CYANAMID -- Manufacture, Chemistry and Uses

Published by
The Chemical Publishing Co.
Easton, Penna.

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Manufacture, Chemistry and Uses

BY

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1913
THE CHEMICAL PUBLISHING COMPANY
EASTON, PA.

LONDON, ENGLAND:
WILLIAMS & NORGATE
14 HENRIETTA STREET, CONVENT GARDEN, W. C.

PREFACE.

This volume is intended to be a review of the present knowledge of Cyanamid, particularly its chemical and agricultural properties. Its purpose is to render some assistance to the investigator who has neither the time nor the library facilities to enable him to make a thorough study, yet who wishes to broaden his knowledge of Cyanamid. Most of the important literature on this subject is written in foreign languages, and many valuable papers occur in journals not found in the ordinary agricultural or chemical library. Moreover, the opinions that have been expressed on almost every phase of the behavior of Cyanamid are so diversified and frequently so deeply buried in controversy that the casual reader is at a loss to know what to accept as generally established facts. It is hoped that the present volume will give to the reader a consistent explanation of Cyanamid that will form the starting point for the acquisition of further knowledge.

In order to arrive at an understanding of the principles underlying particular phenomena it is necessary to adopt at the beginning of an investigation some sort of working hypothesis that will account for the observed facts. Every further fact that is acquired must then verify the original hypothesis or the latter must be modified to fit the facts. The constant remodeling of ideas to agree with observed facts finally leads to a system of knowledge, in which every fact explains to a certain extent every other fact, and in no case contradicts any of them. Such a system of knowledge of Cyanamid, it is believed, is now at hand. The pure chemistry of Cyanamid, its physico-chemical action in the soil, its biological behavior, and its agricultural properties, as presented in this volume, are consistent with each other. Such consistency is believed to induce confidence in the validity of the views expressed. Further experiments may make necessary some slight changes, but the general scheme of the properties of Cyanamid may now be considered as quite definitely established.

There is no question but that Cyanamid will play an important part in the future development of agriculture, and that a great deal of research will be undertaken to broaden the knowledge of its practical application. Much labor has been wasted in the past by the pursuance of faulty methods, and a great deal of work has been but the duplication of earlier efforts, and has contributed little that was not known before. If the publishing of this book will direct research into the fields that still remain more or less unexplored, and if it is helpful in avoiding the errors of past investigations, its purpose will have been accomplished.

NASHVILLE, TENN.
January, 1913.

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CHAPTER I.

Discovery and Manufacture of Cyanamid.

The problem of the artificial fixation of atmospheric nitrogen has engaged the attention of scientists for the greater part of a century. The rapid growth of the fertilizer industry that has attended the development of agricultural science, and the great increase in the number and extent of chemical industries, during the past fifty years, have emphasized the necessity for artificial methods of maintaining and increasing the world's stock of combined nitrogen. One of the influences that stimulated immediate action was the introduction in 1887 by MacArthur and Forest, and at about the same time independently by Siemens & Halske, of Berlin, of the cyanide process for leaching gold and silver from their ores. This discovery produced a strong demand for cyanides, which had hitherto been used to the extent of only a few hundred tons a year, principally in the dye-industry and to a smaller extent in electroplating.

Attempts had been made early in the nineteenth century to bring about the direct synthesis of cyanogen from atmospheric nitrogen and carbon. Among other processes, that worked out in 1847 by Bunsen and Playfair, in which barium carbonate was heated in an atmosphere of pure nitrogen, seemed promising, but did not prove to be commercially successful. The introduction of the electric furnace in 1894 by Moissan and by Willson, for the production of carbides on a large scale, afforded a new instrument for further research. Siemens and Halske, among others, at once adopted the use of the electric furnace for the working out of the problem of nitrogen fixation. In 1895, they worked on the process of Prof. H. Mehner, which consisted in fusing a mixture of sodium carbonate and carbon and conducting nitrogen through the hot mass. In the same year they took up the process of Prof. Adolph Frank and Dr. Nicodem Caro, which consisted in subjecting a mixture of barium carbide, sodium hydroxide, potassium hydroxide and carbon at a high temperature to the action of steam and nitrogen. Frank and Caro, with the co-operation of F. Rothe, found in 1895 that dry nitrogen is essential to successful absorption.

In 1898 it was found that when barium carbide is heated to a temperature of 700° to 800° C., in the presence of nitrogen, about 30 per cent. of the carbide is changed into barium cyanide and the remainder into barium cyanamide. The reactions can be represented by the following simple equations:

$$BaC_2 + N_2 = Ba\ (CN)_2,$$
$$Ba(CN)_2 = BaCN_2 + C.$$

Since it was desired to have all the nitrogen in the form of cyanide, further operations were necessary. The product of the above reactions was fused with soda, when the carbon again reacted with the cyanamide group and produced the cyanide form. The cyanide was leached out with water, and treated with ferrous carbonate to form the ferrocyanide, which was sold as such or fused with sodium to form pure sodium cyanide. The barium carbonate residue was again used to produce barium carbide, as represented by the reactions:

$$BaCO_3 + \text{heat} = BaO + CO_2,$$
$$BaO + 3C = BaC_2 + CO.$$

The fall in the price of cyanides due to the interruption in the production of gold during the Boer War in South Africa made it necessary to seek cheaper methods of manufacture. It was found that calcium carbide could be manufactured at less cost, and also had the advantage of possessing a lower molecular weight. This carbide required a temperature of from 1,100° to 1,200° C. for the absorption of the nitrogen, but combined it entirely in the form of calcium cyanamide, without the formation of any cyanide. By fusion with alkaline salts, however, the cyanamide form, in the presence of carbon, readily goes over to the cyanide form, which can be leached out with water, if desired, and be further purified. When sodium chloride is used as the fluxing agent, the resultant mass contains about 30 per cent. sodium cyanide, and is known as a "surrogate." It is suitable for use directly for the extraction of gold ores.

Agricultural experiments with the crude calcium cyanamide showed that this material is suitable for use as a nitrogenous fertilizer, and patents were issued in 1910 to Dr. Albert R. Frank, son of Prof. Adolph Frank, and to Herman Freudenberg, a co-worker of A. R. Frank, protecting the use of Cyanamid for this purpose. The basic patent protecting the process of manufacture of Cyanamid was issued to Prof. Adolph Frank and Dr. Nicodem Caro in 1908.

The large demands of agriculture for cheap nitrogenous fertilizer materials have directed the efforts of the manufacturers toward the production of Cyanamid rather than of cyanides and other derivatives. At present, the total output of sodium cyanide derived from Cyanamid is only about 2,000 tons per annum, all made in Germany, while the world's production of Cyanamid is estimated at about 120,000 tons per annum. The factory of the American Cyanamid Company, at Niagara Falls, Canada, now has a capacity of 30,000 tons per annum, and extensions now under way will increase this to 60,000 tons per annum. There are thirteen Cyanamid factories abroad, located in Germany, Italy, France, Switzerland, Austria, Norway, Sweden and Japan.

NOMENCLATURE OF CYANAMID INDUSTRY.

With the development of the Cyanamid industry there has grown up a nomenclature that is often confusing to the uninitiated. The terms here defined will be understood to have the following meanings throughout this treatise:

Lime-nitrogen.—Crude calcium cyanamide, ground to a fine powder after removal from the ovens in which it is formed. It contains about 55 per cent. of calcium cyanamide, CN.NCa, about 2 per cent. calcium carbide, and about 20 per cent. of free calcium oxide.

Cyanamid.—This is a trade name for the completely hydrated material prepared for use as a fertilizer in the United States. It contains about 45 per cent. calcium cyanamide, 27 per cent. calcium hydroxide and no carbide. The name is always capitalized and has no final "e."

Cyanamide.—The compound represented by the formula $CN.NH_2$. It is sometimes referred to as acid cyanamide, or free cyanamide.

Calcium Cyanamide.—The chemical compound of the formula CN.NCa, or $CaCN_2$, as it is freqently written.

Calcium Cyanamid.—The name used by the United States Department of Agriculture and by some State Departments of Agriculture to designate commercial Cyanamid. It is sometimes used to indicate the substance represented by the formula CN.NCa, but for the sake of clearness the compound CN.NCa will be called calcium cyanamide in the present paper.

Nitrolim.—The trade name for the material sold in England for agricultural purposes. It is a lime-nitrogen to which has been added just enough water to destroy the carbide. Practically all the free lime is present as calcium oxide.

Kalkstickstoff.—The commercial material manufactured in Germany for use as a fertilizer. It is similar to nitrolim.

Stickstoffkalk.—A crude calcium cyanamide made by nitrifying a calcium carbide which contains about 10 per cent. of calcium chloride. Its manufacture in Westeregeln, Germany, under the Polzeniusz patents was discontinued in 1910.

Calciocianamide.—The Italian commercial product, completely hydrated.

Cyanamide de calcium.—The French commercial product, completely hydrated.

MANUFACTURE OF COMMERCIAL CYANAMID.

The first step in the manufacture of Commercial Cyanamid is the preparation of calcium carbide. This is brought about in the usual manner by fusing in an electric furnace a mixture of lime and coke in accordance with the following equation:

$$CaO + 3C \rightarrow CaC_2 + CO.$$

The carbide is removed from the furnace at regular intervals, is cooled, crushed to a fine powder, and packed in the nitrifying ovens. These are cylindrical, perforated steel cans, set in heat-insulated brick ovens. A carbon pencil through the axis of the can is used to heat the carbide to the combining temperature. On admission of the nitrogen to the cans the following reaction takes place:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C.$$

This reaction is accompanied by an evolution of heat which is just about sufficient to maintain the mass at the combining temperature. The commercial calcium carbide used contains about 20 per cent. of impurities, which so influence its physical and chemical properties that the absorption of nitrogen takes place very readily at atmospheric pressure at a temperature of about 1,100° C. The addition of catalytic agents, principally haloids, suggested by various investigators, is not necessary for the fixation of nitrogen, since the manufacturer can easily regulate the reactions by suitable disintegration of materials and by other mechanical means.

Nitrogen is obtained either by fractional distillation of liquid air, or by means of the copper oxide process. In the latter, air is passed through a red-hot mass of finely divided copper, suspended in asbestos or other inert material. The copper combines with the oxygen and allows the nitrogen to pass through. The copper oxide is easily recovered for use by reduction *in situ* with a suitable gas, such as natural gas.

The nitrogen used must be pure and dry, otherwise, at high temperatures, there is destruction of the carbon pencils, and of calcium carbide, according to the following reactions:

$$\begin{gathered} C + O \rightarrow CO, \\ C + CO_2 \rightarrow 2CO, \\ C + H_2O \rightarrow CO + H_2, \\ H_2O + CaC_2 \rightarrow CaO + C_2H_2, \\ 3O + CaC_2 \rightarrow CaO + 2CO. \end{gathered}$$

Carbon dioxide also destroys the calcium cyanamide with formation of calcium oxide, carbon monoxide and free nitrogen.

The reaction by which calcium cyanamide is formed is reversible:

$$CaC_2 + N_2 = CaCN_2 + C.$$

The temperature of reversal at atmospheric pressure varies greatly with the composition of the carbide used. Thus the temperature of reversal lies at about 1,360° C.,[1] for a crude calcium cyanamide containing 21.1 per cent. combined nitrogen, and made from a commercial carbide of the following composition:

	Per cent.
CaC_2	82.30
C	1.20
CaO	14.72
CaSi	0.06
Ca_3P_2	0.07
CaS	0.13
Ferrosilicon	0.72
Not determined	0.80

An increase of the free lime in the carbide greatly lowers the critical temperature. Thus with a carbide containing 75 per cent. CaC_2 the equilibrium point lies at about 1150° C.[2]

The effect of nitrogen pressure on the equilibrium point has been investigated by M. Thompson, who found that the temperature at equilibrium varies directly as the pressure.[3] Since calcium cyanamide is decidedly volatile at the equilibrium temperature, even as low as 1,050° C., and distils to the colder parts of the apparatus the determination of the equilibrium conditions is open to some errors, but these may not be large enough to vitiate the general conclusions that have been drawn.

It is owing to the reversibility of the reaction that nitrogen

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[1] Caro, Chem. Trade Jour., 1909, p. 622.

[2] LeBlanc & Eschmann, Zeit. für Elek., 1911, 17, 20-34.

[3] Thompson & Lombard, Met. and Chem., Eng., 1910, 617, 682.

cannot be absorbed by liquid carbides as the latter leaves the furnace, since calcium cyanamide cannot exist at the temperature of liquid carbide. As the carbide cools it becomes practically impermeable to gases and absorption takes place only on the surface to a slight depth.

Processes for the nitrifying of a heated mass of lime and coke have not been commercially successful.

The energy consumption for the fixation of one ton of nitrogen as calcium cyanamide is about three horse power years, including the manufacture of the carbide and all subsequent factory operations.

PREPARATION FOR USE AS FERTILIZER.

Cyanamid finds its principal use in agriculture, as a source of nitrogenous plant food, and for this reason practically all the crude calcium cyanamide is converted into a form more suitable for its incorporation in complete fertilizers. To this end, water is added to the crude material in a rotating cylinder; the one or two per cent. of calcium carbide is decomposed and the lime slaked. This powdered Cyanamid is converted to granulated Cyanamid as follows: A small amount of water is mixed with it, and the damp material is run through brick presses. The resulting bricks harden rapidly, and are stored until the material is to be shipped, when they are run through a series of crushing rolls and screens. The coarse material, which passes through a 15-mesh standard screen and over a 60-mesh standard screen, is practically free from dust, and is known commercially as Granulated Cyanamid. The fine material, mostly smaller than 60-mesh, is either incorporated with fresh powdered Cyanamid and again run through the brick presses, or it is mixed with several per cent of an odorless oil to reduce the dustiness, and is sold without further treatment. Both grades of Cyanamid are packed in ordinary fertilizer bags, and are distributed in carload lots to manufacturers of mixed fertilizers. Material so prepared contains nitrogen equivalent to 18 to 20 per cent. of ammonia, and is sold on the basis of its nitrogen content, as determined by analysis.

The following is a typical analysis of commercial Cyanamid.

		Per cent.
Calcium cyanamide	$CaCN_2$	45.92
Calcium carbonate	$CaCO_3$	4.04
Calcium sulphide	CaS	1.73
Calcium phosphide	Ca_3P_2	0.04
Calcium oxide, free	CaO	—
Calcium carbide	CaC_2	—
Calcium hydroxide	$Ca(OH)_2$	26.60
Free carbon	C	13.14
Iron and alumina	R_2O_3	1.98
Silica	SiO_2	1.62
Magnesia	MgO	0.15
Combined moisture	—	3.12
Free moisture	H_2O	0.35
Undetermined	—	1.31
		100.00

COMMERCIAL DERIVATIVES.

Ammonia.—Steam, at a high temperature and pressure, converts calcium cyanamide quantitatively into calcium hydroxide and ammonia, thus forming a convenient source of ammonia for the manufacture of ammonium salts. The carbon, which is in the form of graphite, and the lime, can be used over again for the production of carbide.

Nitric Acid.—By the Ostwald process, ammonia can be oxidized to nitric acid, mixtures of thoria and ceria being used as catalyzers. No external supply of energy is required in this process.

Cyanides.—When calcium cyanamide and carbon are fused together with alkaline salts, in the absence of carbide the calcium cyanamide is converted into calcium cyanide:

$$CaCN_2 + C \rightarrow Ca(CN)_2.$$

The product of this reaction is called a "surrogate." It is used in the recovery of metals by the cyanide process.

The above reaction is completely reversed in the presence of carbides, hence their absence is imperative in this process.

Dicyandiamide.—This derivative is easily prepared by leaching the crude calcium cyanamide mass with hot water, precipitating the lime in the filtrate with carbon dioxide, and concentrating the filtrate. Dicyandiamide is used in the dye industry, and also as a deterrent in nitro-explosives, in place of ammonium oxalate.

Other derivatives, such as urea, guanidine, nitro-guanidine, are being made at the Spandau works, in Germany. A process has also been worked out for the production of synthetic indigo by the action of dialkylcyanamides on Phenylgycine and its derivatives.

Ferrodur and intensit are special mixtures prepared for metallurgical purposes. Ferrodur is a cementing powder used in place of potassium cyanide for hardening iron and steel in ovens. Intensit is a hardening powder for hardening iron and steel in open fires; it is used in place of potassium ferrocyanide. There are other powders of a similar nature with special names differing only in the proportion of active ingredients that they contain. These products are of considerable importance to metallurgy, since they are cheap, yet efficient for the purposes for which they are sold.

CHAPTER II.

Preparation and Properties of Cyanamide.

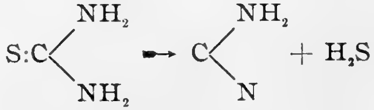
PREPARATION.

Free cyanamide, $CN.NH_2$, was first obtained by Bineau, in 1838, by the action of ammonia on chlorcyan, but it was not isolated by him from the ammonium chloride with which it was formed. The Italian chemists Cloez and Cannizzaro,[1] in 1851, effected the separation, and gave the first description of the compound.

Their method consists in passing chlorcyan into a solution of ammonia in absolute ether, filtering off the crystalline ammonium chloride and evaporating the solution in vacuo below 40°. The reaction takes place according to the following equation:

$$2NH_3 + CNCl \rightarrow CNCl_2 NH_4 + NH.$$

It can also be prepared by the action of freshly precipitated mercuric oxide on thio-urea, in the presence of a little ammonium thiocyanate, which dissolves some of the mercuric oxide as the double thiocyanate, and so renders it more active:



$$S{:}C\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. \rightarrow C\left\langle\begin{matrix}NH_2\\N\end{matrix}\right. + H_2S$$

It is most conveniently prepared from either commercial sodium cyanamide or commercial calcium cyanamide.

From Commercial Sodium Cyanamide.[2]—Twenty-five grams of the salt are gradually added to 37 grams of hydrochloric acid (sp. gr. 1.19) with strong cooling, and the water is removed by distillation in vacuo below 40° C. The residue solidifies on cooling; it is extracted with ether, the ether distilled off from the solution, and the cyanamide caused to

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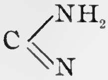
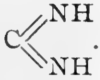
[1] Compt. rend., XXXII, 62. A, 78, 229, and Leibig's Annalen 78, 229.

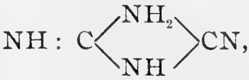
[2] Caro, Schück, Jacoby, Zeit Angew Chem. 1910, XXIII, 2405, 2417.

crystallize by cooling. It is purified by recrystallization from ether. Yield about 5 grams.

From Commercial Calcium Cyanamide.—Fresh commercial Cyanamid or better, the unhydrated lime-nitrogen, is extracted with cold water (solubility about 0.9 grams nitrogen in 100 cc. water). The calcium is removed either with oxalic acid or aluminium sulphate, but preferably with the latter. After removal of the calcium sulphate and alumina by filtration, the filtrate is evaporated in vacuo below 40°, and the residue extracted with ether. It can be purified by recrystallization from ether.

PROPERTIES OF CYANAMIDE.

Cyanamide,[1] $CN.NH_2$, most probably has the formula  $C\begin{smallmatrix}\diagup NH_2\\ \diagdown\!\!\diagdown\!\!\diagdown N\end{smallmatrix}$, although in a very few reactions it seems to act as if it were carbodiimide,  $C\begin{smallmatrix}=NH\\ =NH\end{smallmatrix}$. It is a colorless, crystalline solid, which melts at 41-42° C., as usually prepared. It can be undercooled to 12° without solidifying. On stirring with a sharp-pointed glass rod the undercooled liquid freezes. The carefully purified substance melts sharply at 46° C.[2] It is easily soluble in water, alcohol and ether, and is volatile in steam. It is slightly soluble in carbon disulphide, chloroform and benzol.

Action of Heat.—Pure cyanamide is perfectly stable at ordinary temperatures, but polymerizes slowly on heating above its melting point. Impure cyanamide polymerizes slowly at ordinary temperatures. The principal polymer is dicyandiamide,  $NH : C\begin{smallmatrix}NH_2\\ NH\end{smallmatrix}CN$, or $(H_2CN_2)_2$, which is probably cyan-guanidine. By strong heating, other derivatives are

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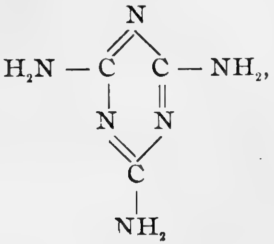
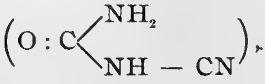
[1] Sidgwick, Organic Chemistry of Nitrogen, p. 216, (Oxford, 1910).

[2] G. Henschel, Diss. Univ. of Leipzig, 1912.

formed, the most important of which are, the polymer Tricyantriamide or Melamine , and Melam, $C_6H_2N_{11}$, and Mellon, $C_6H_3N_9$. Ammonia is evolved during the formation of these bodies. By the action of superheated steam the conversion of cyanamide to ammonia is almost quantitative.

Action of Acids.[1]—Cyanamide reacts readily with acids; with nitric acid forming urea nitrate (95 per cent. conversion); with sulphuric acid and phosphoric acid giving mostly urea, (about 95 per cent. conversion) together with some ammeline, $C_3N_3(NH_2)_2OH$; ammelide, $C_3N_3(NH_2)(OH)_2$; possibly cyanuric acid, $C_3N_3(OH)_3$, and some ammonia.

Cyanamide combines directly with the haloid acids. It combines slowly with free H_2S, readily with yellow ammonium sulphide, with formation of thio-urea. Thio-urea is also formed by the action of thioacetic acid on cyanamide in alcoholic solution. Acetic acid produces principally ammonium acetate (about 80 per cent. conversion) and some urea.

Action of Alkalies.[2]—The strong alkalies KOH or NaOH in aqueous solutions produce almost entirely urea, with no trace of dicyandiamide; weak alkalies, NH_4OH or MgO, produce dicyandiamide almost exclusively at first, and then ammonia. CaO, however, produces a mixture of urea, dicyandiamide, ammeline, amidodicyanic acid  $\left(O : C\begin{smallmatrix} NH_2 \\ NH - CN \end{smallmatrix}\right)$, ammonia and other bodies.

