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

MANUFACTURE OF HIGH-ANALYSIS COMPLEX FERTILISERS
THROUGH UREA-PHOSPHATE ROUTE
FROM WET-PROCESS PHOSPHORIC ACID

By :

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1. SUMMARY

Wet-process phosphoric acid-based fertilisers pose several technological problems when processed for making high analysis fertilisers. The usual concentration obtainable is 28:28:0 for solid N:P complexes. The authors have outlined a process to make urea-phosphate from wet-process acid which on subsequent processing by pyrolysis yields high analysis fertilisers surpassing 30:30:0 in composition. The pyrolysed product forms good N:P base solution for liquid fertiliser manufacture. The urea-phosphate route involving convenient operations and less specialised equipment is, according to the authors, the ideal process for the manufacture of high analysis fertilisers for developing countries.

2. INTRODUCTION

Among the fertiliser manufacturers all over the world, the accent has always been on producing increasingly concentrated fertilisers. This has been especially true during the last decade and a half. Our own country has been no exception to this general trend. Beginning from simple fertilisers containing a low percentage of single nutrients, about 20 years ago, India has now larger capacity plants producing complex fertilisers with as high an N:P ratio as 16:20, 20:20 and even 28:28. Due to various reasons, thermal phosphoric acid plants have not yet found their way into India, although a few are on the immediate future list. Only thermal acid can yield high analysis fertilisers with an N:P ratio more than 28:28, a ratio not exceeded in products from wet-process acid. But since almost all our requirements of chemical grade phosphates are met at present by imports, our first thermal acid may go only towards manufacture of these chemicals.

The main limitation in manufacturing fertilisers with an N:P ratio higher than 28:28 from wet-process phosphoric acid is the presence in it of about 3-4% of impurities, almost half of which is due to free sulphuric acid. These impurities assume higher proportions on removal of the 50-55% water content and thus decrease the percentage of the nutrients. Purification of the acid for subsequent treatment will naturally be highly uneconomical.

The Research and Development Division of Messrs. Fertilisers and Chemicals, Travancore Limited has worked out processes for manufacturing from wet-process phosphoric acid a high analysis complex solid fertiliser as well as liquid fertiliser.

This paper deals with the process details for the above mentioned products from wet-process phosphoric acid through the urea-phosphate route. These processes, worked out first in a bench-scale, have subsequently been put into operation on a pilot plant scale.

3. BENCH-SCALE WORK

When wet-process phosphoric acid is treated with a stoichiometric amount of urea, and the solution concentrated and cooled, urea phosphate crystals are thrown out of solution. These crystals can be easily separated from the mother-liquor by centrifugation and the product urea phosphate contains only less than 0.5% moisture.

Urea-phosphate has a molecular formula $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$, and is over 99.5% pure (on a dry basis) when prepared as above. The crystals are completely water-soluble and are constant in composition. They have an N:P ratio of 17:45, which is nearly the same as that in diammonium phosphate made from wet-process acid, namely, 18:46. Diammonium phosphate is highly hygroscopic, is unstable even at ordinary temperatures losing ammonia (especially in hot climates) and does not crystallise well. On the other hand urea phosphate is very stable, does not so readily take up moisture and can be crystallised to uniformly sized crystals of about 3-4 mm (see figure 1).

Although the existence of urea phosphate has been known for a very long time, and patents for its manufacture existed even as early as 1920 (U.S. Patents), its commercial manufacture has not yet been popularly attempted. This is probably because of insufficient information regarding its agronomic properties; and until such time as these data are available, urea phosphate may not become a popular direct fertiliser.

Our work has, however, shown a promising use for urea phosphate as an intermediary in the manufacture of high analysis fertilisers in which an N:P ratio of +30:+30, may be readily attained.

a) The technique

The possibility of making high analysis fertilisers from urea phosphate depends on the fact that the compound, though made from very impure wet-process phosphoric acid, is very pure and, apart from urea, contains 100% phosphoric acid.

Several possible complex fertilisers of different N:P ratios, but all over 28:28, are discussed below .

b) Simple blending

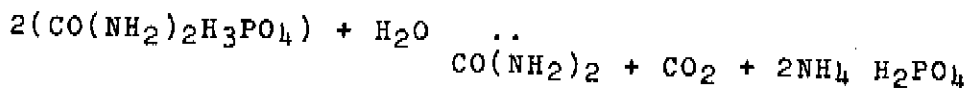
When urea-phosphate is mixed with 61.0% (of its weight) of urea and the mixture melted and cooled, the product has an N:P ratio 28.5:28.5. It can be granulated and the keeping qualities of this product are fair.

