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PRODUCTION OF CYANAMIDE REACTION PRODUCTS

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This invention relates to the conversion of cyanamide and its dimer, dicyandiamide, to other organic nitrogen compounds by processes involving the heating of these materials at high temperatures and pressures in the presence of solvents containing ammonia. More particularly, the invention relates to the production of products from these materials substantially free from contamination by iron by carrying out the conversion in autoclaves consisting of or lined with iron alloys of the type hereinafter described.

Cyanamide and dicyandiamide have recently become important raw materials for the production of a number of organic nitrogen compounds. Thus, for example, melamine can be produced by heating a charge consisting of 1 part of cyanamide or dicyandiamide, from 1–2 parts of anhydrous ammonia and 1–2 parts of methyl alcohol or other organic solvent at temperatures of 120–200° C. for 4–12 hours. This process can also be modified as described in Patent No. 2,221,478, dated November 12, 1940, to produce guanidine salts by introducing equivalent quantities of ammonium salts into the autoclave.

It is a principal object of the present invention to improve these and similar conversion processes involving the reaction of cyanamide or dicyandiamide in the presence of liquid ammonia by conducing them in the presence only of certain alloys of iron and chromium, or of iron-chromium alloys containing certain relatively small quantities of nickel of the type hereinafter defined.

It is a well-known fact that ordinary ammonia, both aqueous and anhydrous, is not corrosive to ordinary iron or steel, even at elevated temperatures. Thus, for example, we have heated samples of hot rolled mild steel boiler plate for 50 hours at temperatures of 180° C. while suspended in a mixture of equal quantities of methanol and anhydrous ammonia without any measurable attack on the metal. It is also a known fact that neither cyanamide nor dicyandiamide will attack iron or steel at ordinary temperatures and, in fact, these compounds have been shipped in ordinary iron containers for many years. Solutions of cyanamide and of dicyandiamide in liquid ammonia, with or without dilution with methyl or ethyl alcohol do not attack iron or steel at ordinary temperatures. It is therefore very surprising to find, as we have found, that when such solutions of cyanamide or dicyandiamide in liquid ammonia, with or without the addition of alcohols or other organic solvents are heated to conversion temperatures of 120–200° C. in an ordinary steel autoclave the autoclave is rapidly attacked and the product is seriously discolored and contaminated with iron.

The rapid attack on the walls of the autoclave by cyanamide and dicyandiamide solutions in liquid ammonia during conversion is a very serious problem in the heat conversion of these solutions, for ferrous equipment is about the only commercially available material that will withstand the pressures involved. Thus, for example, in the above described process for the manufacture of melamine, autoclave pressures of 3000 lb./sq. in. are not uncommon, and comparable pressures are also encountered when guanidine salts are produced. Non-ferrous equipment capable of withstanding such pressures safely, and of a size sufficient to produce the necessary commercial outputs, would be extremely expensive to design and maintain.

We have now discovered a class of ferrous alloys that are not attacked during the conversion of cyanamide-ammonia and dicyandiamide-ammonia solutions, either as such or containing ammonium salts for the production of guanidine salts, under the conditions hereinafter described. These alloys are known commercially as high-chrome steels, since they are alloys of iron with about 8–20% of chromium based on the total weight of the alloy. The alloys are referred to as low carbon steels, since they usually contain from about 0.04% to 0.2% of carbon, and they may also contain other minor materials such as small amounts of sulfur, selenium, manganese, and silicon. The alloys of this class preferably contain nickel to improve their machining properties and ease of fabrication, but we have found that substantial corrosion occurs if an iron-chromium alloy containing more than 15% of nickel is used for the purposes of the invention. We have also found, as an important feature of our invention, that iron-chromium alloys containing up to 15% of nickel must be stabilized by the addition of molybdenum, columbium or titanium. These stabilizers are preferably employed in amounts equivalent to ten times the amount of carbon present in the alloy or more.

We are not able to state the reason for the extremely corrosive action that is attendant upon the conversion of cyanamide or dicyandiamide to melamine, guanidine salts or other conversion products in the presence of liquid ammonia at elevated temperatures of 120–200° C. Several unusual corrosion phenomena appear in carrying out this reaction; thus, for example, ordinary unstabilized "18–8" iron-chromium-nickel alloy is corroded at a relatively rapid rate, whereas a

similar alloy containing small amounts of molybdenum, columbium or titanium is not corroded. On the other hand, a straight iron-chromium alloy containing about 8–20% of chromium is not corroded, even in the absence of a stabilizer. Surprisingly enough, however, any of these alloys will corrode badly if the reaction mixture contains as much as 150 parts per million of dissolved iron, as would be the case if a corrodible steel or iron alloy were present in the liquid in the autoclave. Dissolved iron in the reaction mixture apparently acts as a catalyst or accelerator of corrosion, and for this reason it is highly important to construct the inner surfaces of the autoclave of metal that is not initially corroded. We find that this initial corrosion can be prevented by the incorporation of small quantities on the order of 25–1000 parts per million, based on the total weight of the charge, of an inhibitor such as phosphoric acid (H_3PO_4), ammonium phosphate, or a soluble dichromate such as sodium, potassium or ammonium dichromate, which operates to counteract the corrosive action of any iron that may be dissolved from the autoclave or introduced with the raw materials, and this constitutes another important feature of our invention.

