1. SUBJECT CLASSI- FICATION	A. PRIMARY Agriculture	AF25-0000-0000
	B. SECONDARY Soil fertility,fertilizers,and plant nutrition	

2. TITLE AND SUBTITLE

Urea and superphosphate in production of granular compound fertilisers

3. AUTHOR(S)

Hignett,T.P.; Davis,C.H.

4. DOCUMENT DATE	5. NUMBER OF PAGES	6. ARC NUMBER
1972	27p.	ARC

7. REFERENCE ORGANIZATION NAME AND ADDRESS

TVA

9. ABSTRACT

10. CONTROL NUMBER	11. PRICE OF DOCUMENT
PN-RAA- 217	

12. DESCRIPTORS Complex fertilizers Granular materials Manufacturing Superphosphate Urea	13. PROJECT NUMBER
	14. CONTRACT NUMBER PASA RA (QA) 5-69 Res.
	15. TYPE OF DOCUMENT

AID 590-1 (4-74)

10

UREA AND SUPERPHOSPHATE IN PRODUCTION
OF GRANULAR COMPOUND FERTILISERS

T.P. HIGNETT AND C.H. DAVIS
Division of Chemical Development
Tennessee Valley Authority, Alabama (USA)

Single superphosphate is declining in importance as a source of P_2O_5 in fertiliser as measured by its contribution to the total fertiliser P_2O_5. ISMA data credit superphosphate with about 52 per cent of the world s fertiliser P_2O_5 in 1960 but only 33 per cent in 1970 (1, 2). Further decline to about 22 per cent in 1975 is predicted (3).

The decline was not due to a decrease in production of single superphosphate. In fact, production was higher in 1970 than in 1960 (6.7 vs. 5.2 million tons of P_2O_5), although the 1970 production was less than the peak year of 1966. However, the total production of phosphate fertiliser nearly doubled in the decade, and most of the increase was in materials of higher P_2O_5 content. In 1970, single superphosphate was still the leading form, although complex fertilisers, as a group, were close behind.

The economies in storage, bagging, and transport of high-analysis fertilisers are well known. We should remember, however, that high analysis—rather than an end in itself—is a means to achieve the end of providing the farmer with the lowest cost fertiliser that meets his needs. We do the farmer a disservice if we supply him with a higher analysis fertiliser at incrersed cost per unit of nutrient or if we supply a lower cost fertiliser that lacks some of the needed nutrient elements or contains the wrong proportions of nutrients.

Single superphosphate has merits that should not be overlooked. It is produced by a simple process requiring little investment and only moderate skills. Although the nutrient content is low; often the output from a small single superphosphate plant can be marketed locally, thereby minimizing transport costs. Enormous plants are not necessary to attain economical production. In many countries the facilities are already available and not fully utilized. Low-cost byproduct or spent sulphuric acid is often available in amounts too small to

support an economical scale of phosphoric acid production; often the most economical use for such acid is in superphosphate production. Superphosphate is an excellent basic material for use in granulation of compound fertilisers. And finally, superphosphate furnishes some elements that are lacking in high-analysis fertilisers.

Calcium and sulphur—secondary nutrients necessary in substantial amounts for plant growth—are supplied by single superphosphate but are not present in most high-analysis fertilisers. Of the two, probably sulphur is the most often deficient. Substantial responses to sulphur have been noted in some parts of nearly all states of the United States and in at least 47 other countries, including many developing countries (4). Most soils in tropical and subtropical regions are inherently deficient in sulphur. Sulphur-deficient areas become more numerous and serious when heavy rates of nitrogen and other primary nutrients are applied. Much sulphur is supplied by rainfall in highly industrialized areas where it originates from burning of coal and oil. In these areas, sulphur is seldom needed in fertilisers. However, as plans for prevention of atmospheric pollution materialise, much more need for supplying sulphur in fertilisers can be expected.

Ideally, sulphur should be supplied in fertilisers only when it is needed. To attain this ideal, an alert, efficient agricultural advisory service should be available to every farmer. Even in the most developed countries, this service is often lacking for many farmers. In developing countries, little may be known about the need for sulphur. Sulphur deficiencies may become evident only after several years of cropping with sulphur-free fertilisers.

Most micronutrient elements, such as manganese, zinc, molybdenum, and copper, are extracted from phosphate rock in making phosphoric acid and are therefore present in high-analysis fertilisers as well as in superphosphate to whatever extent they may be present in the rock. Most rocks do not contain enough of these elements to be useful for correction of deficiencies.

Urea is attractive as an ingredient in compound granular fertilisers because of its high analysis, plentiful supply, and low cost per unit of nitrogen. Thus, superphosphate and urea from two of the basic ingredients for manufacture of granular compound fertilisers that may be of particular value in some developing countries and perhaps in the United States. Since the technology for granulating such formulations is not available in the United States, TVA undertook a study to develop the required information. The study—
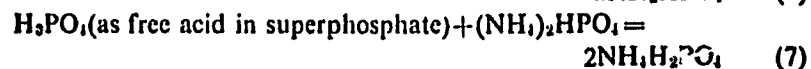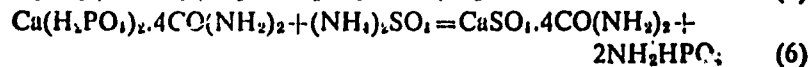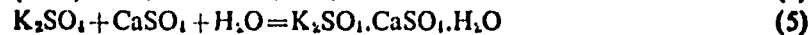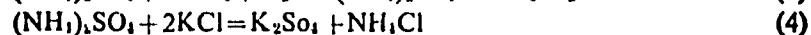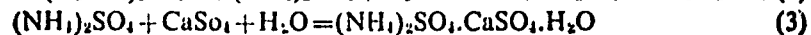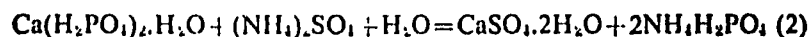
supported in part by the U.S. Agency for International Development—consisted of literature reviews, visits to British granulation plants, personal interviews, and experimental pilot-plant studies. J.T. Procter of Procter Process Engineering, Methwold, Norfolk, England, was quite helpful—both in acquainting TVA with British practice and in countributing on-the-spot suggestions as a consultant during part of the pilot work. This paper reports the results of the work.

