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THE "APEX" PROCESS FOR THE EXTRACTION
OF PHOSPHORIC ACID FOR THE PRODUCTION
OF PHOSPHATIC FERTILISERS AND INDUSTRIAL PHOSPHATES

By :

R. Amanrich
G. Cousserans
A. Mahe
Azote et Produits Chimiques S.A.
France

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SUMMARY

The "APEX" process for the extraction of phosphoric acid for the production of phosphatic fertilisers and industrial phosphates.

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The primary objective of the process developed by A.P.C. under the trade name "APEX" was to provide producers of nitrogenous fertilisers with an economic source of P_2O_5 in a concentrated water-soluble form, and also to avoid the use of sulphur. In its original version the process, after digestion of the phosphate rock with nitric acid, consists of extraction of the phosphoric acid and the excess nitric acid with a selective solvent, purification of the resultant extract, and separation of the two acids by neutralisation with NH_3 . The residue, consisting of an aqueous solution of calcium nitrate, is converted to ammonium nitrate and/or potassium nitrate. The process has proved to be extremely flexible, since it can be used to produce not only NP binaries ranging from pure MAP 12.61.0 to 30.20.0 (the basis of concentrated ternaries such as 17.17.17), but also phosphates of adequate purity for liquid fertilisers (via MAP), detergents (via MAP), and animal feedstuffs (via MAP or dicalcium phosphate).

Cost estimates, in relation to the conditions prevailing in France, show that the P_2O_5 produced by this process is appreciably cheaper than wet-process phosphoric acid. It is also possible to use hydrochloric acid instead of nitric for the digestion of the natural phosphates.

Another interesting development has just been discovered : an economic process for the purification of wet-process phosphoric acid intended for the direct manufacture of industrial phosphates, detergents and feedstuffs.

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LIST OF ABBREVIATIONS

NA	Nitric acid
PA	Phosphoric acid
ML	Mother-liquors from the nitric acid digestion
DL	Nitric acid digestion liquor
AN	Ammonium nitrate
CN	Calcium nitrate
PN	Potassium nitrate
DCP	Dicalcium phosphate
MAP	Monoammonium phosphate
DAP	Diammonium phosphate
MSP	Monosodium phosphate
APP	Ammonium polyphosphates (pyro, tripoly...)
DPP	Dipotassium phosphate

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1. INTRODUCTION

When, at the beginning of 1965, the Research and Development Department of A.P.C. (a Company formed by the merger of O.N.I.A. and P.E.C.) undertook the research work which led to the "APEX" process, the remit was as follows : to find an economic source of water-soluble P_2O_5 suitable for the production of high-concentration solid and liquid fertilisers. It was particularly imperative to avoid the use of sulphur, which A.P.C. do not produce, because of its price which, at the time, was high and rising constantly. Nitric acid, which is low-priced and produced by A.P.C. in large quantities was the obvious choice for the solubilisation of the natural phosphate, especially since the production of nitrophosphate fertilisers was already well-established in our plant. As will be seen later, the "APEX" process is primarily an improved method for the manufacture of ammonium nitrophosphates.

To obtain a water-soluble P_2O_5 product, it was necessary to find a convenient and economic means of separating the phosphoric acid from the calcium nitrate ; liquid-liquid extraction was adopted on account of its flexibility and low cost, the solvent being chosen from among the alcohols. Unfortunately, nitric acid is readily soluble in all the possible solvents for phosphoric acid, thus, in certain cases, there is a problem in separating the two acids. This is particularly so where the manufacture of liquid fertilisers is contemplated, or where it is intended to produce phosphates for detergents or feedstuffs. We sought a simple means of extracting P_2O_5 from the solvent and it has been established that this method, involving neutralisation by solvent-borne ammonia, effects the separation of the two anions. In this way pure crystalline MAP, and AN solution are obtained, without the use of steam and under conditions where serious corrosion problems are not encountered. The fact that MAP is obtained and not phosphoric acid is not detrimental to the process, as it is possible to obtain from MAP, not only a wide range of fertilisers, but also phosphates for use in detergents and animal feedstuffs.

It remained to evaluate the main by-product arising from the nitric acid digestion of the natural phosphates, calcium nitrate, a poor quality fertiliser the market for which has practically disappeared in France.

We foresaw two alternatives, conversion into either ammonium or potassium nitrate. The first of these possibilities has been studied very thoroughly, since it appeared the more profitable and in a plant already producing AN would result in only minor disturbance. The second alternative is promising as potassium nitrate is highly thought of as a fertiliser for certain crops.

We shall describe first the process in its "conventional version" starting from a nitric acid digestion and yielding pure MAP and AN, and then finally we shall examine briefly the possible variants of the process and the more important developments.

2. DESCRIPTION OF THE PROCESS

a) Choice of solvent

After subjecting some hundred solvents to two series of screening tests, we selected isobutyl alcohol as being the most economic. Indeed, this alcohol, a by-product of the OXO synthesis starting from propylene, is very cheap, sparingly soluble in water, and can be recovered easily by azeotropic distillation. Moreover, under our conditions of use, it is for all practical purposes chemically stable.

We list below some of the characteristics of isobutyl alcohol :

- Formula : $(\text{CH}_3)_2 - \text{CH} - \text{CH}_2\text{OH}$
- Molecular weight : 74.12
- Specific gravity at 20° C : 0.803 tonnes/cubic metre
- Boiling point : 108.3° C
- Vapour pressure at 20° C : 9.0mm. Hg.
- Melting point : - 108° C
- Solubility % by weight at 20° C (isobutanol in water : 8.5%
(water in isobutanol : 16.5%
- Viscosity at 20° C : 4.0 cp.
- Mean specific heat between 10 and 100° C : 0.176th/tonne/° C
- Latent heat of vaporisation at 108° C : 138th/tonne
- Isobutanol/water azeotrope : (% by weight alcohol 67.
(Boiling point : 89.8° C
- Flash point : 37.8° C
- Price in France : 400 Francs per tonne

The ternary solubility diagram for the system $\text{H}_2\text{O} - \text{H}_3\text{PO}_4 - \text{iBuOH}$ at 25° C is given in Figure 1.

The table below shows the various partition coefficients of the major constituents that occur in the nitric acid digestion liquor.

The determinations were carried out at 40° C, using a solvent : mixture to be extracted ratio of 1:1 by weight.

Partition coefficient :

$\frac{\text{concentration by weight in the solvent-rich phase}}{\text{concentration by weight in the solvent-weak phase}}$

	<u>Mixture No 1</u>	<u>Mixture No 2</u>	<u>Mixture No 3</u>
H ₃ PO ₄	0.409	0.504	0.588
Ca(NO ₃) ₂	0.087	0.040	0.047
HNO ₃	0.65	very high	very high
Selectivity : $\frac{K_{\text{H}_3\text{PO}_4}}{K_{\text{Ca}(\text{NO}_3)_2}}$	4.7	12.5	12.4
HF			0.093
H ₂ SO ₄			0.042
Al ₂ O ₃			0.342
Fe ₂ O ₃			0.113
MgO			0.066

Composition of the 3 mixtures (% by weight)

	<u>Mixture No 1</u>	<u>Mixture No 2</u>	<u>Mixture No 3</u>
P ₂ O ₅	17.3	10.0	11.34
Ca(NO ₃) ₂	3.1	26.4	33.27
HNO ₃	10.4	8.5	7.2
HF	nil	nil	0.68
H ₂ SO ₄	nil	nil	0.44
Fe ₂ O ₃	nil	nil	0.051
Al ₂ O ₃	nil	nil	0.041
MgO	nil	nil	0.15

The foregoing table clearly demonstrates the selectivity of isobutanol with respect to phosphoric acid, except as regards nitric acid which is much more readily extracted.

b) Description of the process

The first research workers (mainly those from Stamicarbon^{1,2}, and from St. Paul Ammonia) to investigate the preparation of pure phosphoric acid by the nitric acid digestion of natural phosphates used the conventional scheme (Figure 2A) developed by A. BANIEL and R. BLUMBERG of I.M.I.³ : extraction of the phosphoric acid with a C₄ or C₅ alcohol containing some nitric acid to prevent reversion of the dissolution ; purification of this solution to eliminate the extracted calcium nitrate, further extraction by water to remove the nitric and phosphoric acids from the purified alcoholic solution. A portion of the aqueous solution is used as a counter-current in the purification stage, the remaining portion is stripped of the residual alcohol, concentrated and freed from nitric acid by distillation.

This scheme has three main disadvantages :

- The aqueous solution obtained is very weak in P_2O_5 (a more concentrated solution can be obtained by recrystallising part of the calcium nitrate before the extraction stage, but in any case, the final concentration of P_2O_5 will not exceed 15%).
- The distillation of the alcohol in the presence of nitric acid is not without risk.
- The distillation of the nitric acid in the presence of phosphoric acid poses serious corrosion problems.

In order to avoid the latter disadvantage, the Stamicarbon Company proposed⁴ to treat the aqueous solution of phosphoric and nitric acids with a solvent for nitric acid, this secondary solvent being either a ketone or an ether. But then the process becomes very complicated. In effect, it is necessary to add, after the regeneration of the solvent stage in the conventional scheme outlined in Figure 2A, a section for the extraction of the nitric acid, yielding an aqueous solution of phosphoric acid saturated with the secondary solvent which must, therefore, be recovered. The solution of nitric acid in the secondary solvent is treated with water to obtain an aqueous solution of nitric acid which must be likewise stripped of the residual secondary solvent.