Our invention therefore consists in the conversion of cyanamide or dicyandiamide to a reaction product thereof by heating the compound while dispersed in a solvent containing liquid ammonia to reaction temperatures of 120–200° C. in a closed pressure vessel in which substantially all the internal surfaces in contact with the reaction mixture consist of a high chrome steel of one of the types defined above. This high chrome steel may be an alloy consisting of 8–20% of chromium and 0.04 to 0.2% of carbon, the balance of the alloy being substantially all iron with small amounts of impurities of the type outlined above. Preferably, however, the alloy consists of 8–20% of chromium, about 8–12% of nickel (with a maximum of 15%), about 0.04 to 0.2% of carbon and about 0.4–5% or slightly more of a stabilizer of the group consisting of molybdenum, columbium and titanium, or mixtures thereof, the balance being iron and minor materials such as sulfur or selenium and manganese, which improve the machining properties of the alloy when used in amounts of less than about 2%. Any of the above described or similar conversions of cyanamide or dicyandiamide in solvents containing ammonia may be carried out at elevated temperatures and pressures in autoclaves consisting of or lined with the above described alloys without excessive corrosion when care is taken to avoid initial or progresssive contamination of the charge with dissolved iron.

The invention will be illustrated in greater detail by the following specific examples, which show the extent of corrosion that occurs with various alloys in practicing the processes of the invention. It should be understood, however, that various modifications in the compositions of the alloys may be resorted to within the scope of the appended claims, and that the invention in its broader aspects is not limited to the specific examples given.

EXAMPLE 1

Corrosion Tests

Five disk samples of iron-chromium-nickel alloys, some of which were stabilized with molybdenum or columbium were given a metallographic finish and prepared for testing. Two samples of high-chrome steels containing no nickel were also prepared in a similar manner. The samples had the analysis indicated in Table I.

Table I

Sample No.	Per cent composition				Per cent stabilizer			Balance iron, Ti
	C	Cr	Ni	Si	Mn	Mo	Cb	
1	0.06	19	12.67	0.48	2.20	1.88	0.49	------
2	0.15	18	10	0.75	0.75	------	1.2	------
3	0.08	18	8	0.75	0.75	------	------	------
4	0.11	18	11	0.75	1.50	3.00	------	------
5	0.25	25	20	2.00	1.20	------	------	------
6	0.15	12	------	------	------	------	------	------
7	0.12	18	------	------	------	------	------	------
Autoclave liner	0.12	18	8	------	0.50	------	------	0.6

The samples were weighed and were then strung on a glass tube and separated by means of small glass tube spacers. They were then suspended in an autoclave by means of fibre glass cloth so that they were entirely out of contact with the metal thereof.

The autoclave itself was lined with a high-chrome steel alloy, the analysis of which is also given in Table I. After the samples were suspended it was charged with a mixture containing equal parts by weight of dicyandiamide, liquid ammonia and commercial methanol and was then closed and heated in the usual manner. The autoclave required about one hour to reach a temperature of 180° C. and it was then held at 180–190° C. for 2 hours, after which it was cooled quickly to room temperature, the melamine discharged and another charge was put in. The samples were subjected to a total of 23 such runs which amounted to a total of 46 hours at 180–190° C. in addition to the heating and cooling periods.

At the end of this time the samples were removed from the autoclave, cleaned with boiling water, dried and weighed. They were then examined microscopically for surface etching, pits and cracks. The data on corrosion, weights, weight losses, etc., of these samples are given in Table II.

Table II

Sample No.	Wt. (grams) before test	Wt. (grams) after test	Loss in grams	Area ($dm.^2$)	Corrosion rate MDD[2] [1]
1	15.0163	15.0162	0.0001	0.116	0.430
2	9.2585	9.2542	0.0043	0.146	19.3
3	14.0029	13.9915	0.0114	0.134	44.5
4	10.4565	10.4564	0.0001	0.124	0.422
5	15.6491	15.6169	0.0322	0.144	117
6	2.5251	2.5248	0.0003	0.101	1.55
7	2.6829	2.6827	0.0002	0.101	1.04

[1] MDD = mg./dm.²/day (24 hrs.)

Reference to Table II above will show that most of the corrosion occurred in sample No. 5, which contained 20% of nickel, and sample No. 3, which was an ordinary unstabilized "18–8" alloy. This was confirmed by the appearance of the samples under the microscope as they were the most badly stained and etched samples of the lot.

Microscopic examination of the remaining samples showed that Nos. 1 and 4 were as shiny as they were before the test, thus confirming an almost complete lack of corrosion. Samples 6 and 7, containing no nickel, also showed an almost complete absence of change under the experimental conditions, when judged by the appear-

ance of the disks before and after exposure to the test reaction which confirms the low corrosion rate indicated by the data of Table II.