Chemical Reactions

Formulation of compound fertilisers with urea and superphosphate may result (5) in the reaction

$$Ca(H_2PO_4)_2.H_2O + 4CO(NH_2)_2 = Ca(H_2PO_4)_2.4CO(NH_2)_2 + H_2O \quad (1)$$
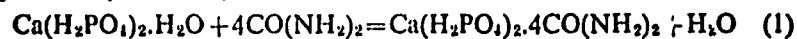
As the reaction releases the water of hydration, the mixture can becon e wet and muddy. This is easily demonstrated by putting the two materials in a bottle and shaking the mixture occasionally. With prilled urea, the mixture becomes damp in a few hours and reaches a muddy state in 2 or 3 days; the reaction probably is not rapid enough to have much effect on conditions in the granulator. When ammonium sulphate and potash salts are included in the mixture, various other reactions may occur—some more rapidly than reaction 1.

$$Ca(H_2PO_4)_2.H_2O + (NH_4)_2SO_4 + H_2O = CaSO_4.2H_2O + 2NH_4H_2PO_4 \quad (2)$$

$$(NH_4)_2SO_4 + CaSo_4 + H_2O = (NH_4)_2SO_4.CaSO_4.H_2O \quad (3)$$

$$(NH_4)_2SO_4 + 2KCl = K_2So_4 + NH_4Cl \quad (4)$$

$$K_2SO_4 + CaSO_4 + H_2O = K_2SO_4.CaSO_4.H_2O \quad (5)$$

$$Ca(H_2PO_4)_2.4CO(NH_2)_2 + (NH_4)_2SO_4 = CaSO_4.4CO(NH_2)_2 +$$
$$2NH_4HPO_4 \quad (6)$$

$$H_3PO_4(\text{as free acid in superphosphate}) + (NH_4)_2HPO_4 =$$
$$2NH_4H_2PO_4 \quad (7)$$

The ammonium and potassium syngenites formed by reactions 3 and 5 are only slightly soluble. Their formation consumes water, which may account for the observed hardening of superphosphate-containing mixtures when ammonium sulphate is added. Ammonium sulphate usually is added in the form of fine crystals, so reactions involving it may proceed more rapidly than with coarser urea prills.

Urea tends to hydrolyse at elevated temperature.

$$CO(NH_2)_2 + H_2O = 2NH_3 + CO_2 \quad (8)$$
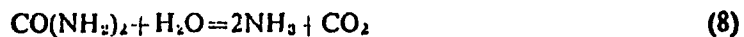
The ammonia generated by reaction 8 reacts with the monocalcium phosphate in the superphosphate

$$Ca(H_2PO_4)_2 + NH_3 = CaHPO_4 + NH_4H_2PO_4 \qquad (9)$$

The result of reaction 9 is a decrease in water solubility of the P_2O_5. The extent of the reaction depends on the time, temperature, and the acidity of the product, so it is desirable to dry the products quickly at a relatively low temperature.

Ammoniation of the superphosphate prior to the granulation operation is undesirable in countries that evaluate phosphate fertilisers on the basis of their content of water-soluble P_2O_5.

British Practice

Several small granulation plants in Great Britain produce granular fertilisers from formulations containing urea, superphosphate, and other materials. Both single and triple superphosphate are used in some plants. Other common materials are monoammonium or diammonium phosphate, ammonium sulphate, add potash salts. Since there is a premium value on water-soluble P_2O_5 in the British market, ammoniation of superphosphate is either avoided entirely or practised only to the extent of neutralising the free acid.

The range of grades is wide—from 7-7-7 to 20-10-10 The 20-10-10 grade is a favourite. The small plants have a competitive advantage in being able to make special grades for their areas, whereas larger plants produce only a few standard grades. With urea in the formulation, the small plants can attain a fairly high nutrient content without depending on their competitors for high-analysis phosphatic materials. (The larger plants mainly produce ammonium nitrate-based compound fersilisers.)

Ammonium sulphate usually is included in urea-superphosphate formulations in Great Britain. One reason may be the favourable chemical effect of hardening the product as discussed previously. Other reasons for using ammonium sulphate are its low cost (by product material) and a general belief that the urea content of compound fertilisers should not exceed 25 per cent. This limitation probably stems from an agronomic consideration; in Great Britain, "combine drilling" is a common practice in which small grain seeds are placed with the fertiliser. In such placement, compound fertiliser containing large proportions of urea may delay or prevent germination of the seed, especially in high pH soils and in dry weather(6). Also, in many formulations if the proportion of urea exceeds about 25 per cent, the liquid phase is excessive for satisfactory granulation.

The higher analysis compound fertilisers are produced with the addition of monoammonium or diammonium phosphate or both. The ammonium phosphate may be purchased or formed in place from phosphoric acid and ammonia. The amount of diammonium phosphate is limited to that which will react with the free acid in the superphosphate to minimise loss of water solubility of the P_2O_5. Neutralisation of free acid is desirable to prevent a wet, sticky condition in the dryer (7).

A typical plant produces 7 to 12 tons per hour. The solid raw materials are prepared by crushing the lumps, if any, weighing, and pre-mixing. The granulator is a rotating drum, typically about 6 feet is diameter by 18 feet long. As compared with usual practice in the United States, the granulator is very long, but the bed depth is shallow. The drum has a retaining ring at the feed end but none at the ·discharge end. With the shallow bed, retention time in the granulator is short—perhaps 3 minutes for some plants. The rotation rate usually is about 40 to 60 per cent of the "critical speed" as defined by Brook (8). For a 6-foot-diameter drum, 50 per cent of the critical speed would be 15.5 revolutions per minute. When ammonium phosphate is formed in the mixture from phosphric acid and ammonia, this is done in a TVA-type continuous ammoniator (9), which may be a separate unit or may be a section of the granulator separated by a retaining ring. The remainder of the plant consists of a dryer, a cooler, screens for recovering product in the desired range of granule sizes, a crusher for oversize, and means for recycling undersize and crushed oversize. The product usually is coated with 1 to 2 per cent of clay together with an oil adhesive.

The free acid content of the superphosphate usually is in the range of 3 to 6 per cent. However, one producer is said to over-acidulate the superphosphate so that neutralisation of the excess acid will provide heat during granulation. Morocco rock is generally used in superphosphate production.

Most operators prefer potash in granular from. When they buy their monoammonium or diammonium phosphate, they prefer that it be granular. Prilled urea is used, although some operators prefer a smaller particle size if it is available. One plant is reported to have tried preliminary crushing of the urea prills but is not pleased with the result, as buildup in the dryer is increased. Ando (10) says that plants in Japan pulverize urea prills to produce compound fertilisers. Some British manufacturers have tried crystalline urea, but caking in storage

makes it unsuitable. Their ammonium sulphate is in the form of fine crystals, and their superphosphate is powdery.

All agree that the temperature in the granulator is important, although the proper combination of temperature and liquid phase is judged more by the appearance of the material leaving the granulator than by temperature measurement. A range of 75° to 85°C seems typical.

