SYNTHESIS OF MEAMINE

A THESIS

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SYNTHESIS OF MELAMINE

Approved:

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THE SYNTHESIS OF MEI AMINE

SUMMARY

Melamine is a crystalline organic compound of major industrial importance. It is employed chiefly in the form of melamine formaldehyde resins for the treatment of paper, textiles, and leather, and for the manufacture of baking enamels, molded plastics, and adhesives. Except for the relatively high cost of these resins, they would find even greater use and importance in these and other applications. These costs are in part due to the difficulty of the final step in manufacture, the conversion of dicyandiamide (also a crystalline organic compound) to melamine. Present methods involve batch operations, high pressures, and the use of liquid ammonia at relatively high temperatures. The principal difficulty apparently is the large heat of reaction, which makes it hard to control the temperature of the process. Because of the excellent temperature control which characterizes the fluidized bed technique so successfully used in the petroleum industry, a study has been made of the possibility of applying this technique to the production of melamine. The results indicate reasonably good yields in a gas-solid system at lower pressures than now used. A fluidized system also has advantages in simplicity of operation.

An examination of the conversion of dicyandiamide (dicy) to melamine in the solid state was made under three conditions: fluidized beds at atmospheric pressure with nitrogen or nitrogen-ammonia mixtures as the fluidizing gas, static beds at atmospheric pressure with nitrogen or ammonia gas, and static beds under elevated pressures of ammonia.

At atmospheric pressure, conversions greater than 50% could not be
obtained under any conditions. The use of various catalysts and ammonia atmospheres to suppress deamination had relatively little effect in improving yields.

In static beds under elevated ammonia pressure, the yields of melamine exceed 90% at pressures above 300 psig. At pressures below 200 psig, there is no appreciable difference in the conversion from that obtained at atmospheric pressure. At approximately 200 psig, there is a sharp change in the general mechanism of the conversion and in the results obtained. Increased pressures above atmospheric reduce the formation of insoluble deamination products to almost negligible quantities at 400 psig. Within fairly wide limits, the particle size of the charge used has no appreciable effect on the conversion. As is the case when dicy is pyrolyzed at atmospheric pressure, at elevated pressure there is a critical temperature at which the conversion proceeds spontaneously. This critical temperature is decreased by increased pressure from a value of about 209°C at one atmosphere to approximately 145°C at 450 psig. Below these temperatures, the conversion proceeds slowly.

The diluents used in the atmospheric operations to determine if they exert any catalytic action had no significant effect on the rate of reaction. However, at elevated pressures, silica-gel gives poor yields of melamine with large amounts of other products and is difficult to handle because of its very high adsorption of ammonia. Alumina yields the same results as are obtained with dicy alone in the charge. There is no positive evidence that any of the diluents tried provide any catalytic action. However, they do prevent any sticking of the charge in both atmospheric and elevated pressure operations.
In the light of the data obtained, the most probable mechanism of the melamine synthesis appears to be a two-stage process involving first the reaction of ammonia with dicy to form water soluble intermediate compounds, and then the reaction of the intermediates with dicy to produce ammonia and melamine.

It is concluded that the conversion of dicy to melamine can be carried out in a solid-gas system with yields of melamine equal to or better, and at pressures appreciably lower, than present commercial processes. However, further study must be made to determine the optimum ratios of diluent to organic necessary in the charge to provide for proper fluidization. Since an equilibrium apparently exists for the conversion of dicy to melamine, a study of the effect of the presence of deamination products in the charge should be made in order to determine if the formation of these compounds can be suppressed by including some of these compounds in the charge. An examination of the problem of separation and purification of the products of the reaction should also be made.
INTRODUCTION

**Industrial Importance.** Melamine is a white crystalline organic compound which has a melting point of about 354°C, and a density of 1.57 g/cc, a little above that of dicy, to which it is related. Melamine sublimes readily at temperatures slightly below the melting point at atmospheric pressure and at temperatures below 300°C at pressures of about 0.1 inch Hg.

Melamine was first discovered by Justus von Liebig in 1834, but, except for a certain amount of academic attention, received no recognition for almost a century. It was then discovered that melamine when combined with formaldehyde produces a thermosetting resin with outstanding resistance to heat, water, and chemical action, thus immediately giving it numerous important industrial and commercial applications.

Perhaps one of the most important of these applications is in the treating of paper, producing paper with increased folding endurance, tensile strength, and bursting strength. In addition, such paper has excellent water resistance, high wet strength, and is lint free. Other sizing materials must be added after the paper sheet is formed and give little but surface protection, or in the case of urea formaldehyde produce noxious fumes. Melamine formaldehyde can be incorporated directly into the pulp mixture. The resinous particles in the pulp are positively charged while the cellulose fibers are negatively charged, thus giving complete protection and bonding of the fibers in the finished paper sheet. Large amounts of melamine resins are therefore
used in maps, towels, tissues, paper board, bags, etc.

Another interesting use of melamine is in the tanning of leather, where it has proved superior to chrome and vegetable tanning in all cases, giving a soft, flexible, decay-proof leather with superior uniformity and wear resistance due to the excellent penetration of the resins during tanning.

Melamine treated textiles retain their shape, are crease resistant, and resist shrinkage during laundering. Melamine has also shown excellent possibilities in improving the shrink resistance of wool fabrics as well as increasing wear resistance.

Still another major application of melamine resins is in synthetic baking enamels for household appliances and automobiles. In addition to being able to produce a pure white enamel, the resins show better heat, wear, chemical, and scratch resistance, and require less baking time than previous synthetic finishes.

Melamine resins in molded plastics have broadened the scope and application of plastics. Together with phenol formaldehyde and urea formaldehyde resins, they constitute the major part of the thermosetting resin field. The melamine resins, however, show better resistance to water and dilute acids and alkalies. They can be produced in all colors and show considerable compatibility with different fillers. They have excellent dielectric strength, wear resistance, heat resistance, and stability. A recent application has been in adhesives, whereby plywood can now be made water resistant as well as heat resistant, so that more rigid standards of wood construction can be met.

Melamine resins in general combine the best properties of the other
thermosetting resins, but with the disadvantage of a higher cost. If the cost of melamine could be reduced by even a small amount, the scope and application of melamine to industry would be correspondingly greater.

Melamine (2, 4, 6-triamino 1, 3, 5 triazine) can be described as the cyclic trimer of cyanamide of which dicy is the dimer. Briefly, the steps in the production of melamine consist of first producing calcium carbide from limestone and coke in an electric arc furnace. Then, nitrogen distilled from liquid air is passed over the hot calcium carbide to form calcium cyanamide. Cyanamide is then liberated from the calcium cyanamide by acid treatment and polymerized to dicy by heating. On further polymerization of dicy, melamine is formed. It is with this last and difficult step that this dissertation is concerned.

Methods of Preparation. At present, the only commercial process (American Cyanamide Co.) used in this country for converting dicy to melamine is carried out by first taking the dicy in solution in liquid ammonia and methyl alcohol and then heating the solution in a batch autoclave, following very carefully a prescribed temperature-pressure-time control template until the reaction is complete at about 110 to 120°C. The resulting melamine is then crystallized and filtered with the liquid ammonia and methyl alcohol filtrate being recovered and sent to underground storage tanks. The yields obtained range from 85 to 90 percent melamine based on the dicy charged. The pressure reactors are installed in "pillboxes" outside the main working area and remote control is used. No personnel are permitted in the reactor area during operations. Reactor pressures during operation are relatively high (75 to 100 atmospheres) due to the vapor pressure of the solution at the temperature
required for the reaction. It is interesting to note that the process
starts with a batch reaction and ends with a batch filtration.

