SYNTHESIS OF MELAMINE FROM UREA, I

By Hideo Kinoshita*

Introduction

As the starting materials of the synthesis of melamine, cyanamide, dicyandiamide, ammonium cyanate, urea, cyanuric acid, ammeline, ammelide, guanyl urea, guanyl cyanamide, etc.[1)2)], have been used. As to the synthesis from urea, several patents are reported.[2)3)4)5)] In those patents, the temperature range is 300～500°C and the maximum pressure is 550 atm. In the patent of American Cyanamide Co.[2)], the equation of this reaction is represented by $6NH_2CONH_2 = (NH_2CN)_3 + 6NH_3 + 3CO_2$. The mechanism of this reaction is not known, but it is reported that biuret, cyanuric acid and ammelide are produced after heating urea for several minutes at 200°C[6)]. In studying the reaction mechanism of the synthesis of melamine from urea, for the purpose of investigating the yield of the intermediate substance and melamine, the author experimented under the following conditions——temperature range 200～425°C, packing ratios 0.1, 0.3 and 0.5 g/cc, and maximum pressure 700 kg/cm².

Apparatus

The apparatus used are much the same as used in the equilibrium experiment of the urea-water system[7)]. It is expected that the reaction vessel, whose capacity is 18.2 cc, steel pipes and high pressure valves must be corroded severely. A favourable alloy in the low nickel system in the test of corrosion[8)] by the urea-water system is used, and it is effective to protect corrosion. The composition of this iron alloy is thus: C, 0.1%; Cr, 24.5%; Ni and Mo, 2%; Mn, Si and Ti, 0.5%.

Samples and Experimental Method

The sample and the experimental methods are all the same as the previous paper[7)] except inspiring the water, namely, urea is recrystallized by water, packed in the reac-

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1) P. P. McClellan, *Ind. Eng. Chem.*, 32, 1186 (1940)
2) Brit. Pat. No. 598,175 Feb. 12 (1948)
3) U. S. Pat. No. 2,550,659 Apr. 24 (1951)
4) Brit. Pat. No. 628,250 Aug. 25 (1949)
5) Brit. Pat. No. 644,374 Oct. 11 (1950)
6) E. A. Werner, *J. Chem. Soc.*, 103, 2275 (1913)
7) R. Kiyama and H. Kinoshita, *This Journal*, 21, 9 (1951)
8) H. Kinoshita, *ibid.*, 21, 16 (1951), To the other systems of alloy, the test of corrosion is executing.

tion vessel and the air exhausts. After reaching a required temperature, the reaction is performed under the pressure produced. The analytical methods of the reaction products are as follows.

After the reaction is over, the products are dried at 65°C to a constant weight and ammonium carbamate and ammonium carbonate etc. contained in the product are decomposed. They are solved in a definite volume of water calculated from the solubility of melamine and cyanuric acid. After filtrating and drying at 65°C, the water insoluble substance is submitted to the analysis of nitrogen content by the method of Kjeldahl. The quantity of water soluble parts are measured by drying at 65°C. As to the water soluble parts, the quantity of urea, melamine, biuret and cyanuric acid are analysed. The experimental methods of the quantitative analysis of the components are as follows.

1) **Urea** According to the method of Xanthohydrol, the quantity of urea is analysed. 5g of xanthohydrol is solved in 100cc of a mixture of methyl alcohol and glacial acetic acid. 5cc of water solution of urea (2 mg urea/cc), 7 cc of glacial acetic acid and 3~5 cc of the reagent of xanthohydrol are mixed. After an hour, the precipitates are washed by 66% acetic acid and methyl alcohol, and dried at 100°C. The quantity of urea corresponds to 1/7 of the dried precipitate.