c) Simple ammoniation

Urea phosphate can absorb ammonia and, if a mixture of urea and urea phosphate is ammoniated, a uniform, completely water-soluble product is obtained. The N:P ratios can be made to suit requirements by adjusting the urea content. One such product made by blending 100 gms. of urea phosphate, and 42 gms. urea and ammoniating to a pH 3.5 analyses at 29.5:29.5:0. This product is really a purer variety of urea ammonium phosphate, the conventional one analysing at only 28:28:0. The reason for this higher analysis is the high purity of the ingredients.

d) Heating in presence of water

Urea-phosphate, in presence of water, hydrolyses to form solid monoammonium phosphate. This, on mixing with urea, can make different N:P grades. A product made by mixing 100 parts of urea phosphate wetted by 6 parts of water and just melted and hydrolysed and later blended with 57 parts of urea, analysed at 29.7:29.7:0. The hydrolysis, which has been quantitatively studied, follows the pattern given below :



In this, 2 molecules of urea-phosphate react with one of water and give one molecule carbon dioxide, one of urea and two of monoammonium phosphate.

e) Decomposition without water (pyrolysis)

Urea-phosphate, when heated slowly, melts to a clear liquid at 102° C, and when the temperature rises to 107-110°, it starts to decompose. Bubbles of carbon dioxide evolve and, eventually, the mass becomes pasty and white. At this stage it can be seen that the preliminary decomposition is completed i.e. one urea molecule, from two of urea phosphate, has decomposed, forming CO₂ and NH₃. The extra oxygen required by the CO of the urea for the formation of this CO₂ is taken up from the P₂O₈ of the urea phosphate molecules forming pyrophosphate. The action is represented by :



This means that a mass of 316 has lost 44 and becomes 272, containing 56 gms. N₂ and 142 gms. P₂O₅. Here, the N:P ratio is 20.6:52.2. When these are equalised by adding enough urea we can have an N:P ratio 30.6:30.6.

The keeping qualities of these fertiliser materials were studied in our laboratory, with special reference to the hygroscopicity of the samples. The temperature of the trials varied between 25° and 31° C during the tests and hygroscopicity was maintained at 100%. The samples were loosely spread on a petri-dish placed in desiccators and the desiccator bottom filled with distilled water. The gain in weight as percentage of the original product was recorded (see table 1).

Table 1

Percentage water absorption of vacuum dried fertiliser material

| | 1st day | 2nd day | 3rd day | 4th day | 5th day | 6th day | 15th day |
|----------------|---------|---------|---------|---------|---------|---------|----------|
| Urea | 1.3 | 2.5 | 2.7 | 2.9 | 3.4 | 4.1 | 4.2 |
| Urea phosphate | 0.8 | 0.9 | 1.2 | 1.5 | 1.8 | 2.2 | 2.4 |
| 28.5:28.5:0 | 0.9 | 1.2 | 1.3 | 1.6 | 2.0 | 2.4 | 2.5 |
| 29.5:29.5:0 | 0.8 | 1.1 | 1.3 | 1.6 | 1.9 | 2.3 | 2.5 |
| 29.7:29.7:0 | 0.9 | 1.1 | 1.4 | 1.6 | 2.0 | 2.4 | 2.6 |
| 30.6:30.6:0 | 0.8 | 0.9 | 1.3 | 1.6 | 1.9 | 2.3 | 2.5 |

The results obtained show that the processed urea-phosphate material has better keeping qualities than urea and urea phosphate.

It has been found possible, by a judicious combination of ammoniation and pyrolysis, to standardise conditons so as to yield a product with an N:P ratio 30+:30+:.

4. USES OF PYROLYSED UREA PHOSPHATE

Pyrolysed urea phosphate is essentially a good fertiliser both as a straight fertiliser and as blends with urea and other materials to form several grades. This aspect has been discussed elsewhere.

The vast potentiality of this fertiliser lies in the fact that it contains almost all phosphates in the non-ortho form. The other methods of production of ammonium polyphosphates are all cumbersome and the product contains a maximum of only 60-70% polyphosphate in the total P_2O_5 present. For this purpose, specialised process equipment and careful operation are essential, starting from polyphosphoric acid. Hence the manufacture of ammonium polyphosphates through the urea phosphate route is expected to be cheaper and highly feasible, especially in developing countries, where sophisticated equipment has to be imported for the presently available process.

We have successfully made liquid fertilisers from wet-process phosphoric acid and the mother liquor of urea phosphate by ammoniation of these materials, and simultaneously adding polyphosphate made from urea phosphate. The polyphosphate could be made into a solution and further ammoniated to get a base solution of N:P ratio 15:35. This base solution is found to possess good keeping qualities and sequestering characteristics.