Other methods of converting dicy to melamine or preparing melamine
have been reported. Foster (1) reported small yields (15 to 30\%) of
melamine obtained by heating dicy in ethylene glycol in the presence of
zinc chloride at 100 to 130°C. Christman and Foster (2) obtained con­
version by heating dicy to its melting point in contact with extensive
surfaces. Henkel and Cie (3) heated dicy in a closed vessel in the
presence of highly compressed nitrogen, hydrogen, or inert gaseous
hydrocarbons. Thurston (4) reported small yields obtained by heating
dicy to 160°C. with an acid condensing agent. Christman and Foster (5)
heated dicy in a rotary furnace at atmospheric pressure and obtained
small yields. Jayne and Day (6) obtained melamine by heating a mixture
of dicy and an alkali metal salt of a weak acid to fusion temperature
at atmospheric pressure.

Wintringham and King (7) obtained fair yields of melamine by
heating a solution of dicy and liquid ammonia in a rotating agitated
vessel. King, Mensing, and Felch (8) obtained good yields by heating a
solution of dicy, liquid ammonia, and methyl alcohol. Almost all other
references to the formation of melamine from dicy are contained in
patent literature, and the methods involve only slight variations in the
manner in which the dicy and liquid ammonia are handled.

As can be readily seen from the preceding paragraphs, most
processes used for the preparation of melamine are directed toward
eliminating or suppressing the formation of undesirable reaction products
by one or more of the following procedures:
(a) By the use of high pressures in order to suppress the deamination of the compounds and the resulting formation of ammonia.

(b) By the use of solvents which act as diluents thus affording a greater heat capacity in the mixture and offering the possibility of evaporation of the solvent to prevent excessive temperature rises. The use of solvents also generally implies high pressures at the temperatures involved.

(c) By the use of catalysts which promote the desired reaction at lower temperatures, thus decreasing the tendency toward deamination and also providing some increase in heat capacity.

(d) By the use of inert diluents which increase the heat capacity of the mixture and therefore prevent an excessive temperature rise even at high reaction temperatures.

The Fluidized Powder Technique. Padgett (9) obtained yields of almost 50 percent melamine by fluidizing dicy with inorganic catalysts at approximately 180°C. in a stream of nitrogen at atmospheric pressure. Since the other methods of preparation of melamine recorded in the literature are batch operations, involving high pressures at relatively high temperatures, or giving very poor yields, it seemed worth while to examine the fluidized technique further. The advantages of a fluidized bed are evident in the easier handling of materials, the better temperature control than possible in a batch operation, and the possibility of developing a continuous process. Considerable experience with the fluidized solids method is already available as a result of its successful use on a large scale in the petroleum industry (10).

Fluidization consists of supporting a bed of solid material in a
gas stream such that movement of the particles in the system closely approximates that of a fluid in turbulent motion. With this system, the possibility of the existence of any large temperature gradient, such as that caused by an exothermic reaction, is remote because of the good heat transfer coefficients obtained. By preventing local overheating due to the reaction, less pressure may be needed to prevent deamination. It is also possible to transport the solid particles in the gas stream to and from a reaction chamber without the usual solids handling difficulties and consequently achieve a continuous operation.

For the conversion of dicy to melamine, the process may be visualized as consisting of a container from which the dicy would be picked up by a stream of ammonia and fed to the reaction chamber. This would consist of a vertical shell, jacketed and perhaps with cooling coils for temperature control. The solid-gas mixture would be carried vertically through the reactor by proper control of the gas velocities. From the reactor the material would be carried to a vessel and would be leached of its melamine content for further processing. If diluents were used, they would simply be mixed with the dicy charge and recirculated through the apparatus after separation from the reaction products. If pressures above atmospheric are necessary, it would only be necessary to provide two raw material tanks and two product tanks. The charge would then be fed intermittently from each storage vessel and the products removed intermittently for leaching and separation, while the reactor would be operated continuously. The fluidizing gas would of course be recirculated.

Chemistry of Dicy and Melamine. Melamine may be obtained by simply heating dicy at atmospheric pressure to approximately its melting point
(209°C.). An exothermic reaction takes place with a considerable temperature rise. Yields of almost 50 percent may be obtained in this way, but with the formation of almost 50 percent of other triazines and deamination products.

Dicy, the dimer of cyanamide, can be represented by the following structural formulas, of which the first best satisfies the many reactions in which it may participate:

\[
N = C - N - C \overset{\text{NH}}{\rightleftharpoons} \text{or} \quad \text{HN} = C = N - C \overset{\text{NH}}{\text{NH}_2}
\]

Dicy may be described as a very fecund parent of almost innumerable commercially important compounds of which melamine is perhaps the most important and is the chief concern here.

The structural formula of melamine is usually represented as an amino form although the imino form is not disproved, and there is evidence of a bond between the hydrogen of the amino groups and the nitrogen atoms of the triazine nucleus even for the amino structure. Therefore, the structure of melamine is represented by the following:

\[
\begin{align*}
\text{HN} & = C \quad \text{or} \quad \text{HN} = C \quad \text{NH} \\
\text{H}_2\text{N} & - C \quad \text{C} \quad \text{NH}_2
\end{align*}
\]

with the former being generally accepted and the one used here in any further discussion.
There is no definitely proven mechanism in the literature for the formation of melamine from dicy. However, several mechanisms have been postulated. One (11) is that dicy and ammonia react to give biguanide, which then dissociates to guanidine and cyanamide. Dicy and cyanamide or dicy and guanidine may then react to give melamine. This mechanism is at least partially borne out by the fact that in pyrolyzing dicy at atmospheric pressure, enough ammonia is formed in the reaction by the decomposition of dicy to allow the process to follow this mechanism and to account for the further polymerized deamination products. Structurally this mechanism may be represented as follows:
Migridichian (12) suggests the following mechanism for the guanidine-dicy reaction:

\[
\begin{align*}
\text{NH}_2 & \quad + \quad \text{HN} =\text{C} - \text{NH}_2 \\
\text{HN} & \quad \rightarrow \quad \text{N} =\text{C} - \text{NH}_2 \\
\text{NH}_3 & \quad + \quad \text{N} =\text{C} - \text{NH}_2 \\
\text{NH}_3 & \quad + \quad \text{H}_2\text{N} -\text{C} - \text{NH}_2
\end{align*}
\]

The chief evidence in favor of the above mechanisms is that cyanamide, guanidine, and biguanide have all been recovered from the reaction mixtures.