2) **Melamine** The quantity of melamine is measured by the absorption spectrum of ultraviolet ray by means of a Beckman-type spectrophotometer. The standard melamine used is recrystallized from water and dried. As the melamine has the maximum absorption at 2350 Å in an acidic solution[9], 2 cc of 0.114 N H_2SO_4 is added to 10 cc of the sample solution in measuring the absorption spectrum. The absorption of 0.0125 g/*l* solution of melamine at 2200 ~ 2500 Å and the relation between the concent-

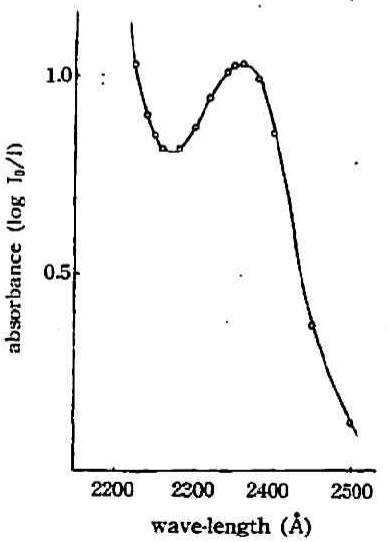


Fig. 1 The absorption of melamine at 0.0125 g/*l* in sulphuric acid solution

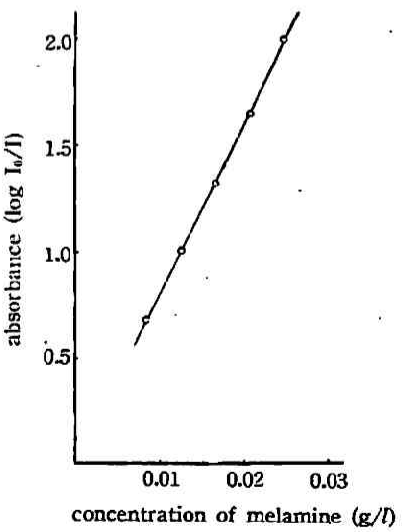


Fig. 2 The relation between concentration and absorbance of melamine at 2350 Å

9) I. M. Klotz and T. Askounis, *J. Am. Chem. Soc.*, 69, 801 (1947)

ration of melamine and the intensity of absorption at 2350 Å are shown in Figs. 1 and 2. The shape and the intensity of the absorption are coincident with the data of Klotz[9].

3) **Biuret** From the reaction of biuret, the quantity of biuret is measured. After coloured by adding alkaline copper sulphate solution, the absorption of visible light is measured. The absorption reaches maximum at 5300 Å. The absorption of 1 g/*l* solution of biuret at 4600 ~ 5600 Å and the relation between the concentration of biuret and the intensity of absorption at 5300 Å are shown in Figs. 3 and 4. The standard biuret is prepared by passing dried hydrogen chloride gas in urea at 150°C and refined[10].