Somewhat on similar lines, the same Company proposed the elimination of the purification section, and the addition of an alkaline sulphate to the aqueous solution of the nitric and phosphoric acids, which still contains much calcium nitrate, followed by removal of the gypsum formed, and the treatment of the resultant aqueous solution with a solvent for nitric acid in order to obtain ultimately a relatively concentrated aqueous solution of the alkaline phosphate (the term "alkaline" also embraces the ammonium radicle).

These two processes are not suitable for industrial use on account of their complexity. Moreover, in an attempt to overcome the three aforementioned disadvantages (viz., very dilute solutions of P_2O_5 , danger of heating the alcohol in the presence of nitric acid, corrosion problems involved in the distillation of nitric acid in the presence of phosphoric acid), research workers in several companies proposed the neutralisation of the alcoholic solution of the nitric and phosphoric acids by ammonia (the ammonia being replaceable by an alkaline salt of sodium).

This neutralisation stage was put forward in two forms :

- Stamicarbon⁶ proposed the following scheme (Figure 2B) : a portion of the alcoholic solution on leaving the purification stage is treated with a counter-current of water, the remainder is neutralised to pH 3.5 with ammonia and two

phases are thus obtained ; a light phase composed mainly of the alcohol and a heavy phase which is an aqueous solution of monoammonium phosphate and ammonium nitrate. Therefore, this process is capable of yielding an NP binary.

- On the other hand the firm of TYPPI OY⁷ as well as some Rumanian workers⁸ proposed the neutralisation of the alcoholic solution with ammonia immediately after the extraction stage, i.e. without effecting any purification. This brings us to the scheme shown in Figure 2C. Under these conditions an NP binary is obtained having a water-solubility dependent on the selectivity of the solvent with respect to calcium nitrate, and which can vary from 80% to 85%.

All these processes give NP binaries of high concentration and good water solubility, but they neither provide a route to the ammonium polyphosphates (liquid fertilisers and 15.61. solid binaries), nor to pure ammonium phosphates (monoammonium phosphate 12.61. and diammonium phosphate 21.53.) whose popularity as solid fertilisers is constantly increasing, nor finally, to industrial phosphates (monoammonium phosphate for fire extinguishers, and sodium phosphate for detergents).

For this reason we directed our research towards obtaining pure monoammonium phosphate from which all the foregoing compounds can be prepared.

We observed that neutralisation to pH 3.5 by the addition of ammonia to an isobutyl alcohol solution containing nitric and phosphoric acids together with 8 to 10% by weight of water, results in the formation of three phases ; a light phase consisting mainly of isobutyl alcohol, an aqueous phase saturated with ammonium nitrate and containing a little monoammonium phosphate, and a solid phase consisting of monoammonium phosphate and a little ammonium nitrate.

This separation into three phases is due partly to the low solubility of isobutyl alcohol in saturated aqueous solutions of salts, and partly to the appreciable difference in the water-solubility of ammonium nitrate and monoammonium phosphate. However, the isobutyl alcohol acts in two ways ; by retaining in the light phase a fair proportion (about half) of the ammonium nitrate formed, and also in reducing the solubility of the monoammonium phosphate in the aqueous phase.

To obtain a solution of isobutyl alcohol containing 8 to 10% water, we no longer use an aqueous solution of nitric and phosphoric acids as the counter-current of the purification stage, but instead the aqueous phase obtained at the neutralisation stage (a saturated aqueous solution of nitrate and phosphate) and we finish up with the lay-out shown in Figure 2D. Any loss of P₂O₅ is prevented by the recycling stage.

This system has the advantage that the extraction is carried out in the presence of large amounts of ammonium ions (the extraction mixture contains effectively 25% by weight of ammonium nitrate. We mean by extraction mixture the digestion liquor together with the solution coming from the purification stage). The extraction of the phosphoric acid is very clearly favoured by the presence of the ammonium ions as is shown in the following table which gives the variation in $K_{P_2O_5}$.

$$\left\{ \begin{array}{l} K_{P_2O_5} = \frac{\text{Concentration of } P_2O_5 \text{ in the solvent-rich phase}}{\text{Concentration of } P_2O_5 \text{ in the solvent-weak phase}} \end{array} \right.$$

for a solution free from ammonium nitrate (i.e. the conventional extraction mixture) and for a solution containing ammonium nitrate (i.e. the extraction mixture obtained from our process). The determinations were carried out at different P_2O_5 concentrations, all the other variables (ratio of solvent to extraction mixture, temperature, etc.) being kept strictly constant.

% P_2O_5 in the extraction mixture	$K_{P_2O_5}$	
	Solution with NH_4NO_3	Solution without NH_4NO_3
10	0.540	0.438
5	0.355	0.272
1	0.315	0.230

Finally, we have noticed in practice that the presence of ammonium ions has quite clearly reduced the formation of deposits in the extractors.

The complete installation (Figure 3) is made up as follows : a digester where the natural phosphate is solubilised with nitric acid ; an extraction stage, maintained at $40^\circ C$, in which the phosphoric acid is extracted with isobutyl alcohol containing 3.00% nitric acid ; a purification stage for the removal of the last traces of calcium from the alcoholic solution.

After purification, the alcoholic solution is cooled to about $10^\circ C$, before entering the neutraliser, where it is brought to pH 3.5 by addition of ammonia (the temperature rises to about $40^\circ C$) ; the neutralised mixture then passes

to a separator for removal of the light phase, and the heavy phase together with the crystalline material is cooled to about 20° C and filtered. After washing with water, the filter cake consists of pure ammonium phosphate (<0.3% NH_4NO_3 and <0.02% alcohol). The wash liquor together with the heavy phase are used to wash the light phase to remove the last traces of P_2O_5 ; this phase, after washing and addition of nitric acid, is returned to the extractor, and the wash liquors together with the heavy phase from the scrubber are used as the counter-current of the purification stage.

The aqueous solution leaving the extraction stage contains all the calcium and ammonium nitrate, and after removal of the alcohol, it is treated with ammonium carbonate to convert the calcium nitrate to ammonium nitrate.

Under these conditions, the overall yield of P_2O_5 (based on the P_2O_5 content of the natural phosphate) is 98%.

It is possible to recrystallise a greater or lesser amount ("strong" or "weak" mother-liquors) of the calcium nitrate prior to the extraction stage. However, in these circumstances the capital investment is slightly higher, and the yield of P_2O_5 is only 94%.

With minor modifications, the process can produce either DCP (by neutralisation with lime, calcium carbonate or CN), or DPP (by neutralisation with potash). In the latter case the PN is precipitated and the phosphate remains as a saturated solution.

c) Current position of the investigation

The preliminary study is practically finished. We have available a small 500 kg P_2O_5 per day unit, which came into operation nearly two years ago, on which we have been able to confirm the main results obtained in the laboratory.

We have found it necessary to develop extractors, capable of being subsequently scaled-up in size, and suitable for the treatment of liquids containing suspended matter.

All the problems raised by the presence in the digestion liquor of insoluble impurities have now been resolved.

3. PERFORMANCE CHARACTERISTICS OF THE PROCESS

The data given in this paragraph have been obtained on the pilot plant, using crude Moroccan phosphate with a P_2O_5

content of 33.5% as the raw material. Phosphates from other sources can, of course, be used instead.

The products manufactured are pure MAP, AN, with calcium carbonate as the by-product.

a) Composition of the products obtained

<u>MAP</u> : N	12.10 - 12.25%)	
)	
F ₂ O ₅	61.4 - 61.60%)	
Fe ₂ O ₃ + Al ₂ O ₃ + MgO.	10 ppm.	approx.)	on the
CaO	10 ppm.)	dried
F ⁻	40 ppm.)	material
NH ₄ NO ₃	less than 0.2%)	
iBuOH	" " 0.01%)	before
)	drying

AN (on the dried material)

Total nitrogen	34.4 - 34.6%	
Nitrogen as NH ₄	17.2 - 17.3%	
Fe ₂ O ₃ + Al ₂ O ₃ + MgO.	less than	0.05% approx.	
SiO ₂	" " 0.02%	"
F ⁻	" " 0.02%	"
SO ₃	" " 0.1%	"
CaO	" " 0.2%	"
MgO	" " 0.1%	"
Organic matter	Nil, even on the dilute aqueous solution coming from the conversion stage	

Almost the whole of the impurities go out with the calcium carbonate, the by-product of the conversion of the calcium nitrate.

b) Overall yields

relative to P ₂ O ₅	98%
relative to nitric nitrogen	93%
relative to ammonia nitrogen	95%

c) Basic data for calculation of manufacturing costs

Battery limits investment = 17 million Francs (valid for France as at April 1970) for a plant to produce :

- 100 tonnes per day of P₂O₅ as wet MAP at 58% P₂O₅
- 237 tonnes per day of nitrogen as wet MAP at 11.6% N, together with a 96% solution of AN (6.20 tonnes per day of AN).

