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

PRE-NEUTRALISATION OF
PHOSPHORIC ACID WITH NITROGEN SOLUTION

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I Introduction

At the ISMA Technical Conference in Helsinki in 1963 we presented the results of a study of the neutralisation of nitrogen solution with sulphuric acid in a pilot pre-reactor. We found that the pre-reactor would make it possible for us to increase the use of domestic nitrogen compounds and sulphuric acid in fertilizer manufacture. Almost all of the nitrogen raw material available in our country is in the form of nitrogen solution. As our work on the pilot plant scale gave promising results, the first large-scale pre-reactor was erected at our Harjavalta factory in the summer of 1963. When a new unit for the manufacture of granulated compound fertilizers was erected at our Harjavalta factory in the spring of 1964, it included its own pre-reactor.

We have been satisfied with the results we have obtained with both these pre-reactors. This applies both to the reactor units themselves and to the product. It is closely similar in composition to the imported basic raw material ammonium sulphate nitrate in which one fourth of the total nitrogen is in the form of nitrate. We have added the pre-solution directly to the granulator and have found that the granulation proceeds more easily than when solid ammonium sulphate nitrate is used.

Facts that determined the course of our subsequent investigations were the following:

- We have two pre-reactors at our disposal, of which we have good experience, for instance in the accurate control of raw material feed.

- A new phosphoric acid factory will be ready for operation in Uusikaupunki by the end of this year. The greater part of the phosphoric acid produced there will be used in compound fertilizer manufacture at Uusikaupunki, but the rest can be used in other ways, either at Uusikaupunki or in our other factories.

- Soil scientists consider it important that our NPK compound fertilizers contain a certain proportion of

nitrate nitrogen. This will be effected in our new compound fertilizer plant based on the use of nitric acid at Uusikaupunki, but we now have four old plants in which granulated compound fertilizers are produced by mixing dry raw materials, and the question of having appropriate nitrate nitrogen levels in these products without using solid ammonium nitrate will have to be solved. It is therefore necessary for us to determine what other nitrogenous raw materials can be used, i.e. whether the nitrogen solution neutralized with phosphoric acid or its mixture with other acids in a pre-reactor can be used in these products.

- Some NPK compound fertilizers used in Finland contain nitrogen and phosphorus pentoxide in the ratio of 1:2.2 - 2.4. This ratio results when nitrogen solution is neutralized with phosphoric acid to give a mole ratio of ammonia to phosphoric acid of 1.0 - 1.15 which is approximately the ratio in monoammonium phosphate (MAP grade). It should be possible to carry this neutralisation out in a simple pre-reactor without incurring excessive nitrogen losses.

In the following, we describe the results we have obtained by neutralising nitrogen solution with phosphoric acid in our pilot-plant pre-reactor.

II Raw Materials

1. Nitrogen solution.

Owing to our varying climatic conditions, the nitrogen solution produced in the winter season differs in composition from that produced in the summer. Thus we have a "winter solution" and a "summer solution". The composition and properties of these two solutions are given in the following table.

	<u>Winter Solution</u>	<u>Summer Solution</u>
<u>Composition:</u>		
Ammonium nitrate	60.0%	65.9%
Free ammonia	24.2%	16.7%
Water	<u>15.8%</u>	<u>17.4%</u>
Total	100.0%	100.0%
<u>Physical properties:</u>		
Crystallization temperature	-18°C	+ 6°C
Boiling point (when total vapour pressure of the solution is 760 torrs)	+19°C	+35°C

Distribution of nitrogen:

Ammonia nitrogen

As NH_4NO_3	10.5%	11.5%
Free ammonia	<u>19.9%</u>	<u>13.8%</u>
Total	30.4%	25.3%

Nitrate nitrogen

As NH_4NO_3	10.5%	11.5%
Total nitrogen	40.9%	36.8%
Guarantee total nitrogen	41.0%	36.85%

Distribution of total nitrogen:

Ammonia nitrogen	74%	69%
Nitrate nitrogen	26%	31%

The nitrogen solution is prepared from an 80% ammonium nitrate solution to which different amounts of ammonia gas are added in winter and summer. The summer solution can be changed into the winter solution by adding 9.8 parts by weight of ammonia to it.

2. Phosphoric acid

We have used two grades of phosphoric acid, one containing 76% phosphoric acid (55% P_2O_5) and one containing 70% phosphoric acid (50% P_2O_5). We were able to use the latter grade without dilution in our experiments and it was then not necessary to use a water feed pump in our pre-reactor unit.

Initially we used a concentrated wet process phosphoric acid (70% $\text{H}_3\text{PO}_4 = 50\% \text{P}_2\text{O}_5$). The solid impurities in this acid interfered with the operation of the feed pump. This interference could be eliminated by installing two parallel filters in the line leading from the storage vessel. However, the use and cleaning of the filters proved inconvenient. We therefore began to use pure 83% electric furnace phosphoric acid (= 60% P_2O_5) and experienced no difficulties in feed or blockages.

3. Degree of neutralisation

The planned degree of neutralisation is expressed as the ratio of ammonia to phosphoric acid designated by $\text{NH}_3:\text{H}_3\text{PO}_4$. A value of 1.0 corresponds to monoammonium phosphate (MAP grade) and a value of 2.0

