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# A MELAMINE PROCESS BASED ON HYDROGEN CYANIDE AND AMMONIA INVOLVING ELECTROLYTIC CONVERSION OF HYDROGEN CYANIDE

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A high yield synthesis of cyanogen bromide has been discovered based on a novel electrolytic conversion of hydrogen cyanide in aqueous ammonium bromide. Subsequent ammonolysis of cyanogen bromide in a selected solvent yields a solution of cyanamide plus solid ammonium bromide which is recycled to the electrolysis step. Satisfactory conditions for trimerization of cyanamide in the solvent to melamine have been demonstrated. Over-all yields of high purity melamine exceeding 90% are achieved in the outlined process. Dilute solutions of hydrogen cyanide in aqueous ammonium bromide are electrolyzed at 100° F. The hydrogen cyanide can be absorbed into the aqueous ammonium bromide from the effluent of a generator using ammonia and a hydrocarbon as feed. The specially designed cell and its operation are described. The selection and optimization of a suitable solvent which serves for both the ammonolyses and trimerization reactions are discussed. Solvents such as dioxane and tetrahydrofuran were particularly useful. The trimerization of cyanamide is shown to be unexpectedly easy and direct compared with other procedures for producing melamine.

OMMERCIAL PROCESSES for melamine are generally based on dicyandiamide (cyanoguanidine) derived from calcium cyanamide (9). Other starting materials which have been reported useful for synthesis of melamine include cyanamide (3), guanidine (13), urea (1), cyanuric halides (7, 8), and hydrogen cyanide plus ammonia (11). In contrast to previously reported hydrogen cyanide-ammonia processes, the melamine process reported here is very efficient. It also offers an economic advantage over the calcium cyanamidebased route where low cost hydrogen cyanide and electrical power are available. The process involves a novel electrolytic conversion of hydrogen cyanide to cyanogen bromide in aqueous ammonium bromide amination of cyanogen bromide in a selected solvent to cyanamide and recycle ammonium bromide, and trimerization of the cyanamide in the solvent to melamine. A simplified process diagram is presented in Figure 1.

The hydrogen cyanide feed for this process can be the pure liquid, or it can be absorbed into the aqueous ammonium bromide from the effluent of a hydrogen cyanide generator operating on an ammonia-hydrocarbon feed. None of the by-products in hydrogen cyanide so produced poses any serious difficulties in the hydrogen cyanide conversion to cyanogen bromide.

Over-all yields of melamine from hydrogen cyanide above 90% are achieved by this process. The bromide losses are negligible and the only significant by-product is hydrogen A more detailed description of the process follows.

# Hydrogen Cyanide-Ammonium Bromide Electrolysis

Cyanogen bromide is produced efficiently in the anode chamber when dilute solutions of hydrogen cyanide in aqueous ammonium bromide are electrolyzed at about 100° F. in a specially designed cell. Aqueous ammonium bromide is used in the cathode chamber. The cell is described in detail below, but the key feature is the use of an ion selective membrane. The membrane prevents mixing of the ammoniacal catholyte with the anolyte and resultant destruction of hydrogen cyanide and cyanogen bromide. At the same time, current densities [100 amp. per sq. ft. (a.s.f.)] at relatively low voltage (3.0) can be maintained by ionic transport through the membrane. The hydrogen cyanide is essentially completely converted to cyanogen bromide. Since the latter is volatile (b.p.  $= 61.6^{\circ}$ C.), it is easily stripped from the analyte for the subsequent conversion to cyanamide and melamine. The cell design permits ready recovery of the hydrogen formed at the cathode. Ammonia escapes with the hydrogen thus maintaining an equilibrium concentration in the catholyte recycle. The cell operates continuously with the anolyte recycled after cyanogen bromide removal and replenishment of ammonium bromide from the amination step.