Requirements based on 1 tonne of P₂O₅ (and on 2.37 tonnes of nitrogen) :

Phosphate at 33.5% P ₂ O ₅	3.05 tonnes
NH ₃	1.70 "
HNO ₃ (100%)	5.25 "
CO ₂	1.25 "
Steam at 13 bars	6.00 "
Electricity	420 kWh.
Sundries equivalent to	30 Francs
Solvent	15 Kg.
Process water	5 m ³
Cooling water	260 m ³

Labour : 10 men per shift including foreman, to whom must be added the ancilliary staff.

d) Comparison of the manufacturing costs of the "APEX" and the wet process

The net cost of 1 tonne of P₂O₅ calculated on the basis of the foregoing requirements, after making an appropriate allowance for the AN, amounts to about 480 Francs for pure MAP, and 450 Francs for the 19.38.0 binary (a mixture of MAP and AN);

these costs are equal to that of a tonne of P_2O_5 in PA obtained from a modern wet process plant of high yield and concentration, when sulphur costs respectively 80 Francs and 45 Francs per tonne.

Therefore, at the present time there is an appreciable price differential in favour of the "APEX" process.

4. THE VERSALITY OF MAP

Figure 4 illustrates the major possible uses of MAP, and shows that for many purposes phosphoric acid can be replaced by it.

Since our Company is very active in the liquid fertiliser fields we were particularly interested in the manufacture of aqueous solutions of ammonium polyphosphates (APP). We have a process operating satisfactorily in the laboratory, and we are now trying it out on a pilot scale.

The following table lists the characteristics of the two types of mother liquor that we obtain.

% N by wt.	% P_2O_5 by wt.	Relative pH P_2O_5 as poly- phosphate	pH	S.G. tonne/m ³	Visc. 20° C	Crystall'n commences at
10.8	37.8	75.5	6	1.390	30 cp.	- 20° C
12.0	40.4	72.5	6	1.437	110 cp.	0° C

The first solution is intended for the manufacture of liquid fertilisers, and the other for suspension fertilisers.

We are also investigating the granulation of MAP, its transformation into diammonium phosphate and its granulation.

We also have on our programme the obtaining of APP in solid form.

Finally, the conversion of MAP to alkaline phosphates is already being carried out on an industrial scale by a Japanese detergent manufacturer.

5. OTHER VARIANTS AND DEVELOPMENTS

The conventional version of the "APEX" process yields MAP and AN from the nitric acid digestion liquor, but there

are many possible alternatives based on the common factors of the extraction of phosphoric acid and its regeneration by neutralisation.

The more important versions of the process are illustrated in the table (Figure 5) which lists the products that can be obtained directly. Among the various possibilities, two recent developments appear to be of particular interest :

- the conversion of CN to NK (13.0.44) by double decomposition : $\text{Ca}(\text{NO}_3)_2 + 2\text{KCl} \longrightarrow \text{CaCl}_2 + 2\text{KNO}_3$

NK is a nitrogen/potash fertiliser which in effect is "tailor-made" for certain crops and its use is tending to increase.

We have developed an original process which gives high yields of K_2O (98%) and nitrogen (95%).

This process will be shortly investigated on the pilot scale.

- purification of wet-process phosphoric acid, with a view to the direct production of alkaline phosphates for detergents.

The purification of phosphoric acid by solvent, leads in general to restricted yields and to a dilution of the acid : we have discovered a process which, starting from filtration acid (20-40%), yields pure alkaline phosphates directly and without dilution and with an extraction rate of 98% based on the P_2O_5 content of the phosphoric acid. The preliminary cost estimates lead us to believe that there are high hopes for the cheapness of this process.

6. CONCLUSIONS

The "APEX" process which we have just described enables us to obtain phosphates, for use in solid fertilisers, from naturally occurring phosphates by digestion with nitric acid : and as such can be considered an economic process for the production of calcium-free ammonium nitrophosphates, leading thence to concentrated fertilisers of virtually complete water-solubility ; the estimates of the manufacturing costs carried out on the basis of a pilot-plant study show, in the case of the conventional version (MAP-AN), an appreciable reduction, of the order of 13%, in the cost of the P_2O_5 (using for purposes of comparison the current costs, of wet-process phosphoric acid and of sulphur).

Moreover, the flexibility of the process which stems from the use of liquid-liquid extraction and direct neutralisation of the solvent phase is in the nature of an additional "trump-card" which allows it to be adapted to the prevailing state of

affairs and to local conditions, whether it be a question of the nature of the acid used for the digestion or of the range of products to be manufactured.

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DISCUSSION

Mr. G. COUSSERANS (Azote et Produits Chimiques, France) : This is the first time, to my knowledge, that there has been in the Technical Meetings of ISMA reference to a process for the manufacture of soluble phosphates embodying nitric acid digestion for the solubilisation, followed by liquid-liquid extraction for separating the calcium. However, this type of process seems to be having a certain vogue, at least at the research stage, since a second paper describing yet another process, similar in principle, is also being presented.

The process which we have christened APEX i.e. from the initial letters of the French word meaning phosphoric acid by extraction, involves the solubilisation of natural phosphates by nitric acid, and extraction, by means of a selective solvent, of the phosphoric acid and excess nitric acid from the raw digestion liquor, followed by purification of the resultant extract and neutralisation with ammonia. This enables the phosphoric acid to be recovered in the form of monoammonium phosphate. The aqueous solution of calcium nitrate, which constitutes the by-product, can be converted into ammonium nitrate, after removal of the solvent, by the classical method of treating with ammonia and carbon dioxide, or along the lines of a more recent alternative which is still under investigation, conversion to potassium nitrate by double decomposition with potassium chloride.

Why did we choose a nitric acid digestion ? The reason is simple. This is the only cheap acid that will solubilise natural phosphates and whose anion is also valuable as an ingredient of fertilisers. Moreover, the Company has for many years been carrying out large scale digestions involving either nitric or nitrophosphoric acid in the production of nitrophosphates. Finally, the work was prompted largely by the recent sulphur crisis.

Why did we choose liquid-liquid extraction ? At first sight it would certainly seem to be an operation somewhat out of place in the fertiliser industry, more suited to the petrochemical or the fine chemical industries, but in point of fact it has turned out to be very simple in use, flexible, economic, and yielding very pure phosphates. Moreover, we already had some years experience with liquid-liquid extractions in other directions.

Why monoammonium phosphate ? Direct neutralisation of the extract with ammonia is the simplest way we have found of effecting the simultaneous separation of the solvent and

each of the acids. Actually, if certain operating conditions are observed, three distinct phases appear when the extract is neutralised with ammonia. A light phase composed of the regenerated solvent which is recycled to the extractor, a heavy phase composed of the concentrated solution of ammonium nitrate which is returned to the extraction stage. The solid phase, monoammonium phosphate needs only to be washed after being separated, and it can then be dried and granulated or converted into ammonium polyphosphate.

After intensive laboratory studies, the process has been tested and developed in a small pilot unit which has been working now for almost two years, during which time we have met many difficulties, but we have been able gradually to overcome them satisfactorily. We feel that we have now acquired all the data necessary to enable us to scale-up the process to the industrial level, and moreover, we are working on the eventual setting-up of a unit to produce 100 tonnes per day of P_2O_5 .

The raw material consists of natural phosphate, either crude or calcined. On the pilot scale we have had experience in the use of Moroccan phosphate, initially calcined and subsequently uncalcined. The liquor coming straight from the digester is subjected to liquid-liquid extraction without any prior separation, either of the calcium nitrate or the insoluble matter remaining after digestion. The solvent used is isobutanol or isobutyl alcohol, a by-product which is in free supply and consequently very cheap. In use it is very reliable and trouble-free, and can be easily recovered. The extraction, purification and separation of monoammonium phosphate are carried out at relatively low temperatures, thus eliminating any serious corrosion problems.

The resultant high-purity monoammonium phosphate is a good fertiliser in itself, and from which can be obtained, by a process that we have also investigated, polyphosphates for the manufacture of liquid fertilisers. Other phosphates such as pure dicalcium phosphate and dipotassium phosphate can be prepared by variations of this same process.

The extraction and separation stages are carried out in the novel liquid-liquid contactors that we found necessary to develop for the treatment of liquids containing suspended matter.

We have not done a great deal of work on the conversion of calcium nitrate to ammonium nitrate, since there are already well-known methods for doing this. We have simply confirmed that, despite the presence of impurities originating from the natural phosphates, the separation of calcium

carbonate is not more difficult on account of these impurities. The latter are found, in the main, with the calcium carbonate, or in the solution of calcium chloride during the production of potassium nitrate.

The overall yields in the production of monoammonium phosphate and ammonium nitrate from crude Moroccan phosphate are 98% for P_2O_5 , 94% for nitric nitrogen and 96% for ammoniacal nitrogen. The last two figures are slightly higher than those you will find on page 14 of the text, as they result from more recent trials based on a plant run of over a month's duration.

The capital outlay for a unit producing 100 tonnes per day of P_2O_5 in the form of moist monoammonium phosphate at 58% P_2O_5 and 240 tonnes per day of nitrogen in the form of a solution of ammonium nitrate at 96% as well as the monoammonium phosphate, is estimated at 17 million French francs as at April 1970 values. You will also find on page 14 of the text the details of the calculation of the costs. According to the estimates that we have made, assuredly in all good faith but inevitably lacking in precision at the time we carried out the investigation, the cost of one tonne of P_2O_5 , after making allowance for the ammonium nitrate produced, amounts to something in the region of Fr. 480 per tonne. When this is compared with the cost of wet-process phosphoric acid produced by a modern process in a plant of comparable capacity, we find a difference of the order of 13% in favour of the APEX process. We do not, of course, take this comparison too seriously, since in the one case we are dealing with a new process which is not yet working on an industrial scale, and in the other case with one that is already well-tried. However, the results serve to encourage us to persevere along these lines.