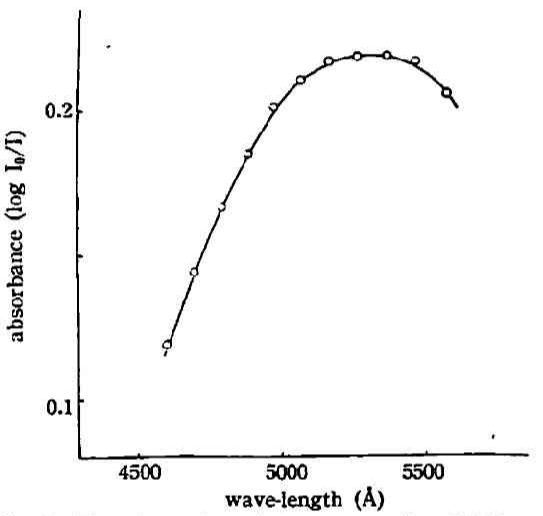


Fig. 3 The absorption of biuret at 1g/*l* in KOH solution

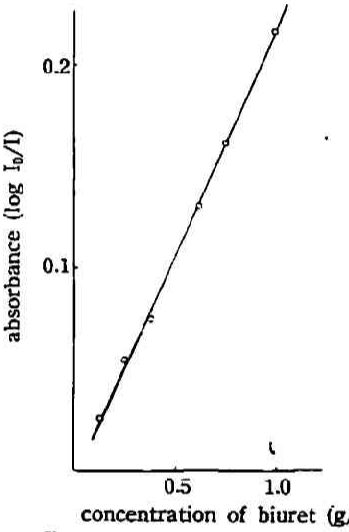


Fig. 4 The relation between concentration and absorbance of biuret at 5300 Å

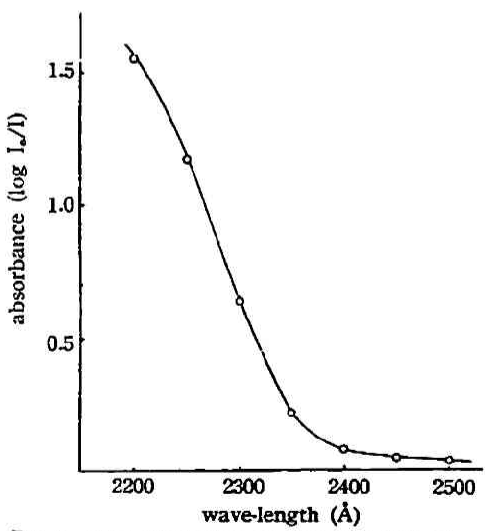


Fig. 5 The absorption of cyanuric acid at 0.0261 g/*l* in 0.1N KOH solution

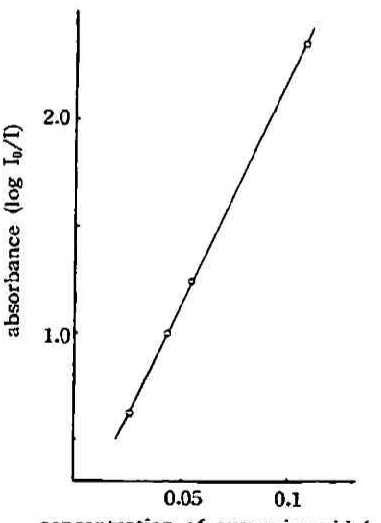


Fig. 6 The relation between concentration and absorbance of cyanuric acid in 0.1 N KOH solution at 2300Å

10) I. Kitawaki, S. Hori and Y. Shimoda, *Bull. Gov. Chem. Ind. Res. Inst., Tokyo*, 32, No. 10 (1937)

4) **Cyanuric acid** The quantity of cyanuric acid is measured by the absorption spectrum of ultraviolet ray as in the case of melamine. There exists no absorption in an acidic solution but the absorption in an alkaline solution has set in from 2400 Å. The absorption of 0.0252 g/*l* solution of cyanuric acid in 0.1 N KOH solution at 2200 ~ 2500 Å and the relation between the concentration of cyanuric acid and the intensity of absorption at 2300 Å are shown in Figs. 5 and 6. The shape and the intensity of absorption are coincident with the data of Klotz[9]. The standard cyanuric acid is prepared by heating urea with $ZnCl_2$ at 220°C and recrystallized[11].

Analysis of the reaction product by the above method shows that there exist three combinations of each component——a) urea and melamine, b) urea and cyanuric acid, c) urea, biuret and cyanuric acid. In measuring the quantity of urea by the way of xanthohydrol, melamine, cyanuric acid and biuret do not interrupt. And the absorption of urea in ultraviolet region in an acidic or an alkaline solution is very slight. So it is capable to measure separately melamine and urea, or cyanuric acid and urea. In the case of the combination c), as there exists the absorption of biuret in ultraviolet region, and the shape of absorption resembles cyanuric acid in the present measurement, so it is not preferable to analyse cyanuric acid with biuret by the absorption of ultraviolet ray. Accordingly, in this case the quantity of cyanuric acid is measured by the subtraction of the quantities of biuret and urea from the quantity of soluble part. The experimental error of each component in each case is within 0.5%.

