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

POTASSIUM MONOPHOSPHATE PRODUCTION BY SOLVENT EXTRACTION

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1. INTRODUCTION

Monopotassium phosphate shows peculiar characteristics as a fertilizer material. The high plant food contents that can be achieved by combining in the same molecule two of the three main plant nutrients, phosphorus and potassium, are evident. Since this product does not contain any chlorine, it is especially well suited for application on tobacco, potatoes, or any crop that may be sensitive to chlorine.

In addition, it is convenient to point out those characteristics of monopotassium phosphate that make it very attractive as an intermediate raw material for various applications.:

1. The high water solubility allows the production of liquid fertilizers with a high potassium and phosphorus content.
2. The ability to be ammoniated, in addition to its high water solubility, makes it of great interest in the granulation of high analysis NPK fertilizers.
3. The ability to undergo thermal dehydration brings about the formation of various high grade potassium phosphate polymers of varying solubility.
4. The excellent behaviour regarding phosphorus and potassium uptake by crops in agronomic studies, makes it an excellent fertilizer material.

Methods of producing monopotassium phosphate for the fertilizer industry have been investigated over many years and those given in the literature may be classified into three main groups as follows :

1. Processes based upon the direct neutralization of wet phosphoric acid with a solution of potassium hydroxide or potassium carbonate (1). This type of process is not economically interesting due to the use of high raw materials.
2. Processes based upon the direct reaction of wet phosphoric acid with KCl. These processes require excess acid and high temperatures to remove the chlorine as hydrochloric acid, since the reaction is negligible at relatively low temperature. This high reaction temperature results in the final product being potassium metaphosphate $(KPO_3)_n$ with poor water solubility characteristics. Moreover, excess acid must be appropriately neutralized with a potassium alkali. All these difficulties have been overcome in the IMI process (2) by the clever use of a heating fluid and 100 % excess acid which leads to a solution of monopotassium phosphate in phosphoric acid as the reaction product.
3. Processes based on the reaction of sulphuric acid, rock phosphate, and potassium bisulphate to yield a solution of monopotassium phosphate in phosphoric acid and gypsum, the latter being separated by filtration, following a technology similar to the production of wet phosphoric acid. Processes of Goulding Fertilizer Ltd (3), Pennzoil Company (4), and S.A. Cross (5) are representative of this group.

This paper will try to describe a new process for the production of monopotassium phosphate based upon the anion exchange behaviour of the alkyl amines. Development of this process has been jointly undertaken by UNION EXPLOSIVOS RIO TINTO and TECNICAS REUNIDAS S.A. through their subsidiary company ESPINDESA.

The main advantage of this new process is the direct production of a granular monopotassium phosphate free of any phosphoric acid contamination which makes it especially suitable for polymerization by thermal dehydration.

The various stages of the process have been developed on the laboratory scale and a pilot plant for process demonstration will be erected in the very near future.

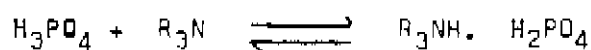
2. PROCESS FUNDAMENTALS

The Espinosa process is based on the direct precipitation of KH_2PO_4 in an organic phase constituted by an alkyl amine, a modifier, and commercial kerosene. Amines are able to extract mineral acids to form their corresponding salts and are excellent anion exchangers. It is well known that the selectivity of anion exchange ability of these amines is generally in the following order :

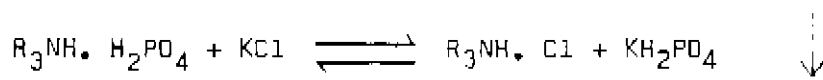


Therefore, PO_4H_2^- can be substituted by Cl^- but it is almost impossible to substitute directly Cl^- by PO_4H_2^- .

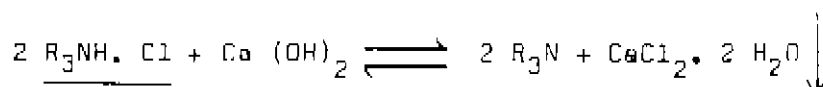
These amines have the property that, when they come into contact with aqueous acid solution thereof, they combine well with acid molecule contained in the aqueous acid solution to produce salts of these amines. For example, when equimolar amine and phosphoric acid are brought into contact, monoamine phosphate is formed according to the following reaction :



If later this organic phase containing the monoamine phosphate comes into contact with solid KCl , an anionic exchange takes place between PO_4H_2^- and Cl^- ions by which the amine is transformed into amine chloride and the solid KCl into $\text{H}_2\text{PO}_4\text{K}$ which is the desired product, according to the reaction :



In order to recycle this organic phase to phosphoric acid extraction, it is necessary to convert the amine chloride into free amine, which is accomplished by lime treatment according to the following reaction :



Thus, this process produces a high water soluble calcium chloride as a solid waste easy to dispose of.

