CYANAMIDES

1. Introduction

It has been suggested that under primordial conditions, cyanamide could have acted as the original peptide-forming and phosphorylating reagent at the beginning of life on earth (1). In 1893, Henri Moissan observed that calcium carbide absorbed atmospheric nitrogen. The resulting compound was subsequently identified as calcium cyanamide. The process was perfected by Frank and Caro in Germany in 1903 and was adopted worldwide almost immediately. It was the first commercial process used to fix atmospheric nitrogen, and production of calcium cyanamide began in 1905 in Europe and 1907 in North America. Calcium cyanamide [156-62-7], $CaNC{\equiv}N$, was first produced commercially around 1900 as fertilizer. A commercial process for manufacturing a pure grade of cyanamide was introduced in 1964. Later, numerous derivatives were developed, the most

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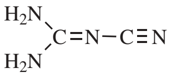
important of which are dicyandiamide (dimer) and melamine (trimer). However, its use in fertilizer has been replaced by ammonia and melamine is made princially by a petrochemical process. Structural formulas of cyanamide, CH_2N_2 (**1**), and its dimer $C_2H_4N_4$ (**2**), and trimer $C_3H_6N_6$ (**3**), are given as follows:

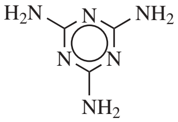
$H_2NC{\equiv}N$

(**1**)



$(H_2N)_2C{=}N{-}C{\equiv}N$

(**2**)



(**3**)

2. Cyanamide

2.1. Properties. Cyanamide [420-04-2], also called carbamodiimide or carbamic acid nitrile, crystallizes from a variety of solvents as somewhat unstable, colorless, orthorhombic, deliquescent crystals (2). Dimerization is prevented by traces of acidic stabilizers such as monosodium phosphate and by storage at low temperature.

The ir spectrum of cyanamide exhibits an intense, poorly resolved doublet at $2225 - 2260\ \mathrm{cm}^{-1}$. The uv spectrum shows only weak absorption below 230 nm, with no maximum observable above 208 nm. Studies of the infrared and Raman spectra (3) support the *N*-cyanoamine structure, $H_2N{-}C{\equiv}N$. The properties of cyanamide are listed in Table 1.

Table 1. **Properties of Cyanamide**

Property	Value	References
molecular weight	42.04	
mp, °C	46	5
bp, °C		
101 kPa[a]	dec	
2.47 kPa[a]	140	
75 Pa[a]	85–87	
density[b], g/mL	1.282	4
refractive index at 48°C	1.4418	
vapor pressure, up to 393 K	$\log \mathrm{kPa}^{a} = \frac{-3.58 \times 10^3}{K} + 8.91$	(4,6)
infrared spectrum, cm^{-1}	2225–2260	
dissociation constants		
K_a	5.4×10^{-11}	7
K_b	2.5×10^{-12}	8
specific heat at 0–39°C, J/(g K)[c]	2.288	9
heat of formation at 25°C, kJ/mol[c]	58.77	10
heat of solution[d] at 15°C, kJ/mol[c]	−15.05	11
heat of combustion at 25°C, kJ/mol[c]	−737.9	10
heat of neutralization[e], kJ/mol[c]	15.48	12

[a] To convert kPa to mm Hg, or Pa to μm Hg, multiply by 7.5.

[b] Calculated.

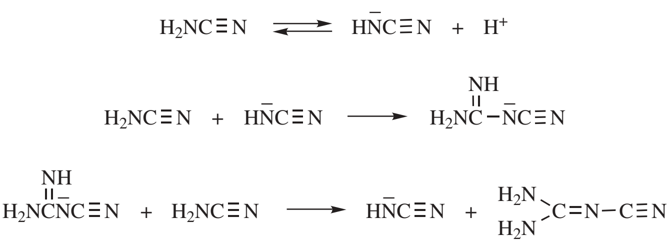
[c] To convert J to cal, divide by 4.184.

[d] In 1000 parts H_2O.

[e] Excess NaOH solution.

Cyanamide is a weak acid with a very high solubility in water. It is completely soluble at 43°C, and has a minimum solubility (eutectic) at −15°C. It is highly soluble in polar organic solvents, such as the lower alcohols, esters, and ketones, and less soluble in nonpolar solvents (4).