Experimental Results

The experimental conditions are as follows: packing ratios 0.1, 0.3 and 0.5 g/cc, temperature range 200 ~ 425°C, and time 0 ~ 6 hours. The quantities of urea at each packing ratio are 2.15, 6.45 and 10.75 g respectively. The weight percentages of the results of analysis of the reaction products, the nitrogen contents of water insoluble substance and the yields of melanine are tabulated in Table 1. The relations between pressure and time at each temperature and packing ratio are shown in Figs. 7, 8 and 9. That the time is zero in the tables means that the reaction vessel is cooled immediately after reaching necessary

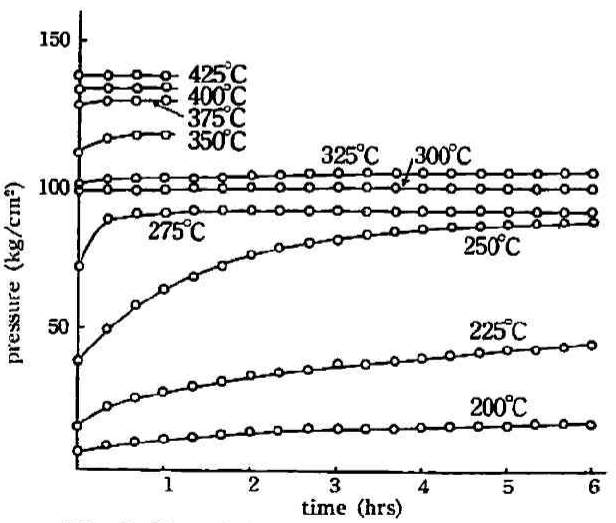


Fig. 7 The relations between temperature and pressure at 0.1 g/cc

11) R. Walther, *J. prak. Chem.*, (2) 79, 126 (1909)

temperature.

Considerations

1) The relation among the reaction products, residual urea, temperature and time As indicated in the tables, the quantity of solid after drying decreases as temperature becomes higher. This means that the quantity of the gas phase increases as temperature becomes higher, but there is no considerable change at a temperature higher than 325～375°C. The quantity of water insoluble substance is trace at 200°C and increases up to 250°C. At 250～275°C it reaches maximum and decreases above 275°C and extinguishes above 325°C. The quantity of water soluble part decreases as temperature becomes higher. There exists a minimum at 275°C in the cases in which packing ratios are 0.1 and 0.3 g/cc. And it becomes greater above 275°C, but there is no considerable change above 325°C. In the case in which the packing ratio is 0.5g/cc, it decreases up to 375°C, and above 375°C decreases very slightly. The quantity of urea decreases as temperature becomes higher, and in the case in which the packing ratio is 0.1g/cc, urea does not exist above 275°C.