5. PILOT PLANT PRODUCTION OF UREA PHOSPHATE

F A C T started production of urea phosphate by the end of 1969, on a pilot plant scale, starting from wet-process phosphoric acid and urea-prills. Laboratory trials earlier had revealed that wet-process phosphoric acid, direct from the dihydrate process plant, could be the starting acid. This avoided an acid concentration unit. The P_2O_5 concentration in the acid from the plant varied between 25 to 30% and averaged 28%. Since our urea production is scheduled only for the end of 1970, we depended upon prilled urea for the trials. As soon as the urea plant is commissioned, we hope to use the urea liquor in place of prills.

Table 2

Composition of material during the pyrolysis of urea phosphate

| | First sample | Second sample | Third sample |
|---|--------------|---------------|--------------|
| P ₂ O ₅ as (NH ₂) ₂ CO.H ₃ PO ₄ | 33.57% | 22.43% | nil |
| P ₂ O ₅ as NH ₄ .H ₂ PO ₄ | 0.95% | 1.08% | 1.17% |
| P ₂ O ₅ as (NH ₄) ₂ H ₂ P ₂ O ₇ | 11.14% | 18.50% | 28.68% |
| P ₂ O ₅ as NH ₄ .PO ₃ | 0.28% | 2.34% | 12.38% |
| Total P ₂ O ₅ | 45.94% | 47.35% | 52.23% |
| Percentage of total P ₂ O ₅ as polyphosphate | 27.22% | 44.02% | 97.80% |

Table 3

Solubility of urea-phosphate at various temperatures in water and alcohols

| TEMP °C | Water | | Methanol | | Ethanol | |
|------------|-----------------------|-------------------|-----------------------|-------------------|-----------------------|-------------------|
| | Gms/100gms sat. soln. | Sp.gr.of solution | Gms/100gms sat. soln. | Sp.gr.of solution | Gms/100gms sat. soln. | Sp.gr.of solution |
| 10 | 41.4 | 1.18 | 25.5 | 0.92 | 8.3 | 0.83 |
| 15 | 45.6 | 1.19 | 28.5 | 0.93 | 9.6 | 0.84 |
| 20 | 49.3 | 1.25 | 31.5 | 0.95 | 11.2 | 0.85 |
| 25 | 52.6 | 1.26 | 34.9 | 0.98 | 13.2 | 0.85 |
| 30 | 56.1 | 1.28 | 40.0 | 0.99 | 16.0 | 0.86 |
| 40 | 62.9 | 1.31 | 50.6 | 1.05 | 23.2 | 0.89 |
| 50 | 68.8 | 1.33 | 54.0 | 1.08 | 31.4 | 0.92 |
| 60 | 73.0 | 1.35 | .. | .. | .. | .. |
| 70 | 76.7 | 1.37 | .. | .. | .. | .. |
| 80 | 80.0 | 1.38 | .. | .. | .. | .. |

In the pilot plant, shown in the flow-diagram, the green acid is pumped into the reaction tank and a stoichiometric quantity of urea is added and agitated to effect complete dissolution. This solution is fed into the vacuum evaporator, where it is heated by steam coils. The evaporation takes place under vacuum. The liquor boils at a vacuum of 18-20" of mercury at a temperature of 75-80° C.

The solution is evaporated to attain a specific gravity between 1.4 and 1.45. The concentrated urea phosphate solution is pumped into the crystalliser, where urea phosphate crystallises, if necessary in presence of seeds. The crystals are separated by centrifuge. The mother liquor collected in storage is sent to the liquid fertiliser section.

The urea phosphate so produced is over 99.0% pure on a dry basis.

The consumption of utilities has been calculated from these pilot plant studies and found to be :

One tonne of product requires 1.55 tonnes of steam at 110 PSIG, 45 kWh electrical energy, and 11 kilo litres of cooling water.

6. PRODUCTION OF 30:30 BLEND

Trial production of 30.0:30.0 was carried out on a small scale in our pilot plant. The operations were carried out batch-wise to get 80 kg product at a time.

The essential parts of the equipment were a jacketed reaction-cum-homogeniser tank, S.S. 316 and an improvised flaker. The open reaction tank was fitted with an agitator of 20 rpm driven by a 0.25 HP motor.

55 kg of urea-phosphate crystals were charged into the reaction tank along with 32 kg of urea. It was not necessary to add the entire urea at this stage, but only part of it, since the presence of urea reduced the melting point and decomposition temperature of urea phosphate. The addition of the required urea initially increased the load on the stirrer, heat requirement and vessel capacity. Hence only one third the quantity was added at first. At this stage the reaction tank was heated by opening steam into the jacket of the reaction tank and, as soon the urea phosphate melted and the agitator shaft was free moving, the agitator was started and the temperature was maintained below 110° C by adjusting the steam. The carbon dioxide escaped (at this stage) with frothing. A careful control of steam can control the frothing but we found it was safe to use surfactants. Several surfactants have been found suitable for suppressing the foam.

