ISMA* Technical Conference

Seville, Spain

20-24 November 1972

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

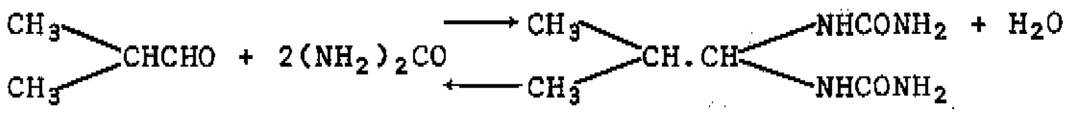
LTE/72/13

MANUFACTURE OF IBDU AND COMPOUND FERTILISERS CONTAINING IBDU

By

Noriyoshi Yanai
Mitsubishi Chemical Industries Ltd., Japan

Isobutylidene diurea or 1.1-diureide isobutane (IBDU) is readily produced as a condensation product of urea and isobutylaldehyde (IBA) in the presence of acid as catalyst, as follows:

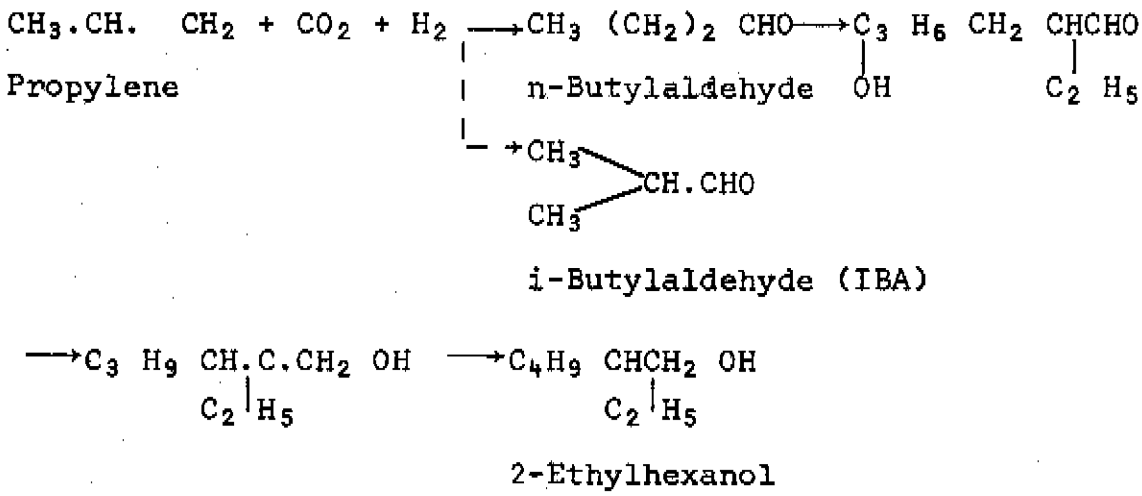


(IBA) (Urea) (IBDU)

The purpose of this paper is to describe the manufacture of IBDU which has been found to be useful as a slow-acting nitrogen fertiliser and for producing compound fertilisers containing IBDU.

Urea is excellent in terms of cheap price, high nitrogen content and completely available form to plants, but its water solubility often causes hygroscopic and caking tendency in storage. Further, these properties are the cause of agronomic troubles such as concentration hazard to plants and nitrogen loss in the soil by leaching, vaporization and denitrification.

To overcome these defects and furthermore to obtain slow-acting or long-lasting nitrogen fertiliser, several urea-aldehyde condensate products have been studied. Isobutylaldehyde (IBA) is produced as a by-product of 2-ethylhexanol process as follows:



We selected IBA as the raw material to be reacted with urea and found that IBDU has many agronomic advantages over the other urea-aldehyde condensate products. We are now offering various grades of compound fertilisers containing IBDU and straight IBDU to the domestic and the USA's markets.