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[1] Ulpiani, Gas Chim., Ital. II, No. 4, 358-417.

[2] Beilstein's Handbuch der Organische Chemie.

Hence, with strong acids and strong bases, cyanamide in aqueous solutions forms principally urea; with weak acids principally ammonium salts; with weak bases dicyandiamide, which decomposes further to ammonia; with lime, a mixture of urea, dicyandiamide and other derivatives.

Action of Oxidizing and Reducing Agents.—In the chapter on availability it will be shown that oxidizing agents convert the nitrogen of cyanamide or its derivatives into forms more insoluble in water and less easily decomposed by strong alkalies.

By the action of zinc and hydrochloric acid, cyanamide yields ammonia and methylamine:

$$CN.NH_2 + H_2 \rightarrow CNH + NH_3,$$
$$CNH + 2H_2 \rightarrow CH_3.NH_2.$$

On heating with potassium nitrite solution a violent reaction takes place, and CO_2, N_2 and dicyandiamide are produced:

$$4CN.NH_2 + 4KNO_2 \rightarrow 2K_2CO_3 + 4N_2 + (CN.NH_2)_2 + 2H_2O.$$

Other Reactions.[1]—In cyanamide, either one or both of the hydrogen atoms can be displaced by metals, alkyl or aryl groups, or by alcohol or acid radicals. It combines with amino-acids, especially in the presence of ammonia. It combines with ammonium chloride at high temperatures, forming guanidine hydrochloride. Heated with ammonium sulphide it yields guanidine hydrosulphide. It combines directly with cyanogen to form a yellow, amorphous powder. With potassium cyanate it forms potassium amidodicyanate, $K.C_2H_2N_3O$. It combines directly with chloral, and also with aldehydes, but with the separation of water.

Metal Salts.—The *dimetal salts* of the alkali metals can be prepared only in the dry way, since in aqueous solution they lose one of the metal ions by hydrolysis. Thus, Na_2CN_2 in aqueous solution yields $NaHCN_2$:

$$Na_2CN_2 + H_2O = NaHCN_2 + NaOH$$

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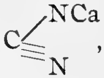
[1] Beilstein, Handbuch der Org. Chem.

Na_2CN_2 on fusion with carbon yields sodium cyanide:

$$Na_2CN_2 + C \rightarrow 2NaCN.$$

Calcium Cyanamide, $CaCN_2$ or  $C\begin{smallmatrix}\diagup NCa \\ \equiv N\end{smallmatrix}$, can be made by the fusion of calcium cyanate:[1]

$$Ca\ (CNO)_2 \rightarrow CaCN_2 + CO_2$$

or by fusion of cyanamide or its polymers with calcium oxide.

Calcium cyanamide forms colorless crystals which sublime at about 1,090° C. at atmospheric pressure. It is insoluble in alcohol, but easily soluble in water (about 2.5 g. in 100 cc. water at 25° C.). Upon solution of the calcium cyanamide in water it is directly hydrolyzed into the *acid calcium cyanamide* and calcium hydroxide.

$$2CaCN_2 + 2H_2O \rightarrow Ca(CN.NH)_2 + Ca(OH)_2.$$

That such hydrolysis takes place as indicated by the equation is shown by the relative amounts of lime and nitrogen existing in solutions of calcium cyanamide. C. Ulpiani[1] investigated the relation of lime to nitrogen in a solution of calcium cyanamide kept at a constant temperature for several weeks. At intervals of several days determinations were made of total nitrogen, nitrogen in the form of cyanamide, and calcium in solution. It was noted that crystals of pure calcium hydroxide, as determined by analysis, were deposited on the walls of the vessel after a day or two. The quantities of lime and nitrogen found in the solution are shown in Fig. 1.

Since the solubility of calcium cyanamide is much greater than that of calcium hydroxide, a concentrated solution of calcium cyanamide is, after hydrolysis, saturated with respect to calcium hydroxide. In addition, there is present lime as a calcium compound of cyanamide. If this compound is calcium acid cyanamide, $Ca(CN.NH)_2$, there will be in solution one atom of calcium to four of nitrogen, or 56 parts by weight

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[1] Beilstein loc cit.

[2] Rend. Soc. Chim. di Roma, n. 4 (1906).

of CaO to 56 of N, or equal weights of each. By reference to the curves in Fig. 1 it is seen that if the ordinate representing the amount of CaO present as $Ca(OH)_2$ is subtracted from the ordinate of total CaO, the ordinate of CaO combined in other forms (with cyanamide) would coincide with the ordinate of nitrogen present as cyanamide; that is, the amounts of CaO and N present are in the relation demanded by the formula $Ca(CN.NH)_2$.

On long standing of the solution, the acid salt $Ca(CN.NH)_2$ decomposes, forming principally urea, some dicyandiamide, and small quantities of melamine, amidodicyanic acid and ammonia. The dicyandiamide diminishes slowly, and finally probably disappears entirely. This is shown in the following analyses by G. Liberi[1] of a solution made by extracting lime-nitrogen containing 18.63 per cent. cyanamide nitrogen, with twenty times its weight of cold water. The nitrogen figures are given as a percentage of the dry lime-nitrogen.

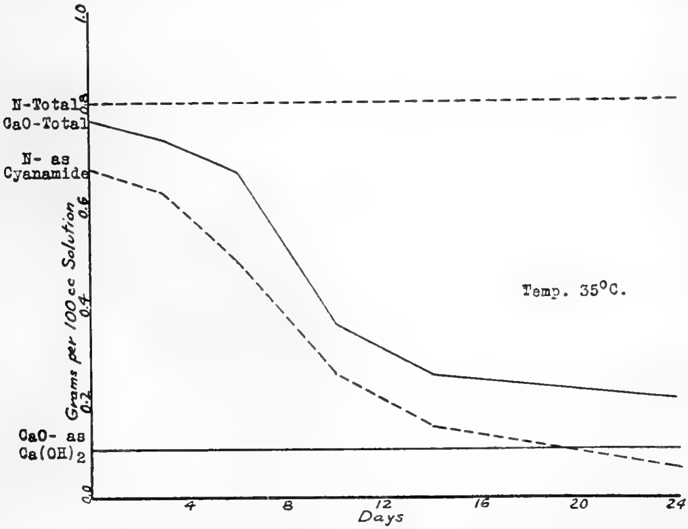

Fig. 1.—Variation of nitrogen and calcium in a solution of lime-nitrogen.

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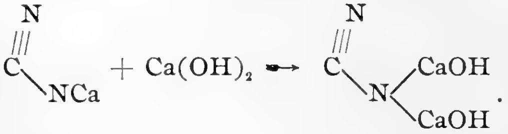
[1] Ann. R. Staz. Chim. Agrar. Sper di Roma., 1911, Vol. V, Series II.

	Nitrogen in solution	
After	As cyanamide Per cent.	As dicyanamide Per cent.
1 day	14.56	0.70
3 days	11.76	1.54
6 days	9.10	2.84
11 days	5.18	2.24
18 days	1.75	1.71
31 days	0.00	1.25
45 days	0.00	0.84
58 days	0.00	0.53
76 days	0.00	0.23

Basic calcium cyanamide is formed in solutions containing an excess of lime:



It can be obtained from lime-nitrogen by extracting with a small portion of water, filtering, and allowing the solution to stand several hours. Long, needle-shaped white to transparent crystals separate out on the walls of the vessel. Filter with suction in the absence of carbon dioxide (under a bell-jar). Dry under a bell-jar over caustic potash.

This salt is almost insoluble in water. In the dry condition it is stable at ordinary temperatures, but when heated to 120° C. it rapidly decomposes to dicyandiamide and calcium hydroxide.

Calcium cyanamide carbonate[1] is readily formed by the action of carbon dioxide on calcium cyanamide in the presence of moisture. It can be prepared by extracting lime-nitrogen with one and one-half times its weight of water, filtering and bubbling CO_2 through the filtrate. In about half an hour a white precipitate forms, which can be filtered and washed with alcohol or ether.

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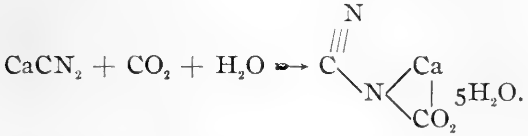
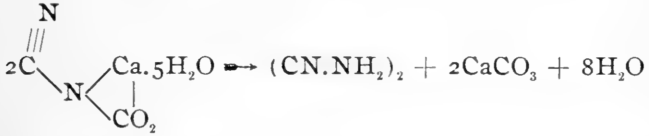
[1] Ulpiani, loc cit.



$$CaCN_2 + CO_2 + H_2O \rightarrow N{\equiv}C{-}N{<}\begin{matrix}Ca\\ |\\ CO_2\end{matrix}\ 5H_2O.$$

Calcium cyanamide carbonate is somewhat insoluble in water, and insoluble in alcohol and ether. On standing in dry air it slowly loses 4 molecules of water of crystallization, and at the same time decomposes to dicyandiamide and calcium carbonate. The same change takes place rapidly when heated:

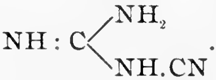


$$2\,N{\equiv}C{-}N{<}\begin{matrix}Ca.5H_2O\\ |\\ CO_2\end{matrix} \rightarrow (CN.NH_2)_2 + 2CaCO_3 + 8H_2O$$

Silver Cyanamide, $CN.NAg_2$.—Obtained on treating an ammoniacal solution containing cyanamide with very dilute (1 : 150) solution of silver nitrate.[1] More concentrated solutions yield a mixture of this salt and double or basic silver salts, containing, however, all the cyanamide.

Silver cyanamide is an amorphous, yellow substance, almost insoluble in dilute ammonia or caustic potash at ordinary temperatures, soluble in hot ammonia solutions, easily soluble in dilute nitric acid. It is easily soluble in alkali cyanide solution, but if an excess of silver nitrate is added, a white, crystalline double salt of silver cyanide and silver cyanamide is precipitated.

When potassium hydroxide is added to a cyanamide solution containing silver nitrate in excess an insoluble mixed precipitate of silver cyanamide and brown silver oxide is formed, which contains all the cyanamide nitrogen.

Dicyandiamide,[2]  $NH : C{<}\begin{matrix}NH_2\\ NH.CN\end{matrix}$.—Obtained by extracting lime-nitrogen with boiling water, concentrating the solu-

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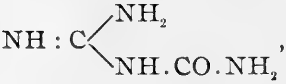
[1] Caro, Schück, Jacoby, loc cit.

[2] Beilstein, loc cit.

tion to a syrup and allowing to crystallize. It forms trimetric plates or thin leaves, melting at 205° C. It is decomposed by heating, with evolution of ammonia and formation of melamine, melam, and other derivatives. Dicyandiamide is somewhat easily soluble in water and alcohol, but almost insoluble in ether. It combines with ammonium chloride at 150°, giving diguanide hydrochloride, $C_2H_7N_5HCl$; with HCl at 150° gives guanidine hydrochloride, CH_5N_3HCl; on boiling with baryta it gives amidodicyanic acid and ammonia; with zinc and HCl yields methylamine and ammonia; with H_2S it gives guanylthiourea; on heating with urea or cyanuric acid it forms ammelin, $C_3H_5N_5O$, and ammonia.

Treated with weak or strong acids, or with strong alkalies, dicyandiamide goes over to *dicyandiamidine*,



$$\mathrm{NH:C}\begin{matrix}\diagup \mathrm{NH_2} \\ \diagdown \mathrm{NH.CO.NH_2}\end{matrix}$$

, caustic crystals, easily soluble in water and alcohol.

Dicyandiamide, treated with silver nitrate solution, forms additional compounds containing, according to the conditions, one, two and three molecules respectively, of dicyandiamide per molecule of silver nitrate. Cold caustic potash added to a dicyandiamide solution containing sufficient silver nitrate causes a white to brown mixture of precipitates of silver dicyandiamide and silver oxide. Silver dicyandiamide is slightly soluble in water, easily soluble in ammonia, soluble in hot nitric acid; on prolonged boiling with caustic potash is converted into silver cyanamide, $CN.NAg_2$, and cyanamide, which polymerizes again to dicyandiamide.

If silver nitrate, then nitric acid, is added to a solution of dicyandiamide, a white precipitate is formed, insoluble in cold, soluble in hot nitric acid or in excess of ammonia. (Identification in mixtures of cyanamide and dicyandiamide. Cyanamide, it will be remembered, gives a yellow precipitate with dilute silver nitrate, soluble in nitric acid, but insoluble in ammonia.)

CHAPTER III.

Analytical Methods.

DETERMINATION OF TOTAL NITROGEN IN CYANAMID.

Practically all the Cyanamid manufactured in this country prior to January 1, 1912, contained about 23 per cent. of its total nitrogen in the form of nitrates. Hence, for the determination of total nitrogen in such Cyanamid it is necessary to use a method that will determine nitrate nitrogen as well as nitrogen derived from Cyanamid. For this purpose the Official Gunning method, modified for nitrates, is suitable. The period of digestion should be at least five hours. The influence of the period of digestion is shown in the following values obtained on a sample of Cyanamid containing nitrates:

	Per cent. nitrogen
2 hours digestion	15.61
3 " "	15.76
4 " "	16.03
5 " "	16.06

All the Cyanamid manufactured in this country since January 1, 1912, is free of nitrates, and therefore, the simple Kjeldahl or Gunning method may be used. The Gunning, which is in general use, is carried out as follows:

REAGENTS REQUIRED.

N/2 (Half-normal) Sulphuric or hydrochloric acid.
N/10 (Tenth-normal) Sodium hydroxide, or ammonium hydroxide.
Sulphuric acid, C. P., specific gravity 1.84.
Sodium hydroxide, saturated solution.
Potassium sulphate, C. P.
Cochineal indicator.

To determine nitrogen weigh out 0.7 gram of finely ground sample. Each cc. of half-normal acid is equivalent to 1 per cent. nitrogen. To determine ammonia weigh out 0.85 gram of finely ground sample. Each cc. of half-normal acid is equivalent to 1 per cent. ammonia.

Procedure.—Place the carefully weighed sample in a Kjeldahl flask of about 300 cc. capacity. Add 10 grams of ground potassium sulphate. Shake until well mixed with the sample. Add 25 to 30 cc. of concentrated sulphuric acid and shake until well mixed. Heat slowly for 30 minutes, then heat with a full flame for one and one-half hours. Cool, dilute, and transfer to a distillation flask. (Distillation can be made from the digestion flask if desired.) Add an excess of sodium hydroxide, and distil 200 cc. into a measured quantity of the standard half-normal acid, containing some cochineal indicator. Titrate the excess of acid with tenth-normal alkali.

DETERMINATION OF CYANAMIDE AND DICYANDIAMIDE.

Caro Method.—Of the various methods for determining cyanamide and dicyandiamide, that of Caro[1] seems to be the best. The reagents used are as follows:

(*a*) Silver acetate solution. 100 grams of silver acetate are placed in a liter flask, covered with 400 cc. of 10 per cent. ammonium hydroxide, and the flask is filled to the mark with water.

(*b*) 10 per cent. solution of potassium hydroxide.

The procedure is as follows: 5 g. of Cyanamid or lime-nitrogen is agitated by hand or in a shaking machine with 450 cc. of water for about 2½ hours, and the flask filled to 500 cc. An aliquot part (250 cc.) is treated with ammonia until it smells strongly thereof and then with silver acetate solution in excess. The precipitate of silver cyanamide salts (p. 12), after shaking and standing a little while, is gathered on a nitrogen-free filter, washed with water until no ammonium salts run through, and the nitrogen in it is determined by the Kjeldahl method.

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[1] Caro, Schück, Jacoby—loc cit.

An aliquot part of the filtrate, now free from cyanamide, is treated with potassium hydroxide solution in excess, and is boiled until no more ammonia comes off. The precipitate contains all the dicyandiamide and some silver oxide. Dilute the solution with an equal volume of water, filter on a nitrogen-free filter, wash with some water, and determine nitrogen in the precipitate by the Kjeldahl method.

Brioux[1] claims that the boiling of the strongly alkaline cyanamide-free solution containing the precipitate of silver dicyandiamide and silver oxide causes a conversion of about 1.5 per cent. of the total nitrogen of the dicyandiamide, and he has modified the method so as to obviate this error. His method is briefly as follows:

Brioux's Modified Caro Method.—Extract the soluble nitrogen from 1 or 2 grams of finely ground sample by frequent shaking for three or four hours in a flask with 250 cc. cold water, and filter through a dry filter without washing. In one aliquot portion of 100 cc. of the filtrate determine cyanamide and dicyandiamide, and in the other determine cyanamide alone.

For combined cyanamide and dicyandiamide nitrogen: For each 0.1 gram nitrogen (approx.) in the solution add 20 cc. of 5 per cent. silver nitrate solution. Then add 20 cc. of 10 per cent. potassium hydroxide solution. A brown precipitate of mixed cyanamide and dicyandiamide salts forms. Filter and wash with cold distiled water. Determine total nitrogen in the residue by the Kjeldahl process, substituting 1 gram copper sulphate in place of the mercury.

For cyanamide nitrogen: In the other portion of the extract from the sample add for each 0.1 gram nitrogen, 20 cc. of 5 per cent. silver nitrate solution. Add an excess of ammonia. A yellowish-brown precipitate forms. Filter and wash with water slightly ammoniacal, finishing with cold distilled water until the washings are free from soluble silver salts. Dissolve the residue in dilute nitric acid (1:2) and determine silver

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[1] Annales de la Science agron. francaise et etrangere, April 1910.

by the sulphocyanate or other convenient method. One atom of silver corresponds to one atom of nitrogen.

In both the Caro and Brioux methods, however, from 25 to 30 per cent. of the urea present is precipitated in caustic potash solution as silver salts along with the dicyandiamide.[1] Since Cyanamid frequently contains more urea than dicyandiamide this occasions considerable error. Henschel[2] found that by the Caro method about 7 per cent. of the nitrogen as dicyandiamide was converted to other forms, presumably by the action of the hot caustic alkali in boiling off the the ammonia. The total nitrogen was not diminished, hence the urea (?) nitrogen was increased at the expense of the dicyandiamide.

Determination of Urea.—Caro determines the total nitrogen remaining in the filtrate from the dicyandiamide separation and designates it as urea. Since, however, some of the urea is precipitated along with the dicyandiamide and since the filtrate may also contain other derivatives, the method can hardly be considered as satisfactory. Caro also recommends Liebig's titration method for the determination of the urea in the filtrate. Ulpiani,[3] however, claims that the mercuric nitrate used for the precipitation of urea in this method, also precipitates cyanamide and dicyandiamide, if present, dicyandiamidine, amidodicyanic acid, ammonia, ammonium salts, and probably all nitrogen compounds found in lime-nitrogen. Ulpiani suggests the direct solution of the sample of lime-nitrogen or Cyanamid with alcohol, but since dicyandiamide as well as urea is soluble in alcohol, this procedure would not simplify the problem very much.

The question of analysis of cyanamide derivatives is much in need of scientific study, but for the present it will be sufficient for most purposes to determine total nitrogen in a given sample of Cyanamid, then to determine cyanamide and

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[1] Brioux, loc. cit.

[2] Georg Henschel, Das Verhalten des technischen Calciumcyanamides bei der Aufbewahrung sowie unter dem Einfluss von Kulturböden und Kolloiden—Diss. Univ. Leipzig. 1912.

[3] Ulpiani, loc. cit.

dicyandiamide by the Caro method, and to consider the difference as being equivalent to the original urea. The other derivatives usually occur in such small quantities that they are practically negligible.

IDENTIFICATION OF AMIDODICYANIC ACID.

The following is based upon the procedure given by Ulpiani[1] for the identification of amidodicyanic acid.

Remove the cyanamide and dicyandiamide (Brioux's method), carefully neutralize the filtrate with sulphuric acid, and treat with copper sulphate. In a day or two greenish crystals of copper amidodicyanate separate out. Sometimes there is also a slight precipitate of copper salts of cyanamide and dicyandiamide, which are easily washed out by rapid decantation, since the copper amidodicyanate is much heavier. The copper amidodicyanate has the formula $Cu(C_2H_2N_3O)_2 . 4H_2O$. It is further identified by mixing the copper salt with ammonia and treating the solution with hydrogen sulphide. The copper sulphide is filtered off, and the filtrate concentrated, when a white precipitate of thiobiuret is formed. This loses water at 100° and melts at 185°. With copper sulphate a solution of thiobiuret gives a white precipitate.

IDENTIFICATION OF AMMELINE.

Ulpiani[2] claims that ammeline can be detected in old lime-nitrogen as follows:

Extract the sample with dilute nitric acid. Filter and just neutralize the filtrate with ammonia. A white precipitate of ammeline is obtained, insoluble in water, soluble in alkalies or mineral acids. Analysis should show the solid to have the formula $C_3H_5N_5O$.

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[1] Gaz Chim. Ital 1908, II No. 4, 358-417.

[2] loc. cit.

CHAPTER IV.

Storage of Cyanamid.

On exposure to the atmosphere, Cyanamid absorbs moisture and carbon dioxide. This absorption of foreign material, of course, increases the weight of the exposed sample, and hence decreases the percentage of the original constituents. Neglect to observe this increase in weight and corresponding decrease of percentages led some early investigators to declare that nitrogen is lost when Cyanamid is stored for any great length of time. It has lately been shown by carefully conducted experiments in the laboratory as well as on a large scale, that under conditions of storage customary for fertilizer materials there is no loss of nitrogen.

Factory Test.—When Cyanamid is stored in ordinary burlap bags only the exposed surfaces can receive moisture and carbon dioxide, and penetration into the interior of the bag or pile is necessarily difficult. Even in damp climates, such absorption is not very large when considered in its relation to the entire pile. Thus, a pile of Cyanamid weighing 94,083 pounds, and analysing 15.63 per cent. nitrogen was stored in a warehouse over and a few feet above the surface of the St. Johns river at Jacksonville, Florida, from July 7th to January 13th, and was then carefully weighed and sampled by the purchaser, the sample being taken from different portions of two out of every three bags in the lot.

	Weight	Per cent. increase in weight. 7 mo's	Analysis nitrogen	Pounds nitrogen
Original........	94,083	....	15.63	14,705
After 7 months.	101,506	7.9	14.52	14,740

Hence, even in this damp climate, where rains occur almost daily during the summer months, the rate of increase of weight is a little more than one per cent. a month, while the nitrogen content remains constant.