3. PROCESS DESCRIPTION

The present process will be more easily explained with reference to the accompanying flow-sheet given in figure 1.

3.1. Monopotassium phosphate precipitation

Commercial wet phosphoric acid is brought into contact with the regenerated organic phase containing free amine in a conventional agitated reactor in order to extract the phosphoric acid into the organic phase resulting in monoamine phosphate. The main gist of this operation is to form a unique liquid phase. In fact, the composition of the organic phase must be such that the amount of water fed to the system with the phosphoric acid does not form a separate aqueous phase. This has been achieved just with one of the ten alkyl amines tested, and only using a suitable modifier.

The reaction between the monoamine phosphate contained in the organic phase and solid KCl is carried out countercurrently in three stages. Each stage includes a mixer and a thickener. The overflow of each thickener constitutes the organic liquid feed to the next mixer and the slurry underflow from each thickener becomes the solid feed to the previous mixer. The solid KCl is fed to the last mixer. The monopotassium phosphate product is removed from the underflow of the first thickener.

This technique of multiple contacts in countercurrent is essential for completing the reaction. As a matter of fact, there is an equilibrium between the solid and liquid phases in such a way that phosphate and chloride concentrations in the organic phase depend upon the composition of the solid phase. Therefore, even though there is an enhanced extraction of chlorides against phosphates, an equilibrium concentration of phosphates in the organic phase and chlorides in the solid phase is reached in a single contact. In other words, substitution of phosphates by chlorides in the organic phase is not 100 % accomplished in a single contact, since one cannot help reaching an equilibrium value between both phases. Typical analysis of both phases in the three stages are given in table 1.

TABLE 1

Analysis of solid and organic phases

	<u>Cl⁻ %</u>	<u>P₂O₅ %</u>	<u>K₂O %</u>
1st stage solid (product)	0.24	47.6	31.4
2nd " "	5.93	42.1	37.5
3rd " "	29.30	9.35	51.2
	<u>Cl⁻ (g/l)</u>	<u>P₂O₅ (g/l)</u>	<u>SO₄²⁻ (g/l)</u>
Organic feed	-	48.2	3.40
1st stage organic	11.6	23.4	2.90
2nd " "	21.0	6.2	1.50
3rd " "	24.4	0.6	0.05

The PK product from this process has an average analysis of 0-48-31 (N-P₂O₅-K₂O), although analysis as high as 0-50-30 have been achieved. Chloride content can be made as low as one wishes depending upon the number of stages in countercurrent and the amine concentration in the organic phase. However, three stages are enough to obtain a product containing less than 0.50 % chlorine, as may be noticed in table 1.

By choosing suitable conditions under which the PK precipitation reaction in the organic phase is carried out, one can obtain the product in granular form with a size distribution rather uniform ranging from 1 to 3 mm. This feature of the process is of overriding importance from an economic point of view, since this is the only way to decrease considerably the amount of organic material carried away in the solid product.

The impurities of the wet phosphoric acid are distributed between the PK product (impurities of inorganic type such as sulphates, iron aluminium etc.) and the organic phase (soluble impurities of organic type)!

The efficiency of the reaction is 98.5 % for P_2O_5 and higher than 99 % for K_2O , feeding to the system a slight excess of phosphoric acid above stoichiometry with respect to chlorides and a still higher excess of free amine, about 10 %. Thus, a product with no chloride and no free phosphoric acid is obtained.

3.2. Amine regeneration

The overflow of the last stage thickener is the "spent" organic phase containing practically all the amine in form of chloride salt. This liquid passes to a special mixer where it is brought into contact with slaked lime. The resulting slurry is sent to a thickener where a completely clear organic liquid containing more than 95 % of the amine in its free form is separated in the overflow and sent back to the first precipitation stage mixer. Thickener underflow contains the solid residue consisting mainly of calcium chloride, excess lime, and dissolved impurities of phosphoric acid which are insolubilized when the medium pH changes to alkalinity.

There again, the conditions under which the reaction is performed are very important in order to obtain a solid residue with good filtration characteristics to decrease the organic material carry away.

3.3. Solvent recovery

The two solids leaving the reaction system : PK product and residue, even after their filtration, carry away a considerable amount of organic phase ranging from 5 to 8 % by weight. In order to make this process economical, it is absolutely necessary to recover all this organic material. Thus, filter cakes are slurried in a cheap hydrocarbon solvent to remove the organic material and, after two stages of washing and filtration, a solid cake practically free of organic impurity is obtained. The filtrate is a solution of organic phase in the solvent used.