# Cyanogen Bromide Ammonolysis and Conversion to Melamine

Cyanogen bromide reacts vigorously with ammonia at ambient temperature. If the temperature is not controlled, a variety of products are formed. Conducting the reaction in ether provides an ether solution of cyanamide (12), but yields are low at practical cyanogen bromide levels owing to the poor solubility of cyanamide in ether. By dissolving the cyanogen bromide in a more suitable solvent such as dioxane or tetrahydrofuran, a controlled exothermic reaction occurs to produce a solution of cyanamide and a crystalline precipitate of ammonium bromide in essentially quantitative yield. The cyanamide solution is filtered or centrifuged free of ammonium bromide, concentrated somewhat, and then autoclaved in the presence of free ammonia to produce melamine in high yield. The ammonolysis of cyanogen bromide is carried out at 100° to 120° F. under slight ammonia pressure. The autoclaving of cyanamide solution is preferably conducted for 1 hour at about 375° to 400° F. and 1500 p.s.i.g. Melamine is recovered by filtration after the ammonia is vented and the solvent slurry is cooled. One recrystallization of the melamine from water produces high purity melamine in yields exceeding 90% from cyanogen bromide.

#### Experimental

**Electrolysis Equipment.** The equipment used throughout this experimental study was commercially available or was fabricated from easily obtained components.

Figure 2 is an exploded view of the modified plate and frame type of electrochemical cell used in the synthesis of the intermediate cyanogen bromide. Basic parts of the cell are the cathode compartment on the left, the anode compartment on the right, and an ion-selective membrane which separates the compartments.

The anode compartment was bounded by a graphite anode (National Carbon Co., grade AGX), the ion-selective membrane, and the anode compartment framing. The latter was made from rubber gasketing and inert plastic materials such as poly(vinyl chloride) or polypropylene to obtain spacings ranging from  $1/_{16}$  to 1 inch. Circulation of the anolyte through the cell was maintained at a low rate by an external pumping loop. Feed to the anode compartment was metered into the pumping loop before the stream re-entered the cell. Production was withdrawn in a slip-stream from the top of the cell through a line equipped with a siphon break.

The cathode compartment comprised a frame, a perforated steel cathode, a felt pad, and the membrane. Rubber gaskets were used wherever necessary in this part of the cell. Catholyte was fed through a manifold system to the top of the cathode compartment frame. Feeders distributed the catholyte evenly over the rear of the cathode. The perforations allowed the electrolyte to run onto the front face of the electrode. The felt pad separated the cathode and the membrane by a low resistance ionic path. The perforations also permitted easy escape of the gases formed on the active face of the electrode during electrolysis. A carbon steel screen with 0.039 inch perforations 0.039 inch thick served as cathode. In the cell shown in Figure 2, the hydrogen and ammonia gases forced out the circulating catholyte through the bottom ports in the cathode compartment. In commercial practice, gas ports would be located conveniently somewhere near the top of the cathode compartment while liquid would leave by gravity.

Direct current power to the cell was provided from a threephase, 1000-A. Udysil rectifier. Electrical connections were made to the cathode with cadmium-plated steel cable connectors and to the anode by polished-end threaded graphite rods. Electrical measurements were made with 2% accuracy meters. Temperature was maintained within  $\pm 4^{\circ}$  F. with cooling water in an external heat exchanger on the catholyte stream and another exchanger in direct contact with the anode.

Ammonolysis-Trimerization Equipment. The ammonolysis reaction was carried out batchwise in a stirred 1-liter Parr autoclave equipped with an internal cooling coil. Liquid ammonia was delivered through a sparging assembly, made from a 2-inch diameter porous 316 SS disk, Grade "X," and mounted directly beneath the downthrusting stirrer. Because of the vigorous exotherm, temperature was maintained within  $\pm 10^{\circ}$  F. with cooling water controlled by a solenoid valve actuated by a West Gardsmen controller.

Trimerizations were conducted in a 1-liter stirred autoclave (316 SS) from Autoclave Engineers, Inc. Temperature was controlled manually during the heating cycle.











Figue 4. Current density as a function of interelectrode distance and applied voltage



Figure 5. Current density as a function of ammonium bromide concentration

# **Analytical Methods**

**Hydrogen Cyanide.** Hydrogen cyanide was estimated using the Liebig-Denigès titration method (4). A sufficiently large sample was used to give a sharp visual end point with from 4 to 40 ml. 0.1N silver nitrate.