As soon as the evolution of gas ceased, the remaining urea was also added and the entire melt became homogeneous. This melt was discharged onto a flaker from where the product was bagged. It has also been found that oil prilling of the melt gives a uniform, granular product of excellent keeping qualities.

The product, analysing at 30.6:30.6:0, weighed 80 kg a batch and was totally soluble in water, giving a clear solution.

7. UTILISATION OF MOTHER LIQUOR

The mother liquor from the urea-phosphate plant is rich in sulphate and metallic ions and is dark green in colour. The effective utilisation of this liquor is highly essential for successful operation of this urea-phosphate plant. In The Fertilisers and Chemicals, Travancore Limited, we carried out the urea-phosphate trials drawing green acid from the Ammonium Phosphate Sulphate Plant where 16:20:0 and 20:20:0 grade ammophos granules are being made. One method of utilising the mother liquor from urea-phosphate plant was to re-cycle back to the ammophos plant where it joins the process streams in the neutralisation tank. A re-cycle ratio as high as 25 per cent P_2O_5 from mother liquor has not been affecting the product ammophos.

Another method of utilisation of this liquor is in the manufacture of liquid fertilisers.

a) Liquid fertilisers

Liquid fertilisers were made by the neutralisation of the mother liquor by ammonia with simultaneous sequestration by pyrolysed urea-phosphate. For best results, the neutralisation pH was maintained between 6.3 - 6.6, with the continuous addition of mother liquor, free phosphoric acid, liquid base (see Section 7) solution 15:35, urea and water, in calculated quantities.

For the preparation of the liquid fertiliser, firstly the quantities of ingredients were determined viz., mother liquor, phosphoric acid, urea, water and liquid-base solution. In fixing the quantity of the base solution, it was determined from experiments that a minimum of 10 to 12 per cent of total P_2O_5 should be from the base-solution for non-potash mixtures and 20 to 25 per cent for mixtures containing potash.

In the neutralisation tank, water was taken and the other liquid ingredients were steadily added in ratio, with

simultaneous ammoniation. The pH was always maintained between 6.3 and 6.6. After the mixing, urea and other solids were added and dissolved.

The liquid fertilisers we made from the mother liquor had an N:P ratio of 18:18. The salting out temperature of this has been found to be 5° C.

8. LIQUID-BASE 15:35:0 SOLUTION

Pyrolysed urea-phosphate as produced according to the process presented earlier makes a 15:35 solution after ammoniation and addition of further urea if necessary. The physical and chemical properties of the solution are given in Table 4.

Table 4

Typical chemical and physical properties of liquid base solution 16:35:0

| | | | |
|--|----|----|------|
| Nitrogen content (percentage) | .. | .. | 15.1 |
| Phosphate - P ₂ O ₅ (percentage) | .. | .. | 35.3 |
| Specific gravity at 25° C | .. | .. | 1.42 |
| Non-ortho phosphate content (percentage of total P ₂ O ₅) | .. | .. | 98.1 |
| Safe storage temperature | .. | .. | 5° C |
| pH | .. | .. | 6.3 |

This solution exhibits marked sequestering properties. Our trials have revealed that, for non-potassic formulations in hot mix plants, only 10-12% P₂O₅ out of the total P₂O₅ content need be in non-ortho form. This quantity becomes 25% when potassic formulations are desired. The keeping quality of the liquid so produced is good and the salting out is at about 5° C, a favourably low temperature in tropical countries.

We envisage that in developing countries this is the best source of sequestering phosphates, since the capital investment and operational cost and electricity consumption to make poly-phosphoric acid either by furnace process or by concentration of wet-process acid cannot be in the immediate capability of many countries. But poly-phosphate production with the existing facilities cannot be a great problem for many of these countries.

9. CONCLUSION

From the foregoing discussion, it is clear that urea-phosphate production opens up new vistas in fertiliser technology. This fertiliser material is so versatile in its characteristics that fertilisers differing widely in physical and chemical properties could be made from it, without much complicated processing. The techniques involved are highly suitable for developing countries, especially because of non-involvement of highly specialised equipment and it is expected that urea-phosphate-based fertilisers will become the most sought after in future, at least in such countries.