Taking into account the physical characteristics of the solid products, washing efficiencies higher than 98 % can be achieved in this operation, so that amine losses are kept below 0.07 % of the PK product.

The solvent used for solid washing is separated from the organic phase by distillation from the filtration liquors. The organic phase is recovered at the bottom of the column.

3.4. Waste disposal

Washed solid residue is dissolved in a small water stream for which sea water can be used if available. Most of the residue is water soluble except the small amount of unreacted lime and the hydrocarbon solvent carry away. The latter is separated in a conventional settler and the aqueous solution is finally sent to a gravity API settler or to a flotation unit where its hydrocarbon content is lowered down to less than 100 ppm. In this way, the aqueous solution of calcium chloride may be discharged into the sea and a significant part of the solvent is recovered and recycled back to the washing section.

4. PRELIMINARY COST ESTIMATION

An estimate of the auxiliary materials and utilities necessary to produce one metric ton of monopotassium phosphate by this process leads to the following costs for the actual conditions at Huelva, Spain :

Capacity	50,000 MT/year of P_2O_5
Chemicals	\$ 17.77
Utilities	1.24
Labour	1.50
Capital cost *	8.00
	<hr/>
Total cost	\$ 28.51/MT of PK (0-48-31)

* This figure includes amortization interest, maintenance and overheads.