In 1963, Mitsubishi Chemical Industries built an IBDU pilot plant at its Kurosaki works and then completed a 13,500 tonnes per year IBDU plant at its Yokkaichi works in 1964. Now Mitsubishi has a 20,000 t.p.y. IBDU plant at its Mizushima works and a 60,000 t.p.y. plant for compound fertilisers containing IBDU at its Kurosaki and Yokkaichi works.

PROPERTIES OF IBDU

Physical properties of IBDU are:

Molecular weight	174.21
Nitrogen content	32.18 (theoretical value)
Appearance	White crystalline powder
Melting point	205°C. with decomposition
Specific gravity	(true) 1.3 (apparent) 0.7 - 0.9
Solubility	0.2 - 0.3 gr/100 ml water at room temperature, hardly soluble in alcohol and ether.
Hygroscopicity	None.

IBDU has the following agronomic characteristics as a slow-acting nitrogen fertiliser.

a) Slight water-solubility - As IBDU is very slightly soluble in water, it has less concentration hazard and a low caking tendency.

b) Mineralization through Urea - The mineralization of dissolved IBDU in the soil water is effected mainly through urea by hydrolisis and is less dependent upon direct decomposition by soil microbes. Therefore, the fertilising effect of slowly released IBDU is as effective as urea and is not affected by soil conditions. Briefly, IBDU can be considered as "slightly water-soluble urea."

c) Control of Slow Action by Granulation - The control of slow action of IBDU is made by checking the dissolution velocity of IBDU. This is made possible by adjusting the size and hardness of straight IBDU or fertiliser granule containing IBDU, as the water-solubility of IBDU is very low, and the dissolution velocity of IBDU can be lessened by granulation which is illustrated in Figure 1.

d) AI Value - The AI value of IBDU measured by the Morgan's procedure is as follows:

TN (per cent)	CWIN (per cent)	HWIN (per cent)	AI Value
32.1	24.9	0.9	96

e) Influence of Aldehyde on Plant Physiology - There is no need to worry about liberated aldehyde except in the case of extraordinarily heavy application, because aldehyde is apt to vaporize into the air and the aldehyde remaining in the soil changes to isobutyric acid which is consumed by soil microbes as other organic acids.

COMMERCIAL PRODUCTION PROCESS FOR IBDU

Both wet process and dry process are available, but the latter is recommended for commercial production because it eliminates the tedious filtration and drying steps required for the former. The wet and dry processes are illustrated in Figures 2 and 3, respectively. However, there are some difficulties about the dry process such as (a) removal of the reaction heat, (b) repression of the secondary reaction and (c) control of the reaction rate.

Removal of the Reaction Heat

Condensation of urea and IBA is an exothermic reaction. As external cooling is ineffective, it is advisable to use a sealed reactor for the entire reaction, using an excess of aldehyde to balance its latent heat of evaporation and heat of reaction, thereby maintaining the desired reaction temperature and cooling and recovering the evaporated aldehyde for re-use. The molar ratio of the two raw materials to be fed to the plant should be 1 for urea to 0.6 - 1.1 for aldehyde.

Effect of Reaction Temperature

If excessive amounts of IBA are used, then normally a considerable amount of by-products are included in IBDU. These by-products are isobutylidene monourea (24.6 per cent N), di-isobutylidene triurea (29.2 per cent N) and di-isobutylidene diurea (24.6 per cent N). They serve no useful fertilising purpose.

However, we have discovered that pure IBDU is obtained at high yield without by-products if the reaction temperature is kept higher than IBA's boiling point in reactor. The reaction rate and the nitrogen content of the product are given in Table 1.

TABLE 1
Effect of Reaction Temperature

Reaction Temperature °C	Reaction Rate of Urea wt per cent	Nitrogen Content of Reaction Product wt per cent
52 - 56	98.7	27.00
56 - 58	98.6	28.63
58 - 64	98.4	30.92
64 - 68	98.4	31.46
68 - 72	98.0	31.84
72 - 76	97.6	32.05
76 - 80	95.4	32.17
80 - 84	90.3	32.17
84 - 88	79.0	32.18
88 - 92	64.0	32.18
92 - 96	35.0	32.18

Note : Reaction Rate (per cent) = $\frac{TN - UN}{TN} \times 200$

Nitrogen Content (per cent) = $\frac{(TN - UN) \times 100}{100 - \frac{UN}{46.65} x} = 100-W$

where TN = Analysis value of total nitrogen
UN = Analysis value of urea nitrogen by urease method
W = Analysis value of nitrogen in urea.

