

MANUFACTURE OF UREA, DICYANDIAMIDE, MELAMINE,  
GUANIDINE CARBONATE AND GUANYL  
UREA SULPHATE.

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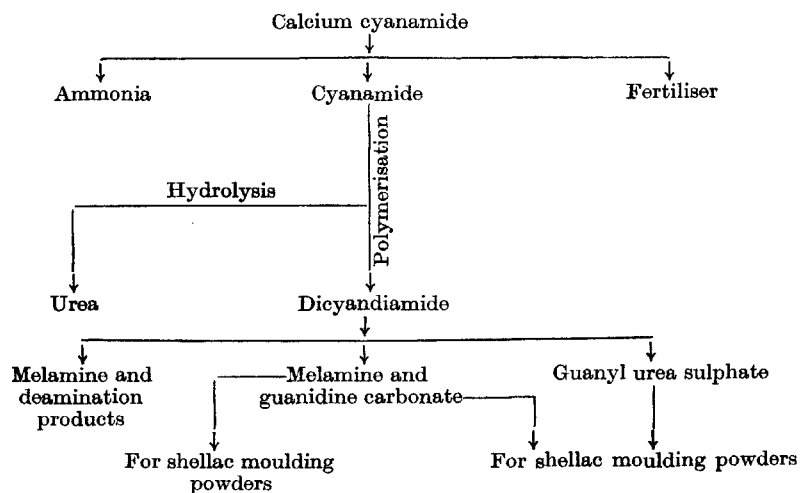
Aminoplastics form one of the main branches of the synthetic plastic industry of modern times. That urea and formaldehyde condense to produce resins when treated under suitable conditions was observed as early as 1884, and since then a great many varieties of urea formaldehyde resins have been prepared suitable for different purposes. In addition to its use as a starting material for synthetic resins, urea finds other wide applications as a fertiliser and in medicine for the preparation of certain specifics like urea-stibamine, etc. The immediate interest that drew the attention of the Indian Lac Research Institute to the production of this chemical on a large scale was created by the fact that shellac when suitably compounded with urea and formaldehyde gives rise to a resin which with proper fillers yields moulding powders which could be used for producing articles in the compression moulding press, working on the Bakelite technique. This powder has been found to be a cheap and suitable substitute for the now very familiar bakelite. In addition to urea, several other related nitrogenous substances like cyanamide, dicyandiamide, and guanidine are known to be usable for the production of synthetic resins. The latest addition to this list is melamine, the resins from which have been found to have very remarkable properties as regards hardness, transparency and heat and water resistance. It finds extensive application in the textile field where fabrics are rendered anticrease with the aid of a melamine formaldehyde resin. It is also known for the readiness with which it forms resins with sugars, phenols, aniline, etc., thereby resulting in a very wide range of products useful for a variety of purposes. Melamine also, like urea and the other chemicals mentioned above, has been found to be useful for the production of shellac moulding powders. Attention was therefore directed to evolve suitable methods for the production of these chemicals on a large scale using, as far as possible, only such raw materials as are readily available or produced in India, in plants that could be made in the country. It is hoped that the manufacture of these chemicals cheaply and in sufficient quantities will not only lead to the establishment of a sound shellac moulding powder industry but also give a great fillip to the starting of urea and melamine resins in this country.

*Urea.*

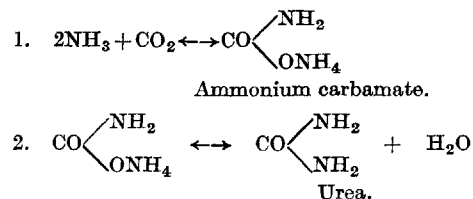
There are several processes known for the production of urea but only two of these are being exploited commercially. The main raw materials are ammonia and carbon dioxide in the one and calcium cyanamide in the other.