Test of Two Bags.—A test on a smaller scale was made by the author, at Niagara Falls, Ontario, in 1912. Two ordinary burlap bags, each holding about 150 pounds of Cyanamid hydrated on November 12, 1911, were exposed November 17, 1911, on a raised platform made of 4-inch strips spaced 4 inches apart. The room was dry, well-ventilated by an open window, and kept most of the time between 10° and 35° C. Samples were drawn and the weight of the bags was taken just before they were laid out on the platform. At the end of each period of exposure as noted below, the bags were carefully weighed, and the contents were removed. After thorough mixing of the material a sample was drawn, and the bags were refilled, tied, weighed, and again laid out on the platform for further exposure. The following data were obtained:

BAG A.—ANALYSES.

Sample drawn	Moisture Per cent.	Carbon dioxide Per cent.	Nitrogen Per cent.	Calcium Per cent.	Ratio $\frac{N}{Ca}$
Nov. 17, 1911	0.00	1.75	16.54	40.34	0.4100
Dec. 17, 1911	0.40	2.12	16.11	39.94	0.4095
Jan. 17, 1912	0.47	2.75	16.11	39.34	0.4095
Feb. 17, 1912	0.46	2.87	15.96	38.94	0.4099
May 17, 1912	0.67	4.05	15.69	37.94	0.4136

WEIGHTS.

Date	Weight pounds net	Gain in weight pounds	Per cent. gain in weight since previous weighing	Per cent. nitrogen calculated	Per cent. nitrogen found	Per cent. nitrogen gained or lost
Nov. 17, 1911	148.25	—	—	—	16.54	—
Dec. 17, 1911	[1]150.75	2.50	1.69	16.266	16.31	+0.04
" " "	[2]149.25					
Jan. 17, 1912	150.50	1.25	0.84	16.131	16.11	—0.02
" " "	149.50					
Feb. 17, 1912	150.50	1.00	0.67	17.024	15.96	—0.06
" " "	150.00					
May 17, 1912	153.25	3.25	2.17	15.683	15.69	+0.01

[1] Before sampling.

[2] After sampling.

BAG B.—ANALYSIS.

Sample drawn	Moisture Per cent.	Carbon dioxide Per cent.	Nitrogen Per cent.	Calcium Per cent.	Ratio $\frac{N}{Ca}$
Nov. 17, 1911	0.00	1.75	16.34	40.53	0.4031
Dec. 17, 1911	0.43	2.10	16.09	39.94	0.4029
Jan. 17, 1912	0.44	2.70	15.87	39.35	0.4033
Feb. 17, 1912	0.46	2.83	15.70	38.94	0.4031
May 17, 1912	0.69	3.96	15.50	38.76	0.3999

WEIGHTS.

	Weight pounds net	Gain in weight pounds	Per cent. gain in weight since previous weighing	Per cent. nitrogen calculated	Per cent. nitrogen found	Per cent. nitrogen gained or lost
Nov. 17, 1911	149.00	—	—	—	16.34	—
Dec. 17, 1911	[1]151.75	2.75	1.84	16.046	16.09	+0.04
" " "	[2]150.75					
Jan. 17, 1912	152.25	1.50	0.99	15.890	15.87	—0.02
" " "	151.25					
Feb. 17, 1912	151.75	0.50	0.33	15.838	15.70	—0.14
" " "	151.25					
May 17, 1912	154.75	3.50	2.31	15.480	15.50	+0.02

The addition of free moisture, chemically combined moisture, and carbon dioxide necessarily increases the weight of the sample, and hence causes a proportionate decrease in the *percentages* of other constituents. It is evident that calcium cannot escape from the stored material either by volatilization, since calcium compounds require at least a red heat before they vaporize appreciably, or by leaching, since the mass remains practically dry for years. The decrease in calcium percentage must therefore be due solely to the addition of other matter, and the ratio of the calcium percentages before and after exposure is equal to the inverse ratio of the weights before and after exposure. Thus in bag A the ratios are $\frac{40.34}{37.94} = \frac{106.32}{100.00}$ or there has been an increase of 6.32 per cent. on the original weight. As shown by the weighings, the in-

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[1] Before sampling.

[2] After sampling.

crease of weight was 5.46 per cent. of the original weight. The failure of the two results to check more closely is due to the difficulty of making accurate calcium determinations in Cyanamid.

Since the absolute quantity of calcium remains constant in the mass exposed, it follows that if the absolute quantity of nitrogen present do not vary, the ratio of nitrogen to calcium must remain constant. Inspection of the data obtained as described above shows that this is actually the case within sampling and analytical limits of error. Recapitulating the results by analysis and by the weights we have:

	Increase in weight		Variation of nitrogen	
	By Ca ratios	by weighing	By N/Ca ratio	By weighing
Bag A....	6.32	5.46	+0.14	+0.01
Bag B....	4.77	5.57	− 0.10	+0.02
Average ..	5.54	5.51	+0.02	+0.015

There has therefore been no loss of nitrogen under ordinary factory conditions of storage, even in the case of a single exposed bag, which exposes a relatively larger surface per pound of material than a large pile would expose.

Of the 5.5 per cent. increase in weight, approximately 0.7 per cent. is due to the addition of free moisture, 2.5 per cent. to addition of carbon dioxide, and 2.3 per cent. to addition of combined water; or, of the total increase in weight, about 13 per cent. is due to free moisture, 45 per cent. to carbon dioxide, and 42 per cent. to chemically combined water.

In the analyses given above, free moisture was determined by the decrease in weight of a sample heated 5 hours at 100° C., in a drying oven free of carbon dioxide. The "combined" water is, properly speaking, not present as water at all, but represents water which has acted hydrolytically upon calcium cyanamide with the production of various organic derivatives. Such hydrolyses are in the main irreversible by drying. The increase in weight suffered by a sample of Cyanamid during storage cannot, therefore, be determined by simply correcting final analyses to the so-called "dry basis," since such a correction is only a small portion of the true correction required. The true increase in weight is best determined by direct weighing of the initial and final sample, or by comparing the calcium content of the initial and final samples. The latter involves very accurate calcium determinations, if the results are to be significant.

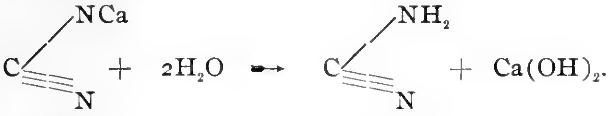
The absorption of "combined water" and of carbon dioxide takes place for the most part in accordance with the following equations, which probably account for the formation of dicyandiamide, urea, calcium cyanamide carbonate, and calcium carbonate:

$$\begin{aligned} 2CaCN_2 + 2H_2O &= Ca(CN.NH)_2 + Ca(OH)_2, \\ Ca(CN.NH)_2 + 2H_2O &= (H_2CN_2)_2 + Ca(OH)_2, \\ CaCN_2 + 3H_2O &= CO(NH_2)_2 + Ca(OH)_2, \\ CaCN_2 + CO_2 + H_2O &= CaCN_2.CO_2.H_2O, \\ Ca(OH)_2 + CO_2 &= CaCO_2 + H_2O. \end{aligned}$$

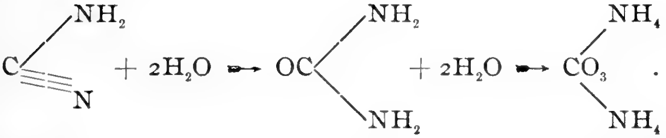
After long periods of exposure there are formed slight amounts of secondary derivatives, so that old Cyanamid will contain the following substances:

Calcium cyanamide	$CaCN_2$
Acid calcium cyanamid	$Ca(HCN_2)_2$
Basic calcium cyanamid	$CaCN_2.Ca(OH)_2$
Calcium cyanamide carbonate	$CaCN_2CO_2.H_2O$
Dicyandiamide	$(H_2CN_2)_2$
Urea	$CO(NH_2)_2$
Amidodicyanic acid	$H_3C_2N_3O$ (slight amounts)
Melamine	$(H_2CN_2)_3$ (slight amounts)
Ammeline	$H_5C_3N_5O$ (slight amounts)
Ammonium hydroxide	NH_4OH (traces)

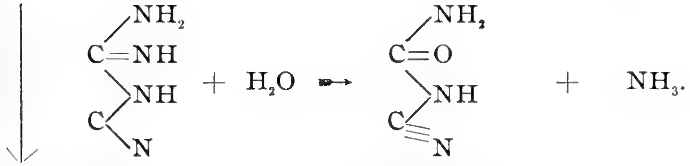
The following scheme shows the relation of some of these forms to each other, and a possible mechanism for their derivation from calcium cyanamide:



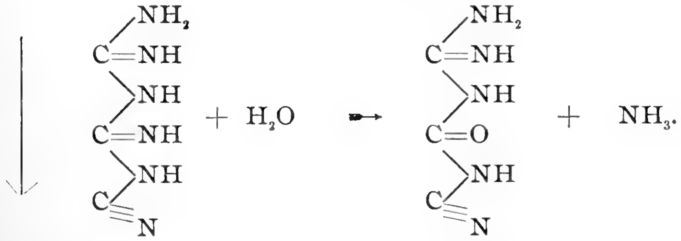
Calcium cyanamide. Cyanamide.



Cyanamide. Urea. Ammonium carbonate.



Dicyandiamide. Amidodicyanic acid.



Melamine. Ammeline.

Relative Amounts of Decomposition Products.—The relative amounts of these decomposition products has been studied in only a few cases, since the total amounts become appreciable only under extraordinarily severe conditions of moisture. A test of this kind is reported by Brioux.[1]

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[1] Annales de la Science agronomique francaise et etrangere, April, 1910.

A sample of lime-nitrogen was exposed on a watch-glass in a bell-jar, the atmosphere of which was kept saturated with moisture by a beaker of water alongside the watch-glass. The 10 gram sample after 8 months exposure weighed 18.75 grams. The analyses before and after exposure are as follows, the third column showing the results corrected to allow for increase in weight.

	Before exposure	After exposure	After exposure corrected
Total nitrogen	17.08	8.99	16.84
Insoluble nitrogen	1.30	0.38	0.71
Soluble nitrogen in form of Cyanamid	15.05	0.14	0.26
Soluble nitrogen in form of Dicyandiamid	0.25	6.87	12.87
Soluble nitrogen in "other forms"	0.48	1.60	3.00

The loss of nitrogen, in the form of free ammonia, has apparently been 0.24 per cent. The soluble nitrogen in "other forms" consists principally of urea, with a small amount of amidodicyanic acid and ammeline.

The above test is unusually severe, and has little bearing upon the question of the storing qualities of Cyanamid. Under similar circumstances it takes less than a week for sodium nitrate, ammonium sulphate and calcium nitrate to entirely dissolve in the moisture they absorb, while basic calcium nitrate becomes pasty and sticky in the same time. The Cyanamid, on the other hand, is still in good mechanical condition at the end of eight months.

A similar test but less severe, and therefore more nearly approaching conditions that may occur in storage on a factory scale, is the following experiment by G. Henschel.[1]

10 to 11 grams of commercial Cyanamid was placed in a thin layer on a watch-glass of about 8 cm. diameter, and set in a desiccator jar, in which was a beaker with concentrated sulphuric acid and another with distilled water. This provided a constant circulation of moist air. In addition, for an hour

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[1] Das Verhalten des technischen Calciumcyanamides bei der Aufbewahrung sowie unter dem Einfluss von Kulturboden und Kolloiden. Inaugural-Dissertation-Univ. of Leipzig, 1912.

each day during the entire 21 weeks of exposure, a current of air was drawn through the desiccator.

	Weight of sample	Per cent. increase in weight	Total nitrogen	Cyanamid nitrogen	Dicyandiamide nitrogen	Urea nitrogen
Original.......	10.609 g	—	13.09	12.031	0.064	0.694
After 21 weeks.	11.343 g	6.92	12.32	9.563	1.221	1.460
Same corrected to original weight......	—	—	13.17	10.224	1.305	1.560

There is therefore no loss of nitrogen, but on the other hand an apparent slight gain, probably due, in the belief of the experimenter, to loss of moisture before the weighing of the sample for analysis. The total increase in weight is 6.92 per cent., which is about the same as the increase in the factory test at Jacksonville, Florida, described on p. 24. The amount of derivatives formed in the latter case was probably, therefore, about the same as in the laboratory test by Henschel. The amount of dicyandiamide formed is about 10 per cent. of the total nitrogen, and the urea is about the same.

The agricultural significance of these changes will be discussed in a later chapter of this volume.

The above are a few of the many records at the command of the author, all of which agree in showing that when the increase in weight is allowed for there is no loss of nitrogen in Cyanamid under the ordinary conditions of storage of fertilizer materials.

CHAPTER V.

Decomposition of Cyanamid in the Soil.

FACTORS INVOLVED.

When Cyanamid is applied to the soil as a fertilizer it must undergo decomposition before the nitrogen can be assimilated by plants. The course of this decomposition, however, has been in dispute since the adoption of Cyanamid in agriculture, and a great deal has been written on the subject. Owing to the incompleteness of many of the reports, and the omission of essential data, no attempt will be made here to review all of them. Of the recent work on the subject the most consistent seems to be that of C. Ulpiani and H. Kappen.

Experiments of Ulpiani.—In 1908 Ulpiani reported the results of some experiments[1] that indicate the difficulties surrounding the solution of this important question. The results of these tests are summarized in the table on page 33.

Aqueous solutions were used containing 0.5 per cent. pure cyanamide, together with various added materials as noted. Calcium was added in the form of calcium hydroxide, two equivalents to one of cyanamide. By "secondary products" is meant dicyandiamide, urea, and traces of amidodicyanic acid and ammonia, amounting to 33 per cent. of the total nitrogen present. Soil was added where shown in the table, in the proportion of 10 grams to 100 cc. of solution. The "nutritive substance for bacteria" consisted of 0.05 per cent. potassium phosphate, 0.01 per cent. asparagine and 0.01 per cent. glucose. Bacteria were introduced into flasks 3 to 8 by extracting soil with the water to be used to make the cyanamide solution. No bacteria were present in flasks 1 and 2. 0.4 per cent. chloroform was present in flasks 7 and 8. Determinations for cyanamide nitrogen in the solutions were made at frequent intervals. The percentages of cyanamide decomposed in 4 and 8 weeks respectively are shown in the table:

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[1] Gaz. Chim. Ital., 1908, II, No. 4, 358-417.

Flask	Calcium	Secondary products	Soil	Nutritive for substance bacteria	Chloroform	Per cent. of cyanamide decomposed	
						4 wks.	8 wks.
1.	Absent	Present	Absent	Absent	Absent	0.63	0.81
2.	Present	"	"	"	"	53.25	73.02
3.	Absent	"	Present	Present	"	50.50	83.03
4.	Present	"	"	"	"	83.00	100.00
5.	Absent	Absent	"	"	"	6.84	16.72
6.	Present	"	"	"	"	40.62	—
7.	Absent	"	"	"	Present	7.58	15.52
8.	Present	"	Absent	"	"	41.04	—

Flasks 1 and 2 were not inoculated with bacteria. Flask 1 therefore shows that a solution of cyanamide, in the presence of its derivatives, is not decomposed even upon months of standing. The mere addition of lime in sterile conditions causes a rapid decomposition of cyanamide. The effect of lime is shown throughout by comparing the even-numbered flasks with the odd-numbered flasks.

Flask 7 shows that under sterile conditions, in the absence of lime, a small amount of soil causes a small amount of decomposition. Flask 5, which differs from flask 7 only in the fact that the sterilizing agent, chloroform, was omitted, shows that the presence of bacteria had no effect whatever upon the decomposition. The same thing is shown by comparing flasks 6 and 8, in which lime was present.

The larger values obtained in flasks 2, 3 and 4 seem to be related in some way to the presence of secondary products, that is, dicyandiamide, urea, and possibly amidodicyanic acid and ammonia. Flasks 1 and 2 were both uninoculated, hence the larger decomposition of flask 2 as compared with flasks 6 and 8 must be due to the simultaneous action of calcium and secondary products of cyanamide. A separate experiment showed, in fact, that the presence of 0.085 per cent. ammonia in a solution of pure cyanamide containing 0.43 per cent. cyanamide effected the complete removal of the cyanamide in 3 months at 30° C., while the cyanamide without an ammonia addition remained constant.

It is interesting to compare flask 1 with flask 3. These differ in two respects, presence of soil and presence of nutritive substance. Now soil in the presence of secondary products may be expected to act similarly to soil in the absence of secondary products, that is, the soil should determine in flask 3 about 7 per cent. of decomposition more than occurred in flask 1. The presence of nutritive substance is therefore probably in this case the controlling factor, but not nutritive substance alone, but nutritive substance in combination with soil and cyanamide derivatives. It is quite possible that a bacterial decomposition that does not take place in the presence of cyanamide alone may take place if other nitrogenous substances are present which are capable of being attacked by bacteria. In fact, Ulpiani determined by separate experiments that the soil bacteria employed by him were not able to decompose pure cyanamide, but that they grew very readily in impure dicyandiamide solutions, while the experiments of Kappen show that micro-organisms do take part in the decomposition in the presence of nutrient solutions and, with the exception of special fungi, in non-sterilized soil. The effect of micro-organisms and of glucose used as a nutritive substance is shown by the following experiment of Kappen.[1]

One hundred grams of a sand soil of low activity was treated with 50 cc. cyanamide solution containing 33 mg. of cyanamide nitrogen. The same treatment was given another 100 grams, but glucose was added. In another case no glucose was added, but the soil was inoculated with cyanamide-splitting cladosporium, a special fungus, occurring in some soils. The subsequent content of cyanamide nitrogen is shown in the following table:

Cyanamide nitrogen in milligrams	With glucose	Without glucose	Without glucose with cladosporium
Applied	33.00	33.00	33.00
Analysed immediately	31.75	32.04	32.48
After 1 day	25.87	23.70	—
After 2 days	23.52	21.16	4.70
After 3 days	19.69	17.93	0.00
After 7 days	8.33	12.55	—
After 9 days	0.00	10.29	—

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[1] Zentr. fur Kunstdünger Ind. XVII, 251, 1912.

It will be noticed that on the third day the amount of cyanamide that had been decomposed was about the same whether glucose were present or not, in fact there seems to be slightly more decomposition when the glucose was omitted, though this is probably accidental. At the end of 9 days, however, the glucose treated sample was entirely decomposed, while the untreated sample still contained about one-third of the original cyanamide. Cladosporium in the presence of soil caused a rapid decomposition, complete in 3 days. It is at once evident that the sand soil used did not contain appreciable amounts of cladosporium, or the decomposition would have been more rapid in the first two cases. During the first three days the samples with and without glucose behaved very much alike, hence the same processes were taking place, and these were probably chemical; then, however, the glucose treated sample became suddenly very active, and this probably represents the beginning of bacterial participation.

It should be noted in the above experiment that the concentration of cyanamide applied was 0.022 per cent., as compared with the 0.5 per cent. used by Ulpiani. It is likely that the latter concentration is too great to permit bacterial activity, except under the most favorable circumstances and then only with certain bacteria. The quantity of cyanamide applied by Kappen is equivalent to about 600 pounds of nitrogen per acre half-foot of soil. In agriculture, 60 pounds per acre is a maximum that is seldom exceeded.

Kappen succeeded in isolating pure cultures of five fungi capable of decomposing cyanamide; two of them, penicillum brevicaule, and the cladosporium mentioned above, grew even in 2 per cent. solutions, but the others required lower concentrations. It is therefore difficult to estimate the importance of these special fungi to this problem. It is certain that they do not occur commonly in all soils (those used by Ulpiani for instance and the ordinary soils of Kappen) to any great extent, and it is doubtful if they ordinarily have much to do with Cyanamid decomposition in the soil.

Ulpiani explains their action as follows: The fungi may decompose the glucose, when it is present, with the production of various aldehydic substances, which, according to well-known chemical reactions unite with the cyanamide with formation of compounds of the type R.CH:N.CN. It is also possible that the fungi produce various products of metabolism which are able to react with cyanamide and so neutralize it, probably in the manner of the formation of antitoxins. He cites in support of this theory the well-known ability of penicillum brevicaule to grow in the presence of arsenical substances.[1]

The above experiments are in agreement with many others by Kappen, as well as with the experiments of Ashby,[2] Behrens,[3] Stutzer and Reis[4] and others, which show that bacteria are active in some stage of the process.

From these experiments of Ulpiani, Kappen and others, the following facts are evident: 1. A solution of pure cyanamide in the absence of other substances is quite stable, and is not decomposed by ordinary soil bacteria. 2. A solution of pure cyanamide may be decomposed by certain special fungi. 3. A solution of cyanamide in sterile conditions is decomposed by lime, by ammonia, and by soil. 4. A solution of cyanamide is decomposed by soil more rapidly in non-sterile conditions than in sterile conditions, provided the concentration is not too great.

The course of the decomposition of cyanamide solutions by lime is very complex (see also p. 28) and leads to the formation of a mixture of urea, dicyandiamide, amidodicyanic acid, ammeline, melammine and other complex derivatives. On the other hand, the decomposition of cyanamide by soil is a simple hydrolysis in accordance with the equation:

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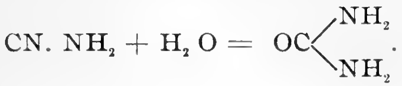
[1] B. Gosio, Studio sulla Bioreazione dell 'arsenico tellurio e selenio. Roma, Tip, Mantellate, 1907.

[2] Zent. Bakt. XX, 704, (1908); XX, 281, (1908).

[3] Jahrs. f. Agrik. 121, (1905).

[4] Jour. f. Landw. Vol. 58, 65, (1910).



$$CN.\ NH_2 + H_2O = OC\langle{}^{NH_2}_{NH_2}.$$

The formation of urea is practically quantitative, and is determined ordinarily solely by physico-chemical means, without the participation of organisms. It will be shown later that the transformation of the urea to ammonia is probably effected by bacteria.

FIRST STAGE OF DECOMPOSITION.