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PHOSPHORIC
ACID 52%

POTASH
KCl 60%

LIME
 $\text{Ca}(\text{OH})_2$

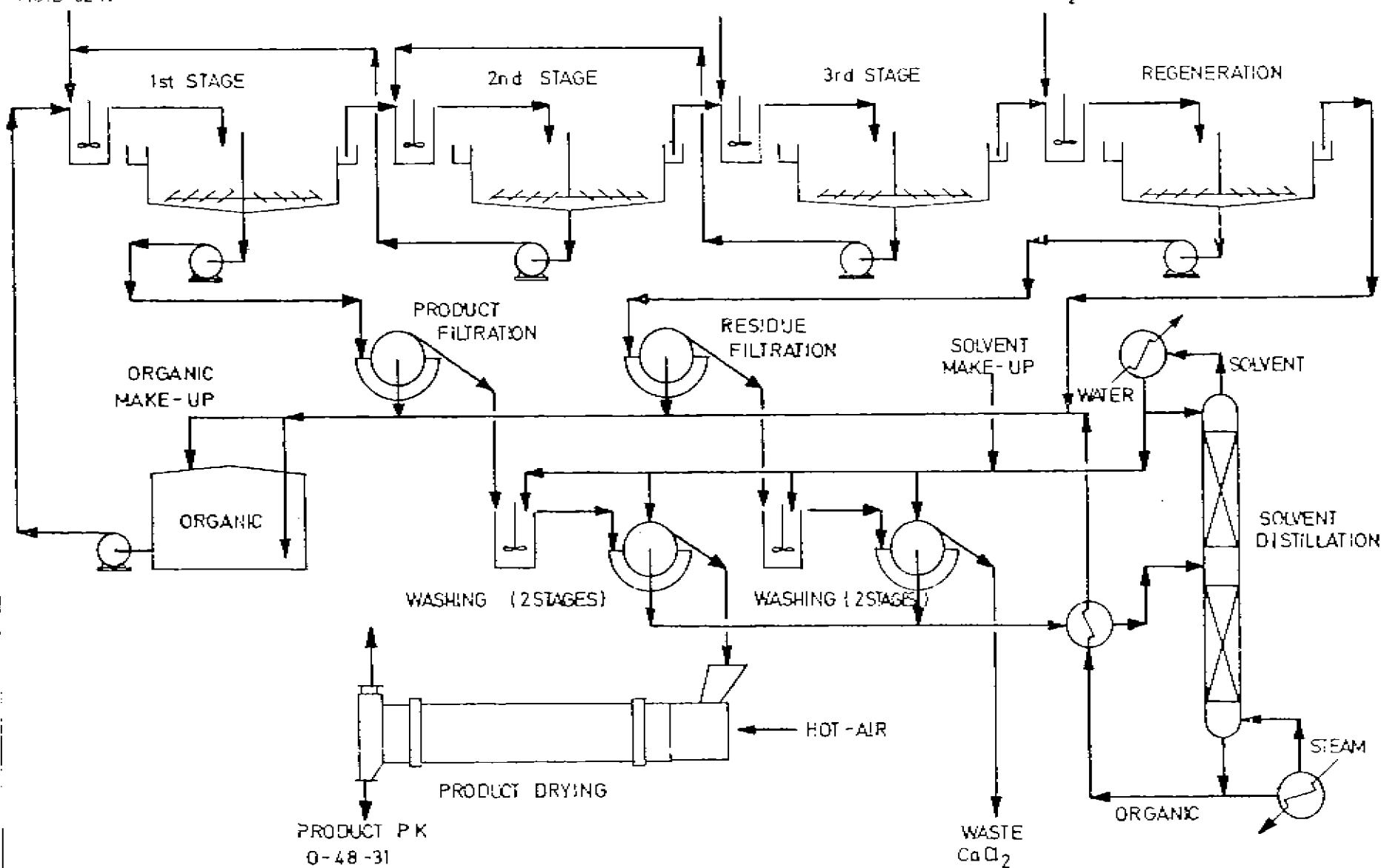


FIGURE-1. SIMPLIFIED PROCESS FLOW-SHEET

DISCUSSIONMr. E.D. NOGUEIRA (Explosivos Rio Tinto, Spain)

Let me start by making clear that what I am going to say is a consequence of a research programme at a laboratory scale and that we by no means pretend to have the know-how of a commercial process for PK production. The main advantage of this novel process is the direct production of a granular monopotassium phosphate 0-48-31 free of any phosphoric acid contamination. Basically the process consists in the direct precipitation of monopotassium phosphate in the body of an organic solution constituted by a commercial secondary amine, namely amberlite LA-2 from Rohm and Haas and a modifier, a commercial kerosene.

1st slide. Fine potassium chloride and wet process phosphoric acid are brought into contact with the organic solution containing the amine and reaction n°1 takes place by which monopotassium phosphate is formed precipitating in the organic phase. Free amine is transformed into amine chloride. In order to reduce the organic solution, it is absolutely necessary to regenerate the amine; this can be accomplished by a treatment with lime according to the reaction n°2. Although reaction n°1 looks quite simple at first glance, there are at least 2 methods for provoking such a reaction producing quite different results indeed: one method may be described by reactions n°3 and 4. Thus when the amine and phosphoric acid are brought together, monoamine phosphate is formed according to reaction n°3. If this organic solution containing the monoamine phosphate comes into contact with solid potassium chloride later on an anionic exchange between phosphate ions and chloride ions takes place according to reaction n°4. The monoamine phosphate is transformed into amine chloride and solid potassium chloride into monopotassium phosphate. This method and reaction n°4 are based upon the very well known fact that in general the order of preference of the weakly basic amines for various monovalent anions follows the sequence shown in the slide. If reaction n°1 is performed into the reactions n°3 and 4, a fine powder of monopotassium phosphate is obtained as the final product. Another method of carrying out reaction n°1 may be described by reactions n°5 and 6. Reaction 5 shows the equilibrium reached when solid potassium chloride is slurried in an aqueous solution of phosphoric acid; of course this reaction is negligible at room temperature. If potassium chloride is mixed with wet phosphoric acid and the resulting slurry dispersed into the organic phase containing the amine, reaction n°6 takes place by which hydrochloric acid is extracted into the organic phase to form amine chloride. Consequently the reaction n°5 proceeds to the right and precipitation of monopotassium phosphate occurs. If reaction n°1 is carried out in this way, rather spherical granules of monopotassium phosphate are obtained as the final product.

Next slide. It shows a simulated representation of a single droplet of the aqueous slurry of potassium chloride in phosphoric acid into the body of organic phase as a consequence of the induced dispersion. Apparently several phenomena are involved: first hydrochloric acid extraction through the aqueous organic inter phase resulting in the formation of amine chloride

into the continuous organic phase; secondly the dissolution of potassium chloride in the aqueous phase through the solid aqueous inter phase resulting in a growing of potassium ions concentration in the aqueous droplet, and finally the precipitation of monopotassium phosphate in the whole body of the aqueous droplet, when its solubility product is exceeded.

Next slide shows a picture of the precipitation reactor taken at the beginning of contact between the aqueous slurry and the organic phase.

Next slide shows another picture of the same reactor taken 5 minutes later. You can see how the slurry droplets which were not visible at the beginning become quite apparent when the monopotassium phosphate has just precipitated into the body of the aqueous droplets. By choosing suitable conditions under which the PK precipitation is carried out, one can obtain the chloride in a granular shape with a rather uniform size distribution with particle sizes within the range of 1 to 3 mm as can be seen in the next slide. This picture is of overriding importance from an economical view point since, in this way, the organic entrainment of the