Carbon dioxide and ammonia are available even under present circumstances, and their availability could be considerably increased by properly organising the existing coke oven and fermentation industries. Besides, limestone being plentiful, a gaseous mixture containing about 30% CO<sub>2</sub> may be readily obtained by burning a 7 : 1 mixture of limestone and coke, the lime obtained thereby being used for the generation of ammonia from ammonium sulphate. Another alternative method would be the burning of coke with a minimum excess of air. The carbon dioxide thus obtained may be passed into potassium carbonate solution to produce potassium bicarbonate, which, on heating, liberates pure carbon dioxide, leaving the carbonate ready again to absorb fresh carbon dioxide.

Calcium cyanamide, the alternative starting material for the manufacture of urea, is itself a fertiliser, and is produced in large quantities in Europe and America. It used to be imported in good quantities before the present war, and is even now available in India in moderate lots. But the establishment of a calcium cyanamide plant in this country is by no means difficult and with the rapid development of our hydroelectric schemes, the day may not be far off when a thriving calcium cyanamide factory makes its appearance. The rise of such an industry will naturally lead to cheaper ammonia, thereby making the entire process more profitable. The utility of calcium cyanamide in the manufacture of certain nitrogenous heavy chemicals will be seen from the scheme below:—



The main reactions in the formation of urea from carbon dioxide and ammonia are as follows:—



The first reaction takes place when *dry* ammonia and carbon dioxide (in the volume ratio of 2 : 1) are passed into a cooled chamber. The ammonia may be dried by passing it through suitable towers filled with lumps of quicklime and the carbon dioxide dried by passing it through a sulphuric acid scrubber. The dry gases in the proper proportion are allowed to mix in a sufficiently large chamber where they combine to form ammonium carbamate with evolution of heat. As the carbamate dissociates even at lower temperatures, the chamber is maintained cold artificially by an external spray of cold water. The temperature is maintained at about 25°C. and on no account should be allowed to rise beyond 30°C. As the reaction is a reversible one, the gases issuing from the reaction chamber, A, always contain the unreacted ammonia and carbon dioxide which can be recovered by passing the mixture through vessels C, C, containing a fine suspension of gypsum in water. Here the ammonia and carbon dioxide get fixed as ammonium sulphate and calcium carbonate respectively. This ammonium sulphate is recovered and re-used for the generation of ammonia. On opening the carbamate chamber, B, plenty of ammonia is evolved and this also may be recovered as stated above.

The collection of ammonium carbamate from the sides of the carbamate plant is rather difficult, as the carbamate forms a rather hard incrustation. Therefore, the plant must be provided with a very efficient scraping equipment as shown in the figure 1.

The next stage is the conversion of ammonium carbamate into urea. This conversion does not usually exceed 43% of the theory, working under the best of conditions (170°–180°C. for six hours). But by conducting the reaction in the presence of a large excess of ammonia the yield of urea may be raised to as high as 80% of the theory, by using both ammonia and carbon dioxide under pressure. The carbamate is packed inside the autoclave of appropriate thickness, the packing ratio being not less than 0.7 gm. (preferably 1 gm.) per c.c. volume of the bomb. The heating may be conducted by gas or electricity and the contents of the autoclave are maintained at about 180°C. for six hours. The pressure registered is about 1,500–1,800 lbs. per sq. inch. As stated before, the conversion proceeds only to the extent of 40–43%, the rest remaining as carbamate and a part hydrolysed as ammonium carbonate. After cooling, the autoclave is opened and the issuing gases (ammonia and carbon dioxide) recovered in the gypsum tower as stated above. Water is

then poured in and the urea dissolved out. The concentrated solution is filtered off from suspended impurities if any and then evaporated till a few c.c. taken on a metal surface solidifies almost immediately. The unreacted carbamate and the carbonate formed decompose during concentration and the gases are recovered as described earlier. The practically fused urea is then poured out into a quadrangular dish of steel or copper lined inside with tin and allowed to set. The urea is pure enough to be directly used for most purposes.