It will be seen from Table 1 that if the reaction temperature is too low (below about 58°C), the reaction rate increases while the nitrogen content of the product drops appreciably and if the reaction temperature is too high (above 84°C), the nitrogen content of the product approximates theoretical value of IBDU while the reaction rate drops considerably.

Effect of pH on the Reaction Rate - Addition of acid as catalyst is necessary for accomplishing the reaction between urea and IBA. Inorganic acids such as sulfuric acid, hydrochloric acid and phosphoric acid, or organic acids are used as catalysts, but sulfuric acid is economical. These acids are employed as 30 to 50 per cent aqueous solution so that the acids come in contact evenly with the starting compounds. The reaction rate shows the highest value at pH 3 as shown in Table 2:

TABLE 2

Effect of pH on Reaction Rate

pH	Reaction Rate (per cent)	pH	Reaction Rate (per cent)
0.5	86.5	5	87.7
1	90.0	6	80.0
2	96.0	7	71.6
3	98.0	8	62.0
4	94.0	9	52.5

Particle Size of Solid Urea - The urea employed in this process is now always in powder form. When prilled urea such as 5 to 20 mesh size is used in this process, there is no trouble.

IBDU Manufacturing Plant - A typical IBDU plant is illustrated in Figure 4. If necessary, any of the sulphuric acid used as a catalyst which remains in the product can be neutralised with an alkali. The analysis of IBDU product at the outlet of a plant of this type is listed in Table 3, which indicates high purity. By this process, IBDU is obtained as granules of 0.1 to 0.4 mm diameter and the distribution can be varied to meet requirements, by changing manufacturing conditions.

TABLE 3

Analysis of Product IBDU

Item	Content
Total Nitrogen, dry weight per cent	32.3
Urea Nitrogen "	0.2
IBDU Nitrogen "	32.2
Water, wet weight per cent	7.5
pH of Neutralized Product (5 g/per 100 ml water)	9.0

PROCESS FOR COMPOUND FERTILISERS CONTAINING IBDU

IBDU is used as a straight fertiliser, but new compound fertilisers containing IBDU as a raw material have been widely marketed. The compound fertilisers containing IBDU are of two classes due to the difference of the phosphatic raw materials.

IB-Compound Fertiliser - When compound fertiliser containing IBDU is used as a fertiliser for paddy fields, it is necessary for the rate of release of available nitrogen to be controlled by adjusting the size and hardness of granules in order to obtain slow-acting or long-lasting availability.

Improvements were achieved by compounding a mixture of IBDU and potassium sulphate or potassium chloride with superphosphate and fused phosphate, by producing the fertiliser in large (5-8 mm diameter) and very hard (destroyed pressure about 10 Kg/granule) granules that keep their form in water for a long time. When the C-P_2O_5 (citric acid soluble phosphate) molar ratio of superphosphate and fused phosphate is 1 ± 0.5, it is in the most suitable form for the production of IB-compound fertiliser. This IB-compound fertiliser, which was originally developed exclusively for rice paddies, was later adapted for application to dry fields as its excellent performance was widely recognised.

The process of IB-compound fertiliser is shown in Figure 5. IBDU, fused phosphate, superphosphate, ammonium phosphate and potassium chloride are continuously fed into the rotary drum granulator (10) through the mixer (9). In the drum, these raw material mixtures are granulated by wetting with urea solution and phosphoric acid or water. The moist granules (2-15 mm diameter), which have 5 to 15 per cent of free water, are led from the granulator to the pre-cooler (11). The moist granules must be kept in the pre-cooler for 10-30 minutes in order to create the strength of the granules, so as not to break in the dryer (12), and then the granules are dried in the rotary dryer at temperature 75-95°C.