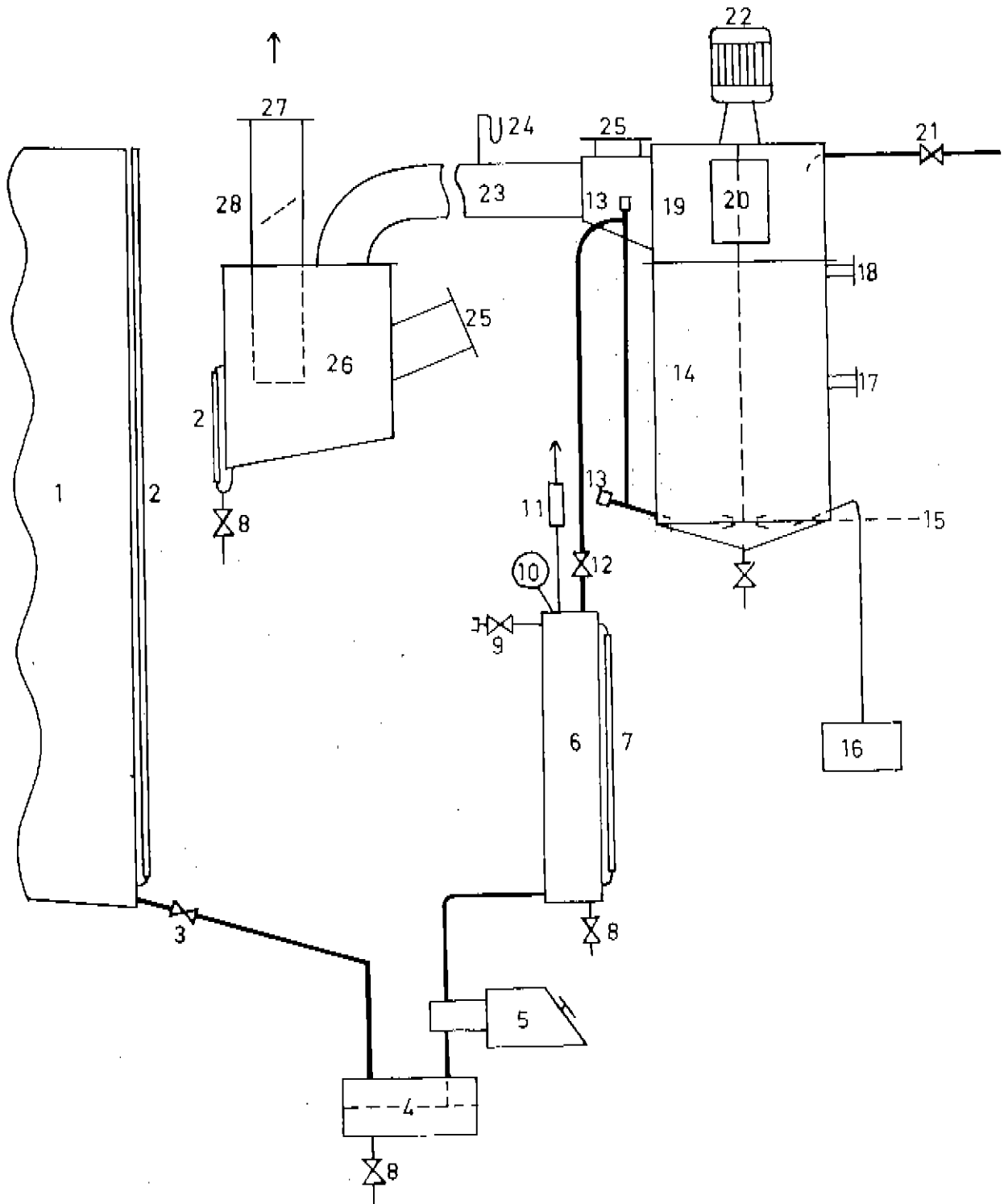
to diammonium phosphate (DAF grade). We employ also the following

$\text{NH}_3:\text{H}_3\text{PO}_4$ planned = planned mole ratio
 " consumed = mole ratio calculated from raw material consumption
 " analysed = mole ratio in product according to analysis.

III Equipment:

- A schematic drawing of the pre-reactor is shown in Fig. 1. The various parts of the equipment are numbered 1 - 28.
1. Raw material tanks.
 2. Glass gauges for measurement of liquid volumes.
 3. Bottom valves of raw material tanks.
 4. Constant-level vessels for raw materials. The suction heights of the feed pumps are kept constant by floats and ball valves in these vessels.
 5. Feed pumps, model Lewa HL1. The pump for nitrogen solution delivers 0 - 185 l/h, the other pumps 0 - 136 l/h.
 6. Counter-pressure vessels for raw materials. The air layer remaining in the upper part of vessels on compression gives the counter pressure required by the feed pump and eliminates surges due to the reciprocating movement of the pump cylinder. The dimension of the vessels are:- diameter 160 mm, and height 1400 mm.
 7. Glass gauges of counter-pressure vessels for following changes in the height of the air layer.
 8. Discharge valves.
 9. Valves for introducing compressed air to replace the air layers during a run.
 10. Manometers for measuring counter pressures.
 11. Safety valves.
 12. Needle valves for producing and regulating the counter pressure.
 13. Screw caps fitted with handles for entry to feed pipes for cleaning.

FIGURE 1: SCHEMATIC EQUIPMENT ARRANGEMENT FOR PRENEUTRALISATION PROCESS.



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14. Pre-reactor. Dimensions:
 Wall thickness 4 mm,
 Inside diameter 375 mm,
 Cross-sectional area of cylindrical part (evaporating surface 11 dm²),
 Height of cylindrical part 625 mm,
 Height of conical bottom 100 mm.
15. Feed plane where the conical bottom meets the cylindrical part. In this plane are located a two-bladed propellor, the ends of raw material feed pipes ($\frac{1}{4}$ ") that pass through the walls of the cylindrical part, and tube pocket for a thermocouple.
16. Temperature meter.
17. One-inch discharge tube through which pre-solution overflows from the pre-reactor. The discharge tube limits the volume of liquid of the pre-reactor to 43.5 l. (31.7 l. when the mixer is rotated).
18. Reserve discharge tube (1"). When the preceding discharge tube (17) becomes occluded, the reactor content may flow through this tube into the mixer or the drain.
19. Cover of pre-reactor, height 335 mm.
20. Covered inspection opening.
21. Valve for rinsing water.
22. Mixer equipped with two-bladed propellor, model Bauknecht eDCF x 1 $\frac{1}{2}$, 2870 r.p.m., 2.2kW.
23. Tube connecting pre-reactor to condensate collector, diameter 184 mm and length approx. 2.5 m. There are openings in the middle of the tube for removing gases for analysis.
24. Manometer, a U-shaped tube.
25. Capped openings for introducing additional air.
26. Vessel for collecting condensate.
27. Connection to washing tower.
28. Adjustable damper.

The pre-reactor and other equipment were made of stainless steel, AISI 316. The material was tested in the form of electrodes (1 x 20 x 50 mm) for corrosion in phosphoric acid.

The test electrodes were immersed in 55, 70 and 85% phosphoric acid (40, 50 and 61% P_2O_5) solutions at 20, 50 and 100°C for 28 days. The first two phosphoric acids were wet process acids. The 85% acid was electric furnace acid. The weight losses in the following table are given in $g/cm^2/year$ and corroded layer thicknesses in $mm/year$.

Temperature, °C	Phosphoric acid		
	55% H_3PO_4	70% H_3PO_4	85% H_3PO_4
20	Corrosion negligible	Corrosion negligible	Corrosion negligible
50	4.5 $mg/cm^2/yr.$ 0.005 $mm/yr.$	4.8 $mg/cm^2/yr.$ 0.005 $mm/yr.$	1.7 $mg/cm^2/yr.$ 0.002 $mm/yr.$
100	188 $mg/cm^2/yr.$ 0.24 $mm/yr.$	362 $mg/cm^2/yr.$ 0.45 $mm/yr.$	189 $mg/cm^2/yr.$ 0.24 $mm/yr.$

IV Experimental

The operation of the pre-reactor was the same as in our previous study. It comprised three stages; preliminary stage, initial or heating stage and the actual run.