2.2. Reactions. Reactions of cyanamide are either additions to the nitrile group or substitutions at the amino group. Both are involved in the dimerization to dicyandiamide.



$$H_2NC{\equiv}N \rightleftharpoons H\bar{N}C{\equiv}N + H^+$$

$$H_2NC{\equiv}N + H\bar{N}C{\equiv}N \longrightarrow H_2N\overset{NH}{\overset{\|}{C}}-\bar{N}C{\equiv}N$$

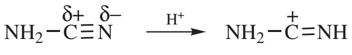
$$H_2N\overset{NH}{\overset{\|}{C}}\bar{N}C{\equiv}N + H_2NC{\equiv}N \longrightarrow H\bar{N}C{\equiv}N + \begin{matrix}H_2N\\H_2N\end{matrix}\!\!>\!C{=}N-C{\equiv}N$$

Dimerization involves addition of the cyanamide anion to the nitrile group of an undissociated molecule to give the anion of cyanoguanidine, or dicyandiamide. This reaction takes place most readily at pH 8–10 where the reactants are present in favorable proportion. The product is a weaker acid than cyanamide and is protonated at once with generation of a new cyanamide anion.

Most of the reactions occurring at the amino group of the cyanamide molecule require the anionic species, $^{-}N{=}C{=}N^{-}$ or $HN^{-}C{\equiv}N$, sometimes in equivalent amount and occasionally as provided by base catalysis. Therefore, the process conditions for dimerization should be created to avoid the use of any metal salt, such as monosodium phosphate (4).

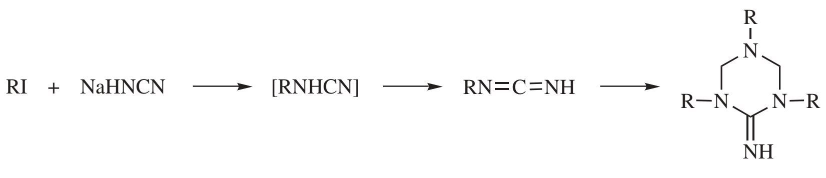
Similarly, nucleophilic reagents are suitable for addition reactions only if they are not so strongly basic as to produce the cyanamide anion in large amounts. In such cases, dicyandiamide is produced or a cyanamide salt is obtained. *N,N*-Disubstituted cyanamides do not ionize, of course, and react easily with strongly basic nucleophiles.

With nitriles in general, addition reactions take place readily in the presence of acids, because of the enhanced electrophilic character of the central carbon atom in the conjugate acid:



$$NH_2-\overset{\delta+}{C}{\equiv}\overset{\delta-}{N} \xrightarrow{H^+} NH_2-\overset{+}{C}{=}NH$$

Substitutions. The cyanamide anion is strongly nucleophilic and reacts with most alkylating or acylating reagents (4); addition to a variety of unsaturated systems occurs readily (4). In some cases, a cyanamide salt is used; in others, base catalysis suffices. Ethyl iodide reacts with sodium hydrogen cyanamide [17292-62-5] to form a trisubstituted isomelamine.



Alkylation with a variety of common alkyl halides or sulfates gives stable dialkylcyanamides. However, the intermediate monoalkylated compounds usually cannot be isolated and cyclic trimers or cotrimers with cyanamide are obtained (13). The reaction can be carried out efficiently in water or alcohol. Allyl chloride is an especially useful reagent, producing diallylcyanamide [538-08-9] (4).

$$\begin{aligned} NaHNCN + 2\,CH_2{=}CHCH_2Cl + NaOH \longrightarrow\ & (CH_2{=}CHCH_2)_2NCN \\ & + 2\,NaCl + H_2O \end{aligned}$$

The amino group in cyanamide is very reactive toward formaldehyde. The reaction produces first an unstable hydroxymethyl derivative that resinifies more or less rapidly, passing through a water-soluble stage which permits various applications. This product can be dried and thermoset. The reactions leading to resinification include condensation to give methylene and methyl ether bridges, hydration of the cyano group if acidic conditions are used, and polymerization of cyanamide residues to give dicyandiamide, melamine, or possibly isomelamine structures (see AMINO RESINS AND PLASTICS).

Cyanogen chloride and NaOH give the potentially useful sodium dicyanamide [1934-75-4] salt (14).

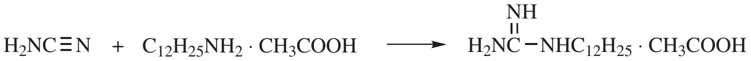
$$NH_2CN + ClCN + 2\,NaOH \longrightarrow NaN(CN)_2 + NaCl + 2\,H_2O$$

Other substitution reactions have been described with ketones, epoxides, anhydrides, acyl halides, amides, and imidates, among others (4).