**Cyanogen Bromide.** Cyanogen bromide was estimated by either of two titration methods, a standard iodometric procedure and a modified Liebig-Denigès procedure. The latter procedure was particularly useful for anolyte solutions which could contain bromine while the former was easier whenever oxidants other than cyanogen bromide were known to be absent. Good agreement was obtained between the two methods (0.2 to 0.5%).

MODIFIED LIEBIG-DENIGÈS PROCEDURE. The total cyanide content of the sample was estimated by adding a sample containing between 10 and 100 mg. of cyanides as hydrogen cyanide to 50 ml. of reducing solution (3.6 grams of reagent grade potassium iodide, 20 grams of reagent grade sodium metabisulfite, 40 grams of sodium hydroxide, and 180 ml. of reagent grade ammonium hydroxide mixed and diluted to 1-liter with distilled water) with vigorous agitation. The resultant solution was titrated with 0.1N silver nitrate to a turbid end point.

The result obtained from the normal titration procedure was used as a blank for the cyanogen bromide content.

**Bromide.** Bromide ion concentration in nonaqueous solution was estimated potentiometrically with 0.1N silver nitrate (14).

**Cyanamide.** Cyanamide concentrations were estimated potentiometrically following the method of Capitani and Gambelli (2).

Melamine. Crude melamine was assayed with a styphnic acid precipitation method (10). Assays for both melamine and water insoluble content were obtained simultaneously.

# **Typical Procedure**

**Electrolysis.** The analyte feed was prepared by mixing pure liquid hydrogen cyanide and known normality ammonium bromide solutions to give the desired cyanide level (by analysis)—e.g., 1.5 w./v. % HCN in 4N NH<sub>4</sub>Br. [w./v. % = (weight  $\times$  100)/solution volume].

At a selected current density  $\sigma$ , the cyanide feed rate  $\gamma$  is adjusted to the desired ratio of electrical to chemical equivalents (expressed in Faradays per mole of hydrogen cyanide, F/ HCN); e.g., F/HCN = 1.95,  $\sigma$  = 200 a.s.f. (100 amp.),  $\gamma$  = 57.4 ml. per min. The anolyte was recirculated at a rate of 180 ml. per min.

The catholyte for this run had been used for over 50 hours. Originally, it had been prepared by mixing 10 pounds of technical concentrated ammonium hydroxide with 3 pounds of technical ammonium bromide and three liters of water. The concentration of ammonia was estimated at 10N from similar runs. The ammonium bromide concentration had been maintained between 2 and 3M by the addition of solid ammonium bromide to the electrolyte. During the run, the recycle catholyte was fed at 75 ml. per min. to the top of the cathode compartment.

The membrane used was AMF-ion A-60. The electrodes were spaced  $\frac{1}{4}$  inch apart.

During a 1-hour recovery run, the cell, operating near the preset conditions, produce danolyte solution containing 175 grams of cyanogen bromide and 2.4 grams of hydrogen cyanide from 54.7 grams of HCN (95.6% conversion; 97.8% ultimate yield of CNBr on HCN) at 3.1 volts across the cell and 35° C. average temperature in the cell.

Cyanogen bromide was recovered readily by distillation of the anolyte. The colorless crystals melted at 48-52° C. and assayed better than 95% CNBr (also contains 1% HCN and the balance H<sub>2</sub>O).

Ammonolysis-Trimerization. The tetrahydrofuran and "glyme" (1,2-dimethoxyethane) used in this investigation were refluxed with sodium metal for several hours. A center cut (10% discarded from both ends) was distilled slowly from the pot through a short (1-foot) column of Berl saddles into a receiver containing sodium-lead alloy. Dioxane was purified by the procedure described by Fieser (5).

A stock solution of cyanogen bromide in the solvent under investigation (approximately 50 w./v.%) was prepared from Sohio cyanogen bromide. The solution was purified from water and hydrogen cyanide with Linde 4A Molecular Sieves (room temperature for 2 hours) and analyzed iodometrically for cyanogen bromide. An appropriate volume of the stock solution was diluted to 700 ml. for a run.