Heat in the granulator is supplied by injecting steam under the bed of material near the feed end of the granulator, by directing gas flames on the surface of the bed, or by the heat of reaction of phosphoric or sulphuric acid with ammonia. A combination of these methos is sometimes used. Heat is conserved by returning the recycle without cooling. In some plants a small amount of spray water is added in the granulator.

Granulation is not completed in the granulator; in fact this unit is sometimes called a "conditioner" which implies that its function is to prepare the material for granulation. Most of the granulation actually occurs in the dryer.

The temperature in the dryer is controlled to prevent hydrolysis of urea and to prevent melting or softening of the granules. The dryer is fired cocurrently with inlet gas temperatures ranging from 130° to 200°C. Maximum permissible product temperature depends on the formulation; 85° to 90°C seems typical. In spite of the relatively low temperature, drying is said to be more rapid than ammonium nitrate-based compound fertilisers because the diffusion rate of water from the granules is faster (11). High-analysis grades are dried to less than 0.5 per cent moisture—low-analysis grades to less than 1.0 per cent.

Undersize screening usually is at 2.0 to 2.5 mm; since few urea prills are as large as 2.0 mm, most of the unincorporated urea prills are returned to the granulator with the undersize. Oversize screening is at 3.5 to 4.0 mm. The ratio of recycle to product usually is between 0.5:1 and 1.5:1

The product cooling is important. If the product is stored at elevated temperature, urea will hydrolyse slowly, releasing ammonia which will combine with the superphosphate and lower the water solubility of the P_2O_5. A decrease of P_2O_5 water solubility from 96 to 78 per cent was reported for 60 days' storage at 45°C, whereas no decrease was detected at 35°C (12).

The cooled products are coated with 0.5 to 1.0 per cent of oil

and 1 to 2 per cent of clay. They seem to have good storage properties when bagged in plastic bags. When stored in bulk, some absorption of moisture from the atmosphere occurs at the surface of the pile. Some manufacturers minimise moisture absorption by covering the stored material with plastic sheets.

Since a large proportion of the materials entering the granulator are already granular, the products are not entirely homogenous. Lack of homogeneity does not cause any serious problems as far as is known. The conditioning operation, with oil and clay, is also effective in masking the lack of homogeneity by covering any unincorporated feeds, such as white urea prills, that were evident in the uncoated product.

Granulation plants of the type just described seem unusually free from dust and fume, even though simple dust catchers are the only recovery equipment. One reason advanced is the absence of ammonium chloride, which is ordinarily the most volatile component of fertilisers. In formulations containing both sulphuric acid and potassium chloride, HCl can be formed by the reaction

$$H_2SO_4 + 2KCl = K_2SO_4 + 2HCl \tag{10}$$

Then some HCl vapour can combine with ammonia above the bed to form the ammonium chloride aerosol. In formulations containing ammonium nitrate and potassium chloride, ammonium chloride is formed rapidly by the reaction

$$NH_4NO_3 + KCl = NH_4Cl + KNO_3 \tag{11}$$

Other reasons for the lack of fume are the low drier temperature and the relatively low, uniform temperature in the granulator, as compared with temperatures reached in formulations involving neutralisation of acids or high degrees of ammoniation of superphosphate.

Japanese Practice

Japanese practice in production of granular compound fertiliser was summarised recently by Ando (10). Production of granular compound fertiliser has increased rapidly in Japan and in 1968 reached 4.5 million tons. Unlike many other countries, Japan seldom includes ammonium nitrate in formulation of compound fertilisers. The nitrogen is derived from ammonium sulphate, ammonium chloride, urea, and ammonium phosphate. Use of ammonium chloride is substantial—reported to be about 200,000 tons per year of nitrogen in

1968. Phosphate materials are mainly single superphosphate and ammonium phosphate. A gradual increase in the use of urea and ammonium phosphate is reflected as an increase in high-analysis products.

As in Great Britain, a high water solubility of P_2O_5 is preferred, so formulations containing superphosphate involve only light ammoniation, sufficient to neutralise free acid. Urea is added mainly in solid form, as crushed prills or crystals. Molten urea is used in some plants where urea is produced adjacent to the granulation unit. Ammonium phosphate may be added either in solid or slurry form. The solid ammonium phosphate may be granular, semigranular, or non-granular; it is produced by the processes developed by Nissan, TVA, Prayon, Scottish Agricultural Industries, Swift, and Fisons.

A variety of granulation processes are used. This is Ando's (10) estimate of the distribution of granulators by type.

	Per cent of total	
	High analysis	Low analysis
Rotary drum	40	60
Pan	15	30
Pug mill (blunger)	25	0
Others	20	10
Total	100	100

The "others" entries include compactors, extruding pelletisers, and fluidised granulators. Information is not available as to which of these granulators are used with superphosphate-urea formulations, although it may be presumed that low analysis grades are based on superphosphate.

Situation in India

In the meeting of The Fertiliser Association of India in December 1969, Mr. A.D. Mango, Chairman of FAI, pointed out the plight of the single superphosphate industry in India. The industry, comprising 29 plants with a total annual capacity of 220,000 tons of P_2O_5, was working at only half capacity (12). He suggested that these plants could make an important contribution if they were permitted to upgrade their products with high-analysis materials to make granular

compound fertilisers, and this became one of FAI's recommendations(13).

At the same meeting, Gupta and Rao (14) reported results of small-scale tests in which a variety of medium-to high-analysis granular compounds were produced from superphosphate urea, diammonium phosphate (DAP), and potassium chloride. One of the problems was loss of water solubility of the P_2O_5 owing to the reactions of DAP with superphosphate. The authors commented that monoammonium phosphate (MAP) would be a desirable material, but it was not available in India.

It may be helpful to point out that plants which make granular DAP can also make granular MAP with only minor changes, and the operation is somewhat simpler (15). In fact, several plants in the United States that were designed to make DAP now make MAP part of the time. India could supply needed MAP from existing and planned DAP plants with very inexpensive alterations.

Developmental Work at TVA

Developmental work on granulation of compound fertilisers containing unammoniated single superphosphate and urea at TVA included studies on bench scale, small pilot scale (45 kg/h of product), and large pilot scale (900 kg/h of product). Several formulations were evaluated for production of fertilisers having 1:1:1 and 1:2:1 ratios. In some tests, DAP was included in the formulation to ammoniate the free acid in the superphosphate.