To conclude, I would like to mention that we have just discovered a purification process for the liquid-liquid extraction of wet-process phosphoric acid, a process leading directly to pure phosphates for detergents and animal foodstuffs.

I must draw your attention to a slight error which has occurred in Figure 2B on page 18 of the text. The direction of the arrows on the two horizontal lines connecting the purification and re-extraction stages should be reversed.

Slide 1 - (Figure 3) you see the lay-out of the APEX process. At the top on the right you have the treatment of the phosphate rock with nitric acid, from whence the digestion liquor is conveyed directly to the extractor in which the two sections for extraction and purification are

situated side by side. The calcium nitrate solution which leaves the left hand side of the extractor goes to the solvent recovery column down which it passes before entering the reactor for treatment with ammonia and carbon dioxide. After removal of the calcium carbonate, the solution is concentrated to a figure of about 96%. Regarding the P_2O_5 stream, the purified extract leaves from the right hand side and after cooling it enters the neutraliser, the small vertical column, and passes finally into the separator which is beneath. The mixture is separated and cooled before the solvent is passed through the small column on the left. There it is washed before being returned to the extraction stage together with fresh solvent. The monoammonium phosphate and the ammonium nitrate solution are withdrawn from the bottom of the separator, for a further separation process (in the case of the figure in the text, this is a rotary filter, and although this was used at the time, we now remove the surplus liquid centrifugally). Finally, the monoammonium phosphate is washed and despatched for a variety of uses.

Slide 2 - (Figure 4) illustrates the various possible uses of monoammonium phosphate. Firstly it can be granulated. In the table it is described as "prilled MAP", but this is already out of date. We did attempt prilling, but we ran into difficulties and so for the moment at least we have dropped this method of granulation. The second possible use is in the production of diammonium phosphate, 21-53-0, which we have carried out on a semi-industrial scale, and thence the production of NP binaries ranging from 25-25-0 where the extra nitrogen is added as ammonium nitrate to 30-30-0 where it is added as urea. We have also produced solid ammonium polyphosphates ranging from 15-61-0 to 18-62-0. Similarly we have prepared polyphosphates in aqueous solution having the composition 11-17-0 in the case of fertilisers in true solution, and having the composition of 12-40-0 for the production of fertilisers in suspension. Finally, we have in fact never tried the other possible use that is mentioned. We do not even know if it will actually work.

Slide 3 - Here we have the lay-out of the pilot-plant for MAP. All the tanks and pumps are on the ground floor, and as you will see later, the extractor and the solvent recovery column are on the first floor.

Slide 4 - This is part of the ground floor in more detail, showing the battery of tanks in transparent PVC and the pumps. This is a close-up of some of the large tanks, the one on the left contains the solvent which is in circulation and similarly for the one on the right.

- Slide 5 - This is a close-up of the multi-outlet metering pump which is used to control the various additives.
- Slide 6 - A view of the extractors, which, from the technological stand point, is where our work all started. Since this picture was taken we have modified the design considerably and those that are to be used as the prototypes for subsequent scaling up in size, which are referred to in the paper, are not quite of the same shape, although they operate on the same principle.
- Slide 7 - A detail of the extractor showing the light phase, i.e., the continuous phase passing through the process.
- Slide 8 - Another prototype representing stage two of our work on extractors. Originally these were cylindrical, but here they have become rectangular and thus lend themselves more readily to being extended in size, at a later date. We now have much larger scale extractors capable of dealing with 10 tonnes per day of P₂O₅.
- Slide 9 - A view of the still attached to the recovery column for the solvent. This was heated originally by a steam coil, and was one of the stages that caused us the greatest problems on account of the deposition of gypsum scale. As a result of this the design of the equipment is now completely different.
- Slide 10 - The head of the solvent recovery column. The solvent distils over as an heterogenous azeotrope, which on condensing, separates into two phases. The solvent-rich phase is returned to the solvent line and the weak phase flows back down the column.
- Slide 11 - This is the equipment that we used up to a year ago for the separation of the monoammonium phosphate. As you see it consists of a rotary filter, and beneath it the tank holding the solution of ammonium nitrate and monoammonium phosphate in suspension which is cooled before being filtered and washed.
- Slide 12 - This shows the MAP leaving the end of the rotary filter band.
- Slide 13 - A close-up of the MAP cake which has a moisture content of about 9%. By the use of centrifugal drying a figure of 2 to 3% can be obtained.
- Slide 14 - This is a view of the control room in which we

have grouped together the various flowmeters, temperature recorders, etc. In the left foreground there is the automatic analyser which enables us to monitor the P_2O_5 content of the calcium nitrate liquor and thereby check the extraction rate. The apparatus also determines the residual calcium in the purified extract. In short, from these two figures we are able to get a pretty good indication as to the smooth running of the plant.

Dr. J.J. MULCKHUYSE (Mekog-Albatros) : I want to thank the authors for their paper and congratulate them on having given us a clear picture of a very interesting and versatile process. Basically this paper describes the extraction and separation of the P_2O_5 -phosphate rock from a nitric or hydrochloric acid solution with an organic solvent, followed by precipitation with ammonia in the organic phase. Starting from this point many variations and combinations seem possible, some of which are briefly indicated by the authors and serve well to make the audience curious for more information.

This process and some similar processes were meant to avoid the use of sulphur, which, as you all remember, went through a rather spectacular and alarming cost-sequence. Starting in 1960 at a low level of U.S. \$ 23 per long ton, it rose to a peak of around U.S. \$ 50 in 1968, after which it rather suddenly, in two years, went down again to U.S. \$ 25 and even lower.

The authors quite understandably mention the fact that their study was undertaken because of the high cost of sulphur at the beginning of 1965 and the question may be asked whether this object still is reached even at the present low level of sulphur prices. The statement on page 14 that it is only at the sulphur-price of Fr. frs. 80 per ton, which is equivalent to U.S. \$ 14.50, that wet-process acid is in a position to compete with the APEX process, makes an accurate investment cost-estimate very important, especially because the indication given per ton of P_2O_5 is rather high.

1st question - What is the accuracy of the investment figures given ? What contingencies are included ?

2nd question - The losses of 7% on nitric N no doubt are partly due to the organic matter in the phosphate rock used by the authors, which was Moroccan rock.

Do the authors have any figures on nitric N-losses for other types of rock or possibly calcined rock ?

3rd question - Somewhat intriguing is the route aluminium phosphates are following. From the table on page 6 we learn that the partition co-efficient for Al_2O_3 is 0.342, that is to say about 1/3 of the Al_2O_3 is present in the solvent rich phase. Normally, on neutralising phosphoric acid with ammonia, aluminium phosphate precipitates readily before the mono-ammonium phosphate mol ratio is reached. Is this not the case in the isobutanol rich phase ?

Some points I missed altogether in this paper. Possibly they were left out for reasons of briefness. It would nevertheless be interesting to have some information on :

4th question - Corrosion and material of construction. Nitric acid/hydrochloric acid and fluorine compounds, as we all know, are not easy to live with in a plant.

5th question - Is there no need for a filtration step between this solution and extraction ? Surely some undissolved matter remains in the slurry and should be removed before the extraction stage. Any remains of organic matter in the phosphate rock may cause very persistent foamy or emulsified layers.

6th question - No mention is made of exhaust fumes or waste gases. Is there a need for a scrubbing system ?

7th question - In your comments mention was made of a gypsum deposit and gypsum scaling. Can you provide us with some more information about it ?

Myself and many others will be very interested in the latest developments as mentioned in the summary and on page 15, viz. the purification of wet-process acid to a degree which apparently makes direct production of feed grade phosphates possible.

No doubt the audience will be grateful for the disclosure of any process information the authors feel free to give at this stage.

Mr. COUSSERANS : With regard to the first question, concerning the figures for capital investment, I have already pointed out that these were derived from estimates based on the present state of our investigation, i.e. after the pilot-plant trials. The figures have been worked out by our cost office, but it is obvious that they can only be in the nature of an approximate estimate, which we can confirm

only when the detailed costs have been worked out for the proposed 100 tonnes per day installation. The figures take into account the difficulties we have encountered in the scaling up of the size, but obviously since we are at present only at the 10 tonnes per day stage, there remains a step of tenfold magnitude still to be accomplished.

Regarding the observed losses of 7% in nitric nitrogen, these do not arise, in the main, from the presence of organic matter. They occur during the conversion of calcium nitrate to calcium carbonate and ammonium nitrate, and also during the difficult operation of filtering the calcium nitrate. Actually, it is the nitrates of calcium and ammonium retained by the calcium carbonate that are the greatest source of these losses. During the six months we have been using uncalcined phosphates, we have not noticed any increased consumption (of nitric acid) due to the presence of organic matter. As to the alternative types of natural phosphate that we have tried in the laboratory, these have been from several sources, Israel, Kola and Carolina, but we have been unable in the laboratory to get an accurate indication of the amounts of nitric acid these require. However, we have observed that these phosphates differ in behaviour to some extent from one source to another, and that they require slightly different operating conditions. However, these phenomena are still not perfectly understood.