Additions. The addition reactions of ammonia and amines to the cyanamide nitrile group have been thoroughly studied (15). For optimum conditions, the reaction should be carried out in an aqueous medium at about 140°C. Gradual addition of the cyanamide to the amine salt minimizes dimerization.

A great variety of amino compounds have been used (4). The two examples given below have practical applications. In many cases it is advantageous to use anhydrous cyanamide in alcoholic solvents.

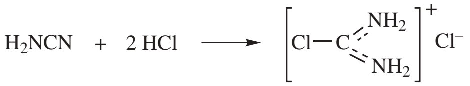
$$H_2NC{\equiv}N + NH_4NO_3 \longrightarrow H_2N\overset{\overset{\displaystyle NH}{\|}}{C}{-}NH_2 \cdot HNO_3$$



$$H_2NC{\equiv}N + C_{12}H_{25}NH_2 \cdot CH_3COOH \longrightarrow H_2N\overset{\overset{\displaystyle NH}{\|}}{C}{-}NHC_{12}H_{25} \cdot CH_3COOH$$

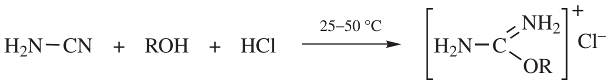
Uses of such guanidine derivatives depend on their strongly basic character and the cationic character of the salts. For example, 2-aminopyrimidine (guanidine derivative) is used in sulfa drugs, guanidine nitrate is used in the production of nitroguanidine (raw material for making explosives), and dodecylguanidine acetate is used as a fungicide (4).

Hydrogen chloride gives a dihydrochloride. Chloroformamidine hydrochloride [29671-92-9] is a convenient anhydrous form of cyanamide that is easily handled and stored (16).



$$H_2NCN + 2\,HCl \longrightarrow \left[Cl{-}C(NH_2)_2\right]^+ Cl^-$$

Addition of alcohols and phenols in the presence of anhydrous hydrogen chloride gives *O*-substituted pseudourea salts (17). The reaction is sluggish except with the lower alcohols, and long reaction time and temperatures up to 100°C are required to obtain good yields.



$$H_2N{-}CN + ROH + HCl \xrightarrow{25\text{–}50\ °C} \left[H_2N{-}C(NH_2)(OR)\right]^+ Cl^-$$

2.3. Manufacture. *Calcium cyanamide* can be manufactured by either the *Frank–Caro batch oven process* (18,19) or continuous processes such a rotary furnace developed by Suddeutsche Kalkstickstoff Werke (SKW) in Trotsberg, Germany (20). In both processes the carbide is first ground to a powder in a ball or rod mill. The charge is further prepared by the addition of 1–2% fluorspar (CaF_2) and recycled calcium cyanamide. The cyanamide dilutes the carbide, thereby preventing a temperature rise that would tend to decompose cyanamide. *Fluorspar* helps promote cyanamide conversion at lower temperatures.

The batch oven consists of a steel shell (2 m diameter and 4.5 m height), lined with a powder insulation and firebricks. It has several gas ports connected to a low-pressure nitrogen supply (25–50 mm w.c.). The prepared carbide charge (about 4 t) is placed in the oven from a special bottom unloading charge container. This container is positioned above with an overhead crane. After charging, a cover is placed on the oven, the nitrogen supply turned on, and a starting electrode inserted to heat a portion of the charge to initiate the reaction. After initiation, the exothermic reaction is self-sustaining. During the reaction the contents sinter to a block or pig. The reaction is completed after 5 days, at which time the fused ingot is removed, cooled, and milled to a powder.

In a continuous nitrogenation process used by SKW in Germany, the kiln is about 20 m long and 2.5 m in diameter. Ground carbide, fluorspar, and calcium cyanamide are mixed with nitrogen and the reaction proceeds. The average residence time of solids in the kiln is 5–6 h. The resulting reaction product is granular or powder, which is then transferred to a cooling drum. The heat released by the reaction is sufficient to bring the starting materials to the desired temperature of 1000–1100°C (21). After the furnace has been started, it can remain in operation without external heating for many months. Kiln capacity is 25 d fixed nitrogen.

To produce a fertilizer grade, water is then added to cyanamide powder to slake unreacted calcium carbide and hydrate free calcium oxide. The wetted cyanamide is processed through a rotating granulating drum to form small balls, which are then hardened in a rotary dryer. The granules are then screened to remove oversize and dust, which are recycled to hydration stage.

2.4. Shipment and Handling.

Granular-grade calcium cyanamide for fertilizer is packaged in 25- or 50-kg bags. Cyanamide is sold anhydrous or as 50% aqueous solution. The solution is stored at refrigerated temperatures with a pH stabilizer to prevent the exothermic polymerization to dicyandiamide. Dicyandiamide powder is sold in bags.