The preliminary stage comprised:

- Ammoniation, when necessary of the nitrogen solution to obtain the winter solution, analysis of the solution and specific gravity determination.

- Programmed dilution of phosphoric acid; concentration and specific gravity determinations.

- Adjustment of feed pumps according to plan.

- Addition of water (10 l) to pre-reactor to cover the ends of the feed tubes and the mixing propellor.

In the initial or heating stage

- The preparation of the pre-solution was begun according to plan.

- The raw material feed and the composition of the pre-solution were adjusted and the initial water was removed.

- The temperature was adjusted.

This stage lasted 50 - 70 minutes and was considered to have ended when the temperature of the pre-solution remained constant.

The actual run:

- When the actual run began, the liquid levels in the tanks were checked and the pre-solution was led through the pipelines to tared vessels for weighing.

- The programmed factors were maintained even at the preselected levels by carrying out analyses at half-hour intervals. The rate of addition of the nitrogen solution was held constant (60 l/h) during the run and the phosphoric acid feed was varied as required.

- The actual run lasted 300 minutes. The raw material consumption was measured and the product was weighed after the experimental run.

The aims of the experiment were

- to neutralise the free ammonia in the nitrogen solution to obtain different ratios of ammonia to phosphoric acid as planned. The planned ratios are given by black triangles in Fig. 2,

- to determine the composition of the pre-solutions produced and the nitrogen losses,

- to study the behaviour of the pre-solutions in a simple granulation process: granulation, drying and cooling.

The conditions during the experiments are presented graphically in Figs. 2 and 3 where data points are joined by straight lines. Each data point represents the mean result in 4 separate experiments. Fig. 2 shows, in addition to the planned levels (abscissal), curves from which the attained mole ratios relative to raw material consumption or to product analyses can be read. The two curves run close together in the MAP range but deviate more and more from each other as the DAP stage is approached owing to nitrogen losses.

The curves in figure 3 plot, per ton of pre-solution, the required weights of raw materials, recovery efficiency, the water added with the raw materials (phosphoric acid and nitrogen solution) to the pre-reactor and the temperature of the pre-solution.

The compositions of the pre-solutions corresponding to the different mole ratios are shown in Fig. 4. The abbreviation AP-N denotes the nitrogen bound as ammonium phosphate. The irregularities in the curve plotting water

FIGURE 2: MOLE RATIO OF AMMONIA AND PHOSPHORIC ACID.

--- = Calculated from raw materials added.
— = Calculated from product analyses.

