in an enclosed vessel at a reactive temperature between 130° C. and 210° C. for a period between twenty-four hours and several minutes to effect reaction therebetween; upon completion of the reaction period, cooling the reaction mass in the said vessel; discharging the reaction mass and crystallizing out guanidine nitrate; filtering, and liberating from the filtrate ammonia and hydrogen sulfide; separating the hydrogen sulfide from the ammonia; and recycling the ammonia to the reaction zone for further production of guanidine nitrate.

7. A process as claimed in claim 6 in which the reaction mass is discharged directly into a cooling bath of ice and water.

8. A process as claimed in claim 1 in which the heating is interrupted at intervals, the vessel is vented and ammonia is swept through the solution to reduce the content of hydrogen sulfide while maintaining the anti-explosive blanket of ammonia about the solution.

9. A continuous process for the production of guanidine nitrate comprising: dissolving ammonium thiocyanate and at least an equimolar weight of ammonium nitrate in anhydrous ammonia; continuously flowing so-prepared solution through a heated reaction zone under a pressure between about 200 and 300 pounds per square inch and at a temperature of at least about 170° C.; releasing the reaction mixture to a zone of lesser pressure; continuously passing gaseous ammonia through the hot reaction mixture in the reduced pressure zone while venting hydrogen sulfide and ammonia therefrom; continuously separating hydrogen sulfide from the ammonia in the vented gases; recycling the sulfide-freed ammonia to the reaction zone; continuously recycling incompletely reacted reaction mass from the reduced pressure zone to the reaction zone and introducing it thereto in admixture with fresh reactants and predominantly recycled ammonia; withdrawing reaction product from the reduced pressure zone at an average rate substantially equal to the rate of formation of guanidine nitrate; and cooling the withdrawn reaction product and separating guanidine nitrate therefrom.

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