Studies on Melamine. I : Influence of Impurities on Direct Preparation of Melamine from Calcium Cyanamide

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Synopsis

In the case of manufacturing melamine directly from calcium cyanamide of poor quality, the influence of impurities contained in the starting material has been studied.

I. Introduction

Synthetic conditions for preparing the intermediate, dicyandiamide, from calcium cyanamide of poor quality (total nitrogen 12.03 per cent, cyanamide nitrogen 11.5 per cent) were, in the first place, looked for according to the methods shown in the literatures.(1)(2)(3) The best condition (A) (Exptl. No. 5, Table 1) and the second best one (B) (No. 9) were determined. In the former case, the ratio of calcium cyanamide and water was 1 : 2, while in the latter 1 : 0.4. And in the direct synthetic method, the B-condition gave better yield of the product than the A-condition (Table 2), which would have due to the amount of the remaining water, impurities and drying condition in the case dried after reaction. For determining the A-condition, the reaction product of calcium cyanamide and water was filtered and the residue was lixiviated with warm water. The amount of dicyandiamide from the filtrate and lixiviated solution was determined for comparison, the first reaction product was dried as the case of the direct synthetic method of melamine.(4)(5) The dried substance was extracted with warm water and the amount of dicyandiamide obtained from the solution was determined. As expected, in the case of the A-condition, the decomposition grade was big (25 per cent), while in the case of the B-condition, it was small (5.8 per cent, Table 3). So it was concluded that the intermediate product, dicyandiamide, was partly decomposed by calcium hydroxide, produced from calcium oxide contained in the starting material and water, during the course of drying. The conversion ratio of the intermediate to melamine was almost equall in the A-(92.7 per cent.) and the B-conditions (95.6 per cent), when the decomposition grade was taken in account. In the case of the A-condition, the decomposition was decreased by drying the product at 100°C shorter than drying at 90°C for longer hour. When dicyandiamide was

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(2) Ja. Dodonow, Ann. Inst. agnon-desaratow (russ), 1, (1923), 1-13, C. Z., 1924, 11,317.
(3) K. Sugino, Japan. Pat., 157218 (1934).
(4) K. Sugino, Japan. Pat., 170177 (1945).
(5) H. Aiya, J. Soc. Chem. Ind. Japan, 50, (1947) 131.

heated with calcium oxide, a main impurity in the starting material, in presence of water at almost the same condition as the drying, the decomposition was approved and its tendency was on the same line.

In conclusion, for preparing diayandiamide from calcium cyanamide of poor quality and water, the ratio of the two components should be 1 : 2. And in the case of direct synthesis of melamine, the amount of water should be minimum and that of sodium hydroxide should be a half amount of dicyandiamide as indicated by Sugino.

II. Experimental part

(1) Synthesis of dicyandiamide from calciumcyanamide.

Dicyandiamide was prepared from calcium cyanamide (total nitrogen 12.03 per cent cyanamide nitrogen 11.51 per cent) under different conditions shown in Table 1. The best condition was that of No. 5 and the second No. 9. When the water was too excess, large amount of a by-product, urea, was produced (No. 7). The filtrate may be concentrated at 60°C or on a water bath without almost difference (Nos. 4 and 5).

Table 1.

Exptl No.	Calcium cyanamide (g)	Water (cc)	Reaction temp. (°C)	Reaction time (hr)	Warm water for extraction (cc)	Residue (g)	Last filtrate after concn (cc)	Dicyandiamide yield (g)	Dicyandiamide yield (%)	Crude urea (g)
1	100*	200	58–60	5	245	117	20	6.6	34.7	
2	100	200	59–61	1	250	119	30	5.5	31.8	
3	100	200	90–91	2	500	118	32	5.5	31.8	1.2
4**	100	200	80–90	1	250	120	38	6.2	35.9	1.0
5	100	200	89–91	1	250	119	36	6.4	37.1	0.8
6	100	200	89–91	½	250	118	35	5.7	33.0	1.3
7	100	500	89–91	1	250	116	37	5.5	31.8	3.5
8	100	100	88–90	1	250	120	41	5.5	31.8	trace
9	100	40	88–90	2	400	119	40	6.0	34.7	trace

* The real weight of calcium cyanamide was 32.9 g.

** 60°C, concentrated under reduced pressure.

In a three necked flask of 1L capacity, 100 g of calcium cyanamide and 200 cc of wate were reacted at 89–91°C for 1 hour under vigorous agitation. The content was filtered while hot. The residue was extracted thrice with hot water, total amount of which being 250 cc. The mixed solution of the filtrate and the extracts was concentrated to 100 cc on a water bath. Separating off the deposited calcium hydroxide while hot, 4 grams of fine crystals of dicyandiamide, m.p 205–209°C, were obtained after cooling. Concentrating the filtrate to 40 cc 2.4 g of the same compound, m.p 204–207°C were isolated. The sum (6.4 g) of the two lots corresponds to 37.1 per cent of the theoretical yield. The last filtrate was evaporated to dryness, boiled with 30 cc of absolute alcohol, filtered and cooled, from which 0.5 g of needle crystals having m.p 130–132°C was separated, which was proved to be urea by melting with a pure sample. From the filtrate, 0.3 g of crude urea was obtained.