The form in which the nitrogen exists in Commercial Cyanamid, neglecting for the moment the alterations produced in storage, is calcium cyanamide. It has been known for many years that this salt is not stable in aqueous solution but immediately hydrolyzes to acid calcium cyanamide and calcium hydroxide:

$$2CN.\ NCa + H_2O = (CN.\ NH)_2Ca + Ca\ (OH)_2$$

Moreover, all investigators agree that the acid calcium cyanamide has but an ephemeral existence in the soil; when applied in normal fertilizer doses the calcium quickly abandons the cyanamide. Löhnis attributes this action to the effect of carbon dioxide in the soil solution, precipitating the calcium as carbonate and setting free the cyanamide:

$$(CN.NH)_2Ca + CO_2 = 2CN.NH_2 + CaCO_3$$

Kappen considers the removal of calcium as a physical process of absorption in the soil, with simultaneous hydrolysis to free cyanamide:

$$(CN.NH)_2\ Ca + 2H_2O = 2CN.\ NH_2 + Ca(OH)_2.$$

He found, for instance, that when 200 grams of clay soil was shaken with 250 cc. of a solution of lime-nitrogen containing 47.8 mg. calcium and 62.2 mg. nitrogen, 39 per cent. of the calcium and only 5 per cent. of the nitrogen was absorbed by the soil in one hour. Such a fertilization, however, amounts to 560 pounds nitrogen per acre half-foot of soil, a quantity far in excess of any ever used in agriculture. The quantity of calcium absorbed in one hour in this test is equivalent to 600 pounds CaO per acre half-foot of soil.

Ulpiani regards the change as taking place with the intermediate formation of calcium cyanamide carbonate:

$$(CN.\,NH)_2Ca + CO_2 = CN.\,NH_2 + CaCN_2CO_2,$$
$$CaCN_2CO_2 + H_2O = CN.\,NH_2 + CaCO_3$$

Whatever the mechanism of this hydrolysis there is no question but that the result is free cyanamide, and consequently the following investigations on the decomposition of cyanamide in the soil were made with the free cyanamide, $CN.NH_2$.

SECOND AND THIRD STAGES OF DECOMPOSITION.

The following experiment by Ulpiani[1] was made to determine the rate of decomposition of cyanamide: 100 grams of earth carefully dried at laboratory temperature, and sieved through a screen with holes of 1 mm. diameter, was placed in a glass tube and to it was added 20 cc. of a solution of pure cyanamide containing 4.2 per cent. cyanamide. The liquid reached almost to the bottom of the tube, hence the soil was not quite saturated. A series of tubes so prepared was stoppered with cork and set in a thermostat at 28° C. After various periods of time the content of cyanamide remaining in the tubes was determined as follows: 80 cc. of distilled water was added and thoroughly stirred with the contents of the tube. After exactly an hour the contents were filtered with suction. Of the filtrate (about 70 cc.), two portions of 25 cc. each were analyzed for cyanamide. The following results were obtained:

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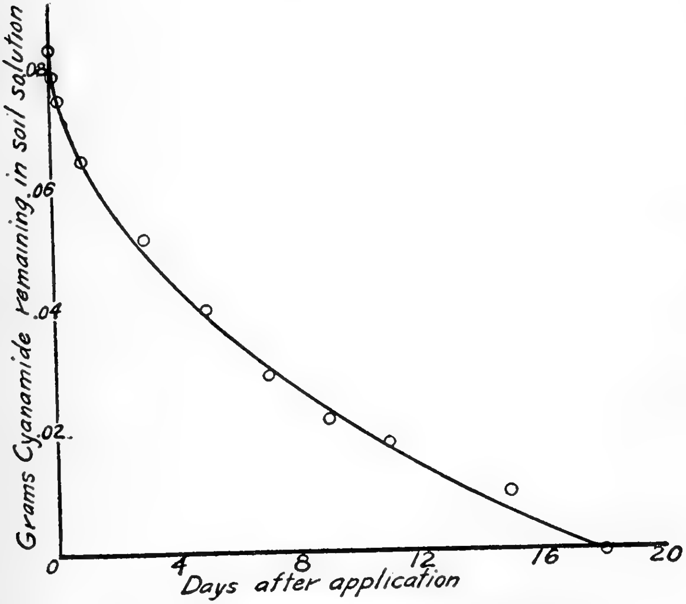
[1] Gaz. Chim. Ital. XL, Parte 1, 1910.

	Quantity of cyanamide Milligrams
Initial	84.0
After ¼ hour	79.2
After 6 hours	75.8
After 1 day	65.9
After 3 days	52.5
After 5 days	40.9
After 7 days	29.8
After 9 days	22.6
After 11 days	18.4
After 15 days	10.0
After 18 days	00.0

The values obtained are plotted in Fig. 2. It is seen that the removal of cyanamide from the soil solution is a maximum in the first few moments of contact. This probably corresponds to an initial period of absorption. It is evident, how-



RATE OF REMOVAL OF CYANAMIDE FROM SOIL SOLUTION.

Fig. 2.

ever, that the cyanamide is not removed solely by a process of absorption, since it is characteristic of absorption processes that a state of equilibrium is usually reached between the substance in solution and in the absorbing surfaces within a day. The substance that is being absorbed never disappears entirely from the solution. In the present experiment, the reaction proceeds to complete disappearance of the cyanamide. The rate of removal of cyanamide is practically constant after the first 9 days, and shows no tendency to become zero thereafter, as it would if an equilibrium were being approached. Such rapid removal of the cyanamide to the very end of the experiment can be due only to chemical conversion of the cyanamide to other forms.

INFLUENCE OF CONCENTRATION.

The following experiment was made by Ulpiani to determine the effect of varying the concentration of cyanamide. In each of a series of glass tubes was placed 100 grams of soil, which was covered with 25 cc. of a solution of cyanamide at various concentrations. At the end of 3 days and at the end of 10 and 30 days, certain tubes, as shown in the table, were taken out, thoroughly mixed with 75 cc. water and after standing one hour were filtered with suction, and cyanamide was determined. The following results were obtained:

Initial quantity of cyanamide		Final quantity of cyanamide			Absolute quantity converted in 3 days Mg.	Percentage converted in 3 days
Concentration Per cent.	Mg. in 25 cc.	After 3 days	After 10 days	After 30 days		
1	25.0	trace	—	—	25.0	100
2	50.0	25.1	—	—	24.2	49
3	75.0	43.5	—	—	31.4	42
4	100.0	60.0	—	—	40.0	40
5	125.0	84.0	—	—	41.0	33
6	150.0	103.4	—	—	46.5	31
9	225.0	171.3	110.8	13.4	53.7	24
12	300.0	231.8	156.8	40.3	68.2	23
15	375.0	302.4	209.1	60.5	72.6	19
18	450.0	352.8	245.2	67.2	97.2	21
21	525.0	420.0	289.8	71.4	105.0	20

In Fig. 3 is plotted the percentage of the cyanamide removed with increase of concentration. This percentage is a maximum at the lower concentrations, but decreases as the concentration increases, until finally a steady value of about 20 per cent. is reached, when the amount of cyanamide disappearing in a given time is constant. The fact that this curve is approximately logarithmic indicates that the primary action is one of absorption, since it is well-known that the more dilute the solution the greater is the percentage of substance taken up by the absorbing surfaces, and that as the concentration of solution increases a condition of equilibrium is reached and the ratio of the concentrations in the absorbing surfaces and in the solution becomes constant.

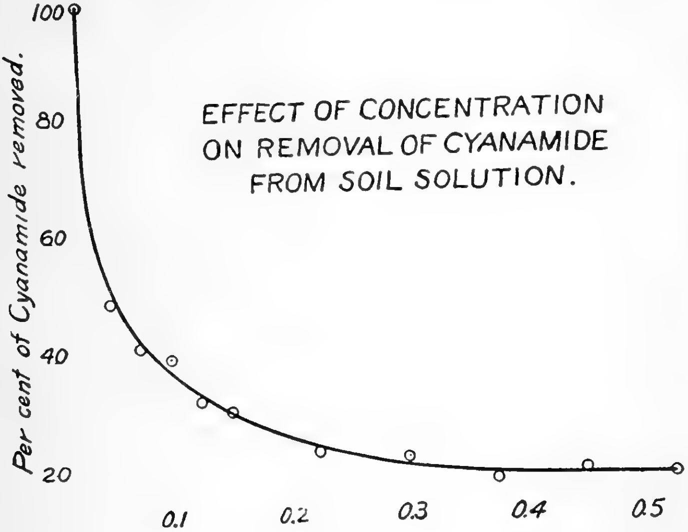


Fig. 3.

Fig. 4 shows the absolute quantity of cyanamide removed as the concentration increases. It is practically directly proportionally to the concentration. This curve shows the same fact as the curve in Fig. 4, namely, that the ratio of the concentrations in the absorbing surfaces and in the solution is a constant, a fact highly characteristic of absorption processes.

In this experiment also, the cyanamide finally disappears entirely from the solution in the course of time, and hence, chemical conversion occurs along with the absorption phenomena.

Taking all the above facts together, it is easy to understand that in the initial period of contact between the cyanamide solution and the soil there is a withdrawal of cyanamide molecules from the solution, and a concentration of molecules in the limiting stratum between the solution and the surface of the solid soil particles. Along with and subsequent to this absorption process there is a chemical conversion of cyanamide molecules, by catalytic action of soil colloids, as we shall show later, the products of the reaction being removed continually and being replaced by new molecules of cyanamide in the limiting stratum.

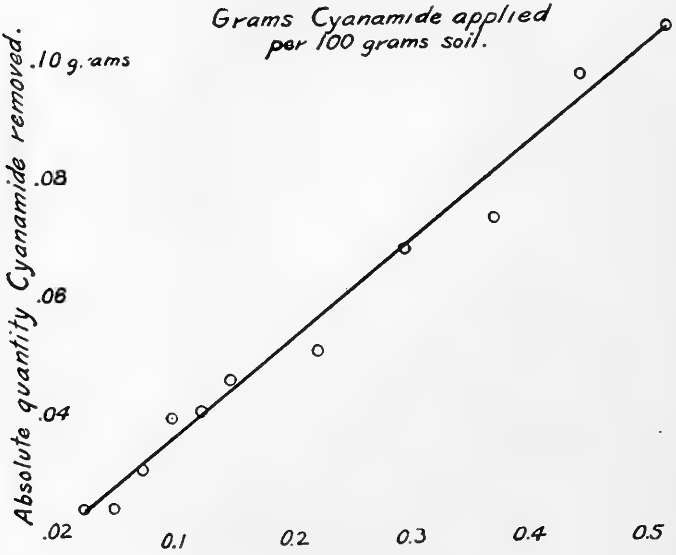


Fig. 4.

That bacteria could take no part in the present experiment is evident, since micro-organisms cannot live in the very concentrated solutions employed.

INFLUENCE OF TEMPERATURE.

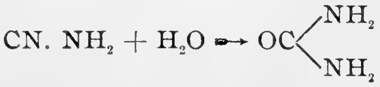
Experiments carried out in a similar manner with 100 grams of soil and 20 cc. of solution containing 4.2 per cent. cyanamide at various temperatures gave the following results:

	At 0°	At 12°	At 30°
Initial quantity of cyanamide....	84 mg.	84 mg.	84 mg.
Quantity present after 2 days...	77	69	51
" " " 4 "	73	59	23
" " " 6 "	69	44	18
" " " 11 "	53	33	trace

The velocity of the reaction increases with the temperature, but even at 0°, where micro-organic life is practically at a standstill, there is a conversion of about 3.5 mg. of cyanamide per 120 grams of damp soil per day.

INFLUENCE OF SOIL AT 100° C.

Two flasks, one containing 100 cc. of a solution with 21 per cent. cyanamide, the other 100 cc. of 21 per cent. cyanamide solution and 500 grams of soil, were heated in a Koch's oven at 100° C. for six hours. After cooling, 400 cc. of water was added to each, and after agitation and filtering, analyses were made. In the flask without soil there was still a large quantity of cyanamide present and considerable dicyandiamide. In the flask with soil, however, there was *no cyanamide or dicyandiamide* remaining after the treatment, but abundant quantities of urea. Under these conditions it is probable that the conversion to urea is quantitative. The reaction must be one of hydrolysis in accordance with the equation.



$$CN.NH_2 + H_2O \rightarrow OC\begin{cases} NH_2 \\ NH_2 \end{cases}$$

NATURE OF PRODUCTS FORMED IN SOIL AT ORDINARY TEMPERATURES.

The formation of dicyandiamide is always accelerated by the action of heat, whether in solutions of cyanamide, or in solutions of cyanamide treated with lime, ammonia or other weak bases. Since there is no formation of dicyandiamide when cyanamide is heated with soil, as shown in the experiment on page 43, there will evidently be none formed at ordinary temperatures. This is verified in the following two experiments.

Four kg. of soil in a balloon flask was sterilized on three successive days by heating for an hour each day in an autoclave at 100°; then was introduced into the flask 800 cc. of a solution containing 4.2 per cent. cyanamide. The flask was stoppered and kept in a thermostat at 25° for 18 days. After agitation with 3,200 cc. water for an hour, and filtering with suction, total nitrogen and cyanamide nitrogen were determined. The results were as follows:

	Grams
Initial nitrogen	2.492
Nitrogen absorbed in soil	1.154
Nitrogen in solution as cyanamide	0.671
" " not cyanamide	0.667
" " as dicyandiamide	none

After the removal of the cyanamide, and concentration on the water bath, addition of nitric acid produced an abundant precipitate of nitrate of urea, which on recrystallization showed a melting point of 140°. This experiment shows that under sterile conditions the product of cyanamide conversion is probably entirely urea.

Under natural conditions, there is little doubt but that the urea is rapidly converted in the soil into ammonium compounds. It was desirable therefore to learn how closely the action of cyanamide resembled that of ammonium carbonate in the soil. In a balloon flask containing 11 kg. of soil was added 200 cc. of solution containing 4.2 per cent. pure cyanamide; and in another flask with 11 kg. of soil was added 200 cc. of solution containing 9.6 per cent. ammonium carbonate, equivalent to the amount of cyanamide used. Each flask was equipped with connections permitting a current of air to pass through the flask, and then through a bottle of dilute sulphuric acid to catch any ammonia evolved in the flask. The balloon flasks were held in a thermostat at 25° for 22 days, at the end of which time 800 cc. water was added. After shaking and standing an hour and filtering with suction, tests showed that there was no cyanamide or dicyandiamide present in the flask to which cyanamide had been added. Determinations were made for total nitrogen, ammoniacal nitrogen and nitric nitrogen in the solution.

The following values were obtained:

	Soil plus cyanamide mg.	Soil plus ammonium carbonate mg.
Initial nitrogen	560	560
Final nitrogen absorbed by soil	450	420
Final nitrogen remaining in solution:		
Ammoniacal	60	70
Nitrate	9	70
Cyanamide	0	—
Dicyandiamide	0	—
Undetermined	41	0

The sulphuric acid in the bottles, through which bubbled the air leaving the flasks, was unchanged, hence, no ammonia escaped from the soil.

Since the 41 mg. of undetermined nitrogen in the solution from the cyanamide flask was not cyanamide, dicyandiamide, ammonia or nitrate nitrogen, it must have been urea, in accordance with the previous experiment. The conversion of the urea to ammonium salts was therefore not quite complete. The conversion of ammonium salts to nitrates was also less than the conversion in the case of ammonium carbonate. The amount of ammoniacal nitrogen in solution is practically equal in the two flasks. It is evident, therefore, that in both cases the absorbed nitrogen exists in the soil in the state of ammonium salts, and these are in equilibrium with the ammonium salts in the solution. Since the soil was not sterilized and low concentrations of cyanamide were used, and large quantities of ammonia were formed, it is very likely that bacteria participated in the decomposition by reacting upon the urea and determining its hydrolysis to ammonium salts.

EFFECT OF CHANGING RATIO OF LIQUID TO SOIL.

When 100 grams of air-dried earth was covered with 20 cc. of cyanamide solution practically all of the soil was wetted, only a little at the bottom of the tube remaining dry. In this condition the mass of water may be considered as being at its maximum distension, each solid particle of the soil being surrounded by a thin film of liquid. This liquid film on the inside, is in contact with a solid phase, and on the outer surface with a gaseous phase, since the interstices of the soil were not filled with liquid.

When 100 grams of soil was covered with 50 cc. of cyanamide solution the interstitial spaces were filled with liquid. There was therefore practically no gaseous phase present.

One hundred grams of soil covered with 100 cc. of cyanamide solution was completely submerged. Series III in the table was thoroughly shaken twice a day during the test. Series IV was not disturbed in any way. The results obtained were as follows:

	Series I 20 cc. not shaken mg.	Series II 50 cc. not shaken mg.	Series III 100 cc. shaken mg.	Series IV 100 cc. not shaken mg.
Initial quantity Cyanamid .	84.0	84.0	84.0	84.0
Quantity after 1 day	65.9	68.0	71.9	73.0
" " 5 days	40.9	53.7	58.1	60.0
" " 9 days	22.6	47.8	54.6	57.1
" " 15 days	10.0	34.8	46.2	49.5
" " 21 days	00.0	26.7	35.7	44.1
" " 31 days	0.0	11.7	35.2	36.9
" " 41 days	0.0	8.4	18.6	33.6

Here again we must exclude bacterial participation, since if bacteria were present they should grow better in the dilute solutions than in the solution of 4.2 per cent. cyanamide in

Series I, yet in the dilute solutions the transformation is very slow.

The above experiment shows that the cyanamide does not react with other soluble substances of the soil, for in such case the maximum activity should occur in dilute solutions; but its conversion is at a maximum when the greatest amount of cyanamide is enabled to come in contact with the solid surfaces of the soil particles. *This condition is obtained when for a given quantity of cyanamide the amount of liquid is a minimum, for then the liquid film about the solid soil particles is its thinnest, the cyanamide is closest to the soil, and the forces of surface tension are at their maximum.*

INFLUENCE OF AERATION.

In order to determine whether oxidation plays any part in the phenomena, an apparatus was arranged so that a current of air in one case and a current of hydrogen in another could be conducted over the samples of soil treated as before with 4.2 per cent. cyanamide solution. The treatment lasted for six days, a portion of the sample being withdrawn in three days. The following results were obtained:

	Initial quantity cyanamide Mg.	Quantity cyanamide present		Per cent. Cyanamide converted in	
		after 3 days Mg.	after 6 days Mg.	3 days	6 days
Air	168.0	110.0	22.0	34.0	86.0
Hydrogen..	168.0	114.0	46.0	32.0	72.0

There is practically no difference in the amounts of conversion in 3 days, and not a great deal of difference between the amounts of conversion in 6 days. The results do not differ enough so that it can be said that oxidation plays any appreciable part in the change. The fact, therefore, that in all of the preceding experiments the tubes were stoppered with cork and sealed with paraffin to prevent evaporation of water could not at any rate increase the conversion.

INFLUENCE OF ELECTROLYTES.

To determine the effect of the presence of various reagents on the course of the conversion, an experiment was made with solutions of cyanamide in balloon flasks without addition of soil, but with various electrolytes. The concentration of cyanamide in the solution was 0.554 per cent.; the other reagents were in the proportion of two equivalents to one cyanamide. The following table shows the amounts of cyanamide remaining in solution.

		554 mg. cyanamide plus			
After	—	$Ca(OH)_2$	KOH	HNO_3	KNO_3
— weeks	554.0	557.0	556.0	451.0	558.0
3.3 weeks	554.0	413.0	420.0	254.0	422.0
8.3 weeks	554.0	369.0	382.0	—	369.0
13.3 weeks	554.0	331.0	340.0	—	303.0
28.3 weeks	554.0	182.0	trace	—	trace

The very slow course of the reactions as compared with the action of soil shows that it is probably not the soluble salts in the soil that are responsible for the hydrolysis of cyanamide but the solid soil particles.

This confirms the conclusion drawn on page 42.

NATURE OF EFFECTIVE SOIL CONSTITUENTS.

In order to determine whether the conversion of cyanamide is caused by the gross solid particles of mineral matter in the soil, or whether it is due to colloids, or various organic debris, the following experiment was made. Soil was allowed to stand a week in contact with concentrated hydrochloric acid, and was then washed free of acid. A portion of soil so treated was saturated with sodium carbonate solution and then washed free of alkaline reaction. A fresh portion of soil was calcined by heating in a combustion furnace in a current of oxygen until carbon dioxide no longer escaped. These samples were treated with cyanamide solutions as in previous experiments, with the following results:

	Initial cyanamide mg.	Final cyanamide after 3 days mg.	Final cyanamide after 6 days mg.	Final cyanamide after 9 days mg.
Ordinary soil	83.8	52.0	36.0	19.5
Soil treated with HCl	83.8	63.5	49.1	36.0
Soil treated with HCl and Na_2CO_3	83.8	55.5	43.2	46.0
Soil calcined	83.8	—	—	77.6

Each of the above treatments has diminished the ability of the soil to convert cyanamide to other forms. The calcined soil has very little power of decomposition. It is evident, therefore, that it is not the gross, solid, mineral particles of the soil that have this power, but certain constituents of the soil mass that are destroyed by heat. These constituents belong to the class of chemical compounds that form colloids or disperse systems in the soil.

We will now examine the results of experiments made with various materials that are known to form part of practically all soils.

EFFECT OF ZEOLITES.

According to Van Bemmelen[1] the colloids of agricultural soil consist principally of amorphous zeolites (amorphous hydrated silicates). These remain for an indeterminate time in suspension in pure water, are coagulated by electrolytes, can be dried into hard compact masses, have in the highest degree the properties of hydrogels, and to their presence is probably due the greater part of the absorptive powers of the soil. Since these substances could not be isolated in their natural state it was necessary to use certain crystallized zeolites, as follows:

Natrolite of Bohemia, hydrated metasilicate of aluminium and sodium.

Scolecite of Ireland, hydrated metasilicate of aluminium and calcium.

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[1] Landw. Ver. Staz. Bd. XXXV, (1888) p. 69.

Analcimite of Tyrol, hydrated trisilicate of aluminium and sodium.

Cabasite of Nova Scotia, hydrated trisilicate of aluminium and calcium.