Bench-Scale Studies : Batch tests of a 15-15-15 grade were made in a small rotary drum with a capacity of 0.9 kg. Three formulations were tested in which supplemental nitrogen and phosphate were added as a granular ammonium phosphate (13-52-0) intermediate between MAP and DAP as powdered MAP (11-55-0) or as granular DAP (18-46-0). The commercial urea was of various particle sizes : (1) regular prills (33 per cent between 1.7 and 2.4 mm and 64 per cent between 1.0 and 1.7 mm), (2) regular prills sized to minus 2.4 mm, (3) regular prills sized to minus 1.7 mm, (4) crushed regular prills (−0.8 mm), and (5) microprills (0 per cent larger than 1.4 mm, 13 per cent between 1.0 and 1.4 mm, 46 per cent between 0.8 and 1.0 mm, and 33 per cent between 0.6 and 0.8 mm).

This was the procedure for the bench-scale tests.

* All raw materials were placed in the drum, and rotation was begun.

* The flame from an acetylene torch was applied directly to the outer shell of the drum for about 5 minutes to supply heat and thus promote granulation.
* After the granules had formed, the heat was removed and the material was allowed to cool and harden in the rotating drum for about 10 to 15 minutes. Occasionally, compressed air was blown into the drum for more rapid cooling to avoid over-agglomeration.

Data from the bench-scale tests are shown in the following tabulation. Granulation was accomplished by the use of flame heat alone; no steam, water, or other materials were required to promote granulation. The water content of the total feed to the drum was about 2.5 per cent. At this moisture level, granulation was good at drum temperatures in the range 60° to 65°C but quite sensitive to control.

Run	A	B	C
Formulation, kg/metric ton of product			
Run-of-pile single superphosphate (0-20-0)	297	299	299
Powdered monoammonium phosphate (11-55-0)	—	165	—
Granular ammonium phosphate* (13-52-0)	175	—	—
Granular diammonium phosphate (18-46-0)	—	—	198
Urea (46-0-0)	277	285	251
Standard red potassium chloride	251	251	252
Granulation data			
Temperature, °C	60	66	60
Calculated total moisture input, per cent of feed	2.6	2.4	2.6
Screen analysis, per cent			
Larger than 3.4 mm	4	11	5
Between 1.7 and 3.4 mm	83	87	73
Smaller than 1.7 mm	13	2	22
Chemical analysis, per cent by weight			
Total N	15.2	15.2	15.4
Biuret N	0.1	0.1	0.1
Total P_2O_5	19.0	15.1	18.3
Citrate-insoluble P_2O_5	0.29	0.70	0.30
Water-soluble P_2O_5	13.4	13.3	14.7
K_2O	14.5	16.1	15.0
H_2O	1.2	1.4	1.85
P_2O_5 availability, per cent of total P_2O_5	98.5	95.4	98.4
P_2O_5 water solubility, per cent of total P_2O_5	71	88	80

* Contains both MAP and DAP with the major part as MAP.

Moisture content of the granular products was about 1.5 per cent. Physical characteristics of the granules were good. About 80 per cent of the product was in the size range 1.7 to 3.4 mm. Water solubility of the phosphate ranged from 70 to 90 per cent of the total P_2O_5 and was lower with formulations containing DAP.

Some individual particles of feed materials could be seen in the granular products. The use of powdered MAP and rushed or microprilled urea improved the homogeneity of the products.

Microscopic examination of the products indicated that the urea-monocalcium phosphate adduct was not formed. The cementing phase binding the component materials into granules was identified as a urea-ammonium chloride complex.

The bench-scale tests indicated that good quality products could be made with this type of process. However, control of the operation to ensure satisfactory granulation was difficult.

Small-Scale Pilot-Plant Studies : After the bench-scale studies, the process was shifted to continuous tests in a small-scale granulation pilot plant with a production rate of about 45 kg per hour. A flow diagram of the process is shown in Figure 1. In the small-
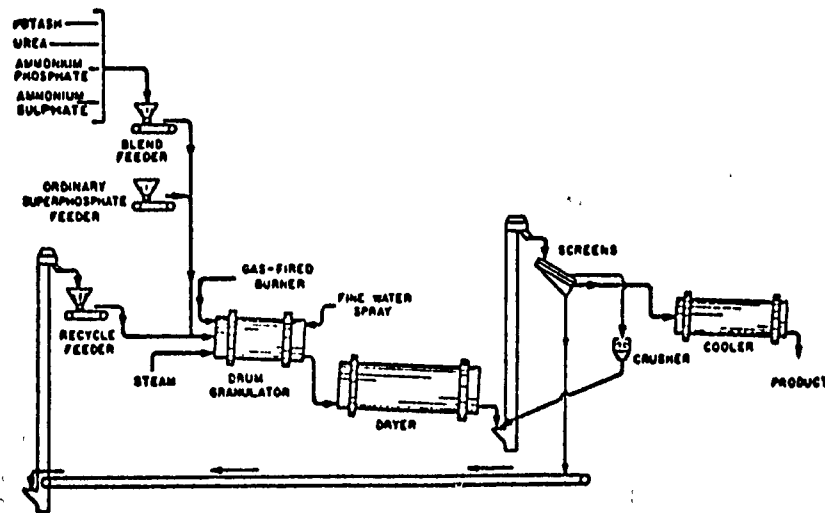

FIG. 1 : GRANULATION OF COMPOUND FERTILISERS
CONTAINING SUPERPHOSPHATE AND UREA

scale pilot plant the product cooler and oversize crusher were not included in the continuous flow system. The dryer product was screened hot. Oversize was crushed batchwise before recycling it to the granulator along with the screen undersize. Onsize product was cooled batchwise by spreading it on the floor.

The drum granulator was 38 by 91 cm and was rotated from a variable-speed drive. A steam sparger 15 cm long provided for addition of steam beneath the bed near the feed end of the granulator. Just downstream from the sparger a burner — fired with natural gas — impinged directly on the bed. Touch-up granulation control was provided by an air-atomizing fog nozzle for introducing small amounts of water near the discharge end of the granulator. The outer shell of the granulator was insulated to hold down heat loss from the small unit.

Retention time in the granulator was about 20 minutes. The granules leaving the granulation section were well formed and were not much changed in size and appearance in passing through the dryer. With the long granulator retention, the water spray at the granulator discharge was particularly helpful for maintaining consistent granulation.

A granulator speed of about 32 revolutions per minute seemed to give best granulation. This is 47 per cent of critical speed and is somewhat greater than the usual granulator speeds.

For convenience in feeding the granulator, the urea, ammonium phosphate, potassium chloride and ammonium sulphate (when used) were pre-blended. The granular ammonium phosphates were crushed to essentially minus 1.7 mm (58 per cent smaller than 0.60 mm) prior to blending. Potassium chloride was fed either as standard particle-size material, which is about 96 per cent between 0.149 and 1.41 mm, or as a special fraction sized to about 95 per cent between 0.84 and 2.4 mm. The ammonium sulphate was crystalline (byproduct, 95 per cent-0.60 mm). Urea for the small-scale pilot plant work was exclusively in the form of microprills (90 per cent -1.4 mm). As all the feeders for solids discharged into a common chute, some premixing occurred ahead of the granulator drum.