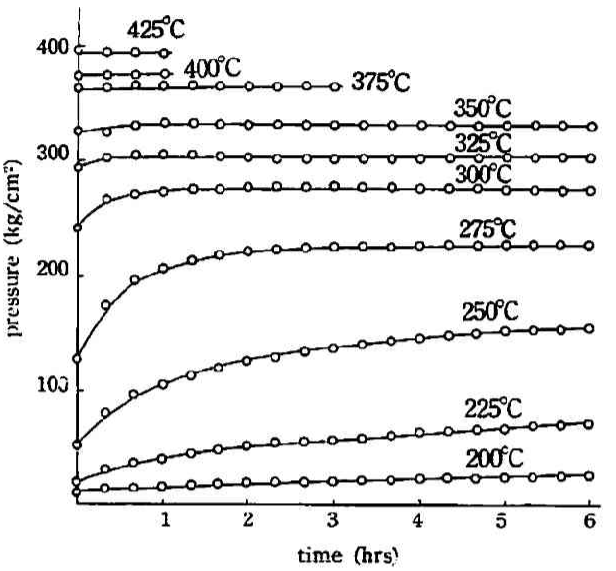


Fig. 8 The relations between temperature and pressure at 0.3g/cc

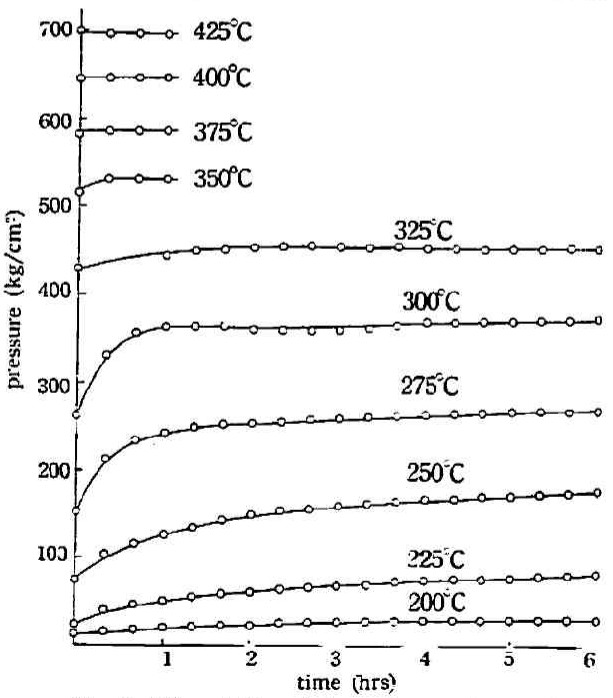


Fig. 9 The relations between temperature and pressure at 0.5g/cc

Melamine is not produced below 250°C, and appears slightly at 275°C. The yield of mela-

mine increases rapidly at 300～325°C and there is no considerable change above 325～375°C (Fig. 10). Biuret does not exist except in the cases of 200°C, 6 hours and 250°C, a few hours. Cyanuric acid exists generally below 250°C.

The relations between each reaction product and time in the following conditions—0.1 g/cc, 250°C and 0.5 g/cc, 300°C—are shown in Figs. 11 and 12. From these diagrams it becomes clear that the quantity of cyanuric acid and urea decreases and that of water insoluble substance increases in the former with the lapse of time and the cyanuric acid disappears in a short time and the water insoluble substance decreases and the melamine increases in the latter.

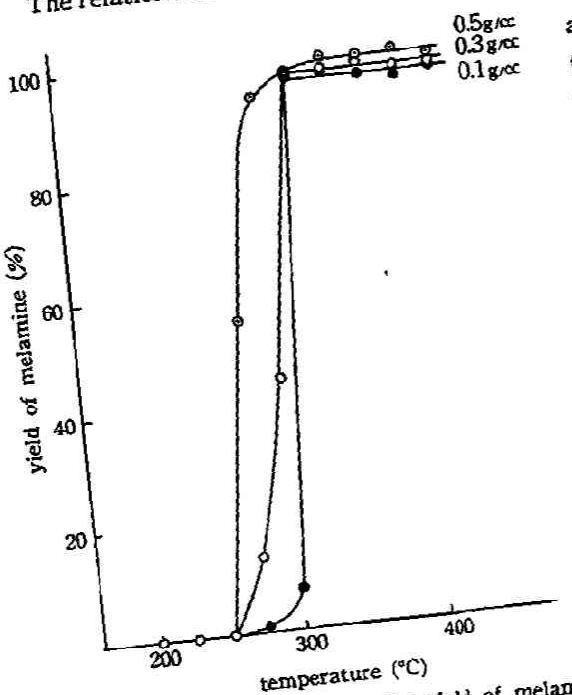


Fig. 10 The relations between the yield of melamine and temperature at each packing ratio

2) **Water insoluble substance**

The nitrogen content of the water insoluble substance is divided into 3 groups,—45～48%, 48～50% and 50～55%. In the case of lower temperature and shorter time, the nitrogen content is 45～48%, and in the case of higher temperature it is near 55% and almost 48～50%. Those