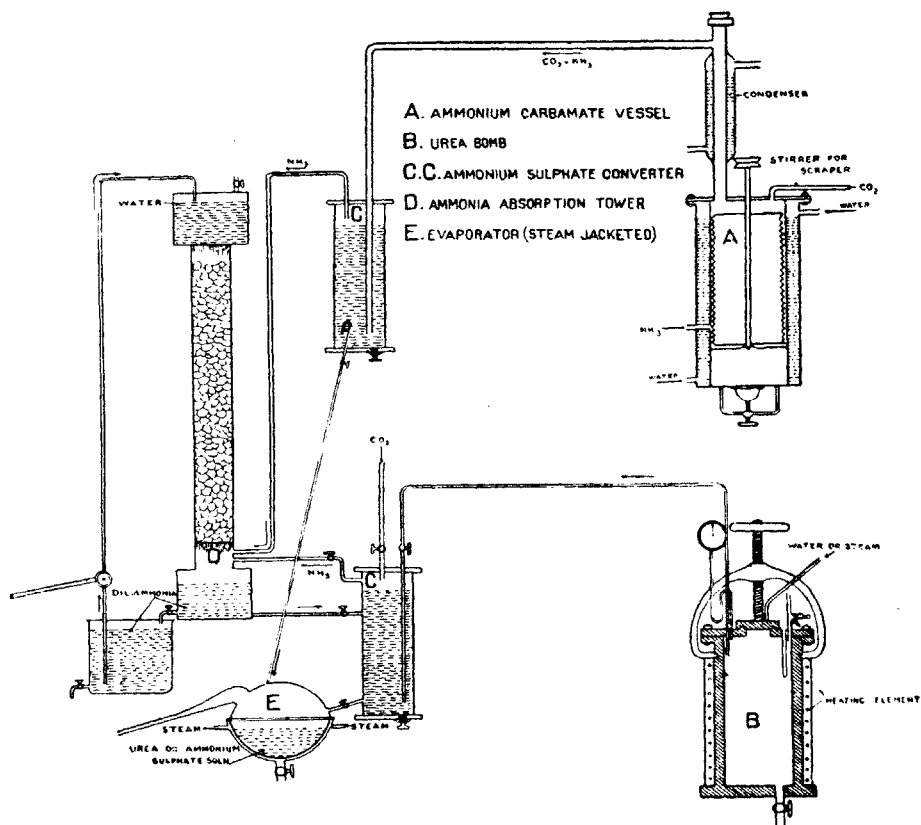


FIG. 1. Urea Plant.

## DIAMIDE, MELAMINE, GUANIDINE CARBONATE &amp; GUANYL UREA SULPHATE. 81

*Cost sheet.*

		Rs.
A. Capital Expenditure—		
4 Urea bombs (1½' diam. × 3' height)	.. .. .	2,800
Carbamate Plant—		
Ammonia generator .. .. .	.. .. .	200
3 Condensation chambers (3' diam. × 6' height)	.. .. .	2,250
3 Ammonia drying towers .. .. .	.. .. .	300
4 Absorption towers .. .. .	.. .. .	400
Evaporating pan (steam-jacketted)	.. .. .	1,000
Small steam boiler .. .. .	.. .. .	3,000
Lime-kiln .. .. .	.. .. .	500
Gas holder 1,000 c.ft. .. .. .	.. .. .	1,500
Compressor .. .. .	.. .. .	1,500
Cylinder for compressed CO <sub>2</sub> .. .. .	.. .. .	150
Filter-press .. .. .	.. .. .	400
Vats, etc. .. .. .	.. .. .	200
Mounting (including pipe lines, etc.)	.. .. .	500
Building .. .. .	.. .. .	2,000
TOTAL ..		16,700
B. Process charges—		
		Rs. A. P.
Depreciation at 10% on block account	.. .. .	5 10 0
Interest at 5% on block account ..	.. .. .	2 13 0
Supervision .. .. .	.. .. .	5 0 0
Labour .. .. .	.. .. .	3 0 0
TOTAL ..		16 7 0
C. Cost of materials—		
Ammonium sulphate 1,056 lbs., @ Rs.190 per ton	.. .. .	89 8 0
Lime 448 lbs., @ Re.1 per cwt. ..	.. .. .	4 0 0
		93 8 0
Less cost of 1,088 lbs. CaSO <sub>4</sub> produced in the reaction, @ Rs.20 per ton	.. .. .	9 12 0
		83 12 0
Plus 5% for impurities cost of 272 lbs. of dry ammonia ..	.. .. .	4 4 0
		88 0 0
1,600 lbs. limestone, @ Rs.10 per ton	.. .. .	7 0 0
800 lbs. coal equivalent to all charges of heating, compression, scrubbing, etc., @ Rs.10 per ton	.. .. .	3 8 0
		10 8 0
Less 896 lbs. lime, @ Re.1 per cwt. ..	.. .. .	8 0 0
		2 8 0
Cost of 352 lbs. CO <sub>2</sub> .. .. .	.. .. .	2 8 0
		88 0 0
272 lbs. of dry ammonia .. .. .	.. .. .	2 8 0
352 lbs. of CO <sub>2</sub> .. .. .	.. .. .	90 8 0
		6 0 0
Plus cost of 6 cwt. CaSO <sub>4</sub> .. .. .	.. .. .	16 7 0
		112 15 0
Less price of 5.5 cwt. of ammonium sulphate ..	.. .. .	52 4 0
		60 11 0
Less price of 4.25 cwt. of CaCO <sub>3</sub> , @ As.8 per cwt. ..	.. .. .	2 2 0
		58 9 0
Cost of 192 lbs. urea or cost per lb. of urea is about 5 annas	.. .. .	58 9 0