DISCUSSION

Dr. K.V. NAYAR (The Fertilisers & Chemicals Travancore Ltd.) : I should like to express my thanks to the organisers of this year's ISMA Technical Conference for giving me the opportunity to be here this morning and to present work on the manufacture of high analysis fertilisers from wet process acid by the urea phosphate route. Before doing this I should like to stress the fact that the whole of the work reported in my paper is the basis of a new process for the manufacture of liquid fertilisers from wet process phosphoric acid. This process consists essentially of adding the required amount of urea to wet process acid of 30-32% strength and seeding it with crystals of urea phosphate when, due to the endothermic nature of the dissolution of urea in wet process phosphoric acid, about 30% of the total P_2O_5 in solution crystallises out as urea phosphate crystals. They can be separated out by filtration, or centrifugation, or any other well known method, and then subjected to pyrolysis, that is treatment by heating, when ammonium polyphosphate and urea will be formed as a molten product. The liquid that filtrates off can be used to dissolve this polyphosphate and the mixture and the solution can be ammoniated to the required pH of 6.5 or so, thereby obtaining after adding sufficient water, the required 18 N : 18 P_2O_5 ratio liquid fertiliser. The paper presents mostly the pyrolysis aspect. I have observed that, if a heat exchanger is used for taking advantage of the heat of evaporation of ammonia, immersed in the liquid to which the urea is added, we can bring about further cooling so that about one third of the total P_2O_5 in solution can be crystallised out. It is not necessary to add more than 15% of the total P_2O_5 in the polyphosphate form if only nitrogen and P_2O_5 liquid fertiliser is required. For potassic formulations we may require higher percentages, as high as 25 to 30% in which case the entire urea phosphate after pyrolysis should be used. Therefore, in cases where a nitrogen/phosphorus liquid fertiliser is the only product required the excess urea phosphate fertiliser produced can be used as a raw material for manufacturing high analysis fertilisers. We have, in a small pilot-plant, been making for several months a product of 30 N : 30 P_2O_5 analysis. I have samples of the relevant products here, if anyone is interested to examine them. There are three products, 30-30 NP, 20-20-20 NPK, and 18-18. I picked 18-18 because that is the composition which can keep well without crystallising at about 5°, which is the lowest possible temperature in much of India. Actually we could even raise this to 20-20 in liquid fertilisers, but on cooling it crystallises out.

Now, with this background, I should like you to read this paper for comments. This process has the advantage that it handles only about 1/3 of the total P_2O_5 for processing, whereas what I would call the conventional existing processes for polyphosphate manufacture handle the entire P_2O_5 right from the concentration stage. You probably have to concentrate it in 2 stages, from 30% to 54% or so, and then again to the polyphosphoric acid stage of 75-76% and then ammoniate it. In our case, after the preliminary stage of crystallising out the urea phosphate, we handle only less than 30% of the total P_2O_5 , which I think should be a great advantage.

Mr. B. CARLSEN (A/S Dansk Svovlsyre-og) : Using urea and wet phosphoric acid Dr. NAYAR and Mr. GOPINATH have demonstrated new ways of producing a number of high analysis complex fertilisers - solid as well as liquid - based on the formation of urea-phosphate.

It is stated that the solid fertilisers, ranging between 28-28-0 and 30-30-0, have very good physical properties, and for the 30-30-0 practically all P_2O_5 is in the polyphosphate form - a fact on which the authors seem to lay great emphasis - not least on account of its sequestering properties, which makes it possible to use it for making highly concentrated liquid fertilisers and to utilise the mother liquor from the urea-phosphate.

For good reasons, I shall not comment much on the chemistry of the processes. Just to be exact I think when you say the ratio N:P you mean N: P_2O_5 , and in table 2 there must be some errors, but as far as I can see they have no significant influence on the results.

Concerning your processes d) and e) on p. 3 and 4, where you heat your urea-phosphate either with or without water, you get half of the urea in the urea-phosphate either hydrolysed or decomposed to ammonia, which reacts with the phosphate with the formation of ammonium-monophosphate or pyro-phosphate respectively.

It seems to be a rather expensive way of producing ammonia ! It is true that by the decomposition in process e) a large part of the ortho-phosphate is converted to polyphosphate, which might justify this process.

In this connection I cannot help referring to the ammonium-polyphosphate process developed in the U.S.A. by T.V.A. and which has just been presented in a paper at this conference. This process starts with concentrated wet

phosphoric acid with 50 to 60% P_2O_5 and liquid ammonia and, by means of rather simple equipment, a melt containing 12-58-0 can be produced. From this melt either slurries or granular products can be made - among them also 28-28-0 in granular form by adding a melt of urea. It is true that in this case only 15 to 25% of the total P_2O_5 is in the form of polyphosphate.

It seems that this process is rather simple too. Certainly it is necessary to concentrate the wet phosphoric acid from 28% P_2O_5 to 50-60% P_2O_5 , but this operation is not much more complicated than concentrating your urea-phosphate solution in a vacuum concentrator and for this purpose you have to crystallise the urea-phosphate and separate the crystals from the mother liquor.