The dried granules (water content 3-4 per cent) are carried to the double deck screen (13). Undersized granules are sent to a hopper (6). Oversized granules with required size (5 - 8 mm diameter) pass through a rotary cooler (15) and are then packed into paper or resin bags.

IB-RINKAAN - In the autumn of 1964, "IB-RINKAAN" - Japan's first synthetic slow-acting fertiliser containing IBDU - was placed on the market. This fertiliser was widely adopted principally for dry fields, as it was found capable of being substituted for relatively expensive organic fertilisers like fish cake and oil cake, which have been used traditionally in large quantities for tangerine and other special crops.

IB-RINKAAN can be produced by mixing IBDU with, for example, ammonium phosphate, ammonium sulphate, potassium salts and urea or ammonium nitrate. In some cases, fritted trace element - Manganese and Boron - is added to IB-RINKAAN. But superphosphate and fused phosphate are not normally used because the available phosphate content is less than that of ammonium phosphate. The resultant product is, therefore, not suitable for high analysis fertilisers.

The process of manufacturing IB-RINKAAN is the same as IB-compound fertiliser except for by-passing pre-cooler (11) as shown in Figure 5. IB-RINKAAN product granules are of 2-4 mm diameter size. Some grades for fertilisers containing IBDU are listed in Table 4.

TABLE 4

Grades of Fertilisers Containing IBDU

Grade IBDU (straight)	Composition of Nitrogen 31 as IBDU	Fertiliser Material IBDU only
IB - Compound Fertiliser		
IB 10-10-10	8 as IBDU, 2 as Urea	IBDU, Urea, SP, FP, KCl, H_3PO_4
IB 10-14-18	3 as IBDU, 2 as Urea 5 as Ammonium	IBDU, Urea, SP, FP, KCl, DAP
IB 10-15-10	6 as IBDU, 3 as Urea 1 as Ammonium	IBDU, Urea, SP, FP, KCl, DAP
IB - RINKAAN		
IB 15-15-15	7.5 as IBDU, 7.5 as Ammonium	IBDU, AS, DAP KCl or K_2SO_4
IB 16-10-14	8 as IBDU, 8 as Ammonium	IBDU, AS, DAP, KCl
IB 18-11-11	6 as IBDU, 4 as Urea, 8 as Ammonium	IBDU, Urea, DAP, K_2SO_4

SP - Superphosphate
FP - Fused phosphate
AS - Ammonium sulphate
DAP- Diammonium phosphate

CONCLUSIONS

The production of slow-acting fertilisers is still only a small fraction of that of general chemical fertilisers in the world. But, slow-acting fertilisers are expected to play an important role in farming in tropic and sub-tropic regions and in areas where heavy rains quickly wash away precious plant food. Japan is most likely to benefit enormously from fertilisers of this type - the country has frequent rainfalls, farm management is on a small scale and farmers are forced to depend on soil productivity, so that huge amounts of fertiliser must be applied in intensive agriculture. Slow-acting fertilisers will also prove a valuable means of reducing manpower requirements, thereby helping the serious labour shortage on Japanese farms today.

A few types of slow-acting fertilisers are available in the market today. Principal among them are urea-aldehyde condensates, IBDU developed by Mitsubishi Chemical Industries being one of them. Interest in IBDU was aroused in different parts of the world when Dr Hamamoto, one of the inventors, lectured on the new fertiliser in Europe at the invitation of the Fertiliser Society in London. Thus, IBDU has gained a fine reputation particularly in the United States, where it is being exported to Swift & Co.