The third question deals with the fate of the aluminium. Certainly, a partition coefficient of 0.34 for aluminium between the aqueous and solvent phases is an indication that aluminium salts will tend to go into solution in the solvent phase. In fact the crude extract as it leaves the extractor contains a not inappreciable amount of the aluminium, as well as a fair quantity of calcium nitrate. The function of the purification stage is the removal of all these impurities by further extraction with the ammonium nitrate solution and their return to the primary extractor. Only very small amounts of aluminium, iron, and magnesium have been found to be present in the MAP.

The fourth question dealt with the problem of corrosion. The first stage of the process, consisting of the nitric acid digestion, is one of our traditional operations. Here the question does, I think, arise, but in our large scale units it has been overcome satisfactorily, but I do not know by what means. In those stages which fall strictly within the APEX process itself, i.e. extraction, purification and separation, there is virtually no corrosion problem, since they are carried out at relatively low temperatures. The maximum temperature encountered in the process is in the region of 60-70° C at the solvent recovery stage.

The extractors and the separator are made from PVC plastic. The remainder of the plant, i.e. the solvent recovery column is in ordinary stainless steel coated with a material to prevent the build-up of gypsum and other substances including, of course, silica.

The fifth question concerns the possible need for a filtration stage between digestion and extraction. When we commenced our investigation of the process, we encountered numerous difficulties due to the presence of insoluble matter in the digestion liquor. When we attempted to clarify this liquor we encountered enormous difficulties and this led us to devise an extractor that would deal with liquids containing matter in suspension without becoming clogged. The problem has now been solved, and for over a year we have been using extractors of this type and without the need for them to be cleaned out.

The sixth question deals with organic matter. This has not been a particular snag for us. Obviously it has made the separation process a little more difficult, owing to the tendency to gel formation. However, this has not been a major problem in the smooth running of the process. In this instance I am speaking solely of Moroccan phosphate, as this is all we have tried in the pilot-plant.

The seventh question concerns the gypsum that arises from the natural phosphates. These always contain a small amount of SO_4 and this is sufficient to create problems when we heat the calcium nitrate solution to recover the solvent. This has been one of the most difficult sources of trouble that we have met.

Finally, you raised the question of the process that we have developed recently for the purification of green wet-process acid. This process embodies liquid-liquid extraction with the object of attempting the direct production of pure phosphates by a single extraction followed by purification. Several processes have been developed already for this, but, in general, the yield of P_2O_5 is rather low, or it is necessary to add a salt to modify the partition coefficient so as to increase the yield of P_2O_5 . In the process on which we have worked, and about which I cannot, at present, give you many details as it is not yet fully covered by patents, there is no addition of other materials. It consists simply of an extraction, followed by purification and neutralisation, broadly speaking in the same sequence as in the APEX process. We have found the operating conditions that enable us to obtain extraction rates comparable with those of the APEX process, i.e. of the order of 98%. At this moment, I cannot say more to you about this.

Mr. Y. DETUNCQ (Péchiney-Saint Gobain, France) :

1. On page 14 of your paper you refer to a solvent process for the purification of phosphoric acid. Is the solvent the same as that in the APEX process or is it another alcohol ?
2. In your conclusions you have estimated a 13% reduction in the cost of P_2O_5 , as compared with wet-process phosphoric acid. Can you state the price of wet-process phosphoric acid and of sulphur that you used for this calculation ?

Mr. COUSSERANS : In the case of the purification of phosphoric acid, I can tell you that the solvent used is of the same family as that in the APEX process. We have under investigation several solvents, but it is quite probable that we shall adopt isobutanol for the basic reason that it is by far the cheapest. The second question is relative to the costs. The price of wet-process P_2O_5 was taken as 554 Francs per tonne and that of sulphur as 160 Francs per tonne, which is roughly equivalent to 26 dollars per short ton.

Mr. M. GITTENAIT (Ugine Kuhlmann, France) : You point out that, when you recrystallise only part of the calcium nitrate, the yield of P_2O_5 is no more than 94%. Can you tell us if the drop in yield is due to a loss of P_2O_5 which is occluded in the crystals of calcium nitrate tetrahydrate, or to a drop in the extraction efficiency. High concentrations of calcium nitrate often favour the extraction of phosphoric acid. On the other hand have you been troubled with problems of emulsion formation, especially during the re-extraction stage ? If so, how have you overcome them ?

Mr. COUSSERANS : As to the first question, about the loss of P_2O_5 . The drop in yield is due essentially to the fall in the partition coefficient for P_2O_5 which occurs when the calcium nitrate content falls. The loss of P_2O_5 by occlusion in the calcium nitrate tetrahydrate is only of the order of 1%, the remainder of the loss being due to the decrease in the partition coefficient obtaining at the extraction stage.

The second question. We have had a great deal of trouble, and for a long time this was a major difficulty in the process. We have succeeded in eliminating it, but I

cannot tell you how.

I should, perhaps, mention that at the outset we were working with the object of producing phosphoric acid, and not monoammonium phosphate. However in this case one meets problems due to the presence of fluoro-silicates or of silicon tetrafluoride, which on hydrolysis give silica gels, and these virtually prevent any separation from taking place. When we changed to monoammonium phosphate, we found that many of these difficulties disappeared, but even so, it was necessary for us to find a complete cure for these problems.

Mr. M. NOIRBENT (Kaltenbach, France) : My first question deals with the purity of the calcium nitrate produced. The APEX process appears to be most attractive from the point of view of the P_2O_5 extracted. However, there is a problem that will be difficult to overcome when the process is eventually operated on an industrial scale. This is the gradual build-up of impurities that will occur in the calcium nitrate solution if this solution is to be treated with ammonia and carbon dioxide, followed by removal of the precipitated calcium carbonate. My question is, therefore, what can be done with this precipitated calcium carbonate, which unlike the pure material from certain other processes, will in this case be impure ? What will be the use for it ?

Secondly the author made a great point of the 98% yield of P_2O_5 . Can he tell us what happens to the remaining 2% which represents a relatively small loss in a complete process for the preparation of P_2O_5 ? On the other hand the yield of nitric nitrogen seems a little low. Is there not a case here for some caution when dealing with a new process, or can the loss of 6-7% nitric nitrogen, which is fairly substantial, be explained ?

Thirdly, the yield of ammoniacal nitrogen is 94%. Can you give the reasons for the loss ?

Finally, my last question deals with the alternative method of converting the calcium nitrate solution which is, indeed, of great academic interest, viz., the double decomposition with potassium chloride, giving calcium chloride and nitrate of potash. By what type of operation does your Company envisage obtaining the purified potassium nitrate, and for such operation what chemical and physical methods will you adopt ? Finally, what do you see as the outlets for the calcium chloride obtained ?

Mr. COUSSERANS : At the moment we do not know what to do with the calcium carbonate, which is certainly impure, containing as it does the major part of the impurities coming from the phosphate ore. A very small quantity could be used as a filler. As for the remainder, there seems no alternative but to discard it.

The second question concerning the 98% yield of P_2O_5 . The other 2% occurs mainly in the calcium nitrate solution from which it separates in part with the calcium carbonate and is consequently lost, and also in part with the ammonium nitrate where it is lost as well. Regarding the yield of nitric nitrogen and also that of ammoniacal nitrogen, these losses are due to the retentivity of the calcium carbonate which becomes impregnated with the nitrate of calcium and ammonia, and is very difficult to wash completely. We have not looked deeply into this aspect, since others have already done this much better. We were content to use the rotary filter that we had available and which only incorporates a single washing cycle. This is not too satisfactory, but the figures I have given are those actually obtained with this type of equipment, and it is possible that this could be improved.

The fourth question concerns the conversion of calcium nitrate to potassium nitrate. In essence this process makes use of the relative insolubility of potassium nitrate, and we work in the presence of a third substance which still further reduces the solubility of the potassium nitrate and also prevents the formation of double salts. The potassium nitrate crystallises out immediately of its own accord. The physical and chemical operations adopted involve essentially the bringing together of the potassium chloride and the calcium nitrate solution, adding the third substance, and recrystallising the potassium nitrate with cooling. This gives yields better than 95% both for K_2O and nitric nitrogen. With regard to the by-product, calcium chloride, there is a possibility of its being used as a snow-clearing agent. I must point out that this application is still rather embryonic as we have not yet carried out the pilot stage studies. This will form part of next year's programme.

Mr. P. MORAILLON (Péchiney-Saint Gobain, France) :
Mr. COUSSERANS has already answered several questions included in a note that I forwarded to him. Nevertheless, I would like, if possible, to have some additional clarification of points raised in my questions.

In my question 2 I asked if the organic matter from the uncalcined Moroccan phosphate accumulates in the solvent to

the stage where the latter becomes unusable.

My question 3. I am surprised by the statement that the presence of calcium fluoride in the calcium nitrate does not adversely affect the treatment with ammonia and carbon dioxide, since it should lead to the precipitation of calcium fluoride and silica, thus rendering filtration extremely difficult. This is probably the explanation for the low yield of nitric nitrogen.

Question 5. Have the authors considered the problems raised by the use of the moist pure MAP for the manufacture of granulated NPK fertilisers, namely the problems of metering and granulation ?