In the experiment No. 9, a porcelain beaker of 500 cc capacity was used and the content was agitated with a hand. Small amount of water was added time to time.

(2) Direct synthesis of melamine from calcium cyanamide

According to the A-(No. 5) and the B-condition (No. 9), melamine was directly prepared form calcium cyanamide; the results were shown in Table 2. The B-condition gave a better yield than the A-condition (Nos. 10 and 12). The amount of sodium hydroxide to be added was sufficient by one half of the dicyandiamide remaining after drying (Nos. 12 and 13).

Table 2.

Exptl No.	Calcium cyanamide (g)	Water (cc)	Reaction timp (°C)	Reaction time (hr)	Drying Temp (°C)	Drying Time (hr)	Weight after drying (g)	Melamine conversion NaOH (g)	Melamine conversion Temp (°C)	Melamine conversion Time (hr)	Water for extraction (cc)	Residue for reaction (g)	Melamine Yield (g)	Melamine Yield (%)	Melamine m p (°C)
10	100	40	87-89	2	89-90	½	126	9.2	210-230	20	4000	130	5.2	30.1	330-345
11	100	200	89-90	1	96-99	1	146	9.2	200-230	20	4000	119	4.3	24.9	338-347
12	100	40	89-91	2	89-90	½	140	2.8*	205-230	20	4000	119	5.4	31.2	343-352
13	100	200	88-90	1	97-100	1	146	2.4**	205-230	20	4000	116	4.45	25.8	347-352

* A half an amount of dicyandiamide in No. 14. of table 3.

** A half an amount of dicyandiamide in No. 15 of table 3.

Table 3.

Exptl No.	Calcium cyanamide (g)	Water (cc)	Reaction temp (°C)	Reaction time (hr)	Drying temp (°C)	Drying time (hr)	Weight after drying (g)	Water for extraction (cc)	Residue (g)	Dicyandiamide Yield (g)	Dicyandiamide Loss * (g)	Dicyandiamide Decomposition (%)
14	100	40	89-92	2	88-91	½	139	400	118	5.65	0.35	5.8
15	100	200	88-89	1	97-100	1	152	400	120	4.8	1.6	25.0
16	100	200	88-90	1	87-91	3	145	400	117	4.3	2.1	32.8

* Differeces between the yields in the corresponding experiments

Table 4

Exptl No.	Dicyandiamide (g)	Calcium oxide (g)	Water (cc)	Reaction temp (°C)	Reaction time (hr)	Water for extraction (cc)	Residue (g)	Dicyandi mide Recovered (g)	Dicyandi mide Recovered (%)	Dicyandi mide Decomposition (g)	Dicyandi mide Decomposition (%)
17	6.5	50	200	97-100	1	400	56.5	4.8	73.8	1.7	26.2
18	6.0	50	40	88-90	½	400	57.8	5.5	91.7	0.5	8.3

The preparing process of dicyandiamide was conducted according to (1). Then it was manipulated as shown in the literature;[4][5] the reacting material was agitated in a porcelain beaker with a hand, adding small amount of water time to time. The extracted solution of melamine was concentrated to 700 cc on a water bath. After separating off the crytals, the filtrate was further concentrated to 90 cc and separated crystals were isolated. The yield of melamine was calculated by summing the two.

(3) Decomposition of the formed dicyandiamide during drying process

The dried product in Table 2 was extracted with 400 cc of hot water of 90°C. The solution was concentrated, filtered, cooled and dicyandiamide was isolated. The difference between thus isolated dicyandiamide and that obtained before drying (Nos. 5 and 9), was assumed to be due to the decomposition during drying; the result was shown in Table 3. When a large amount of water was used, it took long time for drying, resulting the decomposition. Quicker drying, although the drying temperature is higher, will result less decomposition. When the decomposition was taken in account, the conversion ratio of melamine was assumed to be 95.6 per cent in No. 12 and 92.7 per cent in No. 13.

(4) Reaction between dicyandiamide, calcium oxide and water.

As the decomposition of the intermediate product, dicyandiamide, was assumed to be due to calcium hydroxide, the reaction was tried in the corresponding condition; the results were shown in Table 4.

Dicyandiamide, quick lime and water were agitated with a hand in a porcelain beaker under the condition shown in Table 4; and the dried product was extacted with 400 cc of water at 90°C. The solution was concentrated to 60 cc and then to 20 cc. The amounts of the recovered dicyandiamide in the two cases were 4.8 g and 5.5 g respectively.

Summary

(1) The best synthetic condition of dicyandiamide from calcium cyanamide of poor quality was determined.

(2) In the direct synthesis of melamine from calcium cyanamide, the intermediate product, dicyandiamide, was partly decomposed by calcium hydroxide during the course of drying.

(3) When the loss by decomposition was taken into consideration, the conversion ratio of dicyandiamide to melamine was more than 92 per cent.

(4) That the maximum yield of dicyandiamide had been only 37.1 per cent. was assumed to be due to the decomposing action by impurities in the starting material during the reaction.

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