Cyanamide solution dimerizes to dicyandiamide and urea with the evolution of heat and a gradual increase in alkalinity accelerating the reaction. Storage above 30°C without pH stabilizer leads to excessive dimerization and can result in violent exothermic polymerization. Cyanamide should be stored under refrigeration and the pH tested periodically. Stabilized cyanamide can be kept at ambient temperature for a few weeks.

In general, cyanamide should be added to a reaction mixture at such a rate that it is used up as it is added, otherwise a high concentration of cyanamide results which could react violently.

2.5. Economic Aspects.

Generally worldwide production of *calcium cyanamide* has declined since reaching peaks in the 1960s. The major producers of Calcium cyanamide worldwide are listed in Table 2.

Calcium cyanamide production has fallen from a 1960s peak of 1300 to about 320×10^3 t/yr at the time of writing (Table 3). Cheaper ammonia based fertilizers is the main reason for decline, as well as melamine (trimer of cyanamide) now being produced from urea sources instead of from cyanamide.

Cyanamid Canada in Niagara Falls, Canada was the only North American producer of calcium cyanamide and its derivatives (*dicyandiamide*, hydrogen cyanamide, and calcium cyanide) prior to plant closure in 1992. Use of cyanamide as a fertilizer was discontinued in the 1960s, when cyanamide was replaced by less expensive ammonia-based fertilizers. Melamine production from dicyandiamide was also discontinued about 1970 and replaced by plants producing melamine from urea.

Calcium cyanamide and some derivatives are also produced in Japan (Table 3). The fertilizer market is mature and not expected to change significantly.

Polifin in Witbank (South Africa) manufactures calcium cyanamide from carbide as an intermediate in the production of calcium cyanide, for use in gold refining.

Table 2. **Calcium Cyanamide Producers**[a]

	Cyanamide products produced			
Producer	Cyanamide fertilizer	Dicyandiamide	Cyanamide solutions	Calcium cyanide
SKW, Trotsberg, Germany	Yes	Yes	Yes	
Odda Smeltverk AS, Odda, Norway	Yes	Yes		
Polifin, Witbank, South Africa				Yes
Shin-Etsu Kasei, Japan	Yes			
Denki Kagaku Kogyo, Japan	Yes			
Nippon Carbide, Japan	Yes	Yes	Yes	
China	Yes	Yes		

[a] Author's estimate.

Table 3. **Historical Trends of Calcium Cyanamide Production 10^3 t/yr**[a,b]

Region	1960	1980	1997
North America (Canada)	200	40	
Europe	435	340	188
Japan	650	300	104
South Africa	15	20	25
Total	*1300*	*700*	*317*

[a] Excluding China.
[b] Author's estimate.

2.6. Specifications and Analysis. Standards do not exist go for calcium cyanamide or derivatives. Calcium cyanamide can be analyzed by determining nitrogen content using combustion–conductivity or a kjeldahl method. Typical analysis of carbide and cyanamide is presented in Table 4.

2.7. Environmental Concerns. *Calcium cyanamide* production generates some particulate emission that can be controlled by fabric filters. The production of cyanamide from calcium cyanamide results in a calcium carbonate, carbon slurry. The solids, referred to as *diamide lime*, can be recovered, dried, and used as an additive in carbide desulfurization reagent; otherwise they are landfilled in a lagoon.

2.8. Health and Safety Factors. Manufacture of cyanamide and calcium cyanamide does not present any serious health hazard. Ingestion of alcoholic beverages by workmen within several hours of leaving work sometimes results in a vasomotor reaction known as cyanamide flush. Cyanamide interferes with the oxidation of alcohol and accumulation of acetaldehyde probably accounts for this temporary phenomenon. Although extremely unpleasant, it has not been known to result in serious illness or to have any permanent effect.

Commercial grades of calcium cyanamide contain lime and are moderate skin irritants where contact is repeated or prolonged.

Table 4. **Typical Analysis**

	Calcium carbide	Calcium cyanamide fertilizer	Cyanamide 50% solution
CaC_2	79.0		
CaO	13.2	12.7	
C	0.7	12.8	
$CaCN_2$		60.0	
H_2CN_2			50.0
CaF_2		0.6	
Dicyandiamide			1.5
CaS	0.9	0.8	
Mineral impurities (Al_2O_3,SiO_2,MgO,FeSi)	6.2	4.9	
Nitrogen impurities		1.5	0.2
H_2O		6.7	46.3
NaH_2PO_4 (stabilizer)			2.0

Contact or ingestion of cyanamide must be avoided, and precautions taken to prevent inhalation of dust or spray mist. In rat studies cyanamide-100 toxicity ranges from a single oral dose LD_{50} of 280 mg/kg to a single dermal dose LD_{50} of 590 (420–820) mg/kg. The compound is, therefore, considered to be moderately toxic both by ingestion in single doses and by single-skin applications. An aqueous paste of the product is corrosive to rabbit skin. Small quantities of the dry product produced severe irritation when introduced into the conjunctival sac of the rabbit eye.

