

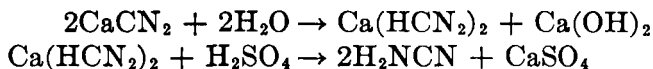
CYANAMIDE

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References

1. GUSTAVSON: *Ann.*, **172**, 173 (1874).
2. MOISSAN: *Compt. rend.*, **113**, 19 (1891).
3. LANTENOIS: *ibid.*, **156**, 1385 (1913).
4. WALKER: *J. Chem. Soc.*, **85**, 1090 (1904).
5. MOISSAN: *Bull. soc. chim.*, [3] **7**, 746 (1892).

9. CYANAMIDE



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Cyanamide, H_2NCN , has been prepared by (1) desulfurizing thiourea with mercury(II) oxide,^{1,6} lead acetate,² or bromine,³ (2) passing gaseous cyanogen chloride into ammonia dissolved in anhydrous ether,⁴ and (3) oxidizing thiourea with alkaline permanganate.⁵ The method described below is an adaptation for laboratory use of a commercial procedure³ that uses calcium cyanamide as a starting material.

Procedure

A. AQUEOUS SOLUTION OF CYANAMIDE

A slurry made by mixing 600 g. of crude calcium cyanamide containing 62.3 per cent calcium cyanamide§ with 600 ml. of water|| is poured into a 10-in. Büchner funnel.¶

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§ Aero Cyanamid, Minimum Hydrate, contains 60 to 63 per cent calcium cyanamide but on storage in a humid atmosphere the calcium cyanamide content will decrease. Samples containing as low as 56.9 per cent calcium cyanamide have been used successfully.

|| In order to obtain the most efficient extraction, it is necessary to have the crude calcium cyanamide finely ground so that 65 per cent will pass through a 200-mesh sieve.

¶ The best results are obtained with a filter cake approximately $\frac{1}{2}$ in. thick.

The outlet of the funnel is connected to a glass spiral condenser, which leads into a filter flask connected to a water pump. Ice water is circulated through the jacket of the condenser to cool the filtrate. The filter cake is extracted with 3.6 l. of water at 60° at such a rate that there is generally only a thin aqueous layer above the cake. The extraction requires about 25 minutes.* The hot water is allowed to remain in contact with the slurry for only a very short time; the resultant solution of calcium hydrogen cyanamide must be cooled immediately to below 20°. Approximately 3.8 kg. of filtrate† is obtained. The filtrate is immediately cooled to 10° and then treated with 20 per cent aqueous sulfuric acid to precipitate the calcium and to lower the pH to 5.1.‡ Approximately 1 kg. of acid will be needed.

The mixture is filtered. Using specified quantities, the filtrate will weigh about 4.1 kg., and will contain about 80 per cent of the cyanamide present in the original calcium cyanamide as a 3.5 per cent solution.

The filtrate may be concentrated with respect to cyanamide by vacuum distillation§ at 40 mm. through a 12-in.

* This operation should be done as quickly as possible, but some lag must be allowed to give time for the water to extract the cyanamide. The recommended leaching system is one in which advantage is taken of the higher rate of solution and hydrolysis of calcium cyanamide in hot water, at the same time avoiding the formation of dicyanodiamide in objectionable amounts.

† Analysis of the filtrate from a typical preparation showed 2.81 per cent cyanamide nitrogen, indicating that 89.2 per cent of the original cyanamide had been extracted.

‡ The pH of the free cyanamide solution should be kept at about 5.0. Previous work at the Stamford Research Laboratories of the American Cyanamid Company, indicates that at a pH of 6 or higher free cyanamide may polymerize violently to dicyanodiamide during the concentration. At a pH of about 3, cyanamide decomposes to urea.

§ The solution must be stirred during concentration to expedite removal of water and to prevent bumping. A simple and convenient stirring device that will operate efficiently for use in systems under reduced pressure is depicted in Fig. 12. A piece of rubber tubing *A* serves as the seal between the shaft of the stirrer *B* and the glass bearing guide *C*. A few drops of glycerol are applied at *B* to lubricate the glass-rubber interface and to permit

column 1 in. o.d. packed with $\frac{1}{8}$ -in. Raschig rings to remove the water. There is a strong tendency for the cyanamide to be carried over into the distillate, and it is therefore necessary to use a column to minimize such losses. Distillation should be carried out behind a safety screen. Aqueous solutions of cyanamide of any desired concentration up to 20 to 25 per cent can be prepared easily in this manner. Such solutions are often employed for synthetic purposes (syntheses 10 and 11) rather than the solid material.

B. CRYSTALLINE CYANAMIDE

If crystalline cyanamide is desired, the concentration of the solution prepared in A is continued until the temperature in the pot reaches 70°.*

The warm solution is filtered to remove the small amount of calcium sulfate that crystallizes during the evaporation. The filtrate is then cooled to 10° to effect crystallization of cyanamide which is separated by filtration and dried in an evacuated desiccator over phosphorus(V) oxide. The crystalline mass should be broken up at intervals in order to

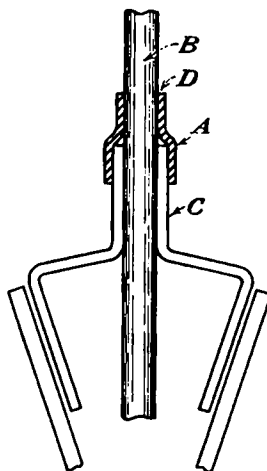


FIG. 12. Stirring device for operation under reduced pressure.

easy rotation. The tube C is conveniently sealed to a male taper joint and can thus be fitted readily to the all-glass distillation apparatus recommended for the concentration operation.