Each zeolite was ground in a mortar and made to pass a screen of fineness Kahl. 00.

One hundred grams of each zeolite was placed in glass tubes moistened with 20 cc. of a 4.2 per cent. solution of cyanamide (2.8 per cent. nitrogen). A fifth tube without zeolite was used as a control. After 12 days in a thermostat the solutions were analyzed with the following results:

	Initial cyanamide grams	Cyanamide after 12 days grams
Solution alone	0.0840	0.0836
" natrolite	0.0840	0.0235
" scolecite	0.0840	0.0148
" analcimo	0.0840	0.0158
" cabasite	0.0840	0.0168

This experiment shows that the crystalline zeolites possess to a high degree the ability to transform the cyanamide, from which we may conclude that the colloidal zeolites as they exist in the soil must have a still greater ability. The crystalline zeolites, according to Zambonini,[1] have a structure analogous to that of the hydrosols, and according to Von Weimarn[2] may act like colloidal substances.

EFFECT OF CARBON.

Ulpiani next desired to learn what effect would be obtained with a material exposing a large surface, but of no chemical activity towards cyanamide. For this purpose a commercial animal carbon was washed with hydrochloric acid and then with water until free from acid, and was dried in an oven at 110° C. In order to obtain a wetting comparable to that in the experiments with soil, 50 grams of carbon was moistened

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[1] Atti. R. Acc. Lincei, XVIII. fasc. II, lst Sem, 1909.

[2] Koll. Zeit. Vol. VI, No. 1, 1910.

with 50 cc. of 4.2 per cent. cyanamide solution. The tubes were kept in a thermostat at 25° for different lengths of time. Just before the analysis 200 cc. of water was added, stirred for exactly one hour, filtered with suction, and cyanamide was determined in the filtrate. The results were as follows:

	Cyanamide present		Total nitrogen in solution	
	mg.	Per cent.	mg.	Per cent.
Beginning	210.0	100	140	100
After 1 hour	161.7	77	112	80
" 6 hours	153.3	73	105	75
" 1 day	132.3	63	102	73
" 3 days	107.6	51	87	62
" 5 "	96.6	46	89	64
" 7 "	75.6	36	89	64
" 9 "	59.3	28	83	59
" 15 "	8.4	4	64	46
" 22 "	0.0	0	77	55

On the 22nd day the solution was distilled with magnesia, giving up 66 per cent. of its nitrogen as ammonia. Hence, of the 55 per cent. remaining in the solution on the 22nd day 22 per cent. was ammoniacal and 33 per cent. ureic nitrogen. A test with nitric acid gave characteristic crystals of urea nitrate.

The experiment was repeated, sterilizing both the carbon and the cyanamide solution. After 2 months the following results were obtained:

	Mg.
Initial nitrogen	560
After 2 months, ammoniacal nitrogen	8
Cyanamide "	0
Dicyandiamide "	0

A test for urea showed the presence of abundant quantities.

These experiments with carbon show that the decomposition of cyanamide is an hydrolysis which is greatly accelerated by the addition of catalysers of various kinds.

EXPERIMENTS WITH NATURAL COLLOIDS.

The experiments of H. Kappen[1] confirm in general the results obtained by Ulpiani. The following experiment of

[1] Zentr. f. Kunstdünger-Industrie, XVII, 234-236, 248-251, 1912.

Kappen shows the relative decomposing ability of some well-known constituents of ordinary soils. These materials were selected so as to differ as widely as possible from one another, so that the effect of individual constituents might stand out. Each substance was used in its natural condition, without being sterilized, but ground to a fine powder. They are all in the class of compounds that form gels in the soil.

1. Meadow iron ore from Guben, Niederlausitz; containing considerable manganese.
2. Meadow iron ore from Otrotschin, Bohemia; contains no manganese.
3. Earth of Siena, yellow natural product containing iron oxide.
4. Umber, brown natural product containing iron and manganese oxides.
5. Laterite earth from Kamerun.
6. Manganese ore, principally manganese hydroxide.
7. Manganese dioxide.
8. Red Bauxite, aluminum hydroxide gel containing iron oxide.
9. White Bauxite, without iron oxide.
10. Kaolin from Meissen.
11. Sandy Kaolin from Türkismühl.
12. Glass sand.

Of the above minerals No's 1, 2, 3, 4, 6, 7, 8, 9 and 12 were used alone, while No.'s 5, 10 and 11 were mixed with an equal quantity of glass-sand. One hundred grams of each was placed in an Erlenmeyer flask and treated with 10 cc. of a 0.5 per cent. cyanamide solution, containing 33 mg. cyanamide-nitrogen. Immediately after the addition of cyanamide, and at the end of various periods of time the content of cyanamide-nitrogen was determined, with the following results:

Cyanamide nitrogen	1. Iron ore	2. Iron ore	3. Earth of Siena	4. Umber	5. Laterite	6. Manganese hydroxide
Initial	33.00	33.00	33.00	33.00	33.00	33.00
After ½ hour	22.96	33.18	33.51	31.75	34.02	8.00
“ 1 day	0.00	0.00	32.04	20.03	19.40	0.00
“ 2 days	—	—	30.87	13.27	11.17	—
“ 3 days	—	—	27.38	5.92	—	—
“ 6 days	—	—	27.04	0.00	4.37	—
“ 7 days	—	—	26.57	—	2.82	—

Cyanamide nitrogen	7. Manganese dioxide	8. Red bauxite	9. White bauxite	10. Kaolin	11. Sandy kaolin	12. Glass sand
Initial	33.00	33.00	33.00	33.00	33.00	33.00
After ½ hour	30.49	32.48	33.04	32.04	32.00	32.00
“ 1 day	11.76	29.40	32.04	32.04	26.16	32.34
“ 2 days	0.00	27.34	30.86	31.16	21.75	32.34
“ 3 dags	—	25.28	30.57	30.57	—	32.34
“ 6 days	—	19.82	30.28	30.28	13.52	32.34
“ 7 days	—	17.68	29.98	29.98	11.76	32.24

Of the greatest activity is manganese hydroxide; second, iron hydroxide containing manganese hydroxide; and third, iron hydroxide free of manganese. The activity of the next most active materials can properly be ascribed to their contents of iron oxide. The difference in the activity of red and white bauxite is very likely due to the difference in iron content. The greater activity of sandy kaolin as compared with kaolin is probably due to the presence in the former of zeolitic substances, which, as Ulpiani found, have a high activity.

The low activity of the kaolin, considering the large specific surface it possesses, suggested that the properties of the various substances are not merely surface phenomena, but that their specific chemical nature is of importance. Manganese hydroxide and the two iron ores were mixed with glass sand in the proportion of 1 gram to 100 grams sand, and a sample of 0.1 gram manganese hydroxide with 100 grams glass sand. These mixtures moistened as before with cyanamide solution containing 33 mg. nitrogen, gave the following results, as compared with the kaolin of the preceding experiment:

Cyanamide nitrogen milligrams	Glass-sand plus Kaolin	1 per cent. manganese hydroxide	1 per cent. iron ore No. 1	1 per cent. iron ore No. 2	0.1 per cent. manganese hydroxide
Initial	33.00	33.00	33.00	33.00	33.00
After 15 hours	—	5.06	25.25	30.80	—
" 2 days	31.16	0.00	14.78	26.48	30.18
" 3 "	30.57	—	8.62	22.79	28.33
" 6 "	30.28	—	4.00	17.24	25.25

It has been shown in the preceding experiment that glass sand has practically no activity. Hence, 0.1 grams of manganese hydroxide is more effective than 100 grams of kaolin. The surface exposed by the kaolin is clearly much greater than that exposed by the smaller quantities of iron and manganese hydroxides, and the catalytic activity of the latter is therefore essentially connected with their chemical properties.

Another experiment was made to compare the activity of iron hydroxide, aluminium hydroxide and silicic acid. The iron and aluminium hydroxides were prepared by precipitation; a sample of each was mixed in the undried condition with 4 times its weight of glass sand, the mixture then containing 2.6 per cent. iron oxide in the one case and 1.6 per cent. alumina in the other. The aluminium hydroxide and the precipitated silicic acid were dried and applied separately to twice their weight of glass sand. One hundred grams of each of the above mixtures was treated with 20 cc. of cyanamide solution containing 33 mg. of cyanamide nitrogen. The subsequent analyses are as follows:

Cyanamide nitrogen in milligrams	Glass-sand plus Iron hydroxide undried 2.6% Fe_2O_3	Aluminium hydroxide undried 1.6% Al_2O_3	Aluminium hydroxide Dried	Silicic acid Dried
Applied	33.00	33.00	33.00	33.00
After ½ hour	31.52	32.48	32.04	32.92
" 1 day	0.00	32.34	31.16	32.63
" 3 days	—	29.56	29.69	31.94
" 6 days	—	—	25.87	31.08

Silicic acid has a slight ability to convert cyanamide; and aluminium hydroxide has somewhat more.

To determine the effect of varying quantities of iron hydroxide gel, the precipitated undried hydroxide was mixed with glass sand in different proportions, and treated as above with the following results:

Cyanamide nitrogen in milligrams	Glass-sand plus iron hydroxide gel containing			
	2.6% Fe_2O_3	1.3% Fe_2O_3	0.65% Fe_2O_3	0.26% Fe_2O_3
Applied..........	33.00	33.00	33.00	33.00
After 1 day......	0.00	4.31	12.32	23.11
" 2 days.....	—	0.00	3.69	13.55
" 3 "	—	—	trace	9.85
" 4 "	—	—	0.00	8.00
" 5 "	—	—	—	5.37

The amount of conversion, therefore, varies with the amount of iron oxide present.

The same iron hydroxide gel was treated in different ways to see what effect would be obtained by changing the form of the material:

Cyanamide nitrogen in milligrams	Precipitated iron hydroxide			
	Untreated	Dried 5 hrs. at 105°C	Heated in steam for 2½ hrs.	Ignited for ½ hrs.
Applied...........	33.00	33.00	33.00	33.00
After ½ day	—	4.31	12.32	—
After 1 day	0.00	0.00	6.46	14.47
" 2 days.....	—	—	1.57	6.16
" 3 "	—	—	0.00	4.00
" 4 "	—	—	—	1.84
" 5 "	—	—	—	0.00

The untreated iron hydroxide has the most activity, which is decreased somewhat by steaming and greatly decreased by ignition.

To determine the effect of iron oxide in the condition of a hydrosol, 250 cc. of iron oxide sol containing 0.8 per cent. iron oxide was treated with 1.25 grams cyanamide. The solution remained clear and fluid during the course of the experiment. For the determination of cyanamide, 10 cc. of the clear solution was pipetted off, flocculated with ammonium nitrate and after dilution and filtration, treated in the usual manner. The following results were obtained:

Cyanamide nitrogen in milligrams	Iron oxide sol. (0.8 per cent. Fe_2O_3)
Applied	33.04
After 18 hours	27.77
" 2 days	22.40
" 4 days	10.08

The condition of sol is favorable to the conversion, but not as favorable as the condition of gel since the dilution of the cyanamide hinders the reaction.

In order to determine whether or not calcium cyanamide reacts as readily as cyanamide, a quantity of lime-nitrogen containing 33 mg. of cyanamide nitrogen was added to 100 g of a mixture of sand with equal weights of manganese hydroxide, and iron ores No. 1 and 2, (see page 52). After 24 hours the quantities of cyanamide nitrogen remaining were:

	Milligram
Manganese	0.00
Iron ores No. 1 and No. 2	0.00
Glass-sand	29.18

With cyanamide, glass-sand left 32.34 mg. in solution after 1 day. The presence of the lime in the lime-nitrogen evidently hastens the decomposition of the cyanamide.

The effect of pure, calcined iron oxide, Fe_2O_3, on cyanamide was determined by mixing glass sand with 5 per cent. of its weight of iron oxide, and treating with cyanamide solution as in the previous experiments.

	Milligram
Cyanamide applied	33.00
" after 1 day	32.42
" " 3 days	30.63
" " 5 days	28.07
" " 8 days	26.56

Iron oxide therefore has a slow action as compared with the metal hydroxides used.

EXPERIMENT WITH STERILIZED SOIL.

All of the above experiments of Kappen were made with unsterilized materials; they therefore do not differentiate between physico-chemical and bacterial processes. In this experiment, soil was sterilized by being held several days in an atmosphere of chloroform vapor, and was compared with untreated soil as in the previous experiments, with the following results:

	With chloroform mg.	Without chloroform mg.
Cyanamide nitrogen applied	33.00	33.00
Cyanamide nitrogen after 2 days	23.00	0.00

The addition of chloroform to the soil therefore greatly hinders the decomposition of the cyanamide, but does not prevent it. It is quite probable that in all of the experiments made by Kappen, except those where high temperatures were employed, bacteria participated in the decomposition of the cyanamide by converting the urea into ammonium salts, thus hastening the hydrolysis of the cyanamide.

CONCLUSIONS.

From the above experiments on the conversion of cyanamide the following conclusions can be drawn:

I. Calcium cyanamide in contact with moist soil undergoes a decomposition to the form of ammonium salts in three independent stages. The first stage is a complete hydrolytic separation of the calcium from the cyanamide, induced by the selective absorption of calcium by the soil, and its probable precipitation as calcium carbonate. (See p. 37). The second stage is a hydrolysis of cyanamide entirely to urea; the third stage is a transformation of urea to ammonium salts.

II. The cyanamide disappears from the soil solution by two processes:

(*a*) Absorption and concentration of cyanamide molecules in the limiting stratum between the soil solution and the soil particles. This takes place during the first few moments of contact. (See pp. 37 and 38).

(*b*) Removal of the cyanamide molecules from the limiting stratum by hydrolysis to urea under conditions of high surface pressure and concentration. (See p. 40).

III. The greatest velocity of hydrolysis occurs when the ratio of soil solution to soil is the least; that is, when the liquid film about the soil particles reaches its maximum distension, and the cyanamide molecules are in closest contact with the soil particles (See p. 42).

IV. The hydrolysis to urea is brought about in the soil by the catalytic action of certain colloidal substances, of which the most effective are the hydroxides of manganese and iron, and certain natural zeolites (hydrated meta- and tri-silicates of aluminium and sodium or calcium (pp. 48-56). Other colloids occurring naturally in the soil have less ability of transformation. Animal carbon is about as active as soil (p. 51).

V. The soil loses its power of effecting the transformation when it is calcined or when it is treated with acids and alkalies; that is, when the colloids are destroyed. Upon addition of the colloids again, it reacquires the property of transformation.

VI. The conversion of cyanamide in sterile conditions is entirely to the form of urea. The urea was isolated and identified (pp. 43, 44, 51).

VII. In the hydrolysis of cyanamide to urea, micro-organisms do not participate, because:

(*a*) The transformation proceeds most rapidly at high concentrations of cyanamide and at concentrations far above those that support life (pp. 40, 43, and 46).

(*b*) The transformation takes place with greatly increased velocity at 100° C. (p. 43).

(*c*) The transformation takes place in the presence of antiseptics and sterilized materials (pp. 44, 50, and 56).

VIII. Unless the greatest care is taken to have perfectly sterile conditions, the urea is converted into the form of ammonium salts. In ordinary soil this change is very rapid (pp. 40, 44, and 57).

IX. The conversion of the urea to ammonium salts hastens the hydrolysis of cyanamide to urea by removing the end-product of the hydrolysis (p. 57).

X. While cyanamide itself is not directly utilized by ordinary bacteria, this fact is of relatively little importance, since the soil bacteria grow in the presence of cyanamide if urea or some other nutrient substance is present; the urea being formed by physico-chemical means from the cyanamide. (See pp. 34, 36, 44, 45, and 57).

XI. The retention by the soil of the nitrogen formed from cyanamide is under the form of ammonium salts (p. 45).

CHAPTER VI.

Retention of Cyanamid Nitrogen in Soil.

The absorption and retention of Cyanamid nitrogen by various soil constituents has been investigated by only a few workers, and very little has been reported that can be regarded as of practical interest. Such tests to be of value should be made with natural soils, and not with pure constituents, such as ignited glass-sand, as has been done by some investigators. The period permitted for absorption should be at least one or two days, and the proportion of aqueous solvent should not exceed that likely to occur in agricultural practice, nor should larger quantities of nitrogen be applied than are likely to be used by the farmer.

The retention of nitrogen is doubtless due to physical processes, as well as to chemical reaction with both the mineral and organic constituents of the soil. (See pp. 39 and 45). Physically, Cyanamid nitrogen is retained in the soil by processes of absorption in the same way as sodium nitrate, or other salts which do not form insoluble compounds by chemical reaction with the soil. By chemical and biological processes, however, Cyanamid nitrogen is quickly converted to the form of ammonium salts, and these are retained in the soil in the form of humic and zeolitic compounds of ammonium. According to A. D. Hall, the weaker the solutions of ammonium salts applied the greater is the percentage of ammonium absorbed by the soil.[1] In the field the amount of soil is so enormously in excess that the absorption of ammonium salts is practically complete.

While plants undoubtedly have the power of directly assimilating the urea[2] that is formed as a transition product during the conversion from cyanamide to ammonium salts, the duration of the urea stage is probably very short in the soil, and

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[1] A. D. Hall, The Soil, New York, 1910, p. 215.

[2] Jour. Agr. Sci., Vol. IV, Part 3, p. 282.

the practical consequences of its brief existence are probably very slight. Hutchinson and Miller have shown that ammonium salts, also, are directly assimilated by plants,[1] but just how effective such processes are it is difficult to estimate. Practically there can be no doubt but that most of the ammonium salts are converted to nitrates prior to their absorption by the plant.

[1] Jour. Agr. Sci., Vol. IV, Part 3, p. 282.

CHAPTER VII.

Nitrification of Cyanamid Nitrogen.

While some of the fertilizing effect of Cyanamid may be due to the presence of urea and ammonium salts, nitrification of cyanamide and its decomposition products may take place very readily in the soil under favorable conditions, providing the concentration of nitrogen is not too great. This is shown in an experiment by Wagner, which was carried out as follows:[1]

Two hundred and fifty grams of sandy-loam soil was mixed with 5 grams of marl and the quantity of nitrogen salts shown in the table below. Each salt was well mixed with 2 grams of gypsum before application in order to facilitate distribution. The mixtures were placed in cylindrical glass vessels 6½ cm. in diameter and 17 cm. high, moistened with 75 cc. water, and covered with 50 grams unfertilized earth. The vessels were allowed to stand at room temperature and the evaporated water was replaced from time to time. After 12, 20, and 33 days respectively samples were drawn from each series and analyzed for nitrate nitrogen. After subtracting the figures obtained in the unfertilized control vessels the following results were obtained:

	Nitrate nitrogen as NO (ccm.)			With the sodium nitrate at 100, the other fertilizers gave as nitrate nitrogen		
Fertilizer application	After 12 days	After 20 days	After 33 days	After 12 days	After 20 days	After 33 days
0.05 grams nitrogen as sodium nitrate	23.7	23.9	24.7	100	100	100
0.05 grams nitrogen as sulphate of ammonia	20.8	22.5	—	88	94	—
0.0125 grams nitrogen as Cyanamid	3.9	5.9	5.9	66	99	96
0.025 grams nitrogen as Cyanamid	4.1	9.9	11.2	35	83	91
0.05 grams nitrogen as Cyanamid	0.3	6.3	14.9	1	26	60

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[1] Landw. Vers. Stat. Vol. 66, No. 4 and 5, 1907.

0.0125 grams nitrogen per 250 grams of soil is equivalent to a fertilization of about 90 pounds of nitrogen per acre. With this large application, even, nitrification of the Cyanamid is complete in twenty days. Larger applications require a longer period, but are of no practical interest. The above results must be considered relatively to each other and not as absolute values, since the conditions were probably very favorable to nitrification.

A similar experiment is reported by Müntz and Nottin.[1] They found that when 0.25 grams of nitrogen per kilogram of soil was used, the relative amount of nitrification in 5 months for different fertilizers was as follows:

	Per cent.
Ammonium sulphate	100
Calcium cyanamide	88
Dried blood	66
Roasted leather	26

The above fertilization is equivalent to about 450 pounds of nitrogen per acre, and has no significance to practical agriculture.

When, however, smaller amounts of Cyanamid were applied, nitrification was very rapid, and further, the bacteria rapidly adjusted themselves to the changed environment and enormously increased their ability to nitrify Cyanamid nitrogen, even when successively increasing doses were applied. This is shown in the following table:

Date applied	Amount cyanamid nitrogen applied each time grams	Amount nitrogen present at analysis before new application	Nitrate nitrogen per kg. of earth by analysis
January 17	0.06	—	—
January 26	0.06	0.06	—
February 7	0.10	0.12	0.01
March 3	0.12	0.22	0.18
April 2	0.22	0.34	0.37
April 25	0.40	0.56	0.58
May 23	—	0.96	0.81

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[1] Annales de l'Institut National Agronomique, 2nd Series, Vol. VI, No. 1, 1907.

The rate of nitrification of Cyanamid is somewhat less than that of sulphate of ammonia when both are applied in large doses. In doses such as would be used in practical agriculture there is probably not much difference. The rate of nitrification must vary greatly in different soils and individual experiments can show but little of general application. As a general average of observations made in Germany, it appears that the duration of Cyanamid nitrogen in the soil is about 70-80 days. In very active soils it is probably less, in cold soils of low bacterial activity it is probably more. Its duration is therefore about midway between that of ammonium sulphate and dried blood.

CHAPTER VIII.

Toxicity of Fertilizers.

A review of the numerous agricultural experiments that have been reported since 1902, indicates that Cyanamid is not equally efficient as a fertilizer in all the conditions in which it has been applied. Cases have been noted where there was apparently an unfavorable action on germination of seeds, unless the fertilizer were mixed with the soil several days before the seed was sown. It is also said to be poorly adapted for use on acid moor soils or on very poor sand soils of low activity. Various explanations have been given of the cause of these undesirable effects. In some cases the occasional harmful action on germination has been attributed to the evolution of acetylene from a crude lime-nitrogen containing free calcium carbide; in other cases the causticity of the lime has been blamed, but usually the unfavorable action on acid moor soils or very poor sand soils is charged to the formation of dicyandiamide by the acids in such soils.