Another suggested mechanism is shown on the following page. This illustrates a possible mechanism which would not postulate the presence of guanidine as an intermediate, but would offer cyanamide as an intermediate and might be favored in the reaction proceeding at different temperatures or pressures.
Data on the heats of formation of the compounds involved in the suggested mechanisms are scarce and not in too good agreement. The most reliable measurements appear to be those of Salley and Gray (13) who report the heats of formation of crystalline cyanamide, dicy, and melamine at 25°C as 14.65, 7.14, and -15.35 Kcal./mole, respectively, as calculated from their heats of combustion obtained from bomb calorimeter data. The heat of formation of guanidine is found to be -30.68 Kcal./mole (14).
Thus, for the over-all reaction, \(3 \text{C}_2\text{N}_4\text{H}_4 \rightarrow 2 \text{C}_3\text{N}_6\text{H}_6\), the calculated heat of reaction would be \(2(-15.35) - 3(7.14)\) giving \(-52.12\) Kcal. or 26.06 Kcal./mole of melamine. The heats of reaction for the most probable mechanism involving biguanide, guanidine, and cyanamide would be as follows, using \(-11.00\) Kcal./mole for the heat of formation of ammonia:

\[
\begin{align*}
\text{NH}_3 + \text{C}_2\text{N}_4\text{H}_4 & \rightarrow \text{C}_3\text{N}_6\text{H}_6 + \text{CN}_2\text{H}_2 \\
H_r & = -30.68 - 11.65 - 7.14 - (-11.0) = -12.17 \text{ Kcal.} \\
\text{CN}_2\text{H}_5 + \text{C}_2\text{N}_4\text{H}_4 & \rightarrow \text{C}_3\text{N}_6\text{H}_6 + \text{NH}_3 \\
H_r & = -15.35 - 11.00 - (-30.68) - 7.14 = -2.81 \text{ Kcal.} \\
\text{CN}_2\text{H}_2 + \text{C}_2\text{N}_4\text{H}_4 & \rightarrow \text{C}_3\text{N}_6\text{H}_6 \\
H_r & = -15.35 - 14.65 - 7.14 = -37.24 \text{ Kcal.}
\end{align*}
\]

The step for the reaction of ammonia with dicy to form biguanide is omitted here, since no data could be found for the heat of formation of biguanide.

The deamination products already mentioned but not included in the mechanisms offered are melam, melam, and melor, which are presumed to be polymerization products with higher molecular weights. Melam is though to have the following structure and relation to melamine:

\[
\begin{align*}
\text{NH}_2 & \quad \text{NH}_2 \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{H}_2\text{N} - \text{C} & \quad \text{H}_2\text{N} - \text{C} \\
\end{align*}
\]

Melamine

\[
\begin{align*}
\text{NH}_2 & \quad \text{NH}_2 \\
\text{C} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

Melam
Further polymerization then yields melem.

The suggested structure of melon is thought to be a condensed group of melem molecules represented as the following; using the symbol, $\Delta$, to represent the nucleus of the melem molecule.

These compounds are nearly insoluble in water even at elevated temperature, and melon is apparently stable to temperatures in excess of 1000°F. The above is not meant to indicate that melamine deaminates at reaction temperature, but rather to indicate the relation of these compounds to melamine and dicy. Even upon sublimation of melamine at above 300°C, at atmospheric pressure, the ammonia liberated due to deamination amounts to only about 0.025 moles per hour per mole of melamine (15).

**Experimental Program.** In the light of the chemistry outlined above, the relatively low yields of melamine obtained by Padgett (9) in
experiments with a fluidized bed at atmospheric pressure are undoubtedly due to deamination of dicy or intermediate compounds in the reaction. Hence, a logical first step in an experimental program would be to explore the effect of temperature, various possible catalysts, and the partial pressure of ammonia on deamination. A preliminary orientation may be secured most conveniently in the laboratory by experiments with a fluidized bed at atmospheric pressure. At the same time, factors such as particle size, degree of fluidization, etc., could readily be studied.

If, as the chemistry of the reaction indicates, ammonia pressure in excess of one atmosphere is needed to suppress deamination completely, further experiments could be made most conveniently with a static bed in a pressure bomb. For this case, the effect of diluents and particle size should also be determined.

To establish the relation between results obtained from fluidized and static beds, the static runs should include some at atmospheric pressure.
**EQUIPMENT**

*Fluidized Bed at Atmospheric Pressure.* The equipment used in this phase of the work is shown in Figure 19. It consisted of a fluidizing chamber of 58 mm. pyrex glass, 30 inches long and tapered at the bottom to 18 mm. To the bottom, a metal two-way stopcock was sealed, one position providing for gas flow during fluidization and the other providing for sampling of the charge in the reactor. Copper tubing was used for carrying all gases except from the reducing valves on the nitrogen and ammonia cylinders to the equipment where rubber tubing was used.

The nitrogen gas was first run through a drying chamber filled with anhydrous calcium chloride and then through a calibrated rotameter fitted with a small capillary at the inlet to suppress the usual bobbing of the rotameter float during fluidization. The gas was then passed through a heater consisting of 8 feet of 3/8 inch brass pipe wrapped with 20 gauge nichrome wire insulated and sealed with sauereisen. The outlet of the heater contained an insulated thermometer well and was connected to the stopcock on the column.

The column itself was first wrapped with asbestos tape over which was wound a nichrome wire heating element sealed in position with sauereisen. Two iron-constantan thermocouples were mounted under the asbestos tape at the top of the taper in the column and about half-way up the column. Over this was placed a section of two inch magnesia pipe insulation. Another calibrated iron-constantan thermocouple was placed in the center of the column at the top of the taper with the leads running...
out through sealed openings in the top and bottom of the column. At
the top of the column a short section of 20 mm. pyrex tubing was attach­
ed by means of a neoprene stopper and filled with glass wool to act as
a filter for any fine particles entrained by the fluidizing gas. Any
solid reaction materials were added at the top of the column after
removal of the stopper and filter.

Control of the temperature of the fluidizing gas and of the
reaction chamber in the earlier runs was done manually by means of vari­
able transformers, however, it was soon found desirable to control the
reaction bed temperature automatically. This was done by installing a
Wheelco Capacitrol with high and low control connected through two
variable transformers set at slightly different output voltages so that
when proper temperatures were reached, the power to the heating coil
would be reduced to just less than would maintain proper temperature.
This prevented the rather large fluctuations in temperature inherent with
"on-off" control in small systems and permitted control to plus or minus
0.5°C at 200°C.

For the runs in which ammonia was introduced with the nitrogen,
a tee was placed in the tubing from the rotameter to the heater and the
ammonia introduced here. The ammonia was run from a standard 50 pound
cylinder of anhydrous liquid ammonia through a special reducing valve and
then through a calibrated flow meter, consisting of a mercury manometer
across a short section of pyrex capillary tubing and a second mercury
manometer for reading the downstream pressure. The ammonia line was also
fitted with a thermometer well and thermometer. The off-gas after pass­
ing through the filter was passed into dilute hydrochloric acid solution
through a porous diffusion plate and then exhausted to the atmosphere.

**Static Bed at Atmospheric Pressure.** The reaction chamber for these runs consisted simply of a pyrex suction flask fitted with a one-hole neoprene stopper through which the nitrogen or ammonia gas could be introduced. The exit gas was drawn off through the side arm of the flask. For the runs in which a pure ammonia atmosphere was used, the exit gas was again run through a porous diffusion plate into an absorption bottle filled with dilute hydrochloric acid solution. The flask was placed in an electrically heated resistance muffle furnace equipped with an indicating-recording controller and stepwise input control to reduce temperature fluctuations.