In the example, 140 grams of cyanogen bromide in tetrahydrofuran solution was placed in the Parr autoclave. The autoclave was closed, pressured to 250 p.s.i.g. with nitrogen and depressured twice, then heated to  $104^{\circ}$  F. in about 10 minutes. Liquid ammonia was metered continuously into the system at a rate such that 57 ml. was added in 11 minutes. The ammonia addition was terminated. After being stirred for an additional 5 minutes, the slurry was stabilized by heating in vacuo at a pot temperature of  $105^{\circ}$  F. The ammonium bromide was filtered from the reaction mixture, washed with three 50-ml. portions of tetrahydrofuran, dried,

#### Table I. Choice of Solvent

Cencentration of BrCN: 25% w./v. Trimerization conditions: One (1) hour, 375° F., 1500–2000 p.s.i.g.

Run No.	$Temp., \\ \circ F.$	NH3 Rate, (M. NH3/M. BrCN/Min.)	Residual Br, Gram-Atoms/ Liter	Yields, %			
				NH <sub>4</sub> Br	Cyanamide	Melamine	Insolubles
			Tetrahy	DROFURAN			
1 2 3 4	104 104 176 176	$\begin{array}{c} 0.05 \\ 0.20 \\ 0.05 \\ 0.20 \end{array}$	0.020 0.028 0.049 0.090	100.5 98.3 96.0 100.1	91.3 85.7 87.5 84.5	92.1 90.2 74.5 73.3	0.7 1.0 1.2 1.6
			1,2-Діметн	OXYETHANE			
5 6 7 8	104 104 176 176	$\begin{array}{c} 0.05 \\ 0.20 \\ 0.05 \\ 0.20 \end{array}$	$\begin{array}{c} 0.150 \\ 0.056 \\ 0.053 \\ 0.089 \end{array}$	99.3 95.9 97.4 97.2	131.0 91.7 90.1 108.1	86.5 86.3 80.6 77.0	2.7 2.3 7.7 9.3
			Dioz	ANE			
9 10 11 12	104 104 176 176	$\begin{array}{c} 0.05 \\ 0.20 \\ 0.05 \\ 0.20 \end{array}$	0.038 0.030 0.053 0.066	101.7 101.7 100.0 97.3	92.2 87.2 87.7 89.0	87.5 86.4 85.7 80.8	0.7 1.4 1.5 1.2

weighed, and analyzed for bromide ion; assay as  $NH_4Br$ , 99.2%; recovery, 98%. The cyanamide solution, 630 ml., contained 47.5 grams of cyanamide (yield, 86%) and was 0.028N in bromide ion.

An aliquot portion of the ammonolyzed solution (450 ml.) was transferred to the high pressure autoclave which then was purged with nitrogen. Liquid ammonia, 160 ml., was added to the mixture. The autoclave was heated over a period of 1 hour to  $375^{\circ}$  F. The pressure rose to about 1600 p.s.i.g. The temperature was maintained for 1 hour and then dropped to room temperature slowly.

The product slurry was withdrawn from the autoclave and filtered. The crude melamine, assayed at 91.9% melamine with 1.0% insolubles, was obtained in 98% yield based on cyanogen bromide. The product was recrystallized and decolorized with a little vegetable charcoal to give essentially pure melamine.

#### **Results and Discussion**

**Hydrogen Cyanide-Ammonium Bromide Electrolysis.** The synthesis of cyanogen bromide was clean and efficient. The only variable influencing the yield significantly was the concentration of hydrogen cyanide in the feed (see Figure 3). Lower concentrations of cyanide favor improved yields of cyanogen bromide. Excellent yields were obtained in this lower range of cyanide concentrations.

The conversion of hydrogen cyanide was nearly in stoichiometric ratio with two faradays of electricity. Thus, operation of the cells was usually restricted to the range around 2 f/ HCN. Since observable amounts of bromine in the anolyte led to excessive anode degradation, the ratio was generally maintained between 1.9 and 1.95 where both high yields and high conversions were obtained. The reaction was independent of temperature over the range 75° to 125° F., current density over the range 50 to 500 a.s.f., anolyte composition from 2 to 5M in bromide and 0 to 2M in hydrogen ion (balance ammonium ion), and cell residence times up to an hour.