Further, by this separation you get the process material split up into two streams, a solid and a liquid, and the ratio between these two streams is fixed. It seems to me that it makes your process a little more difficult compared with the T.V.A. process where solid and liquid fertiliser can be produced at will - naturally at the expense of the concentration of the finished product - but it is still possible to produce a 28-28-0.

These remarks are only put forward to give you the background for my following question :

1. Are the extra costs to get the increase in the content from 28-28-0 to 30-30-0 really justified, for instance by lower handling and transportation costs etc. ?
2. It seems as if you have put very much emphasis on the content of polyphosphate. Is that to obtain a sequestering effect only or do you expect a much better agronomic effect than with ortho-phosphate or both ?
3. By heating the mixture of urea-phosphate one might expect a risk of the formation of biuret. Have you noted such formation and if so what was the content of biuret in the mixture ?
4. Do you intend to produce solid, granular NPK fertilisers from your NP fertiliser and, if so, do you encounter any difficulties in this respect ?
5. Have you made any economic calculation and comparison with other processes for making NP fertilisers, which prove that your processes are more advantageous ?
6. You conclude that the techniques involved in producing

the fertilisers are highly suitable for the developing countries because no highly specialised equipment is needed and you expect that urea-phosphate based fertilisers will become the most sought after in the future. Could you give a brief explanation of this statement ?

It seems to me that Dr. NAYAR has now given quite another approach to the subject, in that he now concentrates on liquid fertilisers. In the paper you could not tell if it was solid or liquid he was aiming at. It seems to me, from what we have just heard, that Dr. NAYAR has found a very interesting process for making liquid fertilisers. However, you need a market for liquid fertilisers if you are going to use this process and this may be some while in parts of Europe. But in any case it seems very elegant process. There might be some delegates who have now had time to prepare some questions, and so I will not go into detail. I will just present the questions based on the paper.

Mr. NAYAR : I think I have already answered question 5. The one advantage I claim for this process for making liquid fertilisers is the fact that in the process only 30-33% of the total P_2O_5 need be handled in the sense that it needs to be subjected to urea processing. Actually the process consists of three or four unit operations and in only one, the most important where the pyrolysis of urea phosphate occurs, do we have to heat the urea phosphate. In this important step, we handle only 1/3 of the total P_2O_5 . The material of construction and the equipment are very simple and cheap compared with any other existing process. We have a small 3 tons a day operational pilot-plant based on the process and we have found that rubber lined mild steel equipment would be quite sufficient except where the pyrolysis step is involved, where 316 stainless steel may be used.

Another question is about the heating of urea phosphate and the risk of formation of biuret. We have studied this problem quite thoroughly and I would state that the formation of biuret can be completely avoided if the temperature of heating is controlled. When a urea phosphate mass is subjected to heating it melts at about 120° (which can still be brought down by the addition of a little more urea) and then, at about 110° C, the evolution of carbon dioxide, that means decomposition of urea, sets in. This liberates ammonia and in situ ammoniation takes place, which is an exothermic reaction. Actually, after the evolution of carbon dioxide has started, you can cut off the heat supply. The reaction maintains itself automatically to completion. In fact, towards the end of the reaction you have to cool the mass to avoid the formation of biuret. It may not be possible to

determine the end of this decomposition from the stopping of the evolution of carbon dioxide, but we have found that certain organic dye stuffs added in parts per million has one colour in the acid medium and an entirely different colour in a medium whose pH is around 3.5 - the pH of the final melt. So this change of colour is very sharp and it starts in the bubbling mass at the top. Once we find a change of colour at the top, we put the cooling system into operation. It is a very simple matter to control the pyrolysis, because you need only control the temperature. Except in the very early experimental stages we have avoided completely the formation of biuret.

Another question asked here was about my putting too much emphasis on the content of polyphosphate. This was not intentional and probably due to the enthusiasm of my colleague in writing out the paper. But we have also found that polyphosphate, in our agronomic field trials, especially if it is about 50% in the solid, has a better effect. However, this is only a preliminary finding. We are waiting for results over 3 or 4 crops before we can say anything about the economic advantage of polyphosphates over orthophosphates.

Our plant has been working on a batch basis and the ammonia used for ammoniation of the first batch is passed through a coil immersed in the wet process acid of the second batch after the addition of urea, so that, in effect, starting with a room temperature of normally 28° where I work, the temperature goes down on the addition of urea in adequate quantities to 15° or 16° C, and it goes down further to 8° C after the heat exchange from ammonia has been effected: thus we find that at 15° or 14° minimum we get about 25% of the P_2O_5 crystallised out as urea phosphate. Of course, it goes without saying that it is not automatic crystallisation and you have to induce it by adding a seeding of urea phosphate crystals in very small quantities. Then, when the temperature goes down due to the ammonia heat exchanger, we have got a maximum of 33 to 34% and a minimum of 30-32% depending on other conditions.