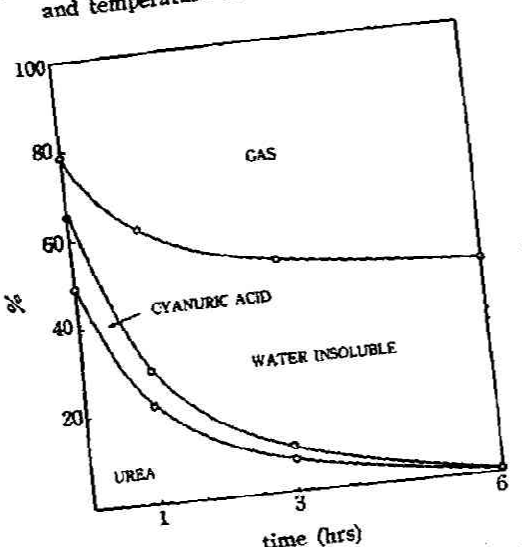


Fig. 11 The relations between each component and time at 250°C, 0.1g/cc

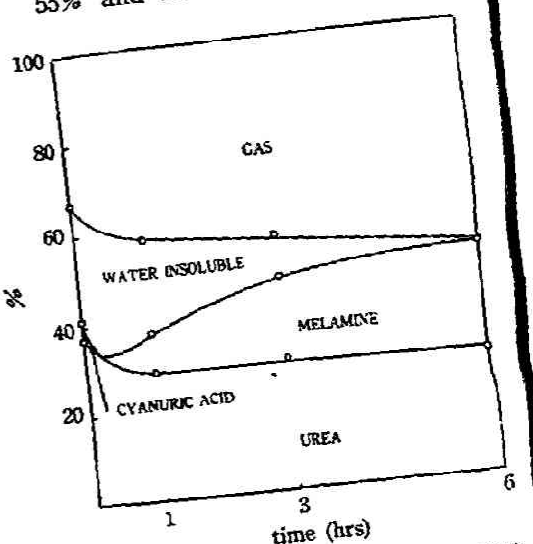


Fig. 12 The relations between each component and time at 300°C, 0.5g/cc

Table 1

Weight percentage of each component, yield of melamine and nitrogen content of water insoluble substance

Exp. No.	Temp. C°	time hrs	solid								
			total	water insoluble		water soluble					
				total	N%	total	urea	melamine total	melamine yield	cyanuric acid	biuret
1	200	6	88.1	trace		88.1	67.0			16.0	5.1
2	225	〃	69.8	23.6	49.8	46.2	32.0			14.2	
3	250	〃	47.7	46.8	49.4	0.9	0.9				
4	〃	3	51.3	41.6	50.3	9.7	6.8			2.9	
5	〃	1	61.1	31.5	49.0	29.6	21.2			8.4	
6	〃	0	78.6	13.4	46.5	65.2	49.4			15.8	
7	275	6	46.5	46.2	49.9	0.3		0.3	1.0		
8	300	〃	46.1	43.5	50.5	2.6		2.6	7.4		
9	325	〃	33.8			33.8		33.8	96.6		
10	350	1	33.7			33.7		33.7	96.4		
11	375	〃	33.5			33.5		33.5	95.6		
12	400	〃	33.2			33.2		33.2	94.8		
13	425	〃	33.5			33.5		33.5	95.6		

Packing ratio 0.1 g/cc (urea 2.15 g)

Exp. No.	Temp. °C	time hrs	solid								
			total	water insoluble		water soluble					
				total	N%	total	urea	melamine total	melamine yield	cyanuric acid	biuret
14	200	6	92.4	trace		92.4	68.1			20.0	4.3
15	225	〃	88.3	17.8	48.9	65.5	51.9			13.6	
16	250	〃	64.5	29.7	49.9	34.8	31.9			2.9	
17	〃	3	66.7	30.5	50.1	36.1	33.1			3.1	
18	〃	1	75.0	16.5	50.2	58.5	49.5			9.0	
19	〃	0	85.5	8.9	47.7	76.6	64.5			10.5	1.6
20	275	6	51.9	33.6	50.3	18.3	14.3	4.0	13.4		
21	300	〃	44.2	19.9	53.6	24.3	10.4	13.9	44.2		
22	325	〃	38.7			38.7	7.1	31.6	97.0		
23	350	〃	36.7			36.7	4.2	32.5	97.3		
24	375	3	36.8			36.8	3.9	32.9	97.7		
25	400	〃	36.8			36.8	4.4	32.4	96.4		
26	425	1	36.3			36.3	3.7	32.6	96.6		