Question 6. Manufacturing costs : in their assessment of costs, have the authors taken sufficient account of all the factors likely to increase the production costs of nitric and ammoniacal nitrogen, eg. the consumption of steam and electricity that a sulphuric acid plant provides at no cost, the use of CO_2 , which is not completely free (it has to be dried), etc. An approximate calculation would show that the total additional costs are of the order of 191 Francs per tonne of P_2O_5 , as against a saving of 0.92 tonnes of sulphur per tonne of P_2O_5 . The equivalent price of sulphur thus works out $191 \times 1/0.92$ which equals Fr. 208 per tonne.

I was surprised at a sulphur equivalent of Fr. 80 per tonne in the case of the MAP, and of Fr. 45 per tonne in the case of the 18-38-0 binary.

Question 7. Disposal of CaCO_3 : many plants making wet-process phosphoric acid take advantage of the solubility in water of gypsum in order to dispose of it either in a fast-flowing river, an estuary or direct into the sea. This method of disposal would not seem to be possible in the case of calcium carbonate which is insoluble. Thus additional costs will also be incurred in disposing of it.

Question 8. Limitations of nitric acid digestion processes : the great disadvantage of all nitric acid digestions is the consequent production of a large quantity of ammonium nitrate (6.2 tonnes per tonne of P_2O_5), which raises commercial and marketing problems. Furthermore, these processes do not allow the manufacture of PK fertilisers, which have undergone rapid development in France. In the case of liquid NP and NPK fertilisers, which do not contain nitric nitrogen, the use of the APEX process would increase the quantity of unwanted NH_4NO_3 and also the problem of getting rid of it.

For these reasons, and for several others, the introduction of a nitric acid digestion process into an existing plant would be difficult to justify on economic grounds, despite the obvious technical merit of certain processes such as the APEX. Nevertheless, the development of such processes is of considerable interest to the fertiliser industry : it will enable the industry, should the need arise, to counter any excessive increase in the price of sulphur. Processes such as the APEX could become very attractive if the price of sulphur were again to rise to a prohibitive level.

Mr. COUSSERANS : Mr. MORAILLON's question 2 relates to the possibility of a build-up of organic matter in the solvent to the point at which it would become unusable. Certainly some of the organic matter does go into the solvent and moreover this is easily confirmed by the colour which the solvent assumes. However, I can say that after two months working, without renewal, the solvent does not contain any appreciable amount of extraneous organic matter - say no more than 0.5%. Its distillation range and solids content are normal, and at all events, we have not detected any drop in activity. However, the solvent now contains organic matter, and it is more highly coloured than when we were using calcined phosphate. On the basis of these two months' working, I do not feel that we shall have problems in longer periods of operation. I have the impression that a certain equilibrium concentration is obtained, and that part of the organic matter is insoluble in the solvent.

Question 3. I had not, perhaps, realised that the filtration of calcium carbonate is considered to be a difficult operation. It is a little more difficult to filter than gypsum, but we began to study the conversion to get some practice in the use of calcium nitrate tetrahydrate obtained from the classical Odda process, which was thus virtually free from impurities. When we changed over to the calcium nitrate solution from the APEX process, which in addition to the calcium nitrate and water, contains the attendant impurities together with ammonium nitrate, we found that it did not filter too badly. This should not be taken to mean that the process was easy, but the filtration rates were of the same order in both cases. On the other hand the presence of the impurities makes the washing more difficult and the yield certainly drops as a consequence. The small percentage losses of nitric and of ammoniacal nitrogen are due largely to the presence of these impurities. Here again, the operation has been carried out in equipment which is not, perhaps, well-suited for this

purpose, as the washing is carried out whilst the material is still on the filter cloth. I believe that for a filtration process of this nature, it would perhaps, be preferable to repulp the calcium carbonate and wash it en masse, but we have not tried it.

Question 5, the use of moist pure monoammonium phosphates in the manufacture of granular NPK fertilisers. We have considered this to the extent of rejecting the possibility, as we encountered too many difficulties when feeding the correct amounts of the moist pure ammonium phosphate to the granulator. On the other hand what we have done is to granulate, experimentally, monoammonium phosphate alone, or as a mixture with ammonium nitrate, i.e., as 5-25-0 binaries. But we have never succeeded in granulating ternaries correctly.

Concerning the question about costs which is indeed formidable. Clearly you have done a very simple calculation which gives results very different from those which we obtained. However, we did not do the calculation on this basis. We based the price of wet-process phosphoric acid on the data that we were given at the last meeting of the Fertiliser Society in London, and we chose an up-to-date process which is not, perhaps, the best or the most economic. We have credited the APEX process with the value of the ammonium nitrate it produces, based on the cost of direct-process ammonium nitrate in the same form, i.e., as a 96% solution. The value of this credit has been worked out for us by our own factory. Because our calculation was not carried out in the same way as your own, I am unable to reply to your question immediately or to explain the discrepancy. Obviously this is considerable, but I have not got all the details at hand to answer this question.

I must admit that we have made no allowance for the disposal of the calcium carbonate, nor have we placed any value on it. Similarly in the case of carbon dioxide, which is freely available in our factory, and consequently we tend to think of it as being free.

Furthermore, you speak of the limitations of nitric acid digestion processes ; it is true they produce a great deal of ammonium nitrate, especially the present process. Nevertheless, we feel that it could be fairly easily integrated into our factory, at Toulouse, where we are already producing considerable quantities of ammonium nitrate, and some of that produced by the APEX process would simply replace part of the ammonium nitrate that is currently produced by the direct process. Thus there would be no problem in this particular instance. But in the case of an entirely new plant or one

which does not already produce much ammonium nitrate, it is obvious that a nitric digestion would create many problems.

Mr. A. DAVISTER (Prayon, Belgium) : I would like to put two questions relating to the end-products. First, the monoammonium phosphate. Can you give us the particle size of the monoammonium phosphate which you obtain ? Then, the solution of ammonium nitrate. What is the level of impurities present in this solution, bearing in mind that it is produced from the phase which retains all the impurities from the phosphate ore ?

Mr. COUSSERANS : The average crystal size of the monoammonium phosphate is 150 microns, which means that they can be separated easily by centrifuging. As to the impurities present in the aqueous solution of ammonium nitrate, I think the answer is to be found, by implication, from the quality of the ammonium nitrate produced, which is detailed in the text. We have concentrated the ammonium nitrate on a semi-industrial scale. We have made 30 tonnes of it in order to see if we met any problems due to the clogging of the evaporators. No problems were encountered, and the composition of the ammonium nitrate, after granulation, is as stated in the text. Since there was no deposition of impurities on the walls of the vessels, these must have remained in the solution. Possibly they were eliminated during the concentration process, at least partially, but we do not know exactly at what stage it could have occurred. What we are sure of is that there was no trace of organic solvent, which is, of course, very important.

Mr. NOIRBENT : It seems that part of the savings in cost of the APEX process is being dissipated by the conversion of the calcium nitrate solution. I feel that this is the moment to raise again the problem of nitrate of chalk 15.5%, which could resolve the general problem of the economics of the APEX process in a most favourable manner. It ought to be possible to come to a very attractive selling price for this nitrochalk in this situation where, on the one hand, there is a very substantial saving in the capital outlay involved and in the elimination of sulphur from the production of P_2O_5 , and on the other hand a considerable reduction in the quantity of nitrogen required to produce one tonne of P_2O_5 . What does the author think of this suggestion ?

Mr. COUSSERANS : I am in complete agreement with you. The nitrochalk produced by this process would be very economic. This was the first possibility that we foresaw, and I have to say that it met with such an unenthusiastic reception from the merchants that there is nothing more to be said about it. Nitrochalk has been ruled out by the stroke of a pen, and we must find some other outlet for the material. However, I remain convinced that economically nitrochalk would have provided the best solution.

Mr. NOIRBENT : I feel that you have been too hasty with the stroke of the pen, because in some countries there are sizeable markets for nitrochalk.

Mr. COUSSERANS : Yes perhaps so. There is another possible outlet with which you are familiar, i.e. urea/nitrochalk, with which we have also done some work. It is a very good fertiliser, but it has had no more success than the other.

Fig. 1

DIAGRAMME TERNAIRE
DE SOLUBILITE

MISCIBILITY TERNARY
DIAGRAM

$H_3PO_4 - H_2O - iBuOH$
at 25°C.