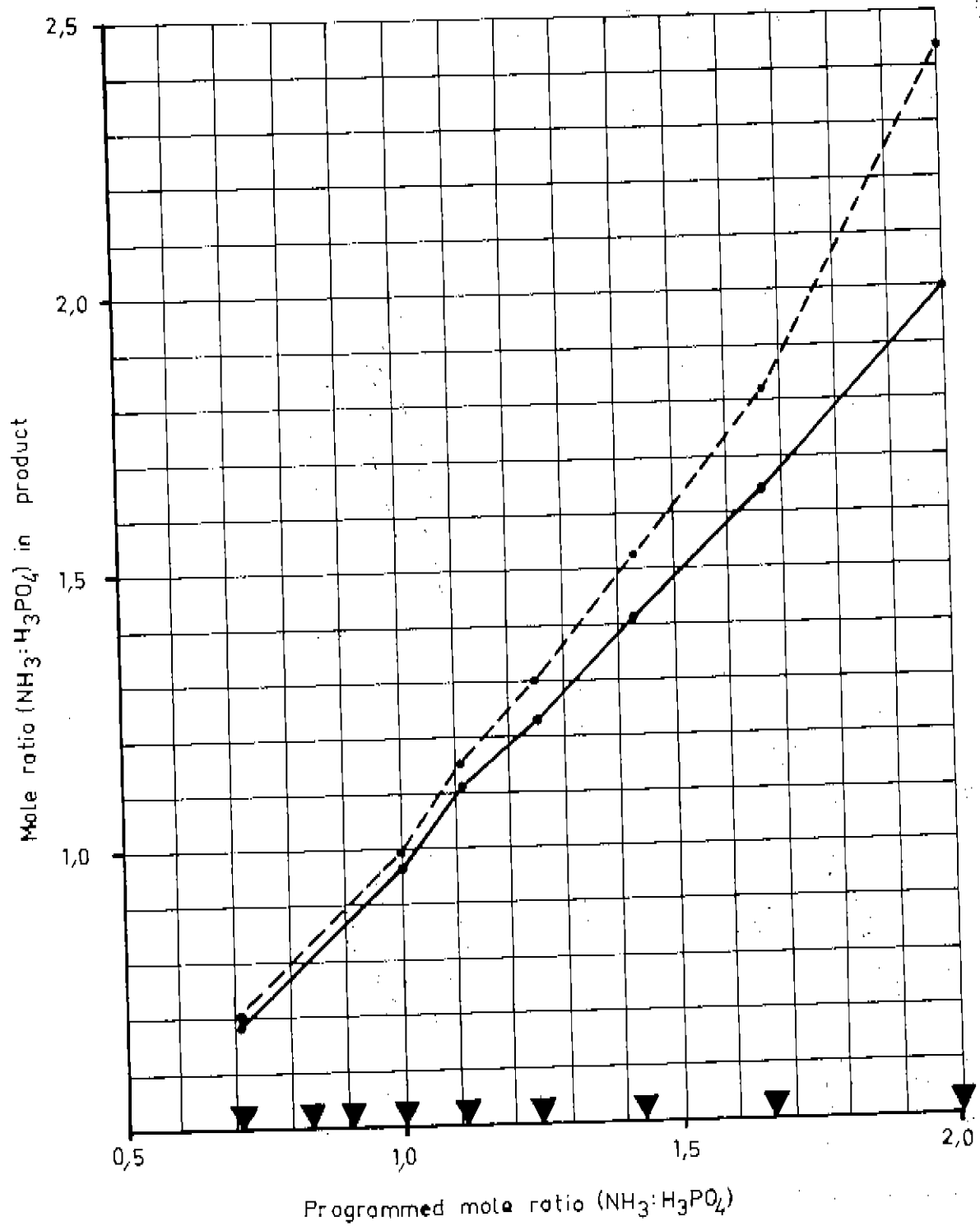
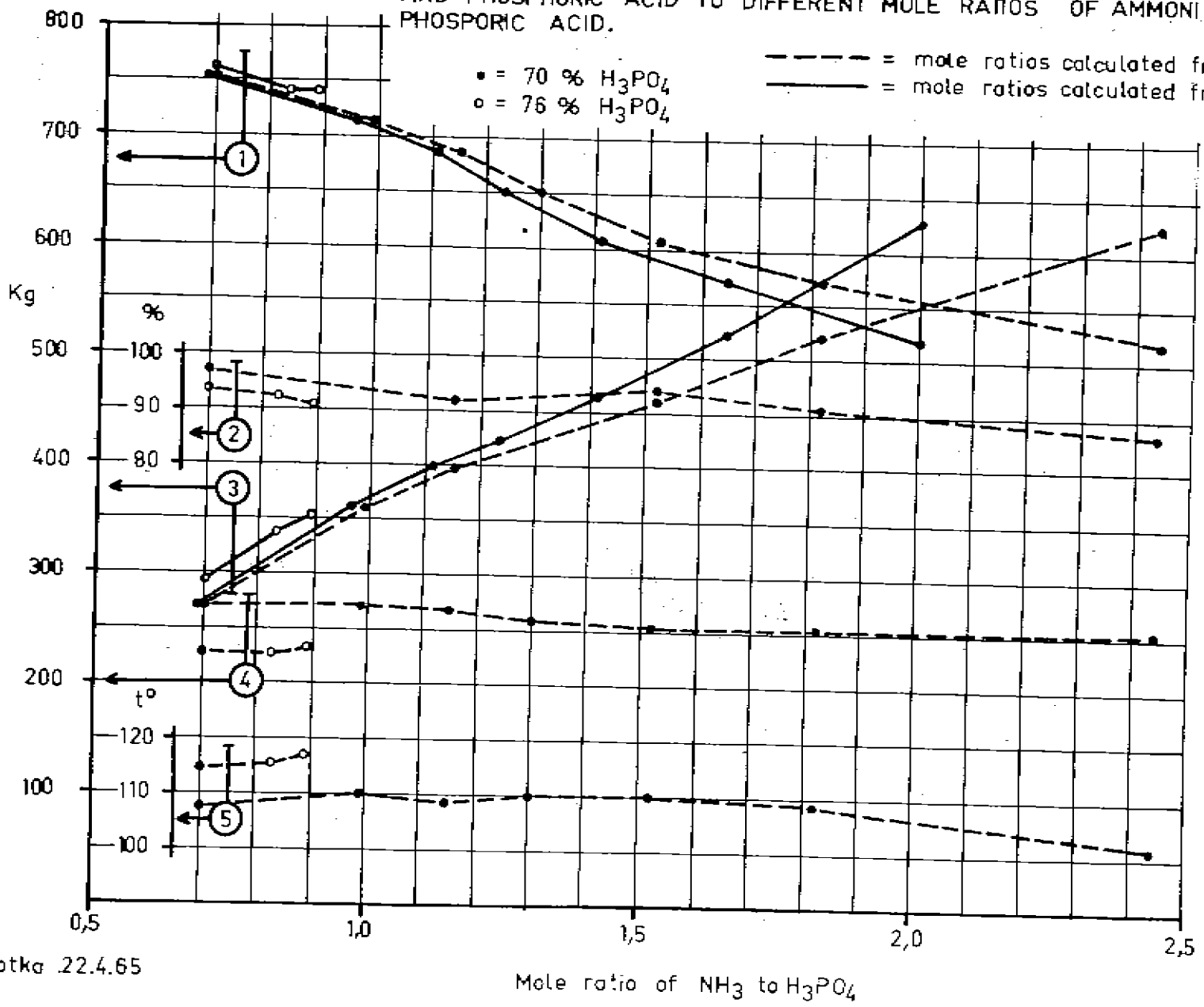


FIGURE 3. PREPARATION OF ONE TON OF PRE-SOLUTION FROM NITROGEN SOLUTION AND PHOSPHORIC ACID TO DIFFERENT MOLE RATIOS OF AMMONIA AND PHOSPHORIC ACID.



- Declarations:
- ① = Phosphoric acid required.
 - ② = Recovery efficiency.
 - ③ = Nitrogen solution required.
 - ④ = Water in phosphoric acid and nitrogen solution.
 - ⑤ = Temperature of pre-solution (°C).

IX
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FIGURE 4: COMPOSITION OF PRE SOLUTIONS.