Packing ratio 0.3 g/cc (urea 6.45 g)

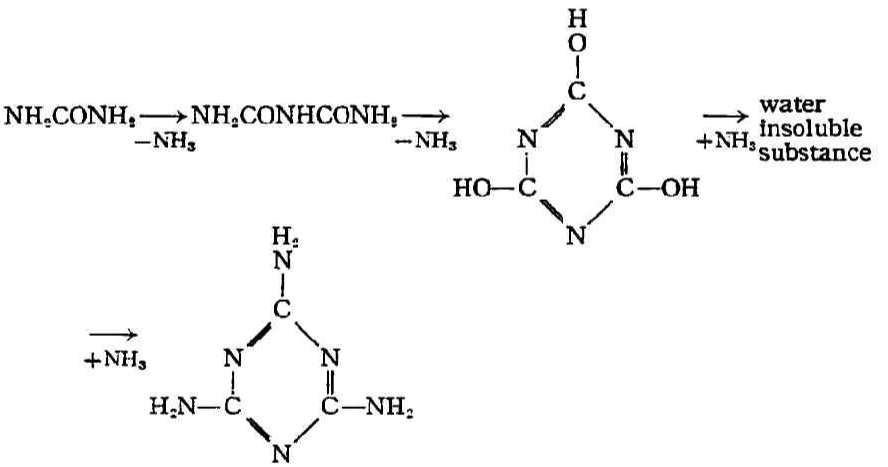
Exp. No.	Temp. °C	time hrs	solid								
			total	water insoluble		water soluble					
				total	N%	total	urea	melamine total	melamine yield	cyanuric acid	biuret
27	200	6	93.5	trace		93.5	75.7			13.9	3.9
28	225	〃	85.5	6.1	50.0	78 4	65.0			13.4	
29	250	〃	73.2	21.2	49.4	52.0	46.8			5.2	
30	〃	3	74.9	22.3	49.9	52.6	49.1			3.5	
31	〃	1	79.9	14.1	50.2	65.8	55.4			8.2	2.2
32	〃	0	88.7	5.9	45.4	82.8	71.2			7.6	4.0
33	275	6	61.4	9.8	49.7	51.6	40.1	11.5	55.0		
34	300	〃	51.1			51.1	27.3	23.8	93.6		
35	〃	3	56.5	9.3	54.1	47.2	29.3	17.9	72.7		
36	〃	1	58.0	20.6	55.7	37.4	28.7	8.7	34.8		
37	〃	0	67.0	25.8	51.1	41.2	37.1			4.1	
38	325	6	46.6			46.6	19.0	27.6	96.2		
39	350	1	44.0			44.0	14.3	29.7	99.2		
40	375	〃	41.4			41.4	10.4	30.0	98.9		
41	400	〃	41.2			41.2	9.7	31.5	99.4		
42	425	〃	40.3			40.3	8.8	31.5	98.1		

Packing ratio 0.5 g/cc (urea 10.75 g)

nitrogen contents are intermediate between cyanuric acid (N-32.6%) and melamine (N-66.7%). So it is capable to consider that the water insoluble substance is the reaction product of cyanuric acid and ammonia—ammelide (N-43.8%) and ammeline (N-55.1%) etc., but this water insoluble substance will be explained in the next report.

3) **Mechanism of the reaction of yielding melamine from urea** From the above results, it seems that the reaction process of yielding melamine is first the escape of ammonia, and secondarily the reaction between ammonia and cyanuric acid will begin as temperature becomes higher, and dehydration will occur at the same time. Namely, biuret is produced by escaping one molecule of ammonia from two molecules of urea, and by the progress of this escaping reaction of ammonia, cyanuric acid is produced. And the water insoluble substance is produced by the reaction between cyanuric acid and ammonia. At higher temperature, melamine is produced by the reaction between the water insoluble substance and ammonia.