Cyanamide-50 is considered to be slightly toxic by ingestion in single dose and moderately toxic by single-skin applications. The degree of irritation to rabbit skin and eye produced by this product is only slightly less than that observed with Cyanamide-100.

2.9. Uses. The most important use of calcium cyanamide is as fertilizer, but it is also effective as a herbicide and defoliant. It was used as a starting material for ammonia until it was displaced by the Haber process. Several derivatives of calcium cyanamide have also been developed: hydrogen cyanamide (intermediate for insecticides, pharmaceuticals, soil sterilants), dicyandiamide (intermediate for flame and fire retardants, viscosity reducers for glues and adhesives, nitrification inhibitors in fertilizers), melamine (thermoset plastic), and calcium cyanide (gold extraction and fumigant). Calcium cyanamide production has fallen from a 1960s peak of 1300 to about 320 10^3 t/y today (excluding China). The use of cheaper ammonia-based fertilizers is the main reason for decline, as well as melamine, which is now being produced from urea sources instead of from cyanamide. Producing countries include Norway, Germany, China, and Japan.

3. Dicyandiamide

3.1. Properties. Dicyandiamide (2) (cyanoguanidine [461-58-5]) is the dimer of cyanamide and crystallizes in colorless monoclinic prisms. It is amphoteric, and generally soluble in polar solvents and insoluble in nonpolar solvents. Its properties are listed in Table 5.

3.2. Reactions. The reactions of dicyandiamide resemble those of cyanamide. However, cyclizations take place easily and the nitrile group is less reactive. Under pressure and in the presence of ammonia, dicyandiamide cyclizes to

Table 5. **Properties of Dicyandiamide**[a]

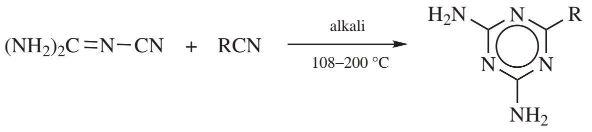
Property	Value
mol wt	84.08
mp, °C	208
bp, °C	dec
acid dissociation at 25°C, K_a	6×10^{-15}
specific heat at 25°C, J/(g · K)[b]	1.41
heat of formation at 25°C, kJ/mol[b]	24.9
heat of combustion at 25°C, kJ/mol[b]	−1382
heat of solution at 15°C, kJ/mol[b]	−24.1

[a] Ref. 40–42.

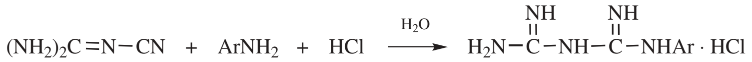
[b] To convert J to cal, divide by 4.184.

melamine. Considerable tonnages of melamine have been made in this manner; however, melamine is produced chiefly by the urea process (22).

Excellent yields of guanamines (23) are obtained when dicyandiamide is heated with alkyl or aryl nitriles in the presence of small amounts of alkali.



Heating with aromatic amines in water in the presence of an equivalent amount of mineral acid gives high yields of aryl biguanide salts (24).

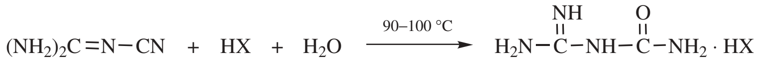


$$(NH_2)_2C{=}N{-}CN + ArNH_2 + HCl \xrightarrow{H_2O} H_2N{-}\overset{NH}{\overset{\parallel}{C}}{-}NH{-}\overset{NH}{\overset{\parallel}{C}}{-}NHAr\cdot HCl$$

Reaction with ammonium salts gives biguanide salts which react further with the ammonium salt forming guanidine salts. Guanidine nitrate [506-93-4] is manufactured by this route (25).

$$(NH_2)_2C{=}N{-}CN + 2NH_3\cdot HNO_3 \longrightarrow 2H_2N{-}\overset{NH}{\overset{\parallel}{C}}{-}NH_2\cdot HNO_3$$