Meaning of "Poison."—It is well to agree at once upon what is meant by the term "toxin" or "poison." Dr. Paul Wagner[1] says "poison, as is known, is a very relative idea, for poisons in great dilution are harmless, and non-poisons in great concentrations are harmful." It is obvious that the term "poison" could be applied to almost any substance if we do not limit the amount which is understood to be used. Unless, therefore, the amount which is said to be toxic is distinctly specified, it is necessary to assume that the amount used is small and popularly regarded as a safe dose. It is also desirable to agree upon the amount of injury that can be sustained before the effect can be pronounced as harmful. Some substances produce temporary exhilaration, followed by serious depression; other substances produce temporary depression, but leave the subject

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[1] Arbeit. der Deut. Landw. Ges., No. 129, p. 267, 1907.

in the long run better than before. Practically, from the standpoint of plant physiology, it seems necessary to define a poison as a substance which, administered in quantities ordinarily considered small, produces functional disturbances ending ultimately in permanent injury or death.[1]

In this connection it may be well to quote entire the conclusions of Dr. Paul Wagner after seven years of experimenting with lime-nitrogen, both in pot cultures and in the field.[2]

CONCLUSIONS OF DR. PAUL WAGNER.

"1. The statement 'lime nitrogen is a plant poison and must be converted by soil bacteria into ammonia and nitric acid in order to act as a fertilizer' has led to many faulty conceptions and is practically not correct. Poison, as is known, is a very relative term, for poisons in great dilution are unharmful, and non-poisons in great concentration are harmful. For instance, perchlorate occurring in nitrate of soda is a decided poison. If one sows 3 kg of perchlorate on a hectare of rye, there will be a poisonous action. Chile saltpeter should therefore contain not more than one-tenth of a per cent. of perchlorate; it should be rejected if it contains more than 1 per cent. of this poison. Likewise, ammonium sulphocyanate is a real plant poison. In the year 1873, in No. 38 of the Hessian Agricultural Journal, I communicated a marked example of sulphocyanate poisoning. On the Rudigheimer estate at Hanau a grain field of 4 hectares was poisoned by an application of 100 kilograms of ammonium superphosphate with 10 per cent. nitrogen, which later investigation showed to contain sulphocyanate. Therefore, this extremely slight amount of sulphocyanate was sufficient to cause a characteristic poisoning and to decrease the yield to about one-third. It has also been learned that ammonium sulphocyanate applied a greater or less time before sowing of

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[1] See also Pfeffer's Physiology of Plants, Ewart, Vol. II, 258.

[2] Arbeit. Deut. Landw. Ges., Heft 129, 1907, p. 267.

the seed, can under certain conditions be decomposed into ammonia, so that is no longer poisonous. Nevertheless, the sulphocyanates to the extent that they remain undecomposed in the soil are decided plant poisons and cannot be applied as fertilizers.

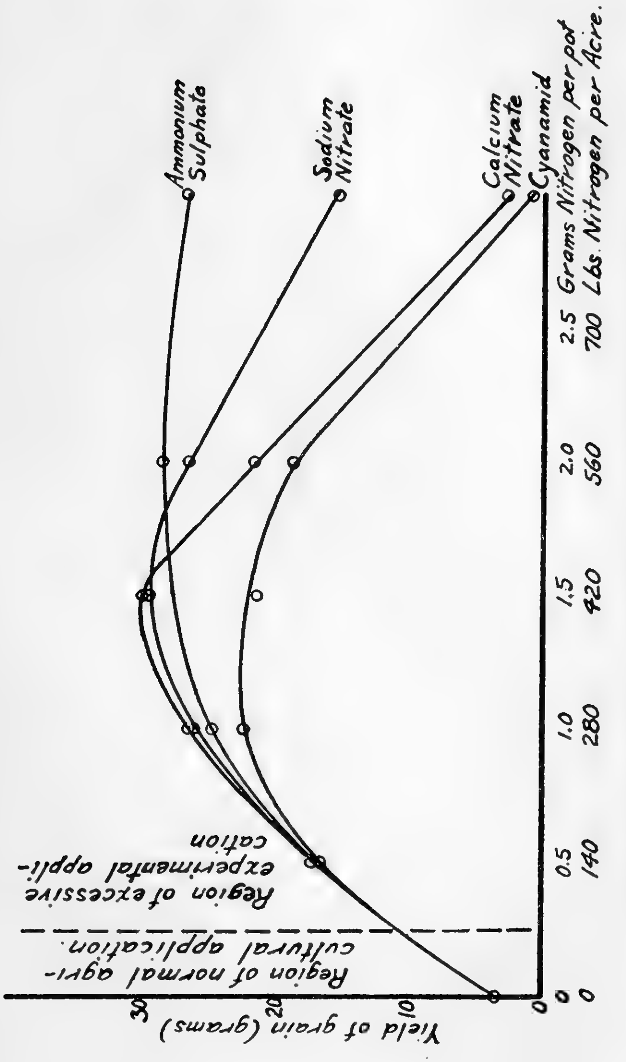
"On the contrary, nitrate of soda, sulphate of ammonia, nitrate of ammonia, and carbonate of ammonia contained in manure, are known as very favorable nitrogen fertilizers and they are still regarded as such, although it is known that under certain conditions they can act disadvantageously. Very concentrated solutions of these nitrogen fertilizers, especially carbonate of ammonia, can, as is evident from our contribution in Volume 66 of the Agricultural Experiment Station Reports, have a depressing action upon the development of plants, and under certain circumstances (which indeed do not occur in agricultural practise) they can produce complete destruction of the plant. No one, however, designates nitrate of soda, sulphate of ammonia or manure as plant poisons. In a similar manner it is known that fertilization with quicklime must be carried out with great care. Professor Tacke has determined by researches upon moor soils a very disadvantageous action of lime fertilization, and I, and others, have found that lime can act harmfully on ordinary soils if the lime is applied in too large quantities or at the wrong time. No one will, however call quicklime, which is known as a highly valuable fertilizer material, a plant poison.

"In just the same way Cyanamid, or so-called lime nitrogen, is to be regarded not as a plant poison, but as a fertilizer, although it, exactly like quicklime and other fertilizers under some conditions, can act harmfully upon the growth of plants. Cyanides, sulphocyanates and similar nitrogen compounds are plant poisons; they act poisonously in very great dilution and cannot serve as fertilizers under any conditions. Cyanamid, however, does not belong to this class, for this compound can act harmfully or poisonously upon plants only in case of very wrong methods of application.

"When Prof. Frank requested me six years ago to test Cyanamid as to the conditions under which it could be used as a fertilizer and its relative fertilizing value, I had already been preparing to undertake the test; but I had expected, on the ground of observations made with cyanides and sulphocyanates, a completely negative result from the experiments.

"Our experiments carried out in the laboratory and on small experimental plots have not confirmed my previous assumption. Our field experiments have shown that the application of lime nitrogen as a fertilizer was attended with less difficulties than one could directly conclude from the experiments carried out in the laboratory and on small experimental plots. Very concentrated solutions of lime nitrogen or exceptionally large applications of this fertilizer act harmfully upon the plants, as is clearly seen from our pot experiments (see page 71 and Fig. 5). Under the normal conditions of agricultural practice, however, a disadvantageous action does not occur, if one follows the directions given for the application of Cyanamid, and these consist essentially in this that the lime nitrogen must not be applied in excessive quantities and further must not be applied upon acid soils or soils which tend to become acid; that it must be distributed as uniformly as possible upon the surface of the field, and must then be worked into the ground, when it is not used as a top dresser, by deep acting tools, or be plowed under.

"To illustrate, it should be noted that in our experiments (see page 71) an application of 1 gram of nitrogen in the form of lime-nitrogen upon 7 kilograms of soil contained in a vessel 20 cm. in diameter did not act harmfully, but acted favorably from the beginning to the end upon the plant growth even when the lime nitrogen was mixed with the soil immediately before planting of the seed. Upon a circumference of 20 cm. diameter, however, one does not apply in agricultural practice 1 gram, but only one-tenth or at the highest two-tenths of a gram of nitrogen. It is therefore clear that one can



EFFECT OF EXCESSIVE APPLICATIONS OF NITROGEN ON YIELD OF OATS

Fig. 5.

regard the disadvantageous action of lime nitrogen, such as happens under applications of exceptionally large quantities in pot experiments as either not occurring in agricultural practice or as immediately disappearing. Practically, one cannot therefore regard lime nitrogen as a plant poison. It is to be regarded as a fertilizer applicable in agricultural practice and having a favorable action, although as is necessary with barn manure, green fertilizers, bone-meal, horn meal, etc., the nitrogen contained in it must be converted by bacterial activity into ammonia and nitric acid in order that it may serve as plant food.

"2. If lime nitrogen is applied in normal quantities, as compared with other fertilizer materials, distributed as uniformly as possible upon the soil, and worked in well with deep-acting tools, it exerts no harmful influence even when applied immediately before sowing of the seed. The idea that lime-nitrogen must be completely, or at least to a great extent, converted into ammonia or nitric acid before it comes into contact with the seed is wrong, although it is possible that the action of lime nitrogen in many cases can be increased if it is applied 8 or 14 days before sowing of the seed.

"3. Lime nitrogen in ordinary field practice can act harmfully only when conditions are such that a part of the calcium cyanamide suffers an unnormal decomposition. Conditions under which this can happen are present especially in acid moor soils or in soils which tend to become acid, or soils very rich in humus, and therefore very poor in lime. It is known that moor soils acts otherwise than normal towards other nitrogen fertilizers as well. Sulphate of ammonia has an unfavorable action upon acid soils. In order to avoid these unfavorable conditions of acid soils previous liming is necessary.

"4. Like all organic nitrogen fertilizers, green substances, barn manure, horn meal, etc., the conversion into ammonia and nitric acid is necessary in order to yield nitrogen assimilable by plants, and like ammonia (although many plants take it up and use it as such), for most plants it has its full effect only when it is converted into nitric acid; so the nitrogen of the lime-nitrogen must be converted into ammonia and nitric acid before it will yield nitrogen that the plants can assimilate.

"5. It is known that the conversion of Cyanamid and the organic forms of nitrogen into ammonia and nitric acid is brought about by the activity of certain soil bacteria and that this conversion, according to the special activity of the soil, sometimes proceeds more rapidly and sometimes more slowly. Upon so-called medium soils in good condition the organic fertilizers as a rule act more completely than upon light dry sandy soils or upon heavy clay soils. The medium loam soils in good condition seem to offer comparatively the best conditions for the action of lime nitrogen. Whether the conversion of calcium cyanamide into ammonia proceeds by an intermediate formation of urea is unproved."

The above was written by Dr. Wagner before the mechanism of the conversion of Cyanamid in the soil had been worked out. These later researches show that the conversion is both physico-chemical and biological, as has been set forth in Chapter V.

The experiments on the effect of concentration to which Dr. Wagner refers were made in vegetation pots with a variety of nitrogenous compounds, on various types of soil, and with various crops. All the results point to the same general conclusion, which is illustrated in Fig. 5. This test was made with oats planted on a sandy-loam soil, in pots 20 cm. high and 20 cm. in diameter. The seed was planted on the day of fertilizing, May 9, 1905, and the grain harvested on July 14, 1905. The lime-nitrogen contained 20.06 per cent. nitrogen, and the calcium nitrate (commercial grade) contained 11.65 per cent. nitrogen.[1] The yields of grain are plotted against the amounts of nitrogen applied to the soil (Fig. 5).

Each of these curves is an illustration of the Law of Diminishing Returns. For the smaller applications of nitro-

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[1] Landw. Vers. Stat., 66, IV-V (1907), p. 346.

gen, the increased yield is almost proportional to the amount of nitrogen applied, but the rate of increase drops off rapidly until a point is reached where further applications not only do not increase the yield but tend to decrease it. If too much fertilizer is applied the plant may even be killed. The "burning" and occasional destruction of vegetation by excessive applications of fertilizer salts is well known to agriculturists. A similar phenomenon has been investigated by Headden and Sackett[1] in Colorado, where it was shown that the formation of excessive quantities of nitrates has caused in some cases the total destruction of all plant life, often over areas miles in extent.

Toxicity, therefore, is a question of the amount of fertilizer applied. All of the common, nitrogenous, mineral fertilizers may have a toxic action if too much is used, but with the ordinary applications of practical agriculture none of these materials is toxic. Experience has determined the maximum quantities of nitrogen that can be economically utilized by the various crops under various soil conditions, and the possible effects of larger quantities than this maximum economical quantity in each case have little interest to the practical farmer. Cotton, corn, wheat, oats, and similar crops seldom economically utilize more than 15 to 25 pounds of nitrogen per acre. Sugar beets and sugar cane may utilize as high as 40 to 50 pounds. Potatoes, truck crops, some fruits, and tobacco may utilize as high as 60 to 70 pounds of nitrogen per acre. With such applications it is doubtful if any of the mineral fertilizers in question would exert a toxic action on the plant, even if they were applied alone, provided the time and method of application were suitable.

As a matter of fact, however, when large applications of nitrogen are desired, it is customary to mix several kinds of nitrogenous materials together and to apply the mixture in several portions, instead of all at one time. Moreover, agri-

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[1] Colorado Exp. Sta. Bulletin 179, 1911.

cultural experience has shown that nitrogenous fertilizers are not utilized as economically when applied alone as when they are used in conjunction with phosphates and potash salts; the presence of phosphorus and potassium seems to greatly modify the ability of the plant to assimilate nitrogen. As a general rule, it is seldom, indeed, that more than 25 pounds of nitrogen, derived from a single source, is applied at one time, unaccompanied by phosphates and potash. In normal agricultural practice, therefore, the question of toxicity of the common nitrogenous fertilizers may be disregarded. If the farmer wishes to depart from the normal practice, it is usually best to follow the instructions issued by fertilizer manufacturers for the use of their products. Such instructions usually designate 20 to 25 pounds of nitrogen per acre as the maximum application, and recommend that the material be applied during the preparation of the soil a week or more before the seed is sown. They also caution against the danger of direct contact of the undiluted fertilizer with the leaves or roots of the plant.

OTHER EXPLANATIONS OF TOXIC ACTION.

Whether or not acetylene, which may be generated by the action of moisture on a lime-nitrogen containing calcium carbide, is harmful to plant life, is of little interest to the Cyanamid industry, since the material prepared for use as a fertilizer does not contain calcium carbide. The lime-nitrogen made in Europe in former years, sometimes contained slight amounts of carbide but it is extremely doubtful if there were any harmful effects from this ingredient. H. Kappen[1] and E. Haselhoff[2] claim that they could observe no harmful effects of acetylene on plant growth. No reports have been found which show that acetylene may be harmful.

The free lime in the German "kalkstickstoff" or lime-nitrogen is in the form of calcium oxide, while in the Ameri-

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[1] Fuhling's Landw. Zeit., Apr. 1908, 286.

[2] Landw. Vers. stat., 68, 1908, Nos. 3 and 4.

can Cyanamid it is in the form of calcium hydroxide and carbonate. The effects of the lime in either form upon plant life have been stated clearly by Wagner in the extract quoted above. Since the amount of total calcium in Cyanamid, expressed as CaO is about 55 per cent. and the amount applied to the soil is necessarily limited by the amount of nitrogen applied, the lime can hardly reach such an amount that it will ever interfere with plant growth.

With regard to the inferior action of Cyanamid on acid moor soils, or on other acid soils, Wagner states that the same thing is true of ammonium sulphate, and that the bad effects should be attributed to the abnormal soil conditions and not to any abnormal action of the fertilizer. Soils which are acid are as a rule unfit for profitable agriculture, and should be put into good condition by previous judicious liming. Fertilizers cannot be expected to overcome the harmful effects of abnormal conditions which constitute the limiting factor in the growth of a crop. The abnormal conditions must be corrected before fertilization will be most economical. Cyanamid, therefore, should not be applied to very acid soils with the expectation of obtaining a profit, unless the unfavorable conditions are corrected by previous liming. The quantity of lime in Cyanamid, while of some assistance, is evidently insufficient on very acid soils, which require frequently as much as one to two tons of slaked lime in order to restore them to a neutral reaction.

The unfavorable action of Cyanamid on very acid soils has frequently been attributed to the possible formation of dicyandiamide from the calcium cyanamide. That there is no chemical or experimental basis for this explanation will be shown in the next section.

DICYANDIAMIDE.

The subject of dicyandiamide has been much discussed in chemical literature. It has been necessary, in order to gain a logical understanding of the subject, to select from the mass of experimental data that have been reported the results that are consistent with all the known facts, and then to reconcile the apparent disagreements with the consistent facts.

Formation.—The researches of Ulpiani[1] show without doubt that acids do not determine the formation of dicyandiamide from calcium cyanamide. Acids acting on calcium cyanamide produce calcium salts and free cyanamide. By the further action of the acids, from the weakest to the strongest, there is formed first urea, and secondly, especially in the case of weak acids, ammonium salts. (See also p. 12). F. Lohnis and R. Moll[2] found that even humic acid, in excess, acting upon lime-nitrogen for 8 days at 40° C. produced not the slightest trace of dicyandiamide. There is no evidence of any kind to show that acids ever produce dicyandiamide from cyanamide. Neither do strong alkalies produce dicyandiamide, but always produce urea and free ammonia. Weak alkalies, however, and especially calcium hydroxide, readily effect the polymerization, although in this case also there is formed considerable urea. The formation of dicyandiamide in lime-nitrogen is brought about by the combined action of moisture, which causes the hydrolysis of calcium cyanamide to cyanamide, and lime which determines its polymerization to dicyandiamide. These reactions take place at ordinary temperatures very slowly, as shown below, but proceed very rapidly above 70° C. At about 100° C. other reactions begin with formation of ammonia and small amounts of other derivatives. Water and heat alone do not cause the polymerization to dicyandiamide; Ulpiani boiled a pure solution of cyanamide 50 hours without any change.[3]

Decomposition.—In a solution of lime-nitrogen, dicyandiamide forms and decomposes simultaneously. This is seen

[1] Gaz. Chim. Ital., 1908, II, No. 4, 358.417.

[2] Centl. Bakt. XXII, 276.

[3] Rend. Soc. Chim. di Roma. p. 4 1906.

in the following table by G. Liberi,[1] showing the content of cyanamide and dicyandiamide nitrogen in solutions of lime-nitrogen made by extracting with cold water and filtering and maintaining at 27° C. The figures are given as percentages of the original lime-nitrogen.

	Dilute solution 1 per cent. lime nitrogen		Concentrated solution 5 per cent. lime nitrogen	
Time elapsed in days	Nitrogen as cyanamide per cent.	Nitrogen as dicyandiamide per cent.	Nitrogen as cyanamide per cent.	Nitrogen as dicyandiamide per cent.
0	18.63	--	18.63	—
1	16.38	0.46	14.56	0.70
2	14.42	0.56	11.76	1.54
6	12.74	0.62	9.10	2.84
11	10.22	0.50	5.18	2.24
18	7.42	0.39	1.75	1.71
31	3.01	0.38	0.00	1.25
45	0.00	0.34	—	0.84
58	—	0.28	—	0.53
76	—	0.22	—	0.23

The maximum amount of dicyandiamide occurs in each case at the end of 6 days' standing. The decomposition of the dicyandiamide is very slow, as is seen in the concentrated solution after the 31st day, when all the Cyanamid has been removed, and no more dicyandiamide can form. Its rate of formation is somewhat faster, and is undoubtedly determined by the concentration of both nitrogen and calcium. The percentage of the total nitrogen transformed to dicyandiamide is about five times as great in the concentrated as in the dilute solution. With the removal of the cyanamide it was observed that crystals of pure calcium hydroxide settled out on the walls of the vessel.

The rapid disappearance of the cyanamide shows that the formation of other derivatives of cyanamide in this solution is much more rapid than the formation and decomposition of dicyandiamide, and it is therefore evident that most of the cyanamide decomposes directly to these other derivatives, and not through the dicyandiamide form. The largest part of

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[1] Annali Staz Chim. Agrar. Sper di Roma Series II, V, 1911.

these other derivatives is urea, and the balance is amidodicyanic acid, melamine and ammeline. (See also p. 29).

Conversion in Soil.—The chemical behavior of dicyandiamide in the soil has not been studied in the thorough manner in which that of cyanamide has been studied, and much of the data at hand is invalidated by the fact that enormous quantities of nitrogen were used. It is necessary to draw our conclusions solely from the vegetation tests that have been reported.

A review of these culture tests will show that they fall into two classes; one, in which chemically pure dicyandiamide was used, and the other in which home-made dicyandiamide was used.

Among the prominent investigators who used pure dicyandiamide are Wagner, Kappen, Sabaschinkoff, Löhnis, Brioux, and C. J. Milo. Their results show that chemically pure dicyandiamide has practically no fertilizing value but on the other hand may have slight toxic action if more than 45 pounds of dicyandiamide nitrogen per acre is applied. The results are in such agreement that it will not be necessary to quote them here. Among those who used dicyandiamide prepared in their own laboratories are Perotti, Ulpiani, R. Inouye and K. Aso. They found that home-made dicyandiamide has a fertilizing value equal to that of ammonium sulphate provided it is not used in quantities exceeding 100 pounds of nitrogen per acre.

Perotti,[1] for instance, in pot tests with wheat, grown to maturity, obtained the maximum crop with 75 pounds of nitrogen per acre in the form of home-made dicyandiamide. The increase in yield over the control pot without nitrogen was about 100 per cent. With buckwheat the maximum crop was obtained with 150 pounds of nitrogen per acre, and the increase in yield was about 200 per cent. With flax the maximum yield was with 300 pounds of nitrogen, and the increase in yield was about 60 per cent.

[1] Cent. Bakt. XVIII, 55, 1907.