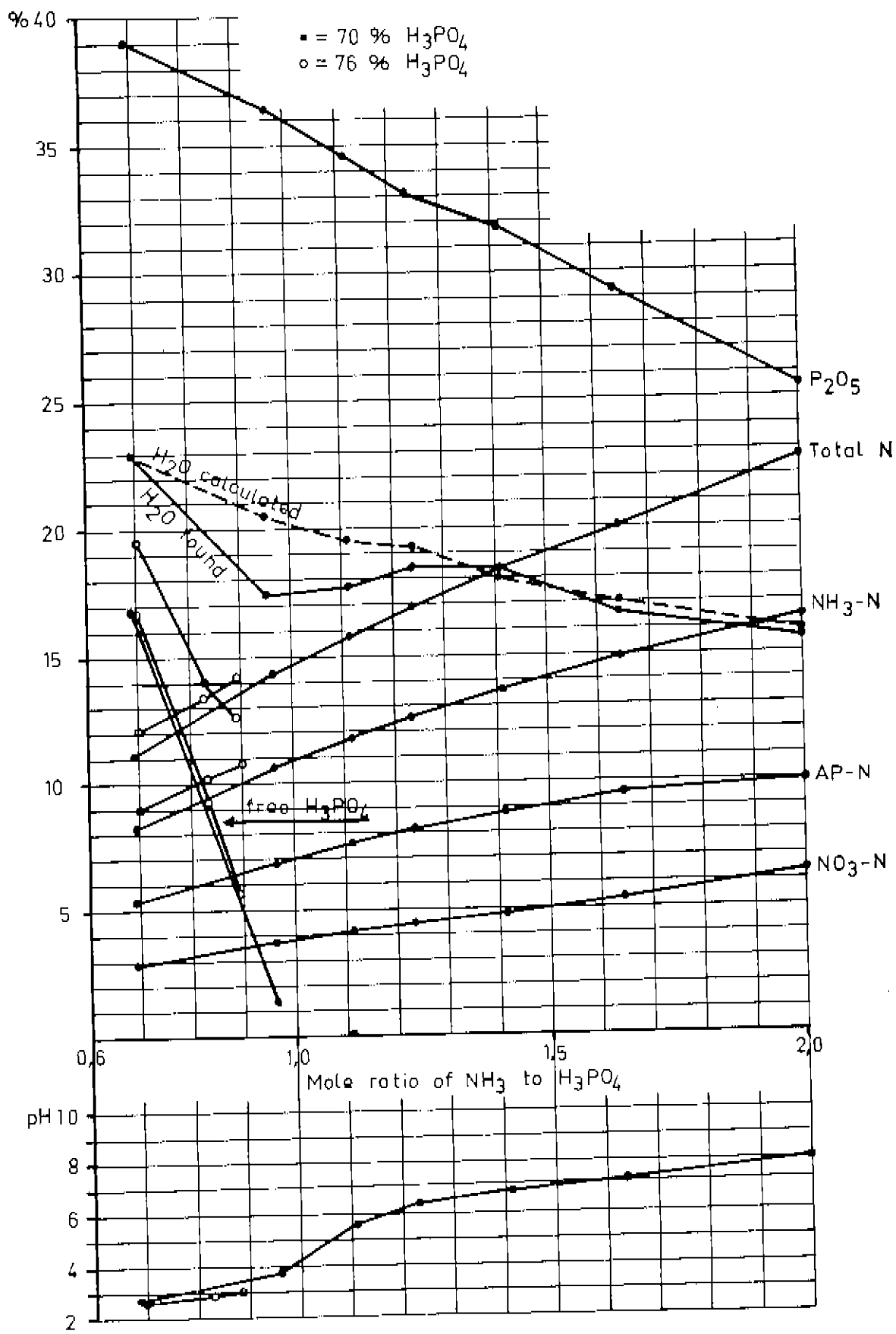
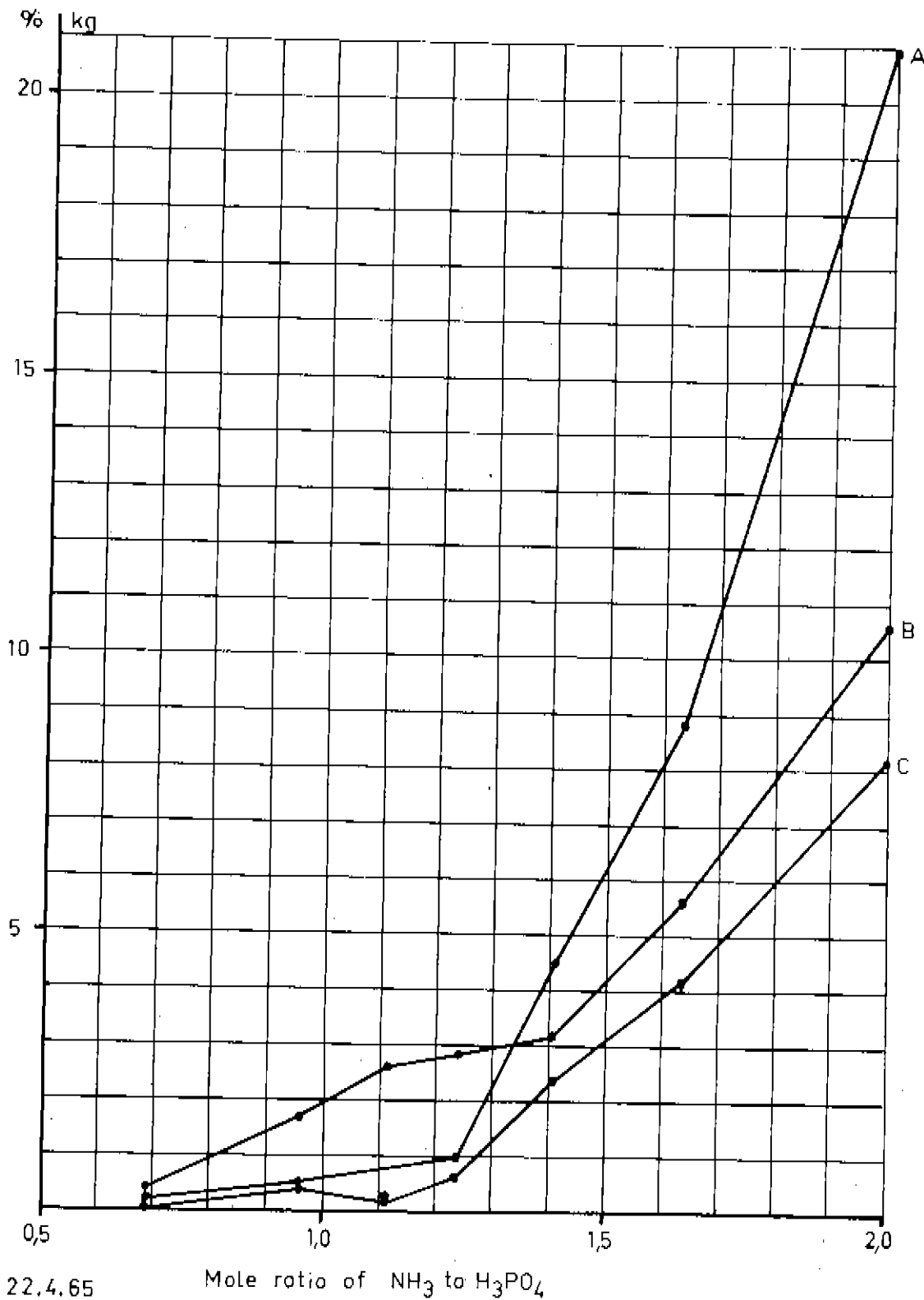


FIGURE 5: TOTAL NITROGEN LOSSES.

- A = Nitrogen loss in kilograms per ton of nitrogen solution according to gas analysis.
 B = Nitrogen loss as percentage of added nitrogen according to material balance.
 C = Nitrogen loss as percentage of added nitrogen according to gas analysis.



content (analyzed water minus calculated water) in the MAP range are due to the insufficient homogeneity of the samples taken for Karl Fischer water determinations. The pH values given in the lower part of the figure were measured on samples obtained by mixing one volume of the pre-solution and 100 volumes of water. The specific gravity of the pre-solution varied within the range 1.43 - 1.47.

The curves in Fig. 5 plot the total nitrogen losses. Curve A gives the total nitrogen losses per ton of pre-solution as calculated from analytical data for the gases emerging from the pre-reactor. Curve B plots the total nitrogen losses computed from the weights and the analyzed total nitrogen contents of the nitrogen solution and the resulting pre-solution: it plots the final nitrogen content as a percentage of the nitrogen added to the reactor. Curve C plots the ratio of the weight given by Curve A to the weight of added nitrogen.