* Toward the end of the concentration process, the pot temperature will rise rapidly from approximately 40 to 70°. A good yield of cyanamide can be obtained if a pressure no higher than 10 mm. and a maximum temperature of 40° are employed, but poor yields are obtained if distillation is attempted at 40 mm. at this same temperature, simply because insufficient water is thus removed. The temperature of the residue in the flask should be kept as low as possible to minimize formation of dicyanodiamide and should never exceed 70°. Evaporation of cyanamide solutions to dryness is hazardous due to the tendency of cyanamide to polymerize with explosive violence when heated in the presence of too little water.

facilitate complete desiccation. The yields of cyanamide, with a purity of 93.5 per cent as determined by analysis, will vary between 110 and 130 g. and average about 120 g. or about 65 per cent of theory based on the calcium cyanamide content of the starting material. Additional cyanamide of lesser purity can be obtained by cooling the filtrate to 0°. It is inadvisable to effect further concentration, however, since explosive polymerizations are very prone to occur at this concentration.

Properties

Cyanamide is a crystalline solid melting at 46°C. and is exceedingly soluble in water, alcohol, and ether. Cyanamide is easily recrystallized from a solution of two parts of benzene and one part of ether. In the presence of acid or strong alkali it hydrolyzes readily to urea, whereas under mild alkaline conditions it polymerizes exothermally to dicyanodiamide (synthesis 10). Cyanamide combines with hydrogen chloride⁹ to form a dihydrochloride and forms salts with metals.^{7,10} It reacts with hydrogen sulfide¹¹ or mercaptans¹² to form thiourea or substituted isothiureas and reacts with alcohols¹³ in the presence of acid to form substituted isoureas. With formaldehyde¹⁴ cyanamide forms methylol compounds; with amines¹⁵ it forms substituted guanidines. Cyanamide can be acylated with acylating agents,^{10,16} or alkylated with alkylating agents.¹⁰ When fused with potassium hydroxide,¹⁷ cyanamide forms potassium cyanate. When treated with hydrazine salts,¹⁸ it forms aminoguanidonium salts. Cyanamide is toxic to the skin and readily attacks iron, steel, copper, lead, and, to a slight extent, Duriron. Glass and enamelware are found to be most resistant.¹⁹

References

1. VOLHARD: *J. prakt. Chem.*, [2] **9**, 6 (1874).
2. WALTHER: *J. prakt. Chem.*, [2] **54**, 510 (1896).
3. RATHKE: *Ber.*, **12**, 776 (1879).
4. CLOËZ and CANNIZZARO: *Compt. rend.*, **32**, 62 (1851).

5. WERNER: *J. Chem. Soc.*, **115**, 1168 (1919).
6. HANTZSCH and WOLVEKAMP: *Ann.*, **331**, 282 (1904).
7. FRANKLIN: "The Nitrogen System of Compounds," A.C.S. Monograph, pp. 93-97, Reinhold Publishing Corporation, New York, 1935.
8. HETHERINGTON and PINCK: U.S. patent 1673820 (1928); *cf. Chem. Abstracts*, **22**, 2816 (1928).
9. PINCK and HETHERINGTON: *Ind. Eng. Chem.*, **18**, 629 (1926).
10. DRECHSEL: *J. prakt. Chem.*, [2] **11**, 284 (1875).
11. HEUSER: U.S. patent 1991852 (1935); *cf. Chem. Abstracts*, **29**, 2180 (1935).
12. ARNDT: *Ber.*, **54**, 2236 (1921).
13. STIEGLITZ and MCKEE: *Ber.* **33**, 1517 (1900).
14. GRIFFITH: U.S. patent 2019490 (1935); *cf. Chem. Abstracts*, **30**, 538 (1936).
15. BISCHOFF: *J. Biol. Chem.*, **80**, 345 (1928).
16. MERTENS: *J. prakt. Chem.*, [2] **17**, 1 (1878).
17. EMICH: *Monatsh.*, **10**, 321 (1889).
18. FANTL and SILBERMANN: *Ann.*, **467**, 274 (1928).
19. Unpublished work of the U.S. Department of Agriculture.

10. DICYANODIAMIDE

(Cyanoguanidine)



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Methods for preparation of dicyanodiamide involve polymerization of cyanamide under controlled conditions in aqueous solutions in the presence of metallic hydroxides or ammonia.¹ Dicyanodiamide is an important chemical intermediate and is used for the preparation of guanidonium nitrate,² biguanide,³ and numerous other derivatives of the ammonocarbonic acids.⁴ The present method is easily adaptable to preparation of laboratory quantities.

Procedure

A neutral aqueous solution of cyanamide (synthesis 9), or a solution made very slightly alkaline with ammonia, is

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