References

1. Kuntze, H.: Z. Pflanzenernahr. Dung. Bodenk., 86, 120-123, 135-141, 206-214, 190-201.

2. Scheffer, F.: ibid, 75, 1-16, German Pat. 972, 352.

3. Jung, J.: German Pat. 1,081,482
   German Pat. 873,242

4. Symes, N.F.: U.S. Pat. 3,061,423

5. Long, M.I.E.: J.Sci. Food. Agric., 11, 441-445 (1960)

6. Lunt, O.R.: J. Agr. Food. Chem., 17, No. 6, 1269-1271 (1969)

7. Hamamoto, M.: The Ferti. Soc. Proceedings, No.90 (1960)

8. Hamamoto, M. et al: Japan Pat. 425,900 (1964)
   Japan Pat. 555,017 (1969)
   German Pat. 1,146,080 (1963)
   British Pat. 949,405 (1964)
   U.S. Pat. 3,322,528 (1967)

9. Yanai, N. et al: Japan Pat. 520,510 (1968)
   Japan Pat. 584,143 (1970)
   Belg. Pat. 664,388 (1965)
   British Pat. 1,099,643 (1968)

MR. N. YANAI (Mitsubishi Chemical Industries, Japan).

It gives me great pleasure to speak to you on the manufacture of IBDU and compound fertilisers containing IBDU.

IBDU is a type of controlled release fertiliser which is generally produced by the reaction between a condensate of urea and IBA in the presence of acid as a catalyst. IBA is a by-product of the 2-ethylhexanol process. The principal properties of IBDU are described on pages 2 and 3 of the paper and I would like to talk about processes for its commercial production. Both wet process and dry process are practicable but the latter is recommended for commercial production because it eliminates the tedious filtration and drying steps required for the former. The wet and dry processes are illustrated in figures 2 and 3 respectively. However, there are some difficulties in connection with the dry process such as removal of the reaction heat, repression of the secondary reaction and control of the reaction rate.

The effect of pH on the reaction rate at about 70°C is shown in table 2. A typical IBDU plant is illustrated in figure 3. There are two variations of the process for producing compound fertilisers containing IBDU, one to give IB and the other IB Rinkaan compound fertiliser. That for producing IB is illustrated in Figure 5 while IB Rinkaan can be produced by mixing IBDU with, for example, ammonium phosphate, ammonium sulphate, potassium salts and urea or ammonium nitrate. The process of manufacturing IB Rinkaan is the same as that for IB compound fertiliser except for the by-passing of the pre-cooler as illustrated in figure 5. Some grades of fertiliser containing IBDU are listed in table 4.

DR. R. NITZCHMANN (B.A.S.F., Germany).

The production of isobutylidene diurea in Ludwigshafen.

We operate IBDU production as a wet process without purification. A urea solution (70%) is reacted with a small excess of isobutyaldehyde. The catalyst: sulphuric acid.

The reaction vessel is a paddle mixer as in the Mitsubishi process, provided with a cooler to condense the excess aldehyde. The resulting solid aqueous reaction product (28-30% H_2O) is neutralised in a second mixer with equivalent quantities of caustic potash solution. (In Mitsubishi NH_3 is used, as far as we know).

It is then dried in a turbulence channel, ground, screened and then either sent for further processing into compound fertilisers or a small proportion is sold under the trade name "Isodur". Our "Isodur" contains 7 - 10% urea, as it is not purified, as stated above. In addition, as a result of the higher water content the product may hydrolyse back into the raw materials, urea and isobutylaldehyde, during drying. Isobutylaldehyde is also obtained by us as a byproduct of oxosynthesis.

The "Isodur" (Isobutylidene diurea, with urea and potassium sulphate impurities) or the compound fertilisers Rasenfloranid 20/5/8/2 or Nitrophiska permanent 15/9/15/2 are used only for the care of lawns, in the cultivation of ornamental plants, in market gardening, tree nurseries, in landscape gardening and for various special crops. We have a licence from Mitsubishi for the use of IBDU as a fertiliser. Mitsubishi has a BASF licence for crotonylidene diurea (CDU).

1) In his lecture Mr. Yanai compares cheap urea with IBDU.

   What are the price relationships between urea and IBDU in Japan?

   Do you think that the consumption of IBDU as a fertiliser will increase appreciably in your country?