The last question to give a brief explanation of the statement that I made, that I thought that urea phosphate based fertilisers will become the most sought-after in the future. However I point out that I also added, if I remember correctly, that this applies in such countries as developing countries where sophisticated equipment has to be imported, for example a concentration plant. The plants I have observed in India never work for more than 180 to 200 working days in any year, the rest of the time being taken by maintenance and breakdowns and so on. So, it is with that in mind and that

alone that this statement has been made because, in the process which I have mentioned in this paper, the operations involved are relatively few in number and far simpler than in any other existing process. That is the reason for this statement.

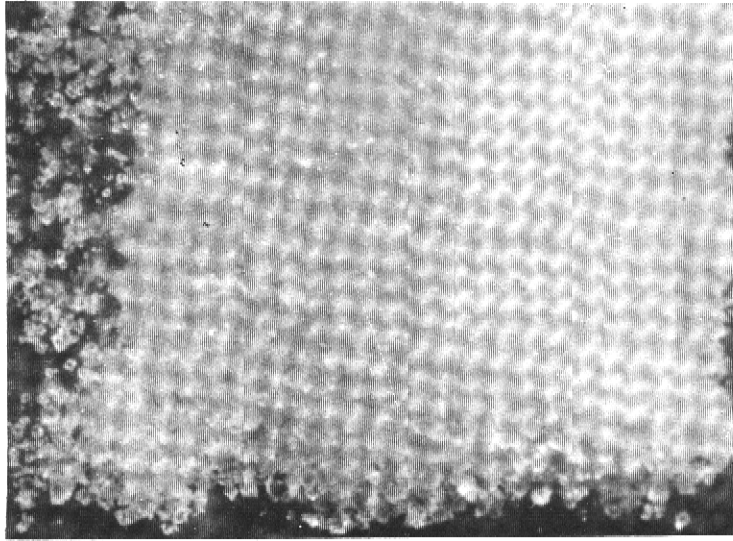


fig. 1

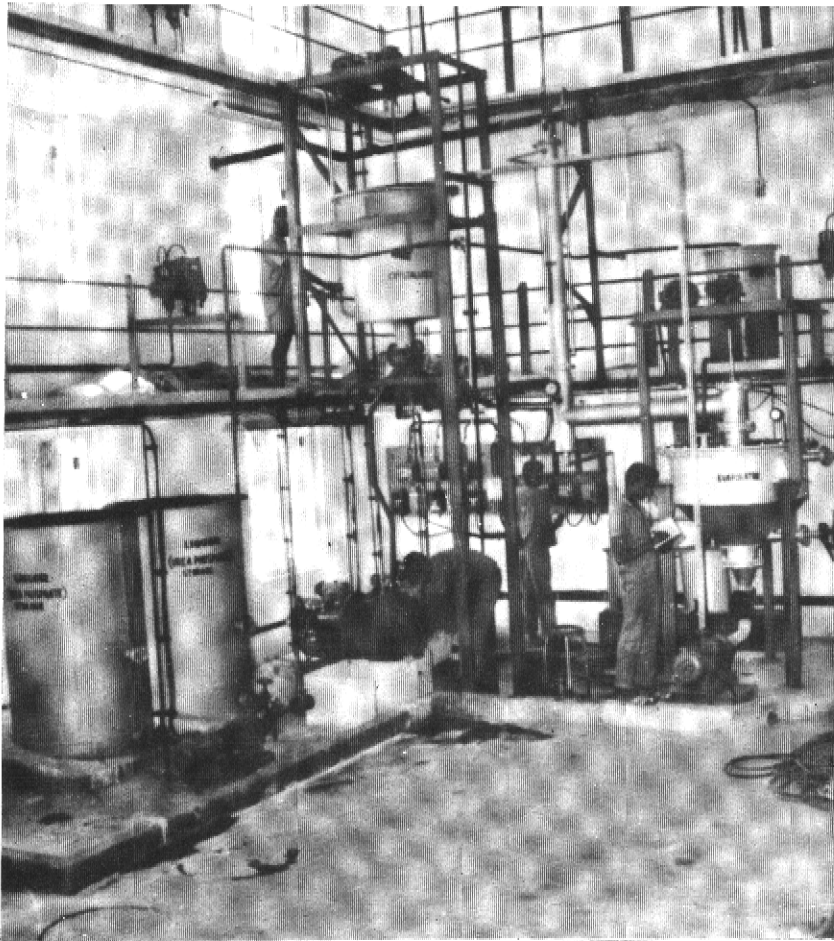
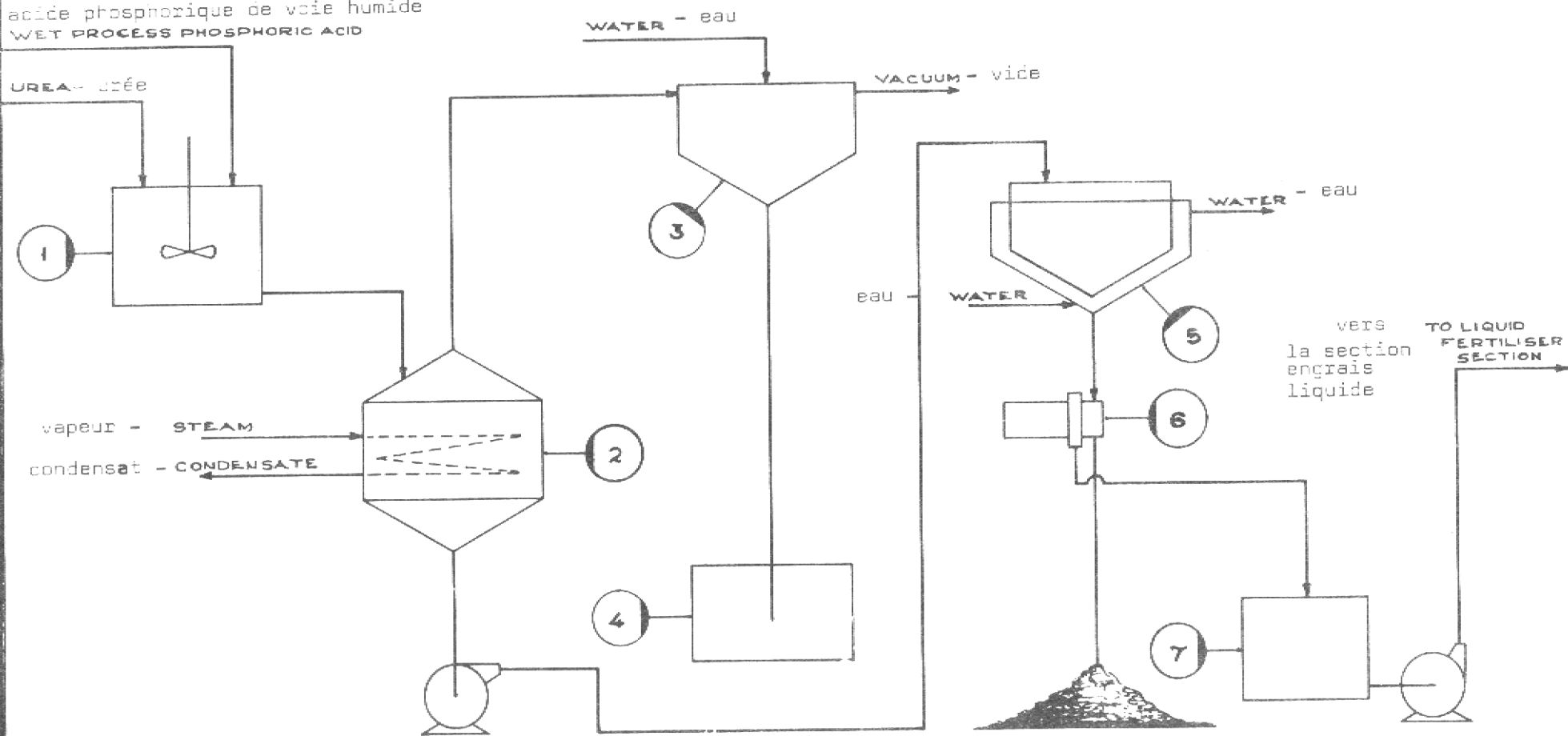


fig. 2

FLOW DIAGRAM FOR THE MANUFACTURE OF UREA - PHOSPHATE.

SCHEMA DE LA FABRICATION DE PHOSPHATE D'UREE

acide phosphorique de voie humide
WET PROCESS PHOSPHORIC ACID



vers
la section
engrais
liquide
TO LIQUID
FERTILISER
SECTION

cuve de dissolution d'urée
1 - UREA DISSOLUTION TANK
2 - VACUUM EVAPORATOR
Evaporateur sous vide

3 - CONDENSER - condenseur
4 - SEAL POT - capacité
5 - CRYSTALLISER - cristalliseur

6 - CENTRIFUGE - centrifugeuse
7 - MOTHER LIQUOR STORAGE
stockage de liqueur mère