Six formulations were tested—two for production of a 15-15-15 grade, three for a 14-14-14 grade and one for a 10-20-10 grade. The formulations are summarized here.

Nominal grade				14-14-14		10-20-10
Formulation identification	A	B	C	D	E	F
Formulation, kg/metric ton						
Crystalline ammonium sulphate (21-0-0)	—	87	72	96	40	—
Granular ammonium phosphate* (13-52-0)	—	198	146	—	—	—
Powdered monoammonium phosphate (11-55-0)	166	—	—	148	—	—
Granular diammonium phosphate (18-46-0)	—	—	—	—	182	227
Run-of-pile single superphosphate (0-20-0)	298	235	319	292	314	477
Granular potassium chloride (0-0-60)	251	250	233	233	234	166
Microprilled urea (46-0-0)	285	230	230	230	230	129
Calculated P_2O_5 water solubility, percent of total P_2O_5	88	90	86	86	83	83
Fraction of total P_2O_5 supplied as single superphosphate, per cent	39	31	46	42	43	48

*Contains both MAP and DAP with the major part as MAP

In tests of the 15-15-15 grade with formulation A (29 per cent of urea), liquid phase in the granulator was excessive. With formulation B (23 per cent of urea and supplemental nitrogen as ammonium sulphate), granulation was not satisfactory because of insufficient liquid phase — probably a result of the lower proportion of single superphosphate in formulation B.

Formulations with 23 per cent of urea generally were granulated satisfactorily when the grade was lowered to 14-14-14 and the proportion of P_2O_5 supplied as single superphosphate was raised from the 31 per cent in formulation B to the range 42 to 46 per cent (formulations C, D, and E).

Formulation F, a 10-20-10 grade, had a urea content of only 13 per cent, and about half of the P_2O_5 was supplied as single superphosphate. This formulation also resulted in satisfactory granulation, but high proportion of steam was required to supply liquid phase, and the product was not adequately dried.

Operating data from three tests with the 14-14-14 grade follow.

GRANULAR COMPOUND FERTILISERS

Nominal grade	14-14-14		
Formulation identification	C	D	E
Granulation data			
Feed rate, kg/h			
Blend[a]	31	30	32
Single superphosphate	15	13	15
Recycle	45	33	58
Steam	0	0.3	0.7
Single superphosphate analysis, per cent			
Total P_2O_5	20.0	21.1	21.0
Available P_2O_5	18.4	19.6	19.5
Water-Soluble P_2O_5	15.6	16.6	16.4
Free acid P_2O_5	1.3	0.3	0.6
H_2O	5.2	1.9	3.6
P_2O_5 water solubility, per cent of total P_2O_5	78	79	78
Temperature, °C	83	73	65
Total input moisture, per cent of feed	0.9	2.5	2.0
Recycle ratio, kg/kg of product	1.0	0.7	1.3
Analysis of exit solids			
Moisture, per cent by weight	0.9	2.2	2.0
Screen size, per cent by weight			
Larger than 3.4 mm	15	34	14
Between 1.7 and 3.4 mm	38	19	48
Between 1.0 and 1.7 mm	20	24	29
Smaller than 1.0 mm	27	23	9
Drying data			
Temperature, °C			
Inlet air	87	116	123
Outlet air	70	76	76
Product	72	68	69
Moisture of exit solids, per cent by weight	0.8	1.1	1.0
Onsize product data			
Chemical composition, per cent by weight			
Total N	13.2	12.9	11.9
Total P_2O_5	15.2	14.2	14.4
Available P_2O_5	14.7	14.0	13.7
Water-soluble P_2O_5	12.4	12.4	9.8
Free acid P_2O_5	0.1	0.3	—
K_2O	14.2	14.9	18.7
H_2O	0.7	1.1	1.0
pH[b]	4.2	3.4	4.8
P_2O_5 availability, per cent of total P_2O_5	96.7	98.6	95.1
P_2O_5 water solubility, per cent of total P_2O_5	82	87	68

[a] The urea, potassium chloride, supplemental ammonium phosphate and ammonium sulphate (when present) were premixed for more accurate control of feed rates.

[b] Determined on a 10 per cent aqueous solution of the product.

The physical appearance of the products was influenced by the particle size of the feed materials. With standard potassium chloride and either powdered or crushed ammonium phosphate, the product had the appearance of most other conventionally granulated products. With granular feed materials, some of the granules escaped incorporation.

Well-dried and suitably coated products stored satisfactorily in tests.

Petrographic analyses indicated that the urea — monocalcium phosphate adduct was not formed. In most of the samples examined, the monocalcium phosphate had reacted with the other salts to give $Ca_2 (K,NH_4)H_7 (PO_4) 4.2H_2O$ (Flatt's salt). Other reaction products were NH_4Cl and KH_2PO_4. The NH_4Cl had reacted with urea to form $CO(NH_2)_2.NH_4Cl$. Additional $CaSO_4.0.5H_2O$ was formed in the reaction of $(NH_4)_2SO_4$ with the monocalcium phosphate.

Water solubility of the phosphate was in the range 80 to 99 per cent of the total P_2O_5 with MAP in the formulation—60 to 70 per cent with DAP. Water solubility for all the products was somewhat lower than desired, because the single superphosphate was low in water solubility (see preceding tabulation).

Large-Scale Pilot-Plant Studies : A few tests were made in TVA's larger pilot plant at production rates of 900 kg per hour. Operation was similar to that of the small pilot plant, except that the dryer product was cooled and screened continuously, with continuous crushing and rescreening of the oversize. During some tests the screened product was also conditioned continuously by coating with clay dust and an oil binder.

The rotary drum granulator was approximately 1 m in diameter by 2 m long. The drum had a 23-cm retaining ring in each end. The discharge ring was recessed 60 cm from the end of the shell. A reciprocating, toothed scraper removed buildup from the shell. The drum was rotated at about 57 per cent of the critical speed. As in the small-scale pilot plant, material in the granulator was heated by a direct flame, and granulation was controlled by introduction of steam and atomized water. Retention time in the granulator was about 5 minutes.