   (In comparison with Germany where this fertiliser can only be considered for use with special crops in view of the high price)

   What are considered to be the possible applications with large-scale crops in agriculture?

2) The lecturer stresses that IBDU affords many agronomic advantages compared with the other urea aldehyde condensates.

   Does this apply only to the urea foraldehyde condensates or also to the crotonylidene diurea?

   In our opinion, however, IBDU is more susceptible to hydrolysis than CDU, especially in the acid medium.

3) In your lecture you refer to a total capacity of 33,500 tons per annum IBDU.

Is this capacity fully utilised by you?

How is the output divided between Japan and exports?

4) Do Mitsubishi operate only the process with dry urea (dry process) or do they employ the wet process as well?

Do you purify in the dry process, or is the quantity of byproducts so small that you are able to dispense with it?

5) Do you have to take pH values into account (on account of the hydrolysis of the IBDU) in the production of compound fertilisers containing IBDU?

6) Does the IBDU's rate of hydrolysis change if the fertiliser granules are bigger and firmer, or are granulated together with the other materials?

MR. YANAI:

In answer to your questions, the reactor in our plant is a paddle mixer and the cooler for vapourised IBDU is a mild steel tube cooler/condenser. The water content of IBDU is about 8%. Sodium hydroxide is used to neutralize IBDU because it is the most economical thing to use in Japan. We have tried the wet process but gave it up because the dry process is easier and more economical. The production capacity of our IBDU plant is 13,500 t.p.y. The total throughput of IBDU is about 25,000 t.p.y. and that of compound fertiliser containing IBDU about 90,000 t.p.y. in Japan. I regret that I cannot give you recent export figures because I do not deal with those matters. Dry process IBDU is of high purity and requires no further purification. The pH and reaction temperature are very important in achieving high purity. The rate of release of IBDU can be slowed down further by granulation. As a raw material, IBDU is expensive and costs more than urea. This is a weak point for sales of IBDU in Japan.

PROFESSOR J. ANDO (Chuo University, Japan).