R. Inouye[1] made pot tests with rape and barley, fertilizing with a dicyandiamide made by himself from lime-nitrogen, and and analyzing 46.7 per cent. nitrogen. The rate of fertilization was equivalent to 2,400 pounds superphosphate per acre, 1,200 pounds potassium carbonate and the amounts of nitrogen shown in the table below, which gives also the yield obtained:

Pounds nitrogen from ammon. sulphate	Pounds nitrogen from dicyandiamide	Average weight of one plant green rape. Grams	Average weight of one plant air-dry, barley. Grams
—	—	5.0	1.8
240	—	59.4	8.3
160	80	62.6	9.0
160	80	64.0	9.0
—	240	8.4	2.5

The dicyandiamide in the fourth pot was applied as a top-dressing. Although the fertilization was very heavy there is no doubt that the results are very good when 80 pounds of nitrogen from impure dicyandiamide is used with ammonium sulphate, although 240 pounds of nitrogen from dicyandiamide alone is little better than no fertilizer. This is clearly an excessive amount of dicyandiamide.

K. Aso[2] made some toxicity tests with a dicyandiamide made by himself from lime-nitrogen, and analyzing 59.88 per cent. nitrogen. Buckwheat and oat plants were grown to a height of about 10 cm. in ordinary soil and were then transferred to flasks containing solutions of different concentrations of dicyandiamide. When the solutions contained less than 0.01 per cent. of nitrogen from dicyandiamide the plants continued growing normally and developed better than in the control flasks. When larger concentrations were used the plants showed the characteristic effects of dicyandiamide poisoning; that is, for increasing doses, first, appearance of a brown color on the tips of the leaves, then drying of the tips, although usually followed by recovery and increased growth; finally, with very large concentrations, curling and drying up of the leaves and destruction of the plant. Here, as with

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[1] Jour. Coll. Agr. Imp. Univ. Tokyo, Vol. I, No. 2, 1909, p. 193.

[2] Jour. Coll. Agr. Imp. Univ. Tokyo, Vol. 1, No. 2, 1909, p. 211.

Cyanamid and other fertilizers, toxicity is a question of concentration, although the specific toxicity of pure dicyandiamide is considerably larger than that of impure dicyandiamide.

Some tests were also made with rice transplanted to field plots (0.83 qm.) manured alike with superphosphate, potassium carbonate and nitrogen compounds at the rate of 90 pounds per acre each of phosphoric anhydride, potash and nitrogen (except control). The nitrogenous substances were ammonium sulphate containing 21.2 per cent. nitrogen, lime-nitrogen with 12.47 per cent. nitrogen, and dicyandiamide with 46.7 per cent. nitrogen. They were applied at different periods before the transplanting of the rice clumps. The total weight in grams of the plants obtained in the air dried state were:

	Fertilized days before planting					
Fertilized with	0	7	14	21	28	35
No manure	229	—	—	—	—	—
No nitrogen	436	—	—	—	—	—
Ammonium sulphate	764	—	—	—	—	—
Lime-nitrogen	614	767	786	807	788	744
Dicyandiamide	507	575	572	670	652	609

The yield of clean grain was as follows:

	Fertilized days before planting					
Fertilized with	0	7	14	21	28	35
No manure	75	—	—	—	—	—
No nitrogen	149	—	—	—	—	—
Ammonium sulphate	266	—	—	—	—	—
Lime-nitrogen	197	259	260	258	280	257
Dicyandiamide	183	208	209	238	244	239

This experiment shows a somewhat lower result with lime-nitrogen than with ammonium sulphate applied at the time of planting, but a somewhat larger yield when the lime-nitrogen is applied 7 days before planting. The dicyandiamide is more effective when applied two or three weeks before planting than when applied at the planting, but it is never as effective as the ammonium sulphate, being at the best about 89 per cent. as effective in producing grain. In the cultivation of rice in America the maximum utilizable application of nitrogen does not exceed 10 pounds per acre. Hence, the above quantities are many times larger than any met in agricultural practice.

A similar experiment was made in pots containing 8 kg. of soil, manured with double superphosphate, potassium sulphate and nitrogen at the rate of 120 pounds of P_2O_5, K_2O and N per acre respectively. The lime-nitrogen contained 11.8 per cent. N and the dicyandiamide 59.9 per cent .N. The yields in grams of air-dry plants were as follows:

	Fertilized days before planting			
Fertilized with	0	7	14	21
Ammonium sulphate	67.5	—	—	—
Lime-nitrogen	65.6	69.6	70.6	74.8
Dicyandiamide	66.6	74.3	73.8	71.5

The yields of grain were:

	Fertilized days before planting			
Fertilized with	0	7	14	21
Ammonium sulphate	29.5	—	—	—
Lime-nitrogen	28.3	30.0	29.5	33.2
Dicyandiamide	30.5	33.5	31.7	33.7

In this experiment the highest results were obtained with dicyandiamide applied a week before planting. When applied at the time of planting the results are about the same as those with ammonium sulphate.

PURE SUBSTANCES AND TOXICITY.

There are several observations reported in the literature that may help us to understand why a chemically pure dicyandiamide should be toxic, while an impure dicyandiamide may have a fertilizing value equal to that of ammonium sulphate.

It has been noted by Sabaschnikoff[1] that a fertilization with chemically pure calcium cyanamide, in comparison with lime-nitrogen containing the same amount of nitrogen, gives only from one-third to one-half as large an increase in yield as is obtained from the lime-nitrogen, both being applied under exactly the same conditions.

C. J. Milo[2] made some experiments on sugar cane, in which

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[1] Mitt. Landw. Inst., Univ. Leipzig, Vol. IX 1908, p. 106.

[2] Archief voor de Suikerindustrie in Nederlandsch-Indie, 20, 482-539.

the sugar cane, in baskets, was watered one month and two months respectively after planting, with solutions of lime-nitrogen (6 per cent. calcium carbide), pure cyanamide, $CN.NH_2$, basic calcium cyanamide, urea and dicyandiamide. The solutions contained each an amount of nitrogen equivalent to an application of 75 pounds per acre. The pure cyanamide proved very toxic and two out of three plants were killed after the second application. About two weeks after the second application, probably when the cyanamide had been converted to other forms, the remaining plants in this basket began to grow luxuriantly. The basic calcium cyanamide caused the plants to look sick temporarily, and they remained inferior. The dicyandiamide (98.5 per cent. pure) was not as intense in its action as pure cyanamide, causing no destruction, but the bad effects lasted longer than those of pure cyanamide, and the plant seemed to lack nitrogen nourishment. The urea caused luxuriant growth from the time of application, and was slightly better than the sulphate of ammonia and lime-nitrogen applications. *The lime-nitrogen and sulphate of ammonia solutions produced full growth and were equally effective.*

It appears therefore, that *the fertilizing value of lime-nitrogen, decidedly can not be judged from the fertilizing action of pure cyanamide or pure calcium cyanamide,* and that the fertilizing value of impure dicyandiamide is quite different from the fertilizing value of pure dicyandiamide. It seems that the plant is unable to utilize these pure compounds of nitrogen, but that in lime-nitrogen there are some substances that neutralize such toxic compounds, or help remove them, or that act upon the plant in such a way as to enable it to withstand the toxic properties until they are destroyed by the conversion of the cyanamide and its polymers by the catalytic action of the soil. It is quite possible for instance, that the lime and the extremely finely divided carbon in lime-nitrogen may play a part in the rapid decomposition of the cyanamide. It is also possible that the urea, and other derivatives that are so easily formed from cyanamide, furnish the plant with nourishment that enables it to withstand otherwise toxic effects that might check growth if such nourishment were not available (see also page 34).

Conclusion.—Toxicity of Cyanamid is simply a question of concentration. Under normal soil conditions and with the normal applications of practical agriculture there are no unusual effects on the germination of the seed or on the growth of the plant. This is verified constantly in the extensive use of Cyanamid in agriculture.

CHAPTER IX.

Agricultural Use of Cyanamid.

Fertilizer Tests.—In the selection of the most economical fertilizer it is necessary to consider, among other things, the nature of the crop, the qualities desired in the plant grown, the type of soil, the effect of long-continued use of the fertilizer, the cost and the relative yields. Thus, the rice-plant seems to be unable to assimilate nitrates easily, but readily assimilates ammonium compounds.[1] The quickly acting forms of nitrogen usually produce rank, heavy growth of the green parts of the plant, with little fiber, while the slowly acting forms produce thinner leaves, and stems with greater strength. For forcing purposes, the nitrates are ideal; for slow, steady growth, the organic forms of nitrogen, Cyanamid, ammonium sulphate, etc., are to be preferred. Soil conditions are often a determining factor. Thus, loose, open soils in regions that receive a great deal of rain do not readily retain nitrates. Soils of low lime content may become acid by the addition of ammonium sulphate year after year: the sulphate radical enters into combination with the lime of the soil and carries away the calcium in the drainage waters.[2] Very acid soils are not economically fertilized with substances like Cyanamid, ammonium sulphate and other materials requiring nitrification, since nitrifying bacteria are notably deficient in acid soils, especially acid sandy soils. Such soils should be put into productive condition by proper judicious liming, some time previous to the fertilization. On light, sandy soils where heavy liming may damage the crop the yearly addition of a small amount of lime as a part of the fertilizer is of great assistance in overcoming the tendency towards acidity. The relative yields per unit of money invested in the different fertilizers is often the controlling factor in their selection, but

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[1] Hawaiian Agr. Exp. Sta. Bulletin 24.

[2] A. D. Hall, Fertilizers and Manures, p. 62, 1909.

since prices vary, it is customary to express the yields on the basis of equal applications of nitrogen.

There is therefore a large number of factors that affect the selection of the most economical fertilizers. The statistical method of merely averaging the yields of a large number of experiments regardless of their character, does not give very much practical information. The errors of experimentation with Cyanamid are usually in one direction, and hence do not offset one another. One of the most common errors is the use of quantities of nitrogen far in excess of what would be applied in practical agriculture, as indicated on page 69. It is shown in Fig. 5 that the relative efficiency of utilization, of the nitrogen in various compounds is not the same at all applications. The relative values at an application of 1 gram per pot are entirely different from the relative values at 0.5 grams, or at lower applications. Moreover, the order of superiority may be different at different applications, as shown on the calcium nitrate curve. At the lower concentrations, such as obtain in practical agriculture, under favorable soil conditions, all of the common nitrogenous mineral fertilizers have about the same efficiency of utilization, in this experiment. Not only is it a mistake to assume that results obtained at one concentration will hold true for other concentrations, but it is, of course, equally wrong to assume that an average of the results at various concentrations will hold true for a particular concentration. The relative efficiencies also vary with the nature of the soil and with the crop. Results obtained on sand may not hold on clay, and vice versa. Acid soils may act differently from neutral or alkaline soils. A nitrogenous fertilizer applied alone usually gives entirely different results when mixed with other nitrogenous fertilizers, or with phosphates, acid or basic, or with potash salts.

A source of error that has probably vitiated many of the reported experiments is the readiness with which unhydrated lime-nitrogen changes in weight, by absorption of moisture and carbon dioxide, especially when stored in small quantities. It is possible that a great many investigators have purchased lime-nitrogen at a certain analysis, have allowed the material to remain exposed to the atmosphere several months, and have then weighed out the fertilizer for the test, assuming that its analysis is practically the same as when it was bought. The error introduced by the weighing up of the fertilizer one month after analysis may amount to 5 to 8 per cent. of the total nitrogen, in the case of a single bag exposed in a damp climate. In America, where the Cyanamid is completely hydrated, the error is much less (see p. 27), but it is still large enough to make it desirable to have the fertilizer weighed out shortly after the analysis is determined.

Another error is the application of Cyanamid only a short time before the harvest. Since Cyanamid may take 70 to 80 days[1] to be completely utilized, it is obvious that the maximum efficiency is obtained only when the application is made not less than 70 to 80 days before the harvest.

The main purpose of a fertilizer test is to determine the relative profits that can be made by the use of different fertilizers. In view of the difficulties of experimentation, and the danger of drawing unwarranted conclusions from insufficient or irrelavant data, as pointed out above, probably *the only fair test of a fertilizer is obtained when it is applied under the conditions that prevail where the consumer uses it.* All other methods require special proof that the results obtained experimentally would also be obtained practically, and such proof is not always available.

To illustrate the considerable variation in the results obtained with different materials in different conditions, a few of the results of prominent investigators are give here. Thus, Strohmer, with sugar beets, obtained as an average of 7 fields, 100 pounds of sugar when sodium nitrate was used, to 104

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[1] Dr. A. Frank, private communication.

pounds of sugar when lime-nitrogen was used.[1] J. Klöppel[2] obtained yields of sugar beets with no fertilizer, sodium nitrate and lime-nitrogen respectively of 100, 127, and 149, while the yields of sugar were 100, 99, and 130. As an average of 10 cereal and root crops in 29 field experiments, Steglich[3] assigned the following values to the various materials: no fertilizer, 81; sodium nitrate, 100; ammonium sulphate, 95; and lime-nitrogen, 96. Schneidewind,[4] as an average of 5 cereal and root crops reports that the increase in yield over the fields unfertilized with nitrogen were comparatively, sodium nitrate, 100; ammonium sulphate, 88; and lime-nitrogen, 73. Wagner, Director of the Experiment Station at Darmstadt,[5] as a summary of 11 field tests on cereals with 27 pounds or less of nitrogen per acre, reports the increased yield over the fields without nitrogenous fertilizer, comparatively as follows: Sodium nitrate, 100; ammonium sulphate, 87; and lime-nitrogen, 94. Müntz and Nottin, as an average of 11 field tests with wheat report the following comparative yields obtained: Cyanamid, 100; ammonium sulphate, 94; dried blood, 96.[6]

USE AS A WEED DESTROYER.

In Germany, lime-nitrogen is used to a considerable extent for the destruction of obnoxious weeds, such as wild mustard, occurring in grain crops, particularly oats. The fine, dry, lime-nitrogen is scattered either by hand or by machine early in the morning when the leaves are wet with dew, or after a rain, at the rate of 60 to 90 pounds per acre. The lime-nitrogen readily clings to the rough, hairy, almost horizontal leaves of the wild mustard, and forms a concentrated solution in the moisture on the leaves. This tends to dilute itself by osmosis and brings

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[1] Oesterr-Ungar., Zeit. fur Zuckerindustrie und Landwirtschaft, XXXV, No. VI, 1906, 676.

[2] Fuhling's Landw. Zeit., **56,** No. 15, 1907, p. 539.

[3] Fuhling's Landw. Zeit., **56,** No. 22, 1907, p. 780.

[4] Arbeit. Deut. Landw. Ges., No. 146, 1908, p. 116.

[5] Arbeit. Deut. Landw. Ges., No. 129, 1907.

[6] Annales de l'Institut National Agronomique, 2nd Series, Vol. VI, No. 1. See also pp. 45-47.

about the destruction of the mustard within a few days. The application is made when the mustard plant is young, best when it has only four or six leaves. The more leaves it has the more lime-nitrogen will be required. The grain crop may be affected a little immediately after the application, and may turn somewhat brown at the tips of the leaves, but it will quickly recover and become much greener than the grain in untreated fields. The leaves of the grain crops, especially oats, stand almost vertical and are comparatively smooth and waxy, so that very little lime-nitrogen clings to them and no permanent damage is done. Practically, this method of destroying wild mustard is quite economical, since the nitrogen applied in this way seems to have as full fertilizing effect as if it were applied under the crop. The mustard, on the other hand, is practically eradicated.

DIRECTIONS FOR APPLICATION AS FERTILIZER.

Very little of the Cyanamid made in this country is applied alone, practically all of it being used as a part of mixed fertilizers. For the guidance of those who wish to use it without admixture with other materials, the following suggestions are offered, although it should be recognized that a true test of the efficiency of the Cyanamid used in this country is made only under the conditions in which it is usually applied, that is, as a part of a mixture containing phosphoric acid, potash, and frequently other forms of nitrogen.

Cyanamid is least efficient when applied as a top-dressing. This is probably due to the quick reaction and fixation in the soil, so that much of the nitrogen is retained in the upper layers of soil where the plant roots do not reach it readily. The application should be made in such a way that the Cyanamid will be buried about where the plant roots are expected to grow. It should be scattered through the lower layers of cultivated soil as much as possible, so as to favor the greatest spreading of the roots. In the event of a dry season, the larger the root system, the better will be the ability of the plant to withstand drouth. Dropping the fertilizer in narrow rows favors the development of bunched root systems, which will do very well as long as the supply of fertilizer lasts and the water supply is good, but are insufficient for the demands of the plant in dry weather. If the application is large broadcasting one-half or two-thirds of the fertilizer before plowing, or after plowing and before harrowing, with the application of the remainder in the row before seeding, or along the row after the plants are up, will be found to produce the best results. Care should be taken that the fertilizer is well mixed with the soil and that pure fertilizer and seed are not in direct contact, thereby avoiding the so-called "burning" of young plants. When the fertilizer is applied alongside the rows after the plants are up, it should be well worked in with the cultivator or with hoes. Care should be taken not to get highly concentrated fertilizers on the leaves of the plant, especially if the plant is wet. Since Cyanamid is a medium-slow-acting fertilizer, it should be applied to the crop not less than 70 to 80 days before the harvest, in order that the nitrogen may be completely utilized by that crop.

The quantity of Cyanamid that can be economically applied at one time is preferably limited to 150 pounds per acre. Experience has shown that the most economical utilization of a nitrogenous fertilizer is obtained when it is used in conjunction with the other fertilizing elements, phosphorus and potassium. For this reason, it is recommended that Cyanamid be used as a part of a fertilizer mixture, rather than that it be applied alone.

If Cyanamid is to be applied to very acid soils, such soils should be put in productive condition by thorough judicious liming some time before the application of the fertilizer. The application of barnyard manure will help to establish the bacteria that are deficient in such soils.

When Cyanamid is applied alone, better results will be obtained if it is applied several days before the seed is sown, especially if the applications are large. For small applications, when care is taken to mix the fertilizer well with the soil, the seed may be planted directly after the fertilizer is spread. Even distribution of the Cyanamid is facilitated by previously mixing it with two to three times its weight of damp earth.

USE OF COMPLETE FERTILIZER MIXTURES.

Since most of the Cyanamid used in this country comes to the farmer as an ingredient of mixed fertilizers, it is as a rule not necessary to have special instructions for its use. From the known chemistry of calcium cyanamide it is very probable that when Cyanamid is mixed with acid phosphate, the phosphoric acid causes a considerable conversion of Cyanamid nitrogen to the form of urea, (page 12). At any rate, the ordinary practice in the use of mixed fertilizers is such that the presence of Cyanamid nitrogen will not require any modification of the usual practice.

CHAPTER X.

Making Fertilizer Mixtures with Cyanamid.

MIXTURES WITH AMMONIUM SALTS.

Cyanamid contains about 55 per cent. CaO, of which about 30 per cent. is present as $CaCN_2$, 21 per cent. as $Ca(OH)_2$, and 4 per cent. as $CaCO_3$ and other forms. Most of the calcium, therefore, dissociates readily and can react when brought into contact with certain bodies. In the presence of ammonium sulphate for instance, a double decomposition takes place as follows:

$$Ca(OH)_2 + (NH_4)_2SO_4 \rightarrow CaSO_4 + 2NH_3 + 2H_2O.$$

Hence, if Cyanamid and ammonium sulphate are mixed alone there will be a large loss of ammonia. The same kind of reaction takes place with other ammonium salts.

If, however, as is practically always the case, there is present an adequate amount of acid phosphate or other acid material, the acid of the acid phosphate immediately fixes the free ammonia and prevents its escape. The ammonia is combined probably as ammonium phosphate or as calcium ammonium phosphates, or both. To prevent loss of ammonia, therefore, it is only necessary to have a sufficient amount of acid material present so that the resulting mixture will be acid in reaction. This condition is obtained when the amount of Cyanamid does not exceed 100 pounds of powdered Cyanamid or 200 pounds of granulated Cyanamid per 800 pounds of ordinary acid phosphate containing 14 or 16 per cent. of available phosphoric acid. Such mixtures have been tested in practical fertilizer manufacturing and show no losses of ammonia. The quantity of ammonium sulphate present is practically immaterial. Acid fish contains some nitrogen as ammonium sulphate, and should be mixed in accordance with the above rule.

MIXTURES WITH ACID PHOSPHATE.

In ordinary acid phosphate analyzing 16 per cent. available phosphoric acid, there is usually found about 5 per cent. as free phosphoric acid, 9 per cent. as mono-calcium phosphate, and 2 per cent. as di-calcium phosphate. When such a phosphate is mixed with Cyanamid there is obviously a neutralization of free acid, and of acid hydrogen of the mono- and di-calcium phosphate, the extent of the reaction depending upon the amount of active lime introduced by the Cyanamid. The neutralization is, of course, attended by evolution of heat, and this heat is the cause of the unfavorable results of mixing large quantities of Cyanamid with acid phosphate.

In America, phosphates are sold on the basis of their content of phosphoric acid soluble in ammonium citrate solution of standard strength, since it has been shown that there is no appreciable difference in the agricultural value of the water-soluble and the citrate soluble part of the phosphate. It is to the interest of mixers of commercial fertilizers to prevent the neutralization of the acid phosphate beyond the di-calcium or citrate soluble stage. With increasing quantities of CaO the following reactions should take place successively, but with relatively decreased velocity:

$$\text{(a)}\quad \underset{\text{Phos. Acid.}}{H_6P_2O_8} + CaO \rightarrow \underset{\text{Water Sol.}}{CaH_4P_2O_8} + H_2O,$$

$$\text{(b)}\quad \underset{\text{Water Sol.}}{CaH_4P_2O_8} + CaO \rightarrow \underset{\text{Citrate Sol.}}{Ca_2H_2P_2O_8} + H_2O,$$

$$\text{(c)}\quad Ca_2H_2P_2O_8 + CaO \rightarrow Ca_3P_2O_8 + H_2O.$$

The last reaction would require a vast excess of CaO, since $Ca_2H_2P_2O_8$ is practically insoluble in water, and is practically undissociated. This reaction does not apply in the practical mixing of Cyanamid and acid phosphate. There is, however, a further reaction, that may take place with prejudicial results.

$$\text{(d)}\quad \underset{\text{Citrate Sol.}}{2Ca_2H_2P_2O_8} + \text{Heat} \rightarrow \underset{\text{Cit. Insol.}}{Ca_3P_2O_8} + \underset{\text{Water Sol.}}{CaH_4P_2O_8},$$

It has been found that with a constant quantity of lime, above a certain minimum, the proportion of citrate insoluble phosphate formed is approximately a logarithmic function of the temperature. The quantity of Cyanamid that can be safely mixed with acid phosphate varies greatly with the nature of the acid phosphate, particularly its content of free acid and of iron and alumina. For some grades of acid phosphate it may be as much as 120 pounds of powdered Cyanamid, for the poor grades of acid phosphate as low as 70 pounds of powdered Cyanamid to 1,000 pounds acid phosphate in a ton of complete mixture.