**Static Bed at Elevated Pressure.** The reaction chamber for these runs (Figure 20) consisted of a pressure bomb 10 inches long, 1-1/4 in. O.D. and 3/4 in. I.D., machined from stainless steel and with a thermocouple well of stainless steel silver-soldered into the bottom. To the top, was attached an adapter section carrying a special ammonia pressure gauge and fitted with a 1/8 inch ammonia needle valve. All gaskets used were of "Teflon." The bomb was heated in a combustion tube furnace, the heat input of which was controlled by a variable transformer. The temperature of the reaction mixture in the bomb was read by means of a Wheelco potentiometer attached to a calibrated iron-constantan thermocouple. After entering the furnace, the thermocouple leads were shielded by means of standard two-hole thermocouple insulators and asbestos tape. A Cenco "presso-vac" pump was used to evacuate the bomb prior to loading it with ammonia from the standard anhydrous ammonia cylinder.
EXPERIMENTAL PROCEDURE

Fluidized Bed at Atmospheric Pressure. All solid reaction materials used in this work were carefully screened on a standard Ro-Tap machine using standard close series Tyler screens in order to obtain narrow size fractions. These materials were then stored in a drying oven until needed, since all exhibit a tendency to pick up moisture. Upon starting a run, the heaters for the gas and fluidizing chamber were turned on with air being introduced instead of nitrogen. The diluent material, such as silica gel or alumina, was removed from the oven, cooled in a dessicator, and weighed, and then returned to the oven. When the reaction chamber reached approximately the desired temperature, a shift to nitrogen gas was made. Then the diluent was added at the top of the reactor. The amount of dicy to be used was then removed from the oven, cooled in a dessicator, and weighed, and returned to the oven. When the desired reactor temperature was again reached and remained constant at the preset value, the dicy was added quickly to the diluent bed through a pyrex glass tube introduced through the top of the reactor. After quickly removing this tube and replacing the filter, the timer was started. If ammonia gas were being introduced with the nitrogen, it was turned on and regulated before the addition of dicy was made.

Readings of temperature, nitrogen flow rate, ammonia flow rate, and ammonia pressure were taken frequently during the runs, although the main efforts were directed toward maintaining all control factors constant during any run. Several samples of the mixture in the reactor were
taken during some of the runs to determine the progress of the reaction. This was done by withdrawing approximately the amount desired through the two-way stopcock at the bottom of the column into a tared weighing bottle, which was then cooled and weighed. A sample was always taken at the end of a run. During the runs with ammonia in the nitrogen stream, samples of the absorbing hydrochloric acid solution were withdrawn by pipette and titrated with sodium carbonate solution standardized against standard 0.1 N hydrochloric acid using a methyl orange indicator. Having withdrawn the last sample at the end of the run, the heaters and gases were turned off, and the remaining charge was withdrawn and weighed to permit checking of the over-all material balance.

**Static Bed at Atmospheric Pressure.** For these runs, the materials, either dicy and silica gel or dicy and alumina, were withdrawn from the drying oven, cooled in a dessicator, weighed, and mixed carefully before placing them in the reaction flask, which was preheated in the drying oven. The gas connections were then quickly made and the flask placed in the heating furnace. The furnace and the gas were then turned on, allowing enough time for any air in the system to be purged before reaction temperature was reached. No attempt was made to take samples during these runs, due to the possibility of the formation of ammeline and ammelide when dicy is exposed to moist air at the temperatures involved. Samples were taken at the end of the run simply to compare the over-all conversion with that obtained in the fluidized bed at similar temperatures. These samples were taken after allowing the flask and its contents to cool with normal gas flow to well below any temperature at which any reaction of dicy might occur. The gas flow was then stopped and the
sample taken in a tared weighing bottle.

Static Fed at Elevated Pressure. For these runs, the bomb was placed in the drying oven for several hours prior to use. The materials used, either pure dicy, dicy and silica gel, or dicy and alumina, were withdrawn from the drying oven, cooled in a dessicator and weighed. If a diluent was used, the dicy and diluent were thoroughly mixed. They were then charged carefully into the preheated bomb, which was immediately attached to the Cenco "presso-vac" pump and a mercury vacuum gauge. The bomb was evacuated very slowly by regulating the gas flow with a screw clamp in the rubber vacuum line to prevent any particles of the charge from being carried out of the chamber. After evacuation to a pressure of 25 microns, the valve on the bomb was closed and the unit disconnected from the vacuum line. It was then attached to the ammonia tank after purging the line on the tank, and ammonia was bled very slowly through the needle valve into the bomb. It was necessary to allow considerable time for completely charging the bomb, particularly for the high pressure runs, since dicy adsorbs ammonia to some extent and silica gel very strongly adsorbs it. If silica gel were used, the pressure in the bomb would return to almost atmospheric, that is, after charging once to a pressure corresponding to the vapor pressure of liquid ammonia at the temperature of the surroundings (usually 140 to 160 psig.). Also, upon charging quickly, the outside of the bomb would become almost too hot to touch due to the heat of adsorption. It is also interesting to note that dicy alone showed an equilibrium adsorption pressure of from 80 to 85 psig. when saturated with ammonia at approximately 32°C.

After the bomb was charged with ammonia to the desired pressure,
it was closed off, wrapped with asbestos tape, and placed in the combus-
tion furnace. The pressure and temperature in the bomb were recorded, 
and the run was immediately begun at the moment the power was turned on. 
Readings were taken very frequently during these runs, often every one-
half minute during the reaction. The power input to the heater was 
maintained constant by controlling the input voltage by a variable trans-
former. No attempts were made to take samples during a run, the chief 
purpose being to determine reaction characteristics under different con-
ditions.

After a run was completed, the furnace was turned off and the 
whole system allowed to cool to a safe temperature, usually below 100°C., 
before opening the bomb. Samples were taken and placed in the drying 
oven to remove any adsorbed ammonia. They were then removed from the 
oven, placed in a tared weighing bottle, cooled in a dessicator, and 
weighed. The bomb was thoroughly cleaned with ammonium hydroxide and 
distilled water before being returned to the drying oven in preparation 
for another run.
ANALYTICAL PROCEDURE

The analytical procedures for determining melamine and dicy in mixtures which might contain several other like compounds are tedious and troublesome and generally cannot be expected to give better than plus or minus one percent accuracy. The procedures used in this work are based on methods reported by Zavarov (16) and Korinfskii (17) and used by Padgett (9) for the determination of melamine and dicy in similar reaction mixtures. The procedure was thoroughly checked on prepared known mixtures of melamine and dicy before any attempts were made to analyze reaction mixtures.

All samples, whether containing just organics or organics and diluents, were treated in the same manner. The weighed sample containing approximately 0.5 gram of organic material was leached in 200 ml. of distilled water in a constant temperature bath at 50°C. for a minimum of two hours. The suspension was then filtered through a weighed Gooch crucible using filtering asbestos in the usual manner. The crucible was then dried over night, cooled in a dessicator, and weighed to determine the amount of insoluble deamination products formed. If the sample contained diluents, the weight of insoluble products was taken as the difference between the amount of undissolved solids and the calculated amount of diluent present based on the proportion of diluent to organic charged. This, of course, assumed a quantitatively representative sample and neglected any ammonia loss.