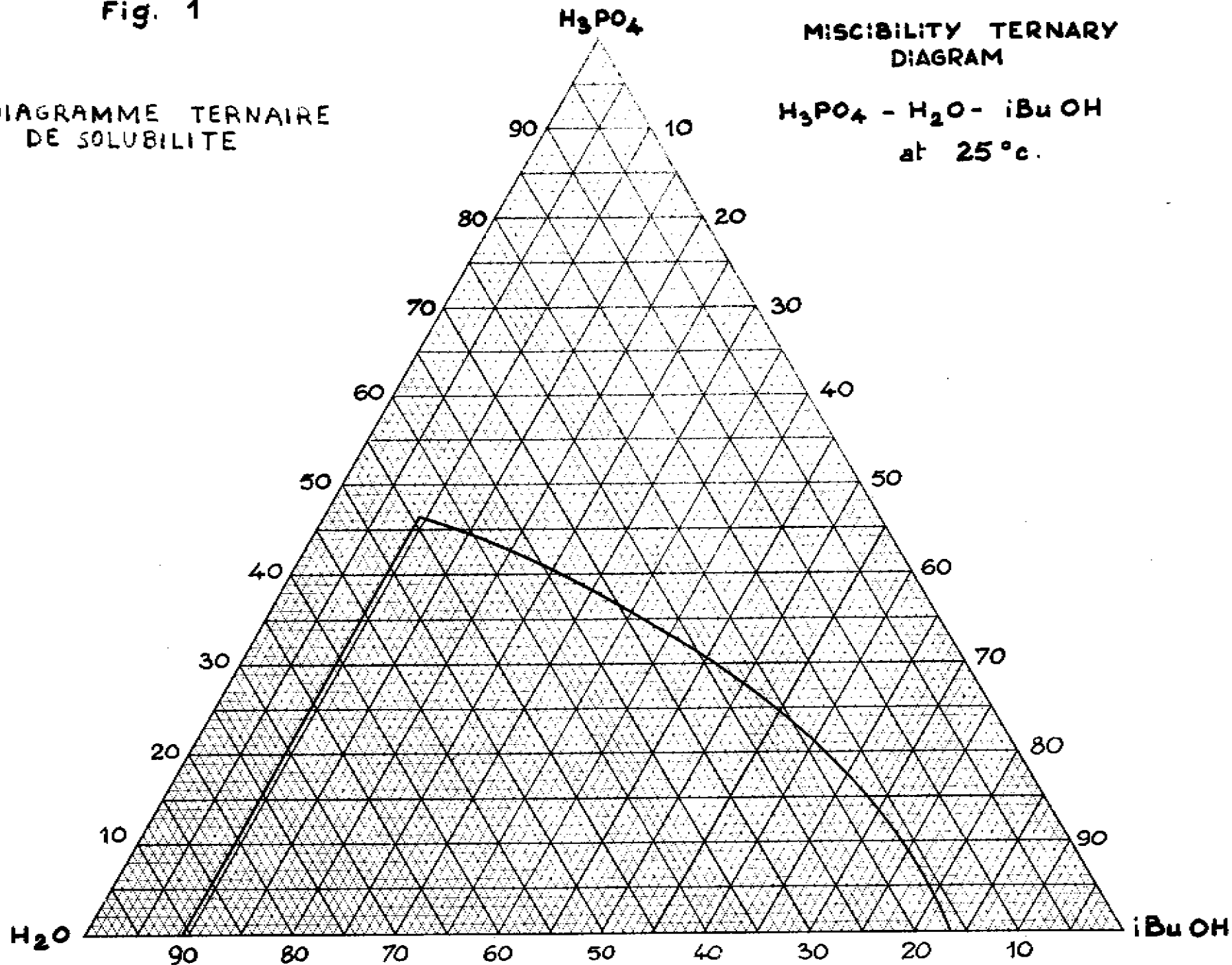
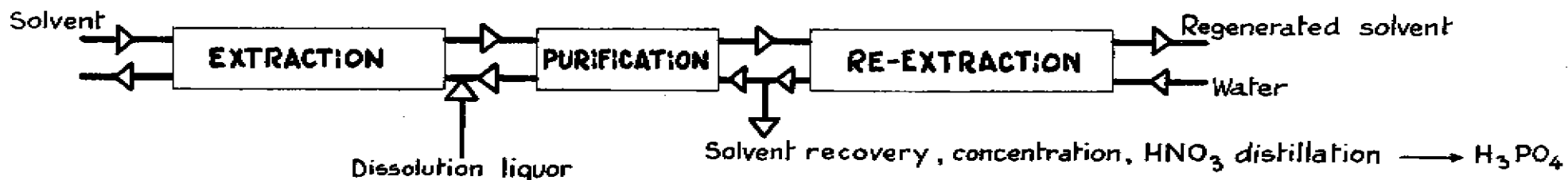


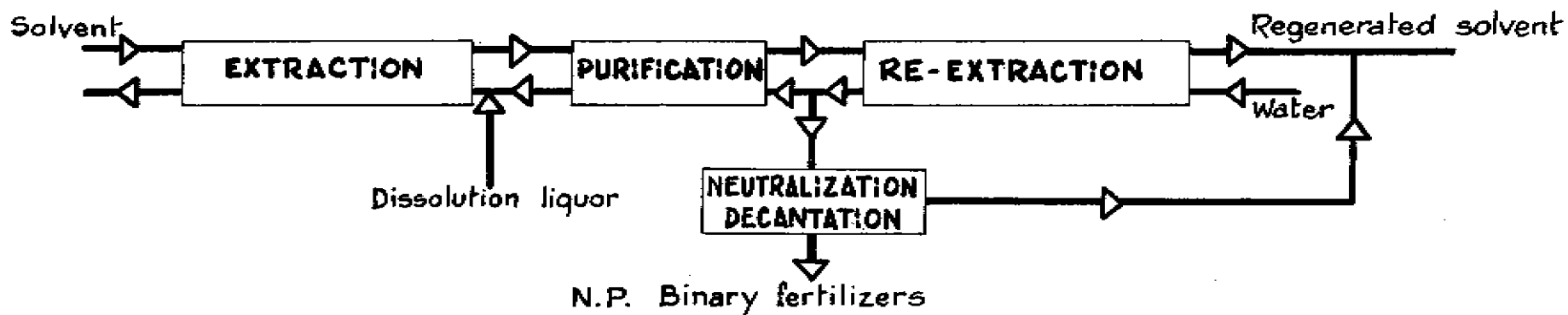
Fig. 2

THE VARIOUS EXTRACTION FLOW-SHEETS

A - CONVENTIONAL FLOW-SHEET

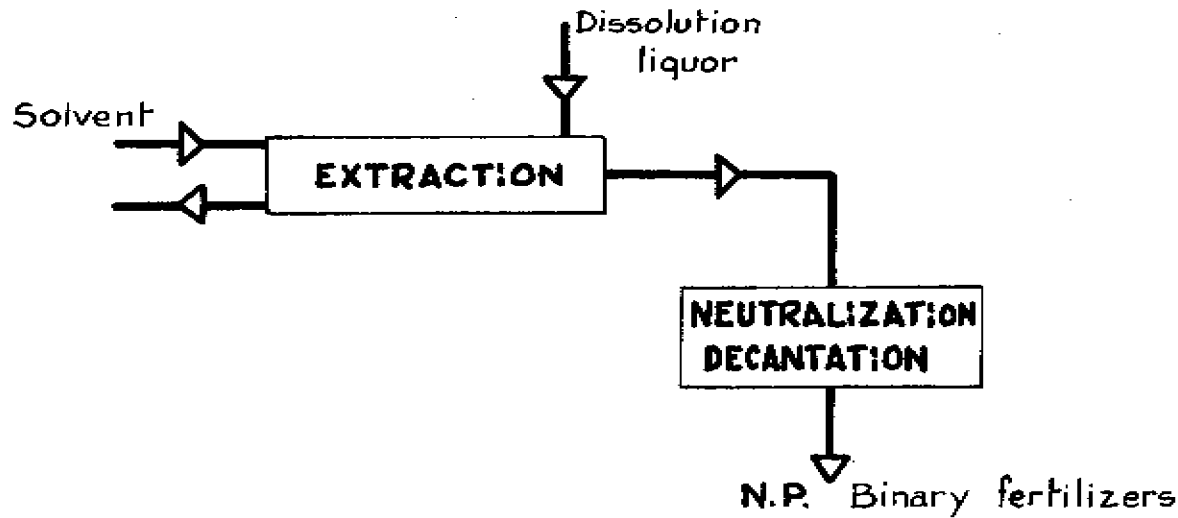


B - STAM:CARBON FLOW-SHEET WITH AMMONIA NEUTRALIZATION

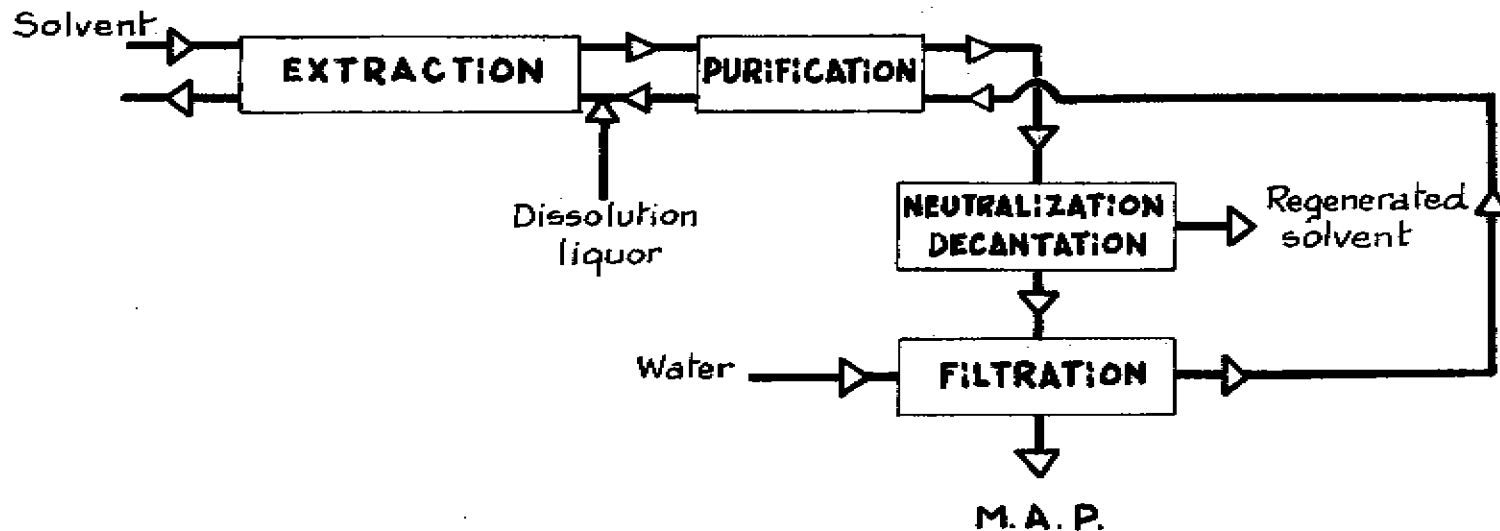


THE VARIOUS EXTRACTION FLOW-SHEETS (CONTINUED)