Hydrolysis (26) of dicyandiamide occurs easily at elevated temperatures in the presence of an equivalent of mineral acid to yield guanylurea salts. This reaction is quantitative and can be used for the determination of dicyandiamide (27).



$$(NH_2)_2C{=}N{-}CN + HX + H_2O \xrightarrow{90\text{–}100\ ^\circ C} H_2N{-}\overset{NH}{\overset{\parallel}{C}}{-}NH{-}\overset{O}{\overset{\parallel}{C}}{-}NH_2\cdot HX$$

Dicyandiamide may be treated with formaldehyde (28) to produce resinous compositions of varying properties (see AMINO RESINS AND PLASTICS), under either acid or alkaline conditions. The reaction can be controlled to give mainly monomethyloldicyandiamide, a very water-soluble compound:

$$(NH_2)_2C{=}N{-}CN + HCHO \longrightarrow HOCH_2{-}NH{-}\overset{NH}{\overset{\parallel}{C}}{-}NH{-}CN$$

3.3. Manufacture. Dicyandiamide is manufactured by dimerization of cyanamide in aqueous solution. The 25% cyanamide solution produced as described above is adjusted to pH 8–9 and held at approximately 80°C for two hours to give complete conversion. The hot liquor is filtered and transferred to a vacuum crystallizer where it is cooled. The crystals of dicyandiamide are separated in continuous centrifuges and passed to rotary driers. The finished material is stored in bulk or in bags. The mother liquor is partly recycled to the cyanamide extraction system and partly purged to keep the thiourea content low. The process is environmentally safe. The process effluent discharges meet local government discharge guidelines. See Table 2 for Producers.

Table 6. **Typical Analysis of Commercial Dicyandiamide**

Assay	Value
dicyandiamide %	99.3
water, %	0.01
melamine, %	0.7
thiourea, ppm	200
heavy metals, ppm	10

3.4. Specifications, Analysis, and Toxicity. Dicyandiamide is identified qualitatively by paper chromatography and quantitatively by ultraviolet spectrometry of the chromatogram. More commonly, total nitrogen analysis is used as a purity control or the dicyandiamide is converted by hydrolysis to guanylurea, which is determined gravimetrically as the nickel salt (29). Methods based on the precipitation of silver dicyandiamide picrate are sometimes used (30). Dicyandiamide can also be titrated with tetrabutylammonium hydroxide in pyridine solution. Table 6 gives a typical analysis of a commercial sample. Dicyandiamide is essentially nontoxic. It may, however, cause dermatitis.

3.5. Uses. In 1893, Henri Moissan observed that calcium carbide absorbed atmospheric nitrogen. The resulting compound was subsequently identified as calcium cyanamide. The process was perfected by Frank and Caro in Germany in 1903 and was adopted worldwide almost immediately. It was the first commercial process used to fix atmospheric, nitrogen and production of calcium cyanamide began in 1905 in Europe and 1907 in North America. Dicyandiamide is used as a raw material for the manufacture of several chemicals, such as guanamines, biguanide and guanidine salts, and various resins. Since 1975, it has also been used in the manufacture of potassium or sodium dicyanamide which are used as insecticides and in chemotherapy. Melamine has extensive applications in the resin and plastic industry; guanamines are used as copolymers (qv) in many resin compositions. Guanidine phosphate [1763-07-1] is employed as a fire retardant in applications where water solubility is not a drawback.

Dicyandiamide, in conjunction with phosphoric acid, is used as a flame retardant for cellulosic materials (31). Cotton fabrics have also been treated effectively in this manner. Use as a fire retardant for wood, particularly shingles, has found commercial application (32).

Dicyandiamide reduces the viscosity of certain colloidal solutions. This property is of commercial significance in the manufacture of glues and adhesives, in the coating and sizing of paper and textiles, and in the conditioning of phosphate drilling muds (see PETROLEUM). This action may prove useful in other applications where control of viscosity is important (33).

Dicyandiamide fluidifies various adhesives and glues. In the presence of dicyandiamide, the initial viscosity of the adhesive formulations is lowered and maintained at a lower range for longer periods of time, thus preventing premature gelling and extending the useful life of the adhesive (see ADHESIVES).

Dicyandiamide, although completely stable at lower temperatures, has found use in surface coating formulations as a flame retardant. When exposed to a flame, the coating composition intumesces or bubbles up, thereby insulating the substrate. In this manner, the substrate retains its physical properties and strength. For example, one effective intumescent formulation includes 10 parts of dicyandiamide, 22 parts of pentaerythritol, 56 parts of monoammonium phosphate, 12 parts of titanium dioxide, 50 parts of latex binder (50% solids), and 33 parts of water. Such a formulation gives good foam volume at low coating weights, and reasonable stability of the foam structure under flaming (34) (see FOAMS).