4) **The yield of melamine** As the reaction yielding melamine from urea is the reaction of dehydration, the water produced in the process of this reaction will decompose urea. Three molecules of water are produced by the dehydration of three molecules



of urea when one molecule of melamine is produced. If one molecule of water decomposes one molecule of urea, one molecule of melamine is produced from six molecules of urea. There exists no urea above 275°C in the case of 0.1 g/cc, and about 4% residual urea above 350°C and about 10% above 375°C in the cases of 0.3 and 0.5 g/cc respectively. The yields of melamine in the tables are calculated by subtracting this residual urea and the yields reach constant values above 325°C at 0.1 and 0.3 g/cc and above 350°C at 0.5 g/cc, and the mean values in this region are 95.8, 97.0 and 98.9% respectively. The yields of melamine are calculated from the above assumption that one molecule of water perfectly decomposes one molecule of urea, but the equilibrium between urea and water must exist, and one molecule of water does not decompose perfectly one molecule of urea, so the yields of melamine must be smaller than the values in the tables. On the contrary, the reaction consuming urea except the above assumption may be the

transformation of urea to ammonium cyanate that is lost in drying the reaction product after the reaction is over. Moreover, the urea may decompose in analysing reaction product——in the case of vaporizing the water that are used in extracting. In a neutral solution, urea is stable at the temperature used, but it is reported that the velocity of decomposition becomes higher in an alkaline solution[12], so the urea may decompose by the alkalinity of melamine. The error is anticipated from the above several reasons, but the author believes that the greatest error is due to the loss by washing out the reaction product from the pressure vessel with pipe line, because the greater the packing ratio is, the closer the yield of melamine is to 100%. The greater the packing ratio is the more the quantity of residual urea. This is because that the pressure of gas phase is higher as the packing ratio is larger, and the escape of ammonia from urea may repress as the pressure of ammonia becomes higher. The effect of ammonia on the yields of melamine from urea may be examined.

5) **The relation between pressure, temperature and time** When the temperature is below 250°C, the pressure is elevated as time passes. The pressure increase is due to the ammonia escaped from urea and to the ammonia and carbon dioxide generated by the reaction between urea and dehydrated water. The pressure reaches a stationary state in 6 hours in large packing ratio at 275°C and in one hour at 300° C (Figs. 7, 8 and 9). There exist the relations of the straight line between temperature and pressure above 300° C in the cases of 0.1 and 0.3 g/cc and above 350°C in the case of 0.5 g/cc(Fig. 13). The liquid phase consists of melamine and urea (only melamine in the case of 0.1 g/cc) and the gas phase ammonia, carbon dioxide, water, etc. at those temperatures and there is no considerable change in the quantities of those components at each temperature above 325～375°C. Consequently, the increase of pressure is chiefly caused by pressure changes with temperature of ammonia, carbon dioxide, water, etc., so the relations of straight line can be understood.

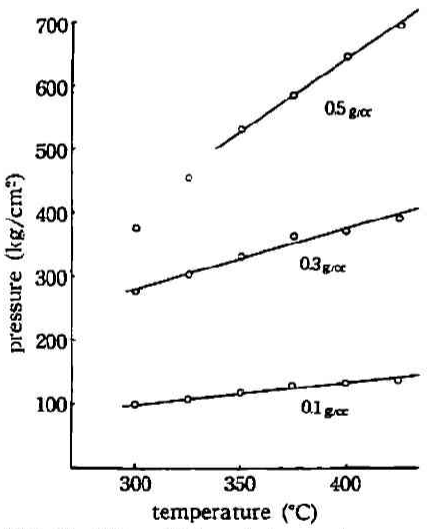


Fig. 13 The ralations between temperature and equilibrium pressure at each packing ratio

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Kyoto University.

12) R. C. Warner, *J. Biol. Chem.*, 142, 705 (1942)