C - FLOW-SHEET OF TIPPY OY PROCESS



D - FLOW-SHEET OF THE A.P.E.X. PROCESS



APEX PROCESS FOR PRODUCING M.A.P. BY SOLVENT EXTRACTION

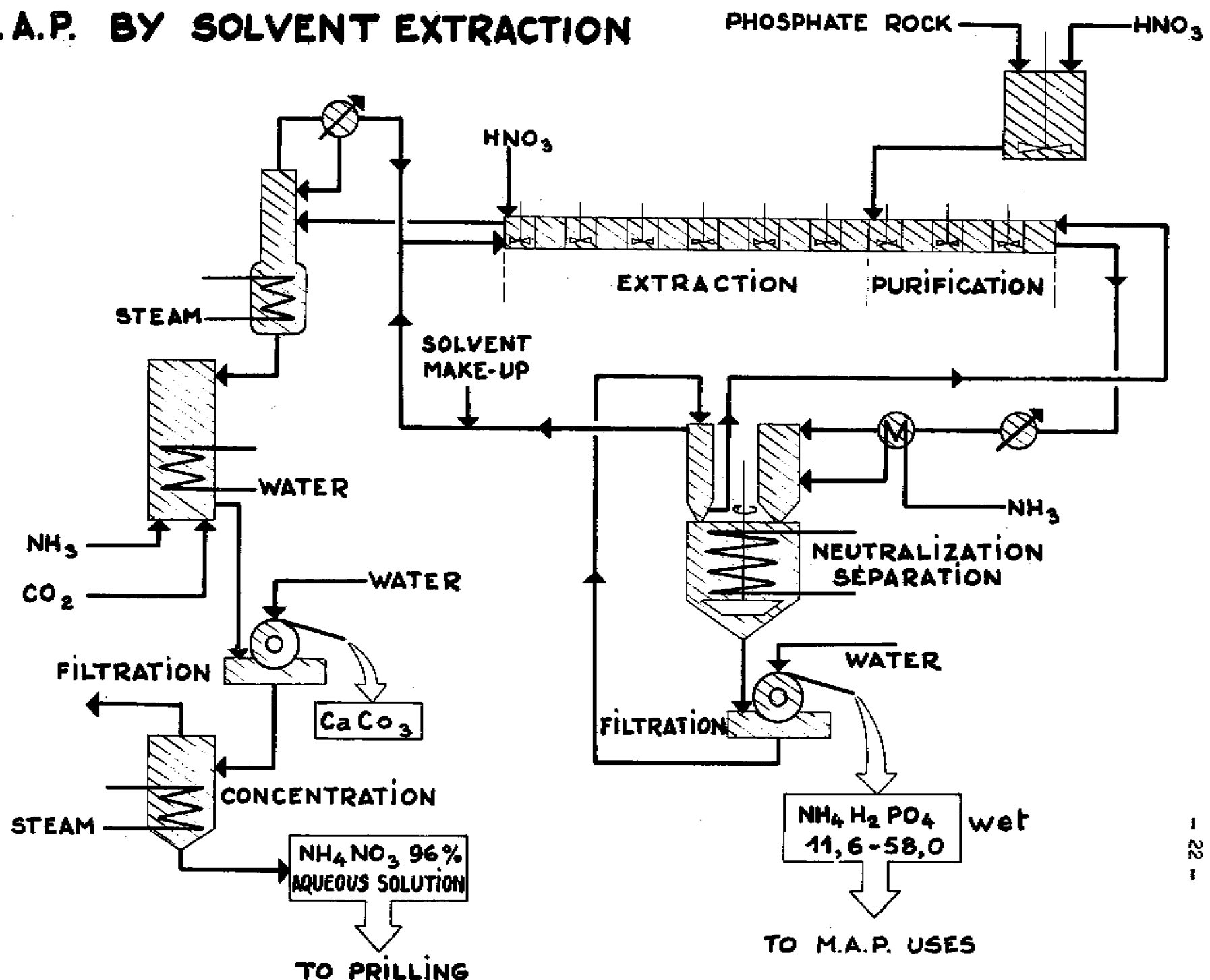


Fig. 4 M.A.P. IS A VERSATILE COMPOUND -2-

WET M.A.P. BY APEX PROCESS

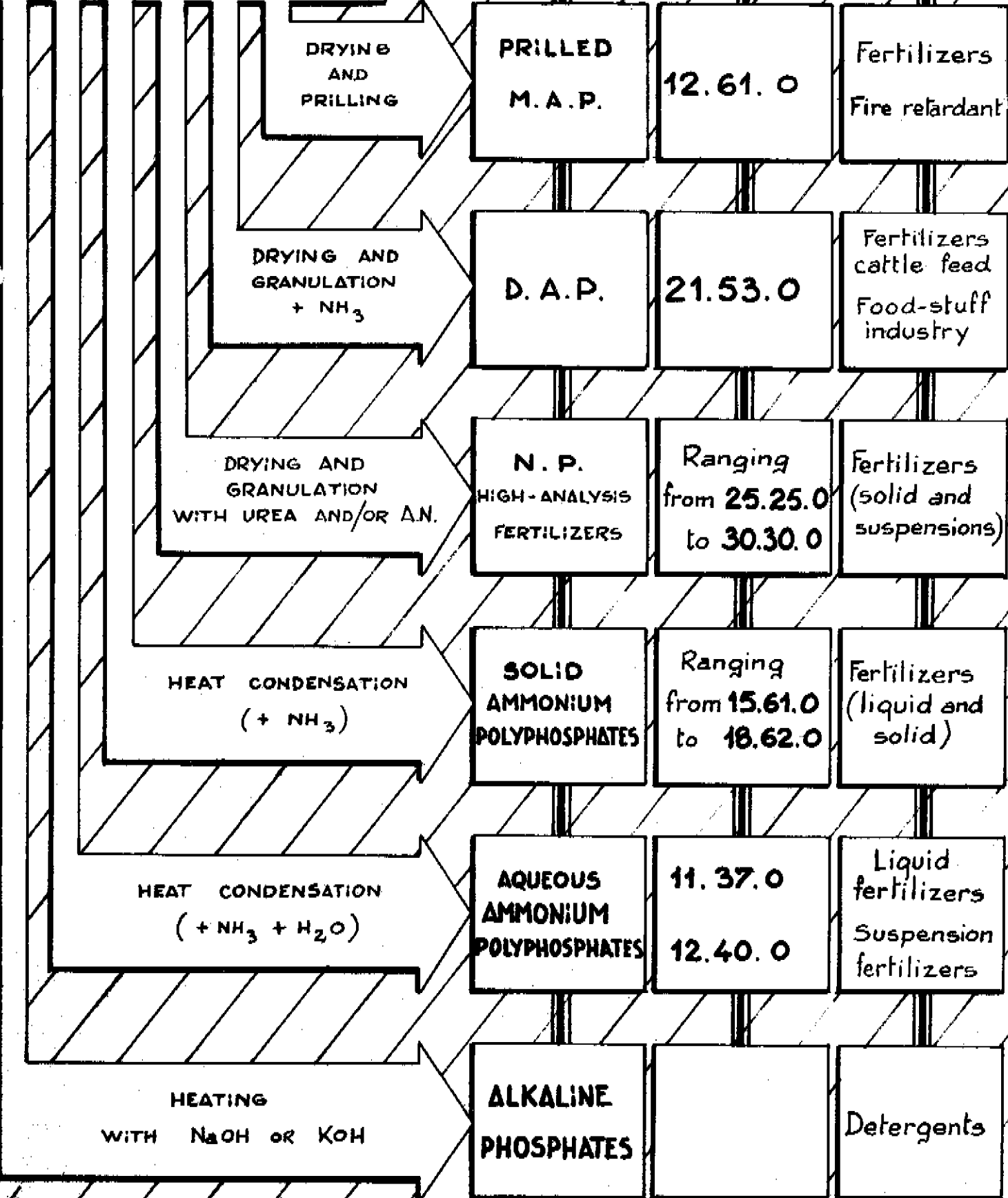


Fig. 5 - Table of the principal variants of the APEX process

* * * * *

Digestion acid	Phosphate product	Co-products
Nitric	MAP (pure or technical) DCP DPP NP Binaries (MAP + NA)	AN or PN
Hydrochloric	MAP DCP MSP	
Sulphuric (purification of PA by wet process)	DAP DCP DPP MSP	