The melamine content of the filtrate was determined by converting
a sample portion to melamine picrate which is insoluble and which can be
separated, dried, and weighed. The solution obtained from the filtration
of the suspension in the determination of the insoluble product was then
diluted with distilled water to 250 ml. in a volumetric flask. A 50 ml.
portion of this solution was then transferred by pipette to a 400 ml.
beaker. To this solution, 50 ml. of glacial acetic acid was added, and
the mixture was heated to 90°C. One hundred milliliters of cold saturated
aqueous picric acid was then added with strong stirring, and the stirring
was continued until precipitation of the melamine picrate appeared almost
complete. This step was perhaps the most troublesome, because an inter­
ruption in the stirring or failure to stir sufficiently frequently yielded
very low amounts of precipitate or almost none. The mixture was allowed to
cool to room temperature and then was placed in a refrigerator over night.
It was then filtered through a Gooch crucible and the precipitate washed
thoroughly with cold saturated aqueous melamine picrate solution, dried to
constant weight, and weighed. The amount of melamine in the sample was
calculated by means of the following formula:

\[
\text{Weight melamine} = 0.356 \times \text{(weight precipitate)} + 0.001
\]

in which the 0.356 is the factor for converting the weight of melamine pic­
rate (M.W. = 355.2) to melamine (M.W. = 126.1) and the 0.001 is a solubility
correction factor for melamine dissolved in the solution as melamine picrate.

The calculated weight of melamine was then divided by one-fifth of
the calculated amount of organic material in the sample to obtain the
percent yield of melamine.

The weight of dicy was determined by converting the dicy to the
silver dicy picrate compound which is insoluble and may be treated
gravimetrically. For the determination of dicy, a separate 50 ml. portion of the solution in the volumetric flask was transferred to a 400 ml. beaker. To this was added 50 ml. of glacial acetic acid. After heating to 90°C, 100 ml. of cold saturated aqueous picric acid and 20 ml. of a 5 percent aqueous solution of silver nitrate were added with stirring. Stirring was again continued until precipitation of the silver dicy picrate seemed to be complete. The mixture was allowed to cool to room temperature, stored in a refrigerator over night, filtered through a Gooch crucible, washed with saturated silver-dicy-picrate solution, and the precipitate dried and weighed. The weight of dicy was then calculated by means of the following formula:

\[
\text{Weight dicy} = 0.2001 (a - b) + \frac{V}{100} (0.0119)(a - 0.0022)
\]

in which \(a\) is the weight of precipitate from the dicy determination, \(b\) is the weight of melamine picrate precipitate, 0.2001 is the factor for the conversion of the weight of silver-dicy-picrate (M.W. = 420.1) to the weight of dicy (M.W. = 214.1), and the second term on the right hand side is the correction factor for the solubility of the precipitates in \(V\) ml. of filtrate. The calculations for percentages were made in the same manner as for melamine.

In the later runs (No. 30 through 61), a simplified dicy determination was made by simply reheating the filtrate from a melamine determination to 90°C, adding 20 ml. of five percent aqueous silver nitrate solution, and stirring until precipitation seemed complete. This mixture was then cooled to room temperature, stored in a refrigerator over night, filtered, washed, and the precipitate dried and weighed in the same
manner. The weight of dicy was calculated by means of the following formula:

\[
\text{Weight dicy} = 0.2001 \times \text{(weight precipitate)} + 0.0041
\]

where 0.0041 is the solubility correction factor for dicy in solution in the filtrate as silver-dicy-picrate. The results obtained with this procedure checked within the limits of accuracy of the procedures used, conserved the sample solution permitting more check analyses, and offered less trouble during precipitation.

An effort was made to determine whether absorption spectra in the ultra-violet range could be used as an analytical procedure. However, since the absorption bands of melamine and dicy are close to each other and other similar compounds interfere, only a qualitative agreement with the gravimetric procedure could be obtained.
RESULTS

The results obtained during the course of this work are shown in Tables I through IV in the Appendix. The significant results obtained from these data are presented in graphical form in Figures 1 through 18. The results of the atmospheric pressure runs are shown in Figures 1 through 8, which include primarily data from the fluidized bed system. However, in order to show the relation of the static system to the fluidized system, data points obtained from the static bed runs are included on these figures where appropriate. The results obtained using static beds with ammonia pressures above atmospheric are shown in Figures 9 through 18.

The progress of the reactions involved during the conversion of dicy to melamine utilizing silica gel as a diluent is shown in Figures 1 through 4. A plot of the weight percent of melamine yield based on dicy charged versus time is shown in Figure 1. The data shown are for runs in which the reaction temperature was between 178 and 182°C. Also included are two data points obtained from static bed runs using a nitrogen or ammonia atmosphere. The weight percent of dicy present versus time is plotted in Figure 2 for runs in which the reaction temperature was maintained at 180°C. A plot of the weight percent of insoluble deamination products formed versus time is shown in Figure 3 for reaction bed temperatures between 178 and 182°C. The weight percent of soluble intermediate compounds is plotted versus time in Figure 4. The points through which this curve is plotted, were obtained by calculating the percent of
solubles as the difference between 100 and the sum of the percent of melamine, dicy, and insolubles read from the curves of Figures 1, 2, and 3.

The weight percents of melamine versus time are plotted on Figure 5 for runs in which the temperatures were maintained above and below 180°C, and include some data points obtained by Padgett (9) on a similar system. The weight percent of dicy versus time is plotted on Figure 6 for reaction temperatures other than 180°C. In order to show the relationship between results obtained at different temperatures, the curves of Figures 1 and 2 are also plotted on these figures, as solid lines, while the data points are shown and designated for other temperatures. The data points indicating the weight percent of insoluble compounds formed at temperatures other than 180°C, are plotted versus time on Figure 7, which includes the curve of Figure 3 as a solid line. Two data points obtained from static runs using nitrogen and ammonia atmospheres, at reaction temperatures of 180°C, are also included for comparison. Data points indicating the weight percent of melamine yields, when diluents other than silica gel were used, were plotted against time on Figure 8, which includes the curves of Figure 5 for comparison.

The results obtained from runs using pure dicy as the charge are shown in Figures 9 through 14. Two typical heating curves for static systems under pressures of ammonia above atmospheric are plotted as temperature versus time on Figure 9. Two typical curves showing the relation of pressure to temperature during runs carried out under elevated ammonia pressure are plotted on Figure 10. The temperature at which the reaction proceeds spontaneously, and referred to as the reaction tempera-
ture, is designated on these two figures. The pressure corresponding to the reaction temperature, and referred to as the reaction pressure, is obtained from curves like Figure 10.

The weight percent of melamine yield is plotted against reaction pressures on Figure 11. However, the average of the melamine yields for the process carried out in static beds at atmospheric pressure with alumina as a diluent and using an ammonia atmosphere is plotted as a data point on this figure. The weight percent of dicy remaining after reaction was complete is plotted versus reaction pressure in Figure 12. The percent of insoluble deamination products formed during the reaction is plotted against reaction pressure in Figure 13 and includes one data point showing the average yield of insoluble products for the process carried out in an ammonia atmosphere using alumina as a diluent. The weight percent of soluble intermediate compounds formed is plotted versus reaction pressure in Figure 11.