The voltage applied to the cell was independent of the type of ion-selective membrane at the high electrolyte concentrations employed in the cell. Figure 4 shows the dependence of the current density on operating voltage and interelectrode distance. Even at quite reasonable interelectrode distances moderate operating voltages produced very high current densities and correspondingly high cyanogen bromide production rates. Figure 5 shows the dependence of current density on the ammonium bromide concentration in the anolyte and catholyte. The bromide concentration in the anolyte was maintained preferably between 3 and 4N. Higher concentrations may be used but did not enhance the cell operation in any way. The concentration of bromide in the catholyte did not affect cell operation greatly. Bromide levels around 2 to 3Nwere quite satisfactory. Free ammonia concentrations in the catholyte up to about 10N did not affect the cell resistance.

### **Ammonolysis-Trimerization**

The choice of solvents for the ammonolysis-trimerization reaction is critical to satisfactory yields and operability. Only those which are inert to cyanogen bromide, ammonia, cyanamide, and melamine under reaction conditions were considered. Equally important, the solvent must dissolve appreciable cyanogen bromide and cyanamide, yet allow ammonium bromide to precipitate in nearly quantitative yield. Beyond this, it was desired to have a solvent with a boiling point in the



Figure 6. Influence of cyanogen bromide concentration on melamine yield



1001 SOLVENT: TETRAHYDROFURAN 90 (%) PURE MELAMINE 80 70 50 100 150 200 TEMPERATURE \*F

Figure 7. Influence of cyanogen bromide concentration on "soluble bromide'

range of 150° to 300° F. to facilitate recovery by distillation and to avoid excessive autoclave pressure.

Considering the above requirements, several solvents were screened briefly from which three were selected for further evaluation, tetrahydrofuran, p-dioxane, and "glyme" (1,2dimethoxyethane). Table I presents data from a 3  $\times$  2 square factorial experimental design to evaluate these solvents. The ammonium bromide, cyanamide, and melamine yields from cyanogen bromide for these solvents are all in the high range (>75%), but some differences among them can be noted. Tetrahydrofuran gave the highest melamine yields using the preferred ammonolysis temperature (runs No. 1 and 2) and was rated a slight favorite. Dioxane is a close second on the same basis while glyme was considered slightly inferior on the basis of ammonium bromide recoveries and melamine yields.

The highest possible cyanogen bromide concentration is desired for maximum process efficiency. Solvent inventory and handling are thus minimized, and the best melamine yields accrue at high cyanamide concentrations. The latter is illustrated in Figure 6. Limiting the cyanogen bromide concentration is the soluble bromide left in the solvent after ammonolysis. The soluble bromide results largely from solvent-cyanogen bromide interreaction. Figure 7 shows how the soluble bromide increases with increasing cyanogen bromide concentration. For batch experiments we chose 25 w./v.% cyanogen bromide as a reasonable compromise. Optimum performance can probably be achieved by using continuous ammonolysis of cyanogen bromide maintained at low instant concentrations. This would achieve high cyanamide concentrations for autoclaving to melamine with residual bromide at a minimum in the solvent.

Yield of melamine is not appreciably influenced by ammonolysis temperature until the latter exceeds 130° to 140° F. (see Figure 8). Lower temperatures (100° F.) are favored to minimize cyanogen bromide-solvent interreactions. Since the cyanogen bromide-ammonia reaction is exothermic, cooling must be provided to maintain these temperature ranges when practical ammonia addition rates are used.

Within a practical range of ammonia addition rates (0.05 to 0.20 mole of NH<sub>3</sub> per mole of CNBr per minute), there is no significant influence of this variable on cyanamide or melamine vields.

Figure 8. Influence of ammonolysis temperature on melamine yield

The trimerization of cyanamide proceeds in high yield under the chosen conditions of temperature, ammonia pressure, and time. As this reaction has been studied by other workers (6, 15) further exploration of these reaction variables was not made. The variable of cyanamide concentration was briefly explored. While data were incomplete, high cyanamide concentrations (equivalent to 25 w./v.% CNBr or higher) favored the best melamine yields.

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