The granulator was built several years earlier for development of processes for continuous and simultaneous ammoniation and granulation of fertiliser materials; it probably was not of optimum design for the urea-superphosphate granulation process. The granulator is shown in Figure 2.
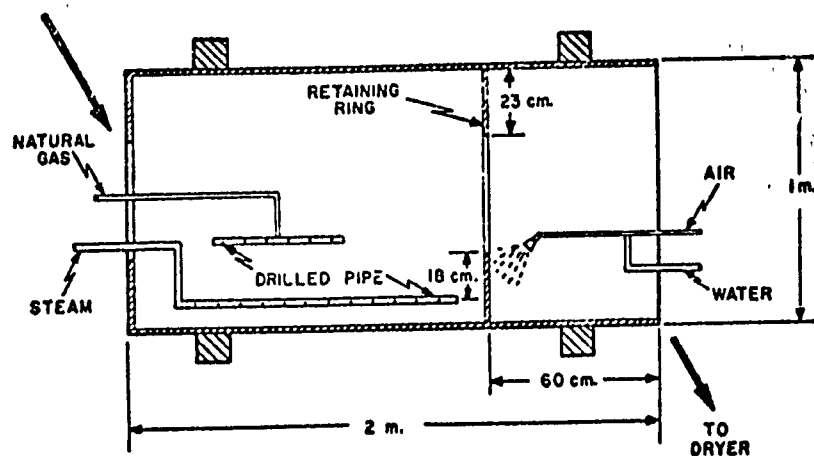
FIG. 2 : SKETCH OF TVA GRANULATOR DRUM

Heat input from the steam sparger in the granulator was about 15,000 kcal per ton of product (saturated steam at 179°C—10 kg/cm²). More than four times this amount of heat was required when the gas flame was the only source of heat because of the heat losses to the air flowing in the granulator. At times, heat was introduced from both sources. Also, steam, water, and gas sometimes were used together.

The pilot work was restricted to testing of 1:1:1 ratio products in three grades, 14-14-14, 12-12-12, and 11-11-11. Here are the formulations.

° 14-14-14—Same as formulation C in the small-scale pilot-plant tests
° 11-11-11—Urea, single superphosphate, and potash
° 11-11-11—Single superphosphate, DAP (to ammoniate free acid in superphosphate), urea, ammonium sulphate, and potash
° 12-12-12—Single superphosphate, DAP (to ammoniate free acid in superphosphate), urea, and potash

Materials for the formulations were standard commercial urea prills, granular ammonium phosphates (incrushed), standard commercial potassium chloride, and byproduct crystalline ammonium sulphate. The single superphosphate used in earlier work was replaced with one considered to be more representative of U.S. commercial products

made from Florida phosphate rock. Its analysis is shown in the tabulation.

Chemical analysis, per cent by weight

Total	C.I.	W.S.	Free acid	H_2O	W.S. P_2O_3 per cent of total P_2O_5
20.9	0.6	16.7	1.2	4.8	80

P_2O_5

Results from granulation of the 14-14-14 grade generally were satisfactory. The mix granulated at a temperature of 70°C with a moisture content of about 1.5 per cent in the granulator product. Recycle-to-product ratio was about 0.7. The product from the dryer, when discharged at a temperature of 70°C, had a moisture content of about 1 per cent. Water solubility of the phosphate was 86 per cent.

The mix was quite sensitive to small changes in temperature or moisture content. Granulation continued during the drying step, and the operators had to monitor continuously the appearance of the discharges from both the granulator and dryer.

Results from testing of the 11-11-11 formulation with only urea, superphosphate, and potassium chloride were not satisfactory. Even without addition of supplemetal heat or moisture, the material was wet and sticky when it left the granulator. The mix could not be dried satisfactorily; it overagglomerated in the dryer as the temperature in the dryer was raised in an affort to remove moisture. The moisture content of the dryer product was about 2 per cent, and the material was too sticky to convey, screen, and crush. Petrographic analysis indicated that the crystalline phases in the product included $CaSO_4$, $Ca_2KH_7(PO_4).2H_2O$, urea-calcium sulphate adduct, and KCl.

Modifying the 11-11-11 formulation by providing sufficient DAP (about 30 kg/metric ton of product) to ammoniate the free acid in the superphosphate and including ammonium sulphate (134 kg/metric ton of product) resulted in improved operation. Granulation was satisfactory with a recycle-to-product ratio of about 0.8, a moisture content of about 1.5 per cent in the product from the granulator, and a temperature of about 79°C. Crysralline phases in the product were identified as urea, KCl, $CaSO_4$, $(NH_4)_2SO_4$, a compound tentatively identified as $Ca_2(NH_4,K)H_7(PO_4).2H_2O$, and smaller proportions of quartz and ammonium phospate.

Omission of ammonium sulphate from the last-discussed formulation raised the product grade to 12-12-12. Operation with the 12-12-12 was reasonably good at a recycle-to-product ratio of about

1.2. The temperature in the granulator was about 54°C, and the moisture content of the discharged product was 1.4 per cent. Even when dried to a moisture level of 1 per cent, the material tended to be somewhat sticky and to overagglomerate during drying. Petrographic analysis indicated that a small amount of the urea-monocalcium phosphate adduct was formed. Apparently the ammonium sulphate in other formulations reacted with the monocalcium phosphate and thus helped to prevent formation of the adduct.

In general, water solubility of the phosphate in TVA pilot-plant products ranged from 70 to 90 per cent, which is somewhat lower than is reported in Great Britain for products of similar processing. The difference probably was due primarily to the lower water solubility of the TVA superphosphate, which was produced from Florida phosphate rock. Morocco rock, which is often used in Great Britain, is said (16) to give a somewhat higher water solubility than Florida rock. Also, there may be a tendency toward a higher degree of acidulation in Great Britain to maximize water solubility of the phosphate. In all the pilot tests the products contained some unincorporated feed materials. The proportion of unincorporated material was inconsequential except for the appearance of the product.

Observations of the exhaust stacks during the pilot-plant tests indicated that practically no dust or fume evolved from the process equipment. The operating areas in the plant were also quite free of dustiness. Absence of visible fume probably resulted primarily from the absence of significant exothermic chemical reactions of the type characteristic of granulation operations involving neutralization of acids. Absence of sulphuric acid from the formulation was helpful in preventing formation of troublesome and highly visible ammonium chloride aerosol.

Conclusions

Granular compound fertilisers can be produced satisfactorily in coventional granulation plants from formulations containing urea and single superphosphate without ammoniation. Products that are adequately dried and coated have satisfactory storage and handling characteristics.

The formulation should contain not more than 25 per cent urea. Diammonium phosphate or some other ammoniating medium should be added to neutralize the free acidity of the superphosphate. Inclusion of ammonium sulphate in some formulations probably is helpful

in avoiding formation of urea-monocalcium phosphate adduct which is detrimental to the physical condition of the products. Drying and cooling temperatures of products should be carefully controlled to avoid hydrolysis of urea and resultant lowering of the water solubility of the phosphate.