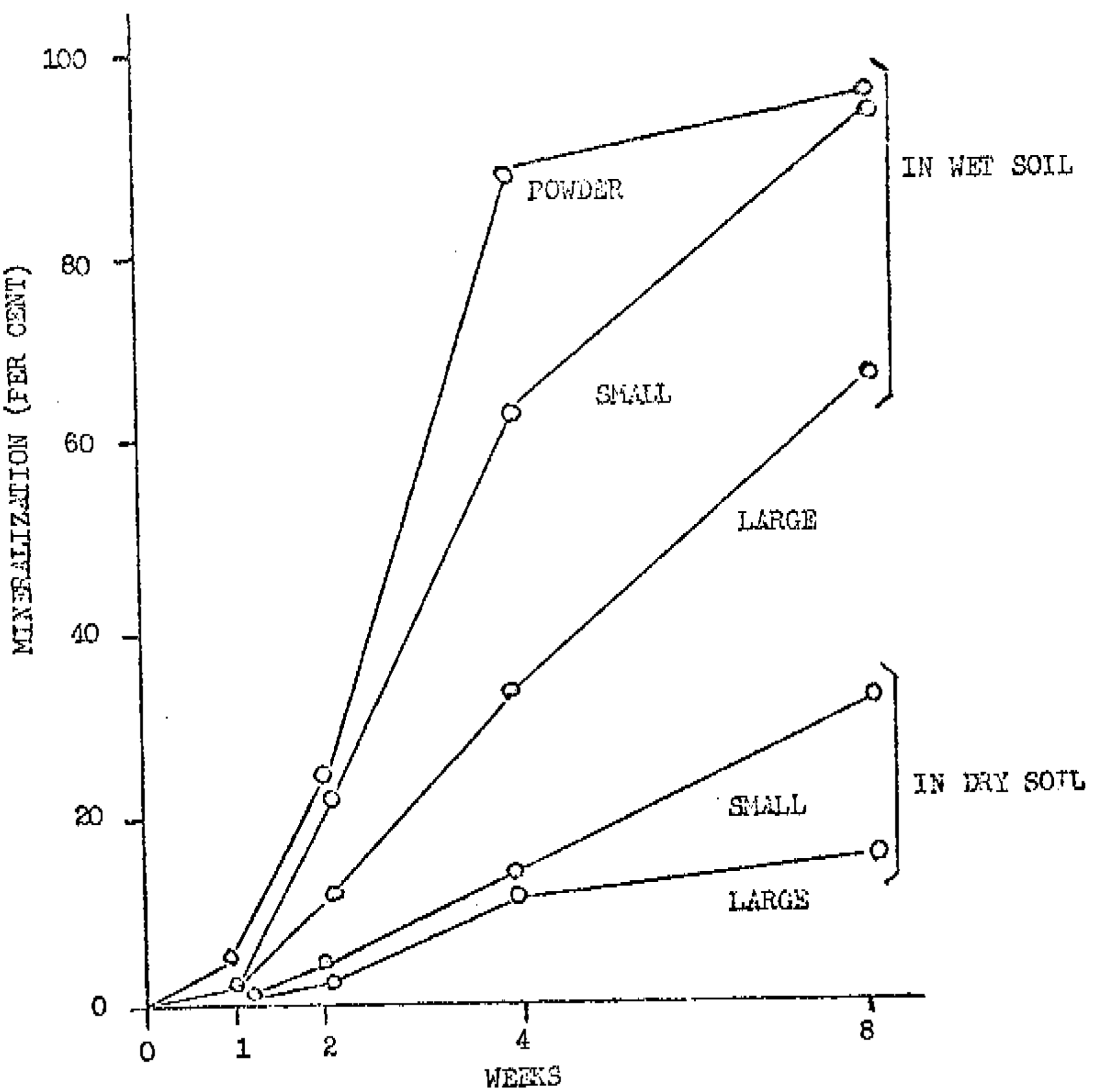
Mr. Yanai is an engineer and this question really concerns future demand for NPK fertilisers. He is not in a position to discuss a subject quite outside his normal sphere of work.

DR. M.M. KOPPER (B.A.S.F., Germany)

In our experience isobutylidenediurea's sensitivity to hydrolysis presents difficulties in production and particularly in use. In acid soils the product hydrolises very quickly again into aldehyde and urea and may have a severely inhibiting effect on the growth of the plant. Many other condensation products containing urea do not show this severe sensivity to hydrolysis with low pH values. I should like to ask Mr. Yanai to comment on this. It would be of particular interest to know whether this problem also occurs with rice in paddy fields and whether there are only a few acid soils in East Asia in which, for preference, crops which cannot be harmed by hydrolysis are grown.

PROFESSOR J. ANDO:

IB compound fertiliser which is granulated in very large granules is particularly suitable for rice paddy fields. It is also expensive, but it is a slow release fertiliser and some farmers like to use it. I think Mr. Yanai would like to emphasise that the use of IBDU-based compound fertilisers for rice growing is increasing in Japan.