For very large-scale operations, liquid ammonia and liquid carbon dioxide are introduced into a pressure and heat resistant bomb where the formation of carbamate and its conversion into urea take place simultaneously. The capital investments on such a plant are naturally considerably more.

*Urea from calcium cyanamide.*

Calcium cyanamide is the other source for the manufacture of limited quantities of urea. Though the price of urea from imported calcium cyanamide is likely to be somewhat higher than when prepared by the above process, the fact that the operation is very much simpler and involves the outlay of only a comparatively smaller capital makes the process attractive for the small-scale producer. The process as worked out at the Indian Lac Research Institute is described below.

Commercial calcium cyanamide (100 lbs.) is mechanically stirred in a large lead-lined wooden vat with 50 gallons of water (temperature 30°-35°C.) and the aqueous extract is then filtered through a filter-press. The filter-cake is again washed with about 10 gallons of water. The collected filtrate is then treated with dilute sulphuric acid (35 lbs. of acid of sp. gr. 1.84 diluted with 1 gallon of water) till faintly acidic. The precipitated calcium sulphate is filtered off and to the clear filtrate is again added 10 lbs. of concentrated sulphuric acid. The solution is then heated in a lead-lined autoclave at 70°C. for six hours in an atmosphere of an inert gas under a pressure of 5 atmospheres.\* After cooling, the excess of sulphuric acid is neutralised with calcium carbonate, the solution filtered and the filtrate evaporated till it registers a temperature of 107°C. At this stage, all the iron and most of the calcium sulphate precipitate out. The filtered solution is re-evaporated to 115°C., when, on cooling, urea, pure enough for most purposes, separates out. The mother liquor on reconcentration to 115°C. deposits a second crop of crystals. The syrupy mother liquor left over can be used for making shellac moulding powder in place of urea.

*Cost sheet.*

	Rs.	A.	P.
Calcium cyanamide 100 lbs., @ Rs.9-8-0 per cwt.	..	..	8 8 0
Sulphuric acid conc. 40 lbs., @ 1 anna per lb.	..	..	2 8 0
Calcium carbonate 12 lbs., @ 1 anna per lb.	..	..	0 12 0
Cost of labour, supervision, depreciation, etc.	..	..	6 0 0
Cost of 25 lbs. urea	..	..	17 12 0
or 1 lb. of urea will cost approximately 11.5 annas.			<u>17 12 0</u>

\* The hydrolysis may also be carried out at the ordinary pressure under the same conditions of temperature and time. The yield of urea in this case is of the order of 20-20 lbs. from 100 lbs. of calcium cyanamide as against 25-30 lbs. when the hydrolysis is carried out under pressure as described above.