EXAMPLE 2

On the basis of the results shown by Example 1, an autoclave was fabricated from a high chrome steel having the following specifications:

	Per cent
Chromium	17.5–20
Nickel	8–10
Carbon	[1] 0.2
Molybdenum	[1] 0.6
Sulfur or selenium	[1] 0.07

[1] Maximum.

Guanidine nitrate was prepared in this autoclave by the following method: 168 grams of dicyandiamide containing 5 parts per million of iron and 320 grams of ammonium nitrate containing 12 p. p. m. of iron were dissolved in 300 grams of liquid ammonia and heated to 160° C. in about 2 hours. The autoclave was heated at 160° C. for 1 hour longer and was then cooled and discharged. The product was pure white guanidine nitrate of excellent color having the following analysis:

	Per cent
Guanidine nitrate	94.1
Dicyandiamide	0.0
NH_4NO_3	0.18

The metallic impurities were determined spectroscopically, and were as follows:

	Per cent
Iron	.0020
Chromium	.0003
Nickel	.00005

Melamine was also prepared in this autoclave from dicyandiamide having the same iron analysis, using the procedure outlined in Example 1. The product was found to contain 0.0008% of iron, 0.0003% of nickel and 0.00005% of chromium.

EXAMPLE 3

An autoclave of about 10 gallons capacity was constructed with an inner liner and internal heating coils and agitator composed of an alloy having the following composition:

	Per cent
Chromium	18.37
Nickel	10.34
Manganese	0.44
Silicon	0.42
Carbon	0.05
Columbium (stabilizer)	0.77
Iron	Balance

This auotclave, as received from the manufacturer, was used for the production of guanidine nitrate by reacting a solution of dicyandiamide and ammonium nitrate in liquid ammonia for 0.5–1.5 hours at 160–170° C., using molar ratios of NH_4NO_3: dicyandiamide of 2:1 and about 2 parts by weight of anhydrous ammonia for each 3 parts of the other two reagents combined.

The first few runs made in this autoclave produced a product which was brown in color and contained considerable quantities of iron, chromium and nickel. Thus, for example, the products from the first two runs contained the following quantities of metal in parts per million:

Fe	Cr	Ni
1,204	285	85
4,610	1,160	100

It was then discovered that the manufacturer had placed an ordinary steel nut inside the autoclave to hold the heating coils. After the removal of this nut the remaining batches were light in color and the content of metallic impurities was almost negligible, averaging 27 parts per million of iron and less than 3 parts per million of Cr and Ni, combined, for a total of 12 additional runs. The high content of chromium and nickel in the first batches indicated that considerable corrosion was taking place in the alloy liner of the autoclave, while the very small values obtained after removal of the steel nut (which contained no chromium or nickel) showed that this corrosion was the direct result of the presence of substantial amounts of dissolved iron during the reaction.

This application is a continuation-in-part of our copending application Serial No. 348,556, filed July 30, 1940.

What we claim is:

1. In the conversion of a compound selected from the group consisting of cyanamide and dicyandiamide to a reaction product thereof, the steps which comprise repeatedly heating dispersions of said compound in a solvent comprising liquid ammonia at temperatures of 120–200° C. in a closed pressure vessel the internal surfaces of which consist of a high chrome steel selected from the group consisting of those having the composition:

Chromium	8–20%
Carbon	0.04–0.2%
Iron	Balance of alloy

and

Chromium	8–20%
Carbon	0.04–0.2%
Nickel	Up to 15%
Stabilizer	0.4–5%
Iron	Balance of alloy

said stabilizer being a member of the group consisting of molybdenum, columbium, and titanium, said process being carried out with substantially iron-free reagents in such a manner and under such conditions that dissolved iron is only slowly built up in the reaction mixture and stopping the reaction before the iron content reaches 0.015% of the reaction mixture, whereby corrosion of the metal in contact with the reaction is minimized.

2. In the conversion of a compound selected from the group consisting of cyanamide and dicyandiamide to a reaction product thereof, the steps which comprise repeatedly heating dispersions of said compound in a solvent comprising liquid ammonia at temperatures of 120–200° C. in a closed pressure vessel the internal surfaces of which consists of high chrome steel having the following composition:

Chromium	8–20%
Carbon	0.04–0.2%
Nickel	8–12%
Stabilizer	0.4–5%
Iron	Balance of alloy

said stabilizer being a member of the group con-

sisting of molybdenum, columbium, and titanium, said process being carried out with substantially iron-free reagents in such manner and under such conditions that dissolved iron in the reaction mixture is only slowly built up and stopping the reaction before the iron content reaches 0.015% of the reaction mixture, whereby corrosion of the metal in contact with the reaction is minimized.

3. A method according to claim 1 in which a small amount of an inhibitor selected from the group consisting of soluble phosphates and dichromates is present in the reaction mixture.

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