The total nitrogen losses included 86 percent ammonia nitrogen and 14 percent nitrate nitrogen.

No losses of phosphorus pentoxide were observed in material balance calculations. Traces of phosphorus pentoxide were detected in the gas analyses.

V The Use of the Pre-Solutions in Fertilizer Manufacture.

To illustrate the use of the pre-solutions in fertilizer manufacture, we present three examples of the preparation of NPK fertilizers of different types for about 500 kg of product on a pilot plant scale. The following procedure was followed. To facilitate the dosage of the pre-solution the fertilizers were manufactured in single batches at one time. Excess water in the pre-solution was eliminated by circulating the recycle. The mixing and granulation were done in the same unit (an Eirich mixer or a drum). The product was sieved after drying and cooling; and the fines and, after grinding, the oversize, were returned to the process.

Example 1. Manufacture of grade 13 - 26 - 19.5 (nutrient ratio 1:2:1½).

Raw Materials

- Pre-solution, prepared from nitrogen solution and phosphoric acid to give a mole ratio of ammonia to phosphoric acid of 1.25. The following is the approximate composition of the solution:

Water	18.5%
Total nitrogen	17.0%

Ammonia nitrogen	12.5%
P ₂ O ₅ content	33.0%
Free phosphoric acid	0.0%
Ratio N:P ₂ O ₅	1:1.94%

- 60% Potassium chloride.

When these raw materials are mixed in the appropriate weight ratio of 70:30, a 13.5 - 26.5 - 20.5 fertilizer with a water content of 0.5 per cent results when the appropriate amount of recycle of suitable composition required to start the process is prepared beforehand.

The starting recycle material available to us had the composition 12.4 - 25.5 - 18.6 and a water content of 0.5 per cent. Its use in the experiment decreased the grade from 13.5 - 26.5 - 20.5 to 13 - 26 - 19.5, but this change had no effect on the granulation process.

The composition of the product was:

	Calculated	Found
Moisture	0.7%	0.7%
Total nitrogen	12.9%	13.1%
Ammonia nitrogen	9.6%	9.6%
P ₂ O ₅	25.9%	26.0%
K ₂ O	19.5%	19.6%

The product contained 53% recycle. After it had passed through the cooling drum, the granulate had the following particle size distribution:

+ 6 mm over size	39.0%
-6+1 mm product	49.0%
-1 mm fines	12.0%

Granulation was very successful and was easily controlled. It was carried out in an Eirich-mixer.

Example 2. Manufacture of grade 16:21:16 (nutrient ratio 1:1.3:1).

Raw materials

- Pre-solution as in the preceding example.
- Ammonium sulphate nitrate, a commercial grade containing 26% N.

- 60% potassium chloride.

Formula:

Raw material		Water + Nutrients, kg			
		H ₂ O	N	P ₂ O ₅	K ₂ O
Pre-solution	570	105	97	188	-
Ammonium sulphate-nitrate	186	2	48	-	-
Potassium chloride	244		-	-	146
Total	1000	107	145	188	146
Water removed on drying	107	Percentage			
Yield of dry product	893	0	16.2	21.1	16.3
Ratio N:P ₂ O ₅			1.0 : 1.3		
Content at 0.5% H ₂ O		0.5	16.1	21.1	16.2

The recycle was expressly prepared for the experiment. In order to determine the nitrogen losses in the drying drum, analyses were carried out before and after the drying. Samples were taken every fifteen minutes.

The following analytical data were obtained:

A = analytical data before drying,

B = preceding data recalculated to moisture content of dried product.

C = analytical data for dried product,

D = formula percentages (for dry product) recalculated to final moisture content of product.

	A	B	C	D
Moisture	5.1	0.9	0.9	0.9
Total nitrogen	15.5	16.2	15.8	16.1
P ₂ O ₅	19.7	20.6	20.9	20.9
K ₂ O	15.4	16.1	16.4	16.2

According to the data in columns B and C total nitrogen, 158 kg/ton of fertilizer, is 97.5% of the calculated nitrogen, 162 kg/ton of fertilizer, and hence the nitrogen loss was 2.5%. The product contained 46% recycle. The particle size distribution in the granulate

after cooling was:

+6 mm over size	30%
-6+1 mm product	60%
-1 mm fines	10%

The granulation was done in an Eirich mixer.

Example 3. Manufacture of grade 16 - 16 - 16.

This experiment differed from the preceding one in that ammonium sulphate nitrate solution was prepared from nitrogen solution and sulphuric acid, and pre-solution (ammonium phosphate solution) from ammonia and phosphoric acid simultaneously in the same pre-reactor.

One ton of the resulting pre-solution contained:

- 296 kg nitrogen solution, containing 21.5% free ammonia and 39.7% total nitrogen.

- 267 kg 70.5% sulphuric acid.

- 72 kg ammonia,

- 505 kg 45.8% phosphoric acid (= 33.2% P_2O_5).

1140 kg

The recovery efficiency was hence 87.7%.

The reactor temperature was $107^{\circ}C$ and the mean total nitrogen loss 4.4%.

Analysis of the mixed pre-solutions gave:

- Moisture	28.2%
- Total nitrogen	16.5%
- P_2O_5	16.5%
- Free sulphuric acid	0%
- pH	6.8%

These mixed pre-solutions and potassium chloride were mixed in the ratio of 78:22 to obtain a granulated fertilizer 16 - 16 - 16 with a moisture content of 1.8%.

Composition of granulated product:

	Calculated	Found
- Moisture	1.8%	1.8%
- Total nitrogen	16.3%	16.2%
- P ₂ O ₅	16.3%	16.1%
- K ₂ O	16.3%	16.2%
- SO ₃		15.4%

The starting recycle was a mixture of ammonium sulphate nitrate, diammonium phosphate and potassium chloride. The amount of actual recycle in the product was 65%. The granulation was carried out in a drum.

Summary

- The pre-reactor initially installed for the neutralisation of nitrogen solution with sulphuric acid proved to be very suitable also for the neutralisation of nitrogen solution with phosphoric acid.

- In order to control the operation of the pre-reactor according to a planned programme it is of prime importance to have reliable feed pumps. This is especially important when several components are to be fed into the reactor at one time.