Dicyandiamide has been marketed as a surface protective coating for printed circuit boards (35), in thermosetting resins (36), as an antistatic agent for cardboard and paper (37), for heat and light stabilization of PVC, retannage of various leathers (38), in improving adhesion of paints (39), as biocide, stabilizer of varnishes (40), and a curing agent for epoxy resins (41).

4. Melamine

Although melamine [108-78-1] (**3**) was prepared for the first time in 1834 by Liebig, almost a century passed before its properties and reactivity were thoroughly investigated. In the late 1930s a commercial process was developed. Since then, uses for melamine reaction products have been developed rapidly in a variety of fields, including plastics, surface coatings, bonding agents, paper and textile finishes, tanning agents, pharmaceuticals, and petroleum and rubber chemicals. Other names for melamine are cyanurotriamide, cyanuramide, and 2,4,6-triamine-1,3,5-triazine.

4.1. Properties.

The outstanding characteristic of melamine, usually a white crystalline matrial, is its insolubility in most organic solvents. This property is also evident in melamine resins after they are cured. On the other hand, melamine is appreciably soluble in water, its solubility increasing with increased temperature. The properties of melamine are listed in Table 7.

The chemistry of melamine has been reviewed (42,43). Melamine, although moderately basic, is better considered as the triamide of cyanuric acid than as an aromatic amine (see CYANURIC AND ISOCYANURIC ACIDS). Its reactivity is poor in nearly all reactions considered typical for amines. In part, this may be a result of its low solubility (see AMINO RESINS AND PLASTICS).

4.2. Manufacture.

Dicyandiamide is converted into melamine by heating. Simple pyrolysis above the melting point leads to an exothermic reaction;

Table 7. **Properties of Melamine**[a]

Property	Value
molecular weight	126.13
mp, °C	350
density, g/mL	1.573
specific heat at 25°C, J/(g · K)[b]	1.23
heat of combustion at 25°C, kJ/mol[b]	−1964
heat of sublimation, kJ/mol[b]	−121

[a] Ref. 42.

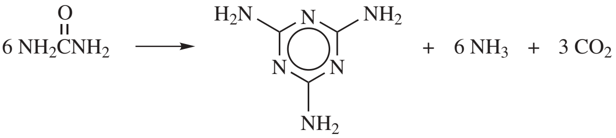
[b] To convert J to cal, divide by 4.184.

however, deammoniation occurs, forming products containing two or three triazine rings as well as melamine. After it was discovered in 1940 that deammoniation can be counteracted by conducting the reaction under ammonia pressure, various methods were developed to control the exothermic reaction on an industrial scale.

Dicyandiamide is used as a nitrification inhibitor and a fire retardant, and in the manufacture of epoxy and other resins.

By now the dehydration condensation of urea [57-13-6] has displaced the dicyandiamide process (see UREA). Although the latter is still used occasionally, the urea process predominates in North America. A flow sheet is shown in Figure 1 (43).

A urea melt is supplied to a one-stage reactor containing a fluid-bed catalyst. The reactor is heated internally by circulating molten salt. Upon entering the reactor, the urea is converted to melamine by the hot catalyst.



The hot ammonia used as carrier gas serves simultaneously as fluidizing agent and inhibits deammonization.

The reactor effluent is rapidly quenched with aqueous mother liquor in specially designed equipment operating at pressures essentially equal to the reactor pressure. This operation yields an off-gas consisting of ammonia and carbon dioxide vapor and a crystalline melamine slurry saturated with ammonia and carbon dioxide. The slurry is concentrated in a cyclone mill. The mother liquor overflow is returned to the quenching system. The concentrated slurry is redissolved in the mother liquor of the crystallization system, and the dissolved ammonia is stripped simultaneously.

This ammonia is recycled to the reactor via a compressor and a heater. Liquid ammonia is used as reflux on the top of the absorber. The net amount of carbon dioxide formed in the reactor is removed as bottom product from the absorber in the form of a weak ammonium carbamate solution, which is concentrated in a desorber-washing column system. The bottom product of this washing column is a concentrated ammonium carbamate solution which is reprocessed in a urea plant. The top product, pure ammonia, is liquefied and used as reflux together with liquid makeup ammonia. The desorber bottom product, practically pure water, is used in the quench system in addition to the recycled mother liquor.