The results obtained in runs in which diluents were used in the reaction mixture are shown in Figures 15, 16, and 17. The data points showing the yields of melamine plotted against reaction pressure are shown in Figure 15. For comparison, the curve of Figure 11 obtained using a pure dicy charge is shown as a solid line on this figure. The weight percent of dicy remaining after reaction is plotted against reaction pressure in Figure 16. The curve of Figure 12 is included as a solid line for comparison. The yields of insoluble compounds versus reaction pressure are plotted on Figure 17 which includes the curve of Figure 13.

The reaction temperature is plotted versus reaction pressure on
Figure 13. The data points included in this figure are designated as to whether the charge consisted of pure dicy, dicy and alumina, or dicy and silica gel. A data point is also included for the temperature at which dicy spontaneously is converted to melamine and other compounds at atmospheric pressure when pyrolyzed.

**Qualitative Observations.** The following information, is not recorded as actual data, but is included here as significant or important observations made during the course of this study:

(a) In the fluidized bed runs at atmospheric pressure, the ammonia evolution due to deamination of reactants approaches a value of one mole of ammonia per mole of dicy charged.

(b) In all cases at atmospheric pressure, whether in a fluidized or static system, some caking of the charge occurs at ratios of diluent to organic of two to one. At higher ratios, there is no noticeable caking.

(c) In operations under elevated pressures of ammonia, the charge shows a slight crust, but is not caked, at ratios of diluent to organic of two to one.

(d) Upon loading of the bomb with ammonia using a pure dicy charge, there is a noticeable heat effect due to adsorption amounting to some 5° to 10°C. at the bomb surface. With silica gel in the charge, the effect is considerably greater.

(e) Using a pure dicy charge, so long as the bomb is loaded with a sufficient amount of ammonia, the ammonia pressure remains constant at from 80 to 85 psig. at approximately 32°C. This pressure may be exceeded only with difficulty by loading with considerably more
ammonia.

(f) There is a noticeable difference in the character of the melamine picrate precipitate on analysis when the melamine yield is low and the amount of insoluble compounds is high. However, this apparently does not affect the accuracy of the analysis.

(g) During the reaction carried out under elevated ammonia pressure in a static bed at the lowest reaction pressure used, the pressure increased to well above normal soon after the initial heat effect of the exothermic reaction was noted.

(h) During two of the runs using elevated ammonia pressure, small leaks developed in the valve on the reaction bomb allowing ammonia to escape very slowly and tending to maintain the pressure constant during temperature increases and also producing a cooling effect due to ammonia expansion. Even though no reaction temperature or pressure data could be obtained, yields of melamine in both runs are above 90%.
Fig. 1. Volatine Yield vs. Reaction Time for Atmospheric Pressure Runs at 180°C, in the Presence of Silica Gel.
Fig. 2. Unreacted Dicy vs. Reaction Time for Atmospheric Pressure Runs at 130°C, in the Presence of Silica Gel.
Fig. 3. Insoluble Products vs. Reaction Time for Atmospheric Pressure Runs at 100°C, in the Presence of Silica Gel.
Fig. 4. Soluble Products vs. Reaction Time for Atmospheric Pressure Runs at 190°C. in the Presence of Silica Gel.
Fig. 5. Effect of Temperature on Melamine Yield vs. Reaction Time for Atmospheric Pressure Runs in the Presence of Silica Gel.
Fig. 6. Effect of Temperature on Unreacted Dicy vs. Reaction Time for Atmospheric Pressure Runs in the Presence of Silica Gel.
Fig. 7. Effect of Temperature on Insoluble Products vs. Reaction Time for Atmospheric Pressure Runs in the Presence of Silica Gel.
Fig. 8. Effect of Diluent and Temperature on Melamine Yield vs. Reaction Time for Atmospheric Pressure Runs.

- Runs at temperature designated - Silica gel diluent
- Run at 130°C. - Filtrol "SR" diluent
- Run at 170°C. - Alumina diluent
- Static Run at 180°C. - Alumina diluent, H3 atmosphere
- Static Run at 200°C. - Alumina diluent, H3 atmosphere
- Static Run at 190°C. - Alumina diluent, H3 atmosphere

Reaction Time - min.

Melamine Yield - wt. %
Fig. 9. Typical Curves of Temperature vs. Time for Runs at Elevated Arsenia Pressure Using Pure Dicy Charges.
Fig. 10. Typical Curves of Pressure vs. Temperature for Runs at Elevated Ammonia Pressure Using Pure Ice Charges.
Fig. 11. Melamine Yield vs. Reaction Pressure for Runs at Elevated Ammonia Pressure Using Pure Dicy Charges.
Fig. 12. Unreacted Dicy vs. Reaction Pressure for Runs at Elevated Ammonia Pressure Using Pure Dicy Charges.
Fig. 13. Insoluble Products vs. Reaction Pressure for Runs at Elevated Ammonia Pressure Using Pure Hicy Charges.
Fig. 11. Soluble Products vs. Reaction Pressure for Runs at Elevated Ammonia Pressure Using Pure Hicy Charges.
Fig. 15. Effect of Diluent on Melamine Yield vs. Reaction Pressure for Runs at Elevated Ammonia Pressure
Fig. 16. Effect of Diluent on Unreacted Dicy vs. Reaction Pressure for Runs at Elevated Ammonia Pressure.
Fig. 17. Effect of Diluent on Insoluble Products vs. Reaction Pressure for Runs at Elevated Ammonia Pressure.
Fig. 18. Reaction Temperature vs. Reaction Pressure for Runs at Elevated Ammonia Pressure.
DISCUSSION OF RESULTS

Runs at Atmospheric Pressure

**Effect of Time.** The progress of the reactions at atmospheric pressure during the conversion of dicy to melamine may be seen by reference to Figures 1 through 4. As shown in Figure 1, the formation of melamine is a relatively slow process at 180°C. At this temperature, approximately 100 minutes are required for the ultimate yield of about 50 percent to be approached. By contrast, the disappearance of dicy itself from the reaction mixture is relatively rapid. As is seen in Figure 2, the disappearance is almost complete after only ten or fifteen minutes. Figure 3 shows that the formation of insoluble products is, like the formation of melamine, a relatively slow process.

Clearly, the rapid disappearance of dicy and the relatively slow formation of melamine and insoluble products must indicate that the major initial products of the reaction are neither melamine nor insoluble compounds, but soluble compounds of some kind. The amount of soluble products at any time may be readily calculated by difference between the weight of the dicy charge and the weight of melamine, unreacted dicy, and insoluble products. The results of such a calculation are shown in Figure 4. This figure emphasizes that a large amount of some intermediate compound or compounds, soluble in water, is formed in the early stages of the process. In succeeding stages, this material is converted relatively slowly to melamine and compounds insoluble in water.

**Static Versus Fluidized Bed.** There is no definite difference
indicated in the results obtained in either static or fluidized beds when using a nitrogen atmosphere, as shown in Figures 1 and 3. However, there is a slight caking of the charge in either case when the ratio of solid diluent to organic is two to one.

**Effect of Temperature.** Figure 5 indicates that the maximum yield of melamine obtainable at atmospheric pressure occurs at a temperature of approximately 180°C. At lower temperature, the formation of melamine is not only slower as might be expected, but the apparent ultimate yield is also lower. Whether this is due to a shift in the equilibrium of the reaction or to competing side reactions is not known. At temperatures above 180°C, the formation of deaminated compounds is presumably favored at a sacrifice of the conversion to melamine.