As granulation is quite sensitive to small variations in the amount of liquid phase, careful control of heat and moisture inputs (gas flame, steam, water) is essential. If the discharge from the granulator contains more than 1.5 per cent of moisture, addition of sufficient heat without melting in the dryer is difficult. Recycling of hot fines helps to conserve heat. High granulator speeds-near 50 per cent of critical speed-are helpful.

Granulation is likely to be influenced significantly by the type of single superphosphate, particularly by its content of moisture and free acid.

As the granulation operation produces practically no dust or fume, control of atmospheric pollution from a commercial plant should be simple.

The present work did not define the optimum design of a granulator for urea-superphosphate formulations. The results of the small-scale pilot-plant work suggest that a longer than usual retention time would be beneficial. The ratio of length to diameter probably should be greater than that (2:1) in the large pilot plant. However, it is believed that most conventional granulation plants can produce acceptable products with urea superphosphate formulations after some experimentation provided there is some leeway in adjusting formulations and selecting grades to be produced.

References

1. *Phosphate Notes*, No. 12, 28-9 (December 1970).
2. *World Fertilizer Review*. No. 1,47 (May 1971).
3. Hignett, T.P., *Proc. 20th Annual Meeting Fertilizer Industry Round Table, 1970* (Memphis, Tenn.), 6-12. Office of Secretary-Treasurer, Baltimore, Maryland 21,212, 1971.
4. Beaton, J.D., Fox, R.I., "Fertilizer Technology and Use," 2nd ed., Chapt. XI. R.A. Olsen. Editorial Committee Chairman, American Society of Agronomy, Madison, Wisc. 1971.
5. Frazier, A.W., Lehr, J.R., Smith, J.P., *J. Agr. Food Chem.*, 15, (2), 345-7 (March-April 1967).
6. Collier, P.A., Hood, A.E.M , Powell, R.A., et al., *J. Agr. Sci.*, Cambridge, 15, 153-60 (1970).

GRANULAR COMPOUND FERTILISERS

7. Yeonmans, P.W., Redman, J.W. British Patent 949, 345. February 12, 1964.
8. Brook, A.T., *Fertiliser Soc. (England), Proc. No. 47* (1957).
9. Nielsson, F.T. U.S. Patent 2, 741, 545. April 10, 1956.
10. Ando, Jumpei, *Proc. 20th Annual Meeting Fertilizer Industry Round Table, 1970* (Memphis, Tenn.), 85-92. Office of Secretary-Treasurer, Baltimore, Maryland 21,212, 1971.
11. *Nitrogen*, No. 66, 29-34 (July-August 1970).
12. Mango, A.D., *Proc. Seminar on Fertiliser Production and Technology*, Fertiliser Association of India (New Delhi), 3-8, 1969.
13. Mango, A.D., *Proc. Seminar on Fertiliser Production and Technology*, Fertiliser Association of India (New Delhi), 711-712 (1969).
14. Gupta, R.K., Rao, A.K., *Proc, Seminar on Fertiliser Production and Technology*, Fertiliser Association of India (New Delhi), 655-665 (1969).
15. Young, R.D., Hicks, G.C., *Com. Fertilizer*, **114**. (2), 26-27 (February 1967).
16. Dee, T.P., Nunn, J.R., Sharples, K., *Fertilizer Soc. (England). Proc.*, No. 42, (1957).

Various aspects of the granulation of urea
with superphosphate highlighted in Mr. T. P. Hignett's
paper, were presented by Mr. A. K. Rao (DCM) who also
initiated the discussion. Moisture as well as
temperature were the governing factors for achieving
proper granulation. It was noted that use of micro
prills or crushed prills of urea and, if possible,
crushed DAP/superphosphate would be helpful. Also
the use of molten urea would contribute to the
granulation. The non-homogeneity of the product
could be masked to some extent by coating. Mr. Rao
enquired the authors con sions regarding the
reversion of water-solubility when DAP was used,
since in his experience with the production of
20-20-0 made by mixing 28 per cent DAP, 32 per cent
urea and 39.5 per cent superphosphate, he had
found good keeping qualities even on prolonged
storage and that water-solubility had stabilised
after a minor reversion initially. He also stated
that DAP or MAP was the main stabiliser for urea-
superphosphate product and not ammonium sulphate
which was a salt of a very strong acid. As an
example, he said that in the 10-10-10 product they
had produced on the lines similar to the Fisons
process, and containing 55 per cent superphosphate,
17 per cent urea and 11 per cent ammonium sulphate,
they observed bleeding and whetting after a few
days. When 6 per cent DAP was incorporated in
the above product they obtained a suitable product.
Also Mr. Rao did not agree that a 14-14-14 product
could not be produced without the use of DAP or
any other P_2O_5 donor as has been mentioned by
Mr. Hignett. He added that DCM had used more than
25 per cent urea in the urea-superphosphate
granulation with success. As Mr. Hignett was not
present during the session, it was decided that
these and other comments would be sent to him
with a view to obtaining clarifications.

Question : It is mentioned in the paper that both single superphosphate and high analysis fertiliser contain micro-nutrients to the same extent as present in the rock. I recall that in a note published by Dr. Sauchelli about 4-5 years ago, the micro-nutrient contents of single superphosphate were shown to be considerably higher than those of high analysis fertilisers using phosphoric acid.

Answer : *Micronutrient Content.* It is a common assumption that single superphosphate contains more micronutrients than concentrated fertilisers. I do not know of any data supporting this assumption. There are hundreds of analyses of phosphate rock, single superphosphate, triple superphosphate and ammonium phosphate showing their content of recognized micronutrients; B, Cu, Fe, Mn, Zn and Mo. In general I think it is a fair conclusion that the micronutrient content of both single superphosphate and higher analysis fertilisers is roughly proportional to the P_2O_5 content. A paper by W.H. Hill, H.L. Marshall, and K.D. Jacob in *Industrial and Engineering Chemistry* (24, 1054-68, September 1932) shows detailed analyses of six wet-process acids and a range of analyses of phosphate rocks from which they were made. Unfortunately there were no analyses of the specific phosphate rocks that were used for making these acids, and the range of micronutrient content for rocks from the same area was rather wide. However, the micronutrient content of the acids usually corresponded to the upper part of the range of that in the rock, and sometimes exceeded it. It was suggested that corrosion of equipment contributed to the Cu, Zn, Mo, Fe and Mn content. It would be nice to have more pertinent data, but I think

the data that we have are sufficient to justify the statement that, on the whole, the micronutrients in high-analysis phosphate fertilisers are as abundant as in single superphosphate. The situation is complicated by the fact that sulfuric acid often contains micronutrients when it is produced from pyrites or smelter operations.