In order to upgrade the melamine, the solution obtained after prethickening and stripping is treated with activated carbon passed over a clarifying filter and fed to a two-stage vacuum crystallization system from which the pure melamine is recovered in a continuous centrifuge. Stainless steel is used as construction material for nearly all parts of the equipment exposed to product streams.

4.3. Analysis and Toxicity. Melamine is determined gravimetrically by precipitation of the insoluble oxalate from a hot aqueous solution (42).

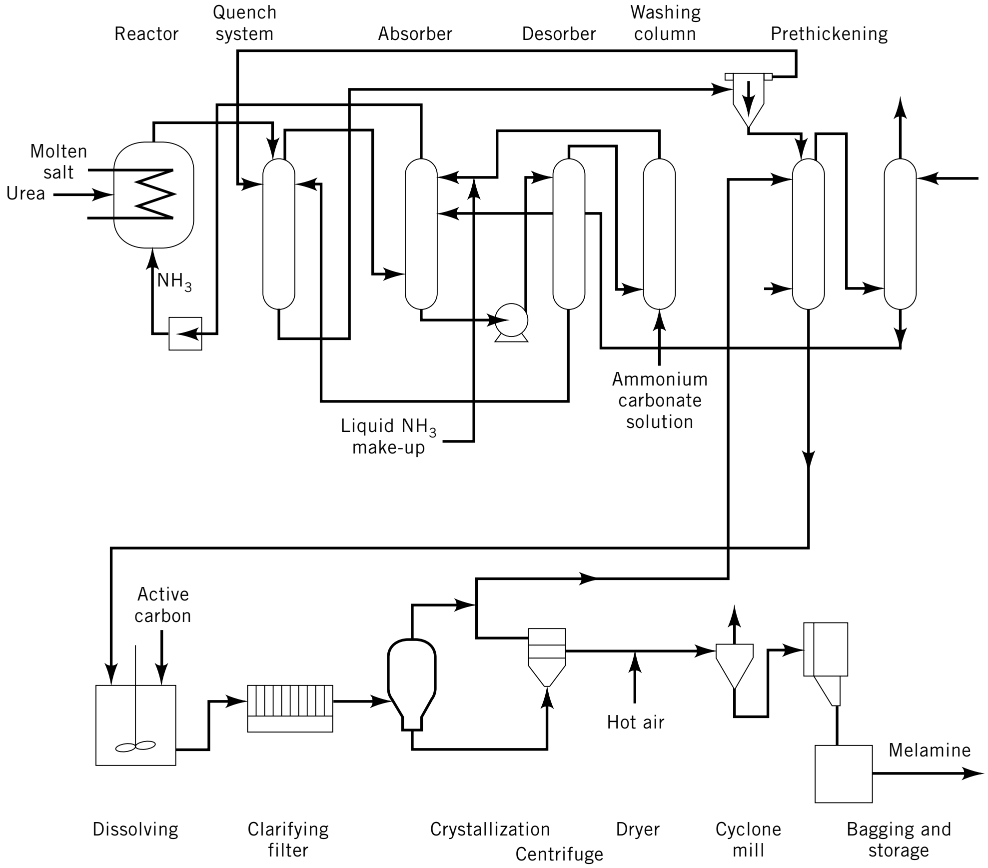


Fig. 1. Production of melamine for urea (43). Courtesy of Gulf Publishing Co.

Extensive toxicity investigations performed with melamine in experimental animals suggest that the compound may have a low order of biological activity. The acute oral LD_{50} for mice was found to be 4.55 g/kg and approximately the same for rats. Chronic feeding tests have been carried out on rats over a two-year period at a dietary level of 1000 ppm and on dogs for one year at a level of 30,000 ppm. Throughout the study, the general health of the test animals did not seem significantly different from that of the controls. Nevertheless, after 60–90 days the dogs showed melamine crystalluria, which persisted throughout the remainder of the observation. However, gross and microscopic examination of the tissues revealed no abnormality attributable to the feeding of melamine.

Melamine in a skin test on rabbits produced neither local irritation nor systemic toxicity. As a 10% solution in methylcellulose, it caused no irritation in the eyes of rabbits. Human subjects were given patch tests with melamine. No evidence of either primary irritation or sensitization was found. Such results suggest that melamine crystal may be handled in ordinary industrial use without special hygienic precautions.

4.4. Uses. Most of the melamine produced is used in the form of melamine–formaldehyde resins (see Amino resins and plastics). Other applications (42) include the use of melamine pyrophosphate [15541-60-3]in fire retardant textile finishes, chlorinated melamine as a bactericide, and melamine as a tarnish inhibitor in detergent compositions, in papermaking, and manufacture of adhesives.

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