The fact that the disappearance of the dicy is so rapid makes it difficult experimentally to get complete and accurate data on the rate of the reaction. The experimental data presented in Figure 6 show that the rate is extremely sensitive to temperature.

The formation of insoluble compounds at different temperatures is shown in Figure 7. There is no definite indication of any relation between the rate of formation of these compounds and temperature. However, the data are quite scattered, a fact which may well obscure any temperature effect. As will be shown later in the discussion of the accuracy of the data, the results of the determination of insolubles are particularly subject to errors because of the difficulty of obtaining truly representative samples of the diluent-organic mixtures.

**Effect of Ammonia.** The effect of pure ammonia atmospheres (used only with static beds) on the dicy to melamine reactions is shown in
Figures 1, 7, and 8. The yields of melamine are greater than those obtained using nitrogen atmospheres or low partial pressures of ammonia, except when using alumina as a diluent at low reaction temperatures. The increase in yield, however, is relatively slight.

As noted in the qualitative observations, measurements of the ammonia evolved in the atmospheric pressure runs using nitrogen or dilute ammonia-nitrogen mixtures indicate that the amount approaches the order of magnitude of one mole of ammonia per mole of dicy charged. Since there are one and one-third equivalent moles of ammonia in the dicy molecule, the deamination is evidently almost complete at atmospheric pressure and at low partial pressures of ammonia. Figure 1 shows that a relatively slight increase in yield of melamine occurs when pure ammonia is used, and this indicates that a pressure of one atmosphere of ammonia has little effect on deamination.

Accuracy of Data. As mentioned in the section on analytical procedure, the methods of analysis for melamine and dicy are accurate to about one percent as determined by comparison with known samples. For example, the analysis of a mixture containing 90% melamine ranges from 89 to 91%, while the determinations on a sample containing 20% melamine range from 19 to 21%. Hence, the analytical technique is quite dependable.

The accuracy of the data is also dependent on the methods of sampling the mixture of diluent and organic material. A clue to the extent of the inaccuracy introduced by sampling is the degree of scatter of the data points on Figures 3 and 7. One can see that the scatter is somewhat greater than can be explained by errors in analysis, but it is
not excessive. A relative measure of the accuracy of sampling and analysis is provided by comparison with the results of Padgett plotted on Figures 1 and 5. The agreement is obviously good.

A point worth noting is that relatively slight errors in sampling have a greater effect on the determination of insolubles than on measurement of melamine or dicy. For example, consider a run in which the charge consists of 100 grams of diluent and 20 grams of dicy, and the true analysis of the reaction products is 39% melamine, 35% insolubles, and 1.5% dicy. If the sample taken is 12 grams and contains 10.5 grams of diluent and 1.5 grams of organic material instead of the proper proportions of 10 and 2, the analysis would show 29% melamine, 51% insolubles, and 1.1% dicy. One should remember then, that the figures on insolubles and also on solubles are inherently somewhat less accurate than the other data. The accuracy of the data is also affected to some extent by the loss of ammonia which occurs during the reactions and which was not measured except during a few runs.

Probable Mechanism of the Dicy-Melamine Reactions. As indicated in Figure 4, which shows the percent of soluble compounds formed versus time, the data show that there must be some sort of intermediate compound or compounds involved in the formation of melamine from dicy, and that most or all of the intermediate material is soluble in water. The intermediates suggested by McClellan (15) and Migridichian (12) are biguanide, guanidine, and cyanamide. All three of these compounds are soluble in water. Hence, the data of this work at atmospheric pressure lend support to the conjecture that the compounds listed above are the ones involved as intermediates in the formation of melamine.
Although not absolutely conclusive, Figure 3 indicates that some formation of insolubles occurs at the expense of dicy. If this were not the case, the curve of Figure 3 would approach the origin with zero slope, instead of the positive slope which it appears to have. Presumably dicy deaminates to form compounds such as melam, melem, and melon already mentioned. A comparison of Figures 1, 2, and 3 reveals that some insolubles are formed at the expense of the soluble intermediates, presumably also by deamination. The fact that most of the formation of melamine occurs after the dicy has almost completely disappeared indicates that at atmospheric pressure and low temperatures (below the spontaneous reaction temperature) the final step in the reactions which produce melamine does not include dicy as a reactant.

Runs at Ammonia Pressure above Atmospheric Heating Effects. As shown in Figure 9, the typical heating rate curves (obtained while maintaining constant power input to the heater) are quite similar for either high pressures (near 350 psig.) or low pressures (near 100 psig.). In both cases, the temperature increases slowly during the first few minutes, partly because of a lag in the heating of the bomb just after the power is turned on and partly because of the heat required for the desorption of the ammonia adsorbed on the dicy charge. Both curves also show that at elevated pressure the reactions during the formation of melamine occur very rapidly. However, the temperature increase after reaction starts is smaller for the runs at higher pressures. This may be attributed partly to the higher heat capacity of the system having the greater ammonia charge at higher pressure. It may
also be due partly to the fact that at higher pressures the reaction begins at lower temperatures with the consequence that the reaction probably proceeds at a slower rate. The heat capacity effect may be noted in the lower heating rate during the high pressure run. For purposes of subsequent discussion, the temperature at which an abrupt rise begins on the temperature-time curve will be called the reaction temperature.

The typical curves of pressure versus temperature, plotted on Figure 10, show considerable differences between runs at high or low pressures. The initial break in each curve in all probability is due to the end of the desorption of ammonia from the charge. After this, up to the next deviation in the curve, the low pressure run shows a close correlation with the calculated pressure-temperature relations at constant volume, taking into consideration the bomb expansion with heat and the slight dissociation of ammonia at higher temperatures. At the dip in the low pressure curve, it is important to note that the pressure decreases prior to any substantial temperature rise, indicating a two step reaction. After the heat of reaction effects begin to appear, the ammonia pressure returns quickly towards normal values and may possibly go above these values, as indicated by still lower pressure runs and by the lag in pressure rise in the bomb during rapid temperature rises. The number of moles of ammonia adsorbed or evolved by the solid during each of the stages can be estimated from Figure 10 with the aid of pressure-volume-temperature data on pure ammonia.

The changes in pressure and temperature as reaction takes place agree with the suggested mechanisms of the conversion of dicy to
melamine. First, in the low pressure runs, as indicated by the lower curve of Figure 10, there is a pressure decrease indicating that ammonia is being used up by some reaction, probably in the formation of biguanide from dicy and ammonia, without any noticeable heat effect. Then there is a strong heat effect with a rapid return of the ammonia pressure, corresponding with the strongly exothermic reaction of the decomposition products of biguanide with dicy to form melamine and ammonia. The tendency of the pressure to exceed the normal value after the dip in the curve of Figure 10 indicates that the exothermic reaction is accompanied by some deamination of the reactants due to the considerable temperature increase. The heat effects, indicated by Figures 9 and 10, which take place during the conversion of dicy to melamine compare favorably with the heats of reaction calculated from the heats of formation of the compounds present, with only about 12 Kcal. evolved during the first stage of the reaction and approximately 10 Kcal. evolved during the second stage.