By the process of granulation, in which the powdered Cyanamid is formed into particles which pass through 15-mesh and over 50-mesh standard screens, the chemical activity of the Cyanamid with acid phosphate is greatly decreased. This is mainly due to the fact that the specific surface exposed by particles of different sizes varies inversely as their diameters. The number of particles per unit of weight varies inversely as the cubes of the diameters. One thousand particles one-hundredth of an inch in diameter, for instance, would be required to make one granule one-tenth of an inch in diameter, and the total surface exposed would be one-tenth as much as before granulation. Since chemical action can take place only on the exposed surface of the solid Cyanamid (the acid phosphate having very little fluidity) it is evident that the localization in a few places of a comparatively large number of widely scattered small particles will greatly decrease the amount of action that can take place.

Practically, it has been found that the chemical activity of the granulated Cyanamid now being manufactured is about one-half the activity of the powdered Cyanamid; hence, about twice as much granulated Cyanamid can be used in acid phosphate mixtures to produce the same effect as a given quantity of powdered Cyanamid. With improvements in the process of granulation the safe amount will be probably further increased.

OTHER MIXTURES.

With other materials commonly used in fertilizer mixtures Cyanamid can be mixed in any quantities, without prejudicial effect on the valuable constituents.

ADVANTAGES OF CYANAMID IN FERTILIZER MIXTURES.

Drying Action.—The free acids in acid phosphate are frequently the cause of dampness and poor mechanical condition in mixed fertilizers, causing caking in the bags and making the fertilizer difficult of application through drills. To correct this undesirable condition it is customary to add to the mixture various drying and neutralizing agents. Since the particles of Cyanamid are soft and porous and usually contain less than 1 per cent. moisture they readily absorb free moisture from the acid phosphate or other damp materials with which they come in contact. More important is the action of the lime on the free acids, calcium phosphates taking the place of the sticky phosphoric acid, while the heat generated by the neutralization aids in dissipating the moisture uniformly throughout the mixture. This drying action is very valuable to the fertilizer compounder.

Preventing Loss of Nitric Nitrogen.—It has long been known by fertilizer manufacturers, and has been demonstrated in the laboratory,[1] that when sodium or calcium nitrate is mixed with acid phosphate, without the further addition of neutralizing agents, there is a loss of nitrogen amounting to from 6 to 10 per cent. of the total nitrate nitrogen added. The loss is due to the action of the free acids in the acid phosphate upon the nitrate salts. Thus, with sodium nitrate the reaction probably is:

$$2NaNO_3 + H_3PO_4 \rightarrow Na_2HPO_4 + 2HNO_3.$$

The nitric acid either volatilizes as such or is decomposed to nitrogen peroxide and oxygen and escapes from the mixture. This loss is prevented by Cyanamid in two ways; the free

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[1] C. S. Cathcart, Jour. Ind. and Eng. Chem., Vol. 3, No. 1, 1911.

phosphoric acid is neutralized by the lime of the Cyanamid, and again, the free nitric acid or nitrogen peroxide is neutralized by the Cyanamid lime immediately after its formation. Whatever the mechanism, it has been shown by careful experiments that Cyanamid prevents this otherwise serious loss of nitrate nitrogen.

Preventing Bag-rotting.—A similar loss of hydrochloric acid gas occurs when potassium chloride, or commercial muriate of potash, is mixed with acid phosphate:

$$2KCl + H_3PO_4 \rightarrow K_2HPO_4 + 2HCl.$$

This loss does not decrease the commercial value of the mixture, but the passage of the acid gases through the cloth of which the bag is made decomposes the bag fiber and causes so-called "bag-rotting." This destructive action is prevented by the addition of Cyanamid to the mixture, causing the neutralization of the hydrochloric acid gas, or the phosphoric acid producing it.

To the fertilizer manufacturer, the drying and neutralizing properties of Cyanamid are decided advantages, since these are not possessed by any other high-grade mineral fertilizer, and no extra charge is made for them in the selling price of Cyanamid. Since the cost of drying and neutralizing agents and the extra mixing expense is saved if the nitrogenous ingredient possesses these properties, Cyanamid has been received with much favor by fertilizer manufacturers. Practically the entire output of the American Cyanamid Company is sold in this way.

CHAPTER XI.

Permanganate Availability of Cyanamid.

In order to have a ready means of determining the agricultural availability of the nitrogen in various organic compounds, certain chemical methods have been adopted that approximately measure this property. The permanganate availability methods are in general use for this purpose. It is generally assumed that nitrogen compounds soluble in water are readily utilized as plant food, but it is also recognized that nitrogen compounds insoluble in water may be utilized by the plant in the course of growth. It seems to be generally true of organic nitrogenous compounds that the solubility in water, together with the relative ease with which the insoluble parts are decomposed by potassium permanganate bears a regular relation to the agricultural availability of the fertilizer. It is interesting to examine whether Cyanamid takes its proper place in the permanganate availability series of values as compared with its agricultural availability, and which of the permanganate methods gives the truest results.

The following experiments on the solubility of Cyanamid nitrogen in water, and its behavior under the influence of potassium permanganate, were made under the direction of the author in October, 1912. The Cyanamid used was a low grade, granulated material analysing as follows:

Nitrogen	13.58	per cent.
Lime (CaO)	50.57	"
Moisture	1.83	"
Carbon dioxide	4.00	"
Size of granules	15 to 50 mesh	

EXPERIMENT I.

Solubility on Filter.—Samples of 1 gram, 2 grams, 4 grams and 8 grams of granulated Cyanamid were placed on filter papers and washed with successive portions of distilled water at 25° C. until the volume of filtrate reached 250 cc. The nitrogen content of each filtrate was determined with the following results:

Sample grams	Grams of N. in sample	Grams of N. in filtrate	Per cent. of total N. in filtrate
1	0.1358	0.1227	90.4
2	0.2716	0.2357	86.8
4	0.5432	0.4729	87.1
8	1.0864	0.8103	74.6

EXPERIMENT II.

Solubility in Flasks.—Samples of 2, 4, 8, 17 and 32 grams of granulated Cyanamid were placed in Erlenmeyer flasks and each covered with 400 cc. of distilled water at 25° C. The flasks were stoppered, and allowed to stand 24 hours, with occasional shaking. They were filtered through dry filters without washing and nitrogen was determined in each filtrate, with the following results:

Sample grams	Grams of N. in sample	Grams of N. in filtrate	Per cent. of total N. in fillrate
2	0.2716	0.2548	93.9
4	0.5432	0.5102	93.9
8	1.0864	1.0119	93.1
16	2.1728	2.0087	92.5
32	4.3456	3.9588	91.1

EXPERIMENT III.

Rate of Solution in Flasks.—In each of five flasks was placed 2 grams of granulated Cyanamid and 250 cc. distilled water at 25° C. Each flask was shaken for 10 minutes continuously, after addition of the sample, and then only occasionally. After filtration without washing, nitrogen was determined in the filtrate. The following results were obtained:

Time	Gram of N. in sample	Gram of N. in filtrate	Per cent. of total N. dissolved
10 minutes	0.2716	0.2055	75.6
30 "	0.2716	0.2298	84.6
2 hours	0.2716	0.2403	88.5
6 "	0.2716	0.2433	89.6
24 "	0.2716	0.2480	91.3

Neutral Permanganate Method.—One of the permanganate availability methods formerly much used is the neutral permanganate method described in Bureau of Chemistry, U. S. Department of Agriculture, Bulletin 107, page 10. In this method a sample of fertilizer containing about 0.075 grams of nitrogen is digested for 30 minutes on a water or steam bath with 125 cc. of potassium permanganate solution containing 2 grams of potassium permanganate. It is then diluted with 100 cc. cold water and filtered and washed until the total filtrate amounts to 400 cc. The nitrogen is determined in the residue; the percentage of nitrogen removed is called the availability. To obtain the effect of the potassium permanganate this method was used, first, with 125 cc. of distilled water in place of the permanganate, and second, with the 125 cc. of permanganate solution.

	Per cent.
Availability with water in place of permanganate	94.34
Availability with permanganate	87.54

Since the only difference in the above experiments was the absence of the 2 grams of potassium permanganate in the first run, it is evident that potassium permanganate has the effect of converting about 7 per cent. of the total nitrogen into insoluble compounds.

Alkaline Permanganate Method.—In this method the availability is measured by the amount of ammonia that is formed and distilled from an alkaline permanganate solution. An amount of sample containing 0.045 grams of nitrogen is digested below the boiling point with 100 cc. of solution containing 15 grams of sodium hydroxide and 1.6 grams of potassium permanganate, for thirty minutes. It is then boiled and the distillate collected until 85 cc. is obtained. The percentage of nitrogen distilled over as ammonia represents the availability. In order to learn the effect of each reagent a run was made by this method using, first, 100 cc. of distilled water in place of the alkaline permanganate solution; second, a run was made with 15 grams of sodium hydroxide in 100 cc. of solution, and a third run was made with both sodium hydroxide and potassium permanganate in 100 cc. solution. The results were as follows:

	Per cent.
Availability with water alone	13.79
Availability with water and sodium hydroxide	53.90
Availability with water and sodium hydroxide and potassium permanganate	4.75

This experiment shows that the nitrogen in Cyanamid is only slowly converted into ammonia by the action of boiling water alone, and that it is much more rapidly converted into ammonia in the presence of sodium hydroxide. By the action of potassium permanganate, however, the formation of ammonia is almost completely prevented, even in the presence of sodium hydroxide.

Hence, in the above methods the addition of potassium permanganate has the opposite effect from what was intended to be the function of potassium permanganate, namely to make insoluble compounds soluble and to convert complex compounds to the ammonia form. In the case of Cyanamid, the neutral permanganate method makes some water-soluble compounds insoluble, and the alkaline permanganate method practically prevents the formation of any ammonia.

The method which is lately coming into favor is the modified alkaline permanganate method adopted by the Agricultural Experiment Stations of New York, New Jersey and the New England States on March 4, 1911.

Modified Alkaline Permanganate Method.—This differs from the other methods in that an amount of sample equivalent to 0.050 grams of nitrogen is first washed on a filter with distilled water at room temperature until 250 cc. of filtrate is obtained. This is intended to remove all the water-soluble nitrogen. As a matter of fact, it removes about 87 per cent. out of a possible 94 per cent. of water soluble nitrogen in a low-grade Cyanamid, and about 89 per cent. out of a possible 96 per cent. in a high-grade Cyanamid. The "insoluble" residue is digested for thirty minutes in a flask with 120 cc. of solution containing 2.5 grams potassium permanganate and 1.5 grams sodium hydroxide, and the ammonia is then distilled by boiling until 95 cc. of distillate is obtained. The sum of the percentage of water soluble nitrogen and of nitrogen in the distillate represents the availability. By this method the sample used in these experiments gave 90.20 per cent. availability.

C. S. Cathcart, State Chemist at the New Jersey Agricultural Experiment Station, made some experiments with samples of powdered Cyanamid, using the regular modified alkaline permangate method, with the following results.

Sample number	284 Per cent.	285 Per cent.	294 Per cent.	295 Per cent.	308 Per cent.
Qualitative test for nitrates	none	none	none	none	none
Total nitrogen	15.76	13.57	13.29	14.00	16.40
Nitrate and ammoniacal (Ulsch-Street)	6.98	5.53	3.50	4.72	7.32
Ammonia salts (magnesia)	0.92	0.57	0.45	0.55	0.91
Water soluble (total)	14.15	11.93	12.23	12.88	14.67
Water insoluble	1.25	1.64	1.06	1.12	1.73
Active insoluble (distilled from alkaline permanganate)	0.17	0.17	0.25	0.32	0.33
Inactive insoluble	1.08	1.47	0.81	0.80	1.40
Total nitrogen as water soluble and active insoluble	93.1	89.2	93.4	94.3	91.5

It is interesting to note that as much as 40 per cent. of the Cyanamid nitrogen is converted to ammonia by the reducing action of the iron and sulphuric acid used in the Ulsch-Street method.[1] The amount of ammoniacal nitrogen originally present is shown by magnesia distillation to be from 3 to 6 per cent. of the total nitrogen. The qualitative test showed no nitrates present.

The water-soluble nitrogen with one washing of 250 cc. distilled water is from 87 to 92 per cent. of the total, the average being 90.6 per cent. By treatment with alkaline permanganate the available nitrogen is found to be 92.5 per cent. as an average of the five samples.

In order to determine the effect of a more thorough initial washing, Cathcart repeated the availability experiments wash-

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[1] For Ulsch-Street Method see U. S. Dept. of Agr. Bureau of Chem., Bul. 107., or Wiley's Principles and Practice of Agricultural Analysis, Vol. 1, p. 445.

ing each sample three times with 250 cc. water each time. The following results were obtained:

Sample number	284 Per cent.	285 Per cent.	294 Per cent.	295 Per cent.	308 Per cent.
Total nitrogen	15.76	13.57	13.29	14.00	16.40
Soluble nitrogen, 1st 250 cc.	14.71	12.13	11.89	12.78	14.50
“ “ 2nd “	0.08	0.32	0.32	0.32	0.49
“ “ 3rd “	0.12	0.12	0.12	0.08	0.33
Total soluble nitrogen	14.91	12.57	12.32	13.18	15.32
Active insoluble nitrogen	0.14	0.22	0.23	0.22	0.31
Inactive “ “	0.71	0.78	0.73	0.60	0.77
Total nitrogen as water soluble and active insoluble	95.5	94.3	94.5	95.7	95.3

It is seen that with this change in the procedure the water-soluble nitrogen averages 93.5 per cent. and the total available 95.1 per cent.

The percentage of available nitrogen revealed by the modified alkaline permanganate method is practically a question of the solubility and the rate of solution of Cyanamid nitrogen in the initial washing with distilled water. The influence of size of sample and of rate of solution is shown in the preliminary experiments on page 96. It is evident that to determine the true amount of water-soluble nitrogen in Cyanamid by the modified alkaline permanganate method a longer period of contact should be allowed between sample and solvent in the initial washing, or more solvent should be used. The simplest way would be to let the sample stand in a flask with distilled water for 24 hours and filter, or to agitate on a shaking machine for about three hours.

Whether or not the availability determined by the permanganate methods corresponds with the fertilizer efficiency of Cyanamid is a question principally of determining what the fertilizing efficiency is, since the permanganate methods are easily carried out in the laboratory. The concensus of opinion seems to be that Cyanamid has about the fertilizing value of sulphate of ammonia, and this is about 95 per cent. of the efficiency of nitrate of soda, as an average of all kinds of conditions, favorable and unfavorable, that might occur in agricultural practice. Both sulphate of ammonia and nitrate of soda, however, show an availability of 100 per cent. by the permanganate methods, while Cyanamid shows about 87 to 89 per cent. by the neutral permanganate method, 4 to 8 per cent. by the alkaline permanganate method, 90 to 94 per cent. by the modified alkaline permangante method, and 94 to 96 per cent. by simple solution in water for 24 hours. The neutral and the modified alkaline methods therefore approximate to a certain extent the values that they should represent, the straight alkaline method is wholly unsuitable, while the simple solution in water gives the most significant results.

CHAPTER XII.

Fire and Water Hazard of Cyanamid.

The combustibility of Cyanamid and its susceptibility to damage by fire and water have been thoroughly investigated by the Underwriters' Laboratories of Chicago, Ill. The following results were obtained through the courtesy of Mr. A. H. Nuckolls, Chemical Engineer, of the Underwriters' Laboratories, and are a part of the report prepared for the information of fire insurance companies:

"The object of the investigation was to determine the nature of recommendations to be made relative to issuance of an opinion upon the fire hazard of the product. This report does not deal with the hazards of mixtures of this product with other fertilizers."

"**Test for Flammable Gases.**—Tests for flammable gases were conducted by placing about 5 pounds of the product in a large bottle, about 6 inches internal diameter by 16 inches in height, and adding an excess of water. The bottle was provided with a loose fitting stopper to which wires were attached for producing an electric spark inside of the bottle. The spark was produced at intervals of about 15 minutes at the beginning of the test. The bottle was allowed to stand for 10 days, the spark being produced about every 3 to 4 hours except during the night. The test was repeated employing a gas testing flame instead of the electric spark and also varying the proportions of gas and air.

"No analysis of the gas evolved was conducted. . . . Mixtures of air with gases evolved when test samples were treated with water did not ignite or burn when brought into contact with electric spark and gas flame."

"**Spontaneous Heating Tests.**—*Acceleration Test.*—This test was conducted by means of an apparatus consisting essentially of a wire gauze cylinder about 1½ inches in diameter and 6 inches long, which is surrounded by a double-jacketed copper water-bath provided with a tight fitting top or lid, a thermometer and inlet and outlet tubes to admit air. The sample was placed in the wire gauze cylinder, and the thermometer inserted so that its bulb was within the sample near its center. The temperature of the bath was maintained at 100° C. for 4 weeks. For the first 6 hours of the test, temperature readings were taken every half hour. Afterwards, readings were taken twice daily until the test was concluded.

"The thermometer showed that the internal temperature of the sample remained at approximately 100° C. during the tests."

"**Test with Water.**—About 10 pounds of the product were placed in a wooden cylinder, approximately 10 inches in height, and 10 inches internal diameter, the walls of the cylinder being about 1 inch in thickness. The temperature of the sample was allowed to become the same as that of the room, and then about 4 pounds of water, the temperature of which was observed, were added with stirring. The mixture was then allowed to stand and its temperature observed for a period of about a week.

Test started at 10.30 A. M.	Degrees C.
Temperature of room during test, about	18
" " water at start	18
" " test sample of product at start	17
" " mixture at 11.00 A. M., about	20

"No material rise in the temperature of the mixture was observed."

"**Acid Tests.**—One pound samples of the product were treated with concentrated hydrochloric, sulphuric, and nitric acids and the results observed.

"The acids reacted readily with the samples with considerable evolution of heat, compounds of these acids and lime being produced, and the Cyanamid ($CaCN_2$) was also attacked and decomposed. No combustion or explosive action took place."

"**Behavior of Product when Heated.**—Two 20-gram test samples were heated in a large porcelain dish by means of a Bunsen burner. The heat was gradually increased until the temperature of the samples was above a bright red heat. During the test a small gas-testing flame was constantly applied to the samples.

"At the start oil vapors were given off but not in sufficient quantity to form a flame. The samples were decomposed but no material amount of combustion occurred."

"**Test with the Oil Used.**—A sample of oil employed in the manufacture of Cyanamid was obtained directly from the manufacturer. Small samples of the oil were also obtained from the product by extraction with petroleum ether.

"*Specific Gravity.*—Specific gravity was obtained roughly by means of a Bé. hydrometer. The specific gravity was found to be approximately 30° Bé. at 19° C.

"*Flashing Point.*—The flashing point was determined with the Pensky-Martens tester, the standard method of test with this apparatus being followed. The flashing point was found to be 150° C. (221° F.) closed cup.

"*Evaporation.*—An evaporation test was conducted by heating about ½ gram of a sample of the soil, spread out on a watch-glass, for 5 hours at 100° C. in an ordinary oven and determining the loss of weight of the sample. The loss by evaporation was found to be 1.1 per cent. by weight in 4 hours.

"*Spontaneous Heating.*—This test was conducted by heating 14 grams of the oil, disseminated over 7 grams of cotton, at a temperature of 100° C. for 48 hours in an apparatus consisting essentially of a wire gauze cylinder, about 1½ inches in diameter and 6 inches long, surrounded by a double-jacketed copper water-bath provided with a tight fitting top, thermometer, inlet and outlet tubes to admit air. The oiled cotton was placed in the wire gauze cylinder, and the thermometer inserted so that its bulb was within and near the center of the oiled cotton. Observations were made to note if any difference between the temperature of the sample and the water-bath occurred.

"The internal temperature of the test sample remained slightly below 100° C. during the first 5 hours of heating, and never exceeded 100° C. the temperature of the surrounding bath."

"**General Behavior when Treated with Water.**—A stream of water at about 75 pounds pressure from a ½ inch nozzle was applied to a bag for 15 minutes, the stream being directed so as to wet the entire external surface of the bag. The bag was then allowed to stand about a week, and an average sample was analyzed according to the method of Gunning.

"The sample did not readily absorb water, owing to the presence of oil which retarded immediate contact of the water with the lime-nitrogen compound. Water was, however, gradually absorbed with a very slow evolution of gas in small quantity. A marked odor of ammonia was noted. When allowed to dry in air, the sample hardened to some extent, or in other words 'caked.' This 'caking' was in a measure due to absorption of carbon dioxide from the air.

	Per cent.
Nitrogen in sample before wetting	14.44
Nitrogen in sample after wetting	13.10
Apparent loss of nitrogen	1.34

The following conclusions were drawn with regard to the fire and water hazard of Cyanamid:

"It is readily decomposed by high temperatures, and also by mineral acids which attack it somewhat violently with the evolution of considerable heat. Its decomposition by water is not accompanied by a material rise in temperature or the formation of hazardous products in dangerous quantity. It is not liable to spontaneous ignition.

"The product is non-flammable, and is not combustible to a material extent. The product is decomposed by high temperatures such as are produced in burning buildings. It will be noted that a relatively small amount of oil (4.2 per cent.) and carbon 13.25 per cent.) are present. The high temperature to which the free carbon is subjected in the electric furnace renders it sufficiently graphitic to be difficulty combustible.

"The product is susceptible to damage to a material extent by fire or water. The product does not readily take up water, and is not a good conductor of heat. In case of fire it will, therefore, probably be only partially damaged by the heat and water.

"The product is considered non-hazardous except in respect to susceptibility to damage by fire and water."

In the process of manufacture, the cans containing the crude calcium cyanamide are withdrawn from the nitrifying ovens at a temperature of more than 1,000° C., and are allowed to cool in the open air, without noticeable injury to the calcium cyanamide.

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