*Melamine from calcium cyanamide.*

## Dicyandiamide.

Calcium cyanamide (10 lbs.) is stirred well with water (5 gallons) at 45–50°C. for half an hour. It is then filtered and the residue washed with a further 1 gallon of water. The total volume of the filtrate is noted. Sulphuric acid (sp. gr. 1.7) is prepared by mixing concentrated acid (sp. gr. 1.84) and water in the ratio of 8 : 1. The total volume of this acid required to neutralise the whole of the filtrate was determined by titrating a known volume of the latter against a suitably diluted portion of the former (40 to 1,000 c.c.). The filtrate is then treated with exactly half this volume of acid and the temperature then rapidly raised to 80°. At this stage the rest of the acid is added drop by drop in the course of 1½ to 2 hours with constant stirring. The calcium sulphate precipitated is then filtered off and the solution evaporated to crystallisation. The dicyandiamide separates on standing in the form of long needles, M.P. 210°C. The yield is 12 to 13% of the theory. The mother liquor contains some more dicyandiamide together with smaller quantities of urea, melamine, etc. which may be recovered.

Dicyandiamide (600 gms.) is mixed with 125 c.c. of ammonia (sp. gr. 0.90) in a tin-lined steel autoclave and the mixture heated under pressure to 140°C. At this temperature, the highly exothermic reaction begins and the temperature rapidly rises to 160°C. and the pressure to about 700 lbs. per sq. inch. The mass is maintained at 150° to 160°C. for about 1½ hours. After cooling, the bomb is opened and the issuing ammonia recovered.

The sludge in the autoclave is then removed and digested with cold water (2,000 c.c. in 3 lots). After filtration, the filtrate which contains guanidine carbonate is concentrated till a drop on a glass slide immediately deposits crystals. After cooling, the crystals are collected on a filter, washed with a small quantity of water and dried. The yield of guanidine carbonate varies from 150 to 180 gms.

The residue is boiled with enough water, filtered off from the insoluble matters and the filtrate allowed to stand. Beautiful shining plates of melamine separate out on standing, M.P. 350°C. Yield 160–180 gms.

*Cost sheet.*

					Rs. A. P.
Calcium cyanamide 100 lbs.	..	..	..	..	8 8 0
Sulphuric acid 32 lbs.	..	..	..	..	2 0 0
					<hr/> 10 8 0
Less cost of 44 lbs. of calcium sulphate, @ Rs.3 per cwt.				..	1 3 0
Cost of 12½ lbs. dicyandiamide	..	..	..	..	9 5 0
i.e. the cost per lb. is about 12 annas.					<hr/> <hr/>

					Rs. A. P.
Dicyandiamide 10 lbs., @ As.12	..	..	..	..	7 8 0
Ammonia 12 lbs., @ As.5	..	..	..	..	3 12 0
					<hr/>
Less cost of 3 lbs. guanidine obtained as by-product	..	..	..	..	11 4 0
					<hr/>
Process charges	..	..	..	..	8 4 0
Cost of 3 lbs. melamine or Rs.3-4-0 per lb.	..	..	..	..	1 8 0
					<hr/>
					9 12 0
					<hr/> <hr/>

By treating the dicyandiamide in dry alcohol with gaseous ammonia under 3 atmospheres pressure and heating as described above the yield of melamine has been raised to 450 to 480 gms. resulting in a very much lower cost of production.

#### *Guanyl urea sulphate.*

Dicyandiamide is dissolved in a slight excess of 2N sulphuric acid by heating to about 80°C. when the exothermic reaction begins and the temperature rises rapidly to 100°C. It is then maintained at this temperature for 1 hour and then filtered and the filtrate allowed to stand overnight. The guanyl urea sulphate separates out in the form of tiny crystals. The yield is practically quantitative and the mother liquor from one charge may be used for the next one.

#### *Cost sheet.*

					Rs. A. P.
Dicyandiamide 10 lbs., @ 12 annas per lb.	..	..	..	..	7 8 0
Sulphuric acid (1.80) 6.25 lbs., @ 1 anna per lb.	..	..	..	..	0 6 3
Processing charges	..	..	..	..	1 12 0
					<hr/>
Total cost of 15 lbs. of guanyl urea sulphate	..	..	..	..	9 10 3
∴ Cost per lb. = As.10.25					<hr/> <hr/>