Question : It is mentioned that "the amount of diammonium phosphate is limitted to that which will react with free acid in the superphosphate to minimise loss of water solubility of the P_2O_5". This is not understandable. Additional quantities of DAP would upgrade P_2O_5 just as MAP would. The reduction in water solubility with DAP is probably due to neutralization of free acidity similar to when ammoniating superphosphate.

Answer : The intention of the statement is to say that "It was the usual practice (in Great Britain) to use no more diammonium phosphate than that which would react with the free acid in the superphosphate." The purpose of this limitation was to avoid loss of water solubility which would occur with larger proportions of diammonium phosphate according to the reaction

$(NH_4)_2HPO_4 + Ca(H_2PO_4)_2 \rightarrow 2NH_4H_2PO_4 + CaHPO_4$
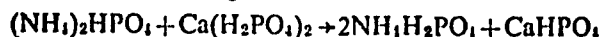
The reaction may or may not be complete during granulation, but it does go to completion (or nearly so) during chemical analysis and thus reduces the water solubility as reported by analytical procedures.

Question : The observation in the paper that the reduction of water solubility is maximum when using DAP as the P_2O_5 donor is not borne out by the figures given for bench scale runs A, B & C. The water solubility appears to be lowest when using 13:52:0 containing MAP and DAP.

Answer : After inspection of the original data, it appears that the products from the bench-scale tests were not adequately cooled or dried before storage. The loss in water solubility was partly due to hydrolysis of urea, liberating ammonia which reacted with superphosphate while the products were stored in a sealed container at relatively high temperature (probably about 40° to 50°C) before final analysis.

For instance, the product from Run A (with 13-52-0) had a P_2O_5 water solubility of 91 per cent when first made; the final analysis about 10 days later showed 71 per cent. Thus, the data from the bench-scale tests probably are inadequate for any conclusion on the effect of the form of ammonium phosphate on water solubility. They do emphasize the need for good cooling and control of storage temperature. These factors were under better control during the pilot-plant tests, so we think the data from these tests are more reliable.

Question : In the table on the operating data from three tests with 14-14-14 grade it is not clear how water soluble P_2O_6 as a percentage of total P_2O_5 is more in the drier product than in the granulator product.

The conclusion that water solubility of phosphates is 60-70 per cent with DAP and 80-90 per cent with MAP is not borne out by the data in the table. Whereas in formulations C & D there is an increase in the water solubility from the granulator to the drier product, in case of formulation E containing DAP, there is a loss of water solubility from 78 to 68%. Something takes place during drying.

Answer : The P_2O_5 water solubility given in this context is that of the single superphosphate only. The water solubility of the product leaving the granulator was not determined. The "calculated" water solubility shown is the weighted average of the water solubility of the phosphatic materials in the formulation. There was good agreement between the calculated and actual water solubility in formulation D which contained MAP. There was some loss in formulations C and E which contained 13-52-0 and 18-46-0, respectively. The loss was especially heavy with formulation E.

Question : As a result of the work done by us, it is my opinion that the limit on the maximum urea that can be incorporated is not absolute at 25 per cent, but depends on an optimum balance between single superphosphate, urea and the ammonium radical contributing constituent (DAP/MAP/Ammonium sulphate), and possibly with more precise work it should be possible to define the

range of formulations possible on a triangular composition diagram. It is our observation based on pilot plant studies on wide range of mixtures viz., 20:20:0, 15:15:15, 18:18:9, 15:15:7½, 20:10:10, 10:20:10, 9:27:9, 5:16:0 that without the use of DAP, MAP or ammonium sulphate only 10 per cent urea can be admixed with unammoniated single superphosphate without producing a pasty mass in the granulator, whereas when an ammonium radical contributing constituent is incorporated, the percentage of urea which can be tolerated increases with the increase of the ammonium radical concentration. For example, in a 20:20:0 formulation as much as 32 per cent urea could be used.

Answer : I agree that maximum urea use is not an absolute percentage, and probably depends on many factors. We should have qualified our statement that the formulation should not contain more than 25 per cent urea.

Question : There has been considerable interest in this field in India based on our work. The participants in the Seminar may wish to know regarding cost considerations, especially with regard to granulation losses and fuel and steam consumption during the manufacture of granulated mixtures using high contents of single superphosphate and urea. Any data you can provide on this would be helpful.

Answer : It would be risky to estimate costs based on pilot-plant operations, which were not entirely successful. We are continuing our study and hope to have more complete information later.

WRITTEN QUESTIONS BY MR. S.L. AGRAWAL,
FCI, Trombay (India)
ANSWERED BY MR. T.P. HIGNETT,
TVA, Alabama (USA)

Question : It is indicated that granules are coated with 1 per cent of oil. Is it advisable to use this oil, I suppose it is of organic origin, on compositions based on Ammonium Nitrate Phosphate and Potassium Chloride as it might initiate cigar burning type decomposition creating fire hazard ?

Answer : The oil used to coat the granules is a petroleum-based hydrocarbon. It is a common practice in the United Kingdom and some other countries to use such oil for coating granular compound fertilizers, including compositions containing ammonium phosphate, ammonium nitrate, and potassium chloride. I understand that at least one company in the United States uses this treatment. Presence of the oil does not initiate cigar-burning type of decomposition.

Question : In the sketch TVA Granulator Drum (Figure-2) natural gas is being used directly for burning in order to provide heat to the granules. Would it not create fire hazards and decomposition specially on formulations based on Ammonium Nitrate Phosphate containing Potassium Chloride ?

Answer : We do not use direct gas flames for heating the granules when using ammonium-nitrate-based formulations. Other methods of heating are more effective, such as steam or reaction of ammonia with sulfuric or phosphoric acid. There might be a fire hazard in case the rotation of the granulator accidently stopped and the flame was left burning.

WRITTEN QUESTIONS BY DR. R. MAUDGAL,
IEL, Kanpur (India)
ANSWERED BY MR. T.P. HIGNETT,
TVA, Alabama (USA)

Question : Is it technically feasible to produce on commercial scale high analysis NP/NPK granulated products such as 23:23:0, 16:16:16 and 19:19:10, etc. from Urea/Triple Superphosphate/Muriate of Potash ?

Answer : TVA has produced 23-23-0 in the pilot plant from urea, triple superphosphate and ammonia. There was no particular difficulty in granulating the product. We would expect that the other formulations would be feasible also.

Question : Will it be necessary to ammoniate TSP, if so, to what extent and what will be the water soluble P_2O_5 content of such granulated products as mentioned above ?

Answer : We regarded ammoniation as necessary in our process. The water solubility of the P_2O_5 was reduced to about 50 per cent by ammoniation. Some commercial operations in the United Kingdom have used urea and triple superphosphate in granulation formulations without ammoniation or with very light ammoniation. However, I believe that ammonium salts, particularly ammonium sulfate, were included in the formulation.