At higher pressures (the upper curve of Figure 10), after the first break in the pressure-temperature curve due to desorption, the curve tends at first toward reasonable agreement with calculated pressure-temperature values. However, there is an appreciable upward deviation of the pressure as the temperature is increased. Apparently, at the start of a run at high pressure, ammonia is adsorbed in two ways; one, a simple adsorption of ammonia on dicy, and the other, a chemisorption of ammonia by dicy. The adsorbed ammonia is quite easily driven off at relatively low temperatures, while the other requires quite high temperatures to release the ammonia-dicy bond. If reference is made
to the structure of dicy and biguanide, it is quite apparent that the \(-\text{CN}\) group of the dicy molecule should very readily accept ammonia. It is believed, then, that this bond still exists at least to some extent as the melamine reaction temperature is reached. This is also in agreement with the fact that there is no pressure drop prior to the temperature effect upon reaction to melamine. It is to be noted that the pressure rises more slowly after the exothermic reaction begins, and this is attributed again to the lag in pressures with very rapid temperature increases in the bomb. Agreement is also found with the mechanism suggested for the conversion of dicy to melamine, however, with the formation of biguanide at lower temperatures due to the higher pressure of ammonia.

**Effect of Pressure.** The effect of pressure on the dicy-melamine reactions, when pure dicy charges are used, is shown in Figures 11 through 14, in which the yields of melamine, dicy, insolubles, and solubles are plotted against the pressure at the reaction temperature. At pressures up to 200 psig., there is no noticeable change in the ultimate yield of melamine obtained during the reaction from that obtained at atmospheric pressure. However, at about 200 psig., there is an abrupt increase in the yield of melamine obtained. The yields above 200 psig. are generally above 80 percent and increase further with still higher pressure. This contrasts with yields nearly constant at about 50 percent below 200 psig. It is presumed that this phenomenon is caused by the difference in ammonia adsorption characteristics of dicy at low and high pressures. Adsorption of this type, previously discussed, characteristically shows sharp changes in the degree of adsorption at certain pressures. This
pressure is presumably at about 200 psig, for the dicy-ammonia system in the rather narrow range of reaction temperatures involved. This would result in the whole charge remaining as dicy almost to the reaction temperature at low pressure, while at higher pressure, much of the dicy would already have become essentially biguanide due to the chemisorption of ammonia prior to reaching reaction temperature.

Further light is thrown on the mechanisms involved by a consideration of the effect of pressure on the amount of dicy remaining after the reaction, which is shown in Figure 12. Despite the fact that Figure 10 indicates a reaction between ammonia and dicy in runs at low pressure, Figure 12 reveals the presence of large amounts of unreacted dicy after the dip is passed. The most probable explanation of this fact seems to be that in the low pressure runs the dip in the curve in Figure 10 is caused by reaction between ammonia vapor and the dicy molecules at the surface of the particles of solid. Once the surface molecules react, further reaction between ammonia vapor and dicy proceeds at a vastly reduced rate because of the necessity for diffusion of ammonia through the solid phase to reach the unreacted dicy in the interior of the particles.

Turning to the high pressure region of Figure 12, one finds that the amount of dicy remaining after the reaction is quite low. Evidently, reaction of the dicy with the ammonia is completed very rapidly if an adequate amount of ammonia is adsorbed throughout the solid phase at the time when reaction temperature is reached. One can say that the key to success in achieving high rates of reaction and high ultimate yields of melamine in the synthesis of melamine in the solid phase is to pretreat
the charge with ammonia before reaction temperature is reached, employing sufficient pressure and time to insure the adsorption of an adequate amount of ammonia and its thorough diffusion into the solid.

The fact that the percentages of melamine and dicy remaining in the product are substantially independent of pressure above 300 psig., as indicated by Figures 11 and 12, suggests the existence of an equilibrium conversion of dicy to melamine, when an adequate supply of ammonia in the solid phase is assured.

The effect of pressure on the formation of insolubles is shown in Figure 13. There is a continued decrease in the percent of insolubles formed as the reaction pressure is increased. This effect is as to be expected, with the higher pressures suppressing the deamination of the reactants. Figure 14 shows that the percent of soluble compounds produced changes only slightly at pressures up to about 200 psig., and that above this pressure there is a gradual decrease in the amount of these compounds. However, since the amount of solubles is calculated by difference, it is not thought that there are any significant trends in these data except possibly at the higher pressures.

**Effect of Possible Catalysts.** The effect of diluents in the charge is shown in Figures 15, 16, and 17. The presence of alumina shows essentially no effect on the reaction under any conditions. However, silica gel shows an adverse effect on melamine formation, with yields no better at 250 psig. than are obtained at atmospheric pressure. This may be explained by the fact that two of the intermediates, guanidine and biguanide, are strong bases with which silica gel would almost certainly act as an acid, forming a complex and preventing further reactions in the
formation of melamine. This also may account for the rather large amounts of soluble products formed.

**Effect of Pressure on Reaction Temperature.** The reaction temperature is obtained by noting the first sharp upward deviation from the normal heating curve during a run. Consequently, these temperatures coincide with the start of the first major exothermic reaction or reactions and not necessarily with the very start of the intermediate reactions, particularly at the lower pressures.

The effect of pressure on this reaction temperature is shown in Figure 13. The reaction temperature is decreased by increased pressure from a value of about 210°C. at atmospheric pressure to about 145°C. at 450 psig. This effect seems to agree with the proposed mechanisms, since these mechanisms suggest that the first step in the conversion of dicy to melamine involves a reaction of dicy with ammonia, which would certainly be favored at lower temperatures under higher pressures of ammonia. The diluents used in these runs show no significant effect on these reaction temperatures.
BIBLIOGRAPHY

1. Foster, George H., United States Patent 2,206,603.


17. Korinfiskii, A. A., Zavodskaya Laboratoriya, 12, 413 (1946).
Table I. Data of Fluidized Bed Runs at Atmospheric Pressure.

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* No measurement of insolubles

** No analysis made — charge caked

T Trace
Table II. Data of Static Bed Runs at Atmospheric Pressure

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T Trace
Table III. Data of Static Fed Runs at Elevated Ammonia Pressure Using Pure Dicy Charges.

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T Trace

80 - 100 mesh charge
Mel. in charge - 5 gms.
Table IV. Data of Static Bed Runs at Elevated Ammonia Pressure Using Alumina or Silica Gel Diluents

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* No reaction temperature or pressure data taken

** Maximum temperature and pressure reached during run

T Trace
Table V. Typical Data for Static Bed Runs under Elevated Ammonia Pressure

Run No. 36

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Table VI. Typical Data for Static Bed Runs under Elevated Ammonia Pressure

Run No. 36

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Table VII. Typical Data for Static Bed Runs under Elevated Ammonia Pressure

Run No. 46

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Controller
110v.
Variable Transformers

Gas Heater

Thermometers

Filter

Absorption Bottle

Ni3 Flow Meter

Rotameter

Drier

Figure 19.
Fluidization Equipment

x Thermocouples
Figure 20.
Full Scale Pressure Reactor

- 1-1/4" Stainless Steel
- 3/8" N.P.T. Pressure Tape
- 7/16" N.F.
- 1-1/2" Iron Steel
- 5/32" N.P.T.