SIZE

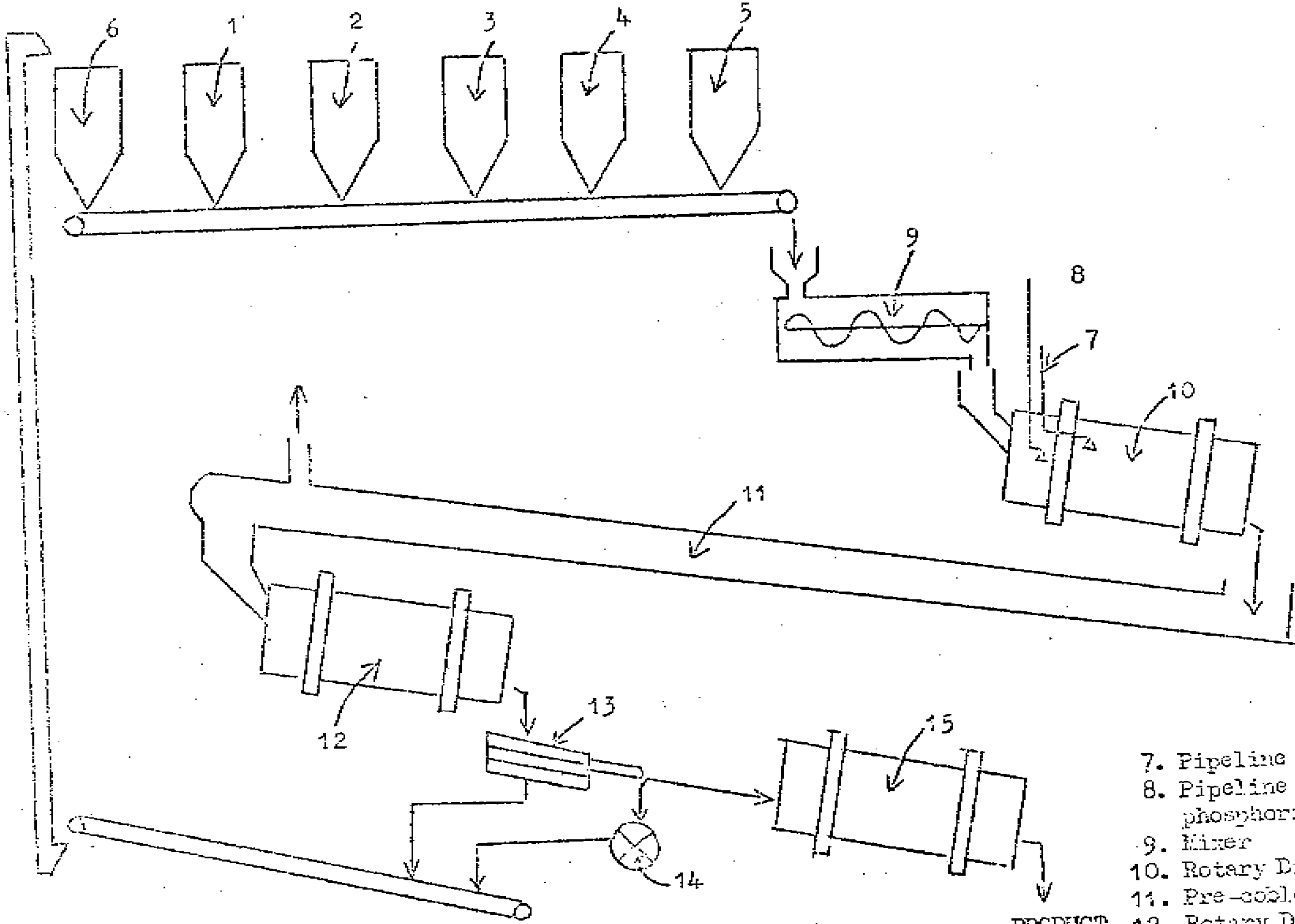
SMALL (0.8 to 1.4 MM)
LARGE (1.7 to 2.4 MM)

MOISTURE

WET SOIL 34 per cent
DRY SOIL 22 per cent

FIG. 1 : MINERALIZATION OF IBDU. INFLUENCE OF GRANULAR SIZE AND SOIL MOISTURE

[25 mg.N/70 g. soil at 25°C expressed as nitrate-nitrogen]



7. Pipeline for Urea Solution
8. Pipeline for Water or phosphoric acid
9. Mixer
10. Rotary Drum Granulator
11. Pre-cooler
12. Rotary Dryer
13. Double Deck Screen
14. Crusher
15. Rotary Cooler

FIG. 5 IB-COMPOUND FERTILISER PLANT

1. Hopper for IBDU
2. Hopper for Fused Phosphate
3. Hopper for Superphosphate
4. Hopper for Ammonium phosphate
5. Hopper for Potassium chloride