- The preparation of the pre-solution, its discharge from the reactor and the dosage was easily carried out if the water content of the pre-solution exceeded 15%. If it fell below 14%, it proved difficult to avoid blockage of the pipeline leading from the reactor to the next stage. It was for this reason that we had to give up the 76 per cent phosphoric acid (= 55% P₂O₅) and use 70 per cent phosphoric acid (= 50% P₂O₅) instead. Another solution would naturally have been to increase the added volume of water.

- When ammonia gas is introduced into the reactor, the end of the feed pipe is very easily blocked, but by using two pipelines, one of which is in use while the other is being cleaned, the gas flow can be kept constant.

- The nitrogen losses in our pilot reactor, determined by different methods, deviate most from each other at mole ratios of ammonia to phosphoric acid in the range 0.9 - 1.4, but even in the worst case they were not greater than 3 per cent. When the mole ratio exceeds 1.4, it is advisable to recover the nitrogen (in a scrubber). A slightly higher ratio may be possible if the dimensions of the reactor are changed.

- The pre-solution prepared from nitrogen solution and phosphoric acid to a mole ratio in the range 0.9 - 1.4 can be used as a nitrogen and phosphorus source for fertilizers in which the weight ratio of nitrogen to phosphorus pentoxide is 1:3.5 - 1:1.20. Such fertilizers are a low-nitrogen fertilizer

(N:P₂O₅:K₂O = 1:2.5:2.5), a chloride free fertilizer (1:2.7:3) and a boron-containing fertilizer (1:2.2:2).

- The pre-solution with a mole ratio of ammonia to phosphoric acid of 1.25, to which 33 per cent of ammonium sulphate nitrate is added, represents the fertilizer with the ratio 1:1.3 of nitrogen to phosphorus pentoxide which is most commonly used in our country (fertilizer example 2). It may also be used to increase the grade of our present low-nitrogen fertilizers based on superphosphate. The ammonium sulphate nitrate can, of course, be replaced by a pre-solution prepared from nitrogen solution and sulphuric acid, which we call a montan solution.

- The relatively simple pre-reactor unit can be used to produce fully soluble high grade fertilizers and to increase the grade and solubility of our low-grade fertilizers based on superphosphate and its ammoniation.

DISCUSSION

Dr. T. K. VAHERVUORI (Rikkihappo Oy, Finland) : Fertiliser consumption in Finland in recent years has exceeded all forecasts and has posed many urgent and difficult problems for fertiliser manufacturers. This increase has almost entirely centred on compound fertilisers. The production of mixed fertilisers by Rikkihappo in 1964 was over 36% higher than in 1963. This has led to the rapid and extensive erection of new processing units by our fertiliser industry. As a result of new process developments and of the new production units, the variety of our multi-nutrient fertilisers will change, and the share of complex fertilisers and average nutrient contents will increase. Since our earlier processes mainly involved only mixing operations, the change will naturally bring forth many new problems requiring investigation when we modify our processes to serve domestic needs, utilising locally available raw materials.

At the ISMA Technical Conference in Helsinki in 1963, we presented the results of a study of the neutralisation of nitrogen solution with sulphuric acid. On the basis of these results, we have erected full scale reactors, the operation of which has fulfilled our expectations. We also stated that we would extend our studies to other acids. The paper now before you is hence the second part of our investigations, following the first part presented to you in Helsinki.

The choice of phosphoric acid after sulphuric acid for our continued studies is closely associated with the present expansion of our company. The new fertilisers which we shall manufacture will at first be based on ammonium phosphate. By using nitrogen solution, our production can be diversified, and it will be possible to vary the ratio of ammonia and nitrate nitrogen contents, as well as the grade in general. Because the pilot plant and the full scale pre-neutralisers which we erected for nitrogen solution and sulphuric acid have functioned entirely satisfactorily, it was natural to extend our studies to their suitability for phosphoric acid. These studies have given us valuable experience in the operation of this type of reactor and have clarified the special requirements associated with the use of phosphoric acid and the manufacture of fertilisers from this type of neutralised slurry.

Mr. R. ARDOUIN (Union Francaise d'Engrais, France) : The paper by Dr. Vahervuori and Mr. Virtanen is a sequel to that presented at Helsinki two years ago, relating to the use of sulphuric acid. The results now reported with the use of phosphoric acid are most interesting. The authors are to be congratulated on the competence and fulness of detail with which they have presented to us a serious work, beset with problems which certain of us know well in practice. I say certain of us, for many companies have studied ammoniation, but from different aspects, as anhydrous ammonia in either gaseous or liquid form gradually became used in larger quantities in the fertiliser industry. Progress achieved so far is considerable; but

research continues and other methods are being evolved and will gain acceptance.

In our industry, we started with the incorporation of nitrogenous and potassic salts mixed with superphosphates in a granulating drum, into which water was sprayed. Then very acid superphosphate was ammoniated by the formation of the ammonium salts corresponding to the acids used, following the injection of ammonia into the mass. The difficulties encountered are well known: scaling of the drum, necessitating a method of cleaning it, and N and P_2O_5 losses in the flue, mostly as the result of a deliberately fairly strong current of air entraining dust and gases from the raw materials. However, these difficulties have been partially overcome.

At the same time, a new direction has been taken with processes involving the reaction of phosphate rock with nitric acid which, as far as NP fertilisers in Europe are concerned, account for the majority of the production and constitute a most rational solution.

Then came the direct use of fertiliser materials. For example, ammonium nitrate solution and ammonium phosphate slurry, prepared in advance, have been used for the manufacture of ternary fertilisers, the incorporated solid salt having most often been potassium chloride, using a fairly high coefficient of fines recirculation.

But in general, the water must always be evaporated at some stage. If solutions are used instead of crystalline salts, the water is eliminated in the dryer instead of removing it by concentrating the solution to obtain the crystalline salt. Thus the heat balance may well be just as good in both cases, and it is important to know what it is before choosing the granulation apparatus.

The heat balance is particularly favourable if heats of reaction are used for the partial or total evaporation of the water.

The paper presented by Mr. Baynham to this conference offers still another innovation, since ammonium phosphate and ammonium nitrate are manufactured "in situ", separately, during granulation.

The paper by Messrs. Vahervuori and Virtanen must, I think, be understood from the point of view of the Finnish economy, which seeks above all to use its own national nitrogenous raw materials in order to avoid massive imports of other nitrogenous materials, the cost of which would be higher. But having said this, since the aim of the study is the production of high analysis ternary fertilisers, is this in fact the best method from the technical and economic standpoint?

The nitrogen solutions which are used, called Barrett Liquor in France and Nitrona and Urana solutions in the U.S.A., contain a certain amount of water which is additional to that contained in the phosphoric acid.

In considering the apparatus described by the authors for the

neutralisation of phosphoric acid, as shown in figure 1, I have the following comments:

Firstly, the control of temperature in the pre-reactor is of prime importance. To avoid nitrogen losses, the apparatus must be simple, efficient and quick acting. If difficulty in controlling temperature is encountered around the 107°C level shown in the graph of figure 3, these losses may be high if action is delayed. Now, according to your paper, 50 to 70' are required to achieve a constant temperature in a pilot plant. How would you obtain it on an industrial scale?

Instead of the pre-reactor which you use, one can use a saturator - a simple apparatus which overcomes the difficulties mentioned above. In a saturator, the increase of the reaction temperature is overcome by means of a circulation of water, cooling the slurry as it forms.

The pipeline blockages which you mention do not occur if one takes care to have the ammonia pipeline arriving internally to the bottom of the saturator, with the phosphoric acid emerging a few centimetres from the surface of the liquid. In this way, these two feed-lines are constantly heated, and this avoids obstructions and permits the use of wet process phosphoric acid, which is cheaper than the thermal acid which you recommend.

In order to maintain the temperature of the ammoniated phosphoric slurry at around 70°C , which is a satisfactory temperature for good granulation in the presence of superphosphate, and for which the vapour pressure of ammonia remains low up to a ratio of $\text{NH}_3:\text{P}_2\text{O}_5$ of 1.75, the rise in temperature is controlled by means of water circulation. This is achieved in Inco spirals placed within the saturator, the flow of cooling water being controlled in accordance with the temperature of the slurry. A pH of 7.3, corresponding to the ratio of 1.75 mentioned above, can be achieved without risk of nitrogen losses.

According to the graph in your paper, these losses, with your process, seem fairly substantial above a ratio of 1.5. At 1.25, you already have a loss of 2.5%, and in example No. 3, for the manufacture of a 16-16-16 fertiliser, you use ammonia and not Barrett liquor to neutralise the phosphoric acid. In this case, the $\text{NH}_3:\text{P}_2\text{O}_5$ ratio is 1.825 and losses have seriously increased. The reason for these losses is that the saturation is made at too high a temperature. On the one hand, you mention a rate of recovery of 87.7%, and on the other, nitrogen losses of 4.4%. How do you reconcile these two figures?

Perhaps in your installation it would be worthwhile operating in two stages, i.e. in a first stage up to a ratio of 1.25 with a pH of 6.5, in which case the vapour pressure of the ammonia is acceptable and there is no entrainment of ammonia in the effluent gases; and then in a second stage, for other fertiliser formulations, you could proceed above the 1.25 ratio by cooling the slurries or by operating a pre-saturation up to a ratio of 1.5 in a boiler saturator

fitted with a recovery scrubber. Saturation would be terminated by ammonia injection into the granulator. This is the TVA system, which works very well for the industrial manufacture of di-ammonium phosphate. These slurries of various compositions would then serve for the preparation of NPK ternary formulations.

I must admit that cooling is a costly solution, since the calories given off by the saturator are evacuated as a pure loss, whilst they could contribute to the evaporation of water - unless, which is sometimes the case, this hot water is used in the factory.

With regard to the incorporation of nitrate nitrogen in the formulations, some firms use an 83% or even stronger solution of ammonium nitrate simultaneously with the ammoniated phosphoric slurries.

The flow of ammonium nitrate solution is measured by means of a magnetic flow meter which we have used and which has worked perfectly after a fairly rapid adjustment.

I do not think the authors envisage the simultaneous pre-neutralisation of sulphuric and phosphoric acids by Barrett liquor in the same apparatus, for the mixture of these two acids, particularly when hot, is very violent, and corrosion of the construction material would certainly occur, unless your trials have caused you to study this particular case?

Thus the manufacture of ammoniated phosphoric slurries is an economic proposition if one seeks to eliminate nitrogen losses as far as possible and providing one aims to make only well defined types of slurries for the production of high analysis ternary fertilisers.

In work currently undertaken by various companies, two trends emerge: some prefer to obtain a preliminary production of crystalline salts which are then mixed together and agglomerated (as described by Mr. NILSSON in his interesting paper), and some use liquids.

In the first case, crystallisation is a fairly costly operation, and feeding in salts is less accurate than with liquids or slurries. In the second case, one is dealing with a whole range of more or less good efficiencies which are cumulative and which finally make operations equally costly.

I shall not conclude with any further description of the advantages and disadvantages of these two trends, because each case is conditioned by its own commercial and economic priorities. But the most logical solution would be that which profited from the various heats of reaction to obtain a very dry product which could be bagged immediately after production. From the investment point of view, the installation which would give most satisfaction would be that comprising a simplified apparatus without a drier, cooler or de-dusting section, which are sources of trouble. Moreover, storage capacities could be reduced to the strict minimum, as well as the size of buildings. Certain companies are already studying this problem.

However, we think that for formulations of average concentration the classical granulation plants developed for superphosphate will probably remain economic.

Dr. VAHERVUORI : Thank you, Mr. Ardouin, for your interesting and constructive contribution. You asked whether there is any difference between the start-up time of 50-70 mins. for the pilot plant and that for the full scale plant. We have not yet used phosphoric acid in this way on an industrial scale, and so we do not have any exact figures. But if we take the pilot plant trials and the full scale production based on sulphuric acid and nitrogen solution as indicative, it seems reasonable to think that the start-up time using phosphoric acid will be about the same with the full scale plant as in the pilot plant trials.

You refer to our stated recovery rate of 87.7% compared with a figure of 4.4% for nitrogen loss, and you ask how we reconcile these figures. The figure of 87.7% relates to the yield of nitrogen solution, whilst the 4.4% relates to the nitrogen loss in the drier.

You asked whether we have used sulphuric and phosphoric acid simultaneously in our pre-neutraliser. We have done this, and there is, of course, a corrosion problem. We used AISI 316 stainless steel, and we found afterwards that the AISI 317 quality, with a slightly higher molybdenum content, gave better results.

Mr. H.S. SCHOEMAN (Fisons (Pty) Ltd., South Africa) : The author mentions on page 17 that the ammonia inlet to the reactor is very easily blocked. We are now in the course of commissioning a small MAP plant in South Africa, and this was the first problem we encountered. After a few hours operation, our pipe was completely blocked. Unfortunately, we do not have enough room in our reactor to put in a second line, as suggested by the author; but I should like to ask him what is the design of his ammonia feed inlet into the reactor.

Dr. VAHERVUORI : We have just a straight open tube. At least for our pilot plant, this gives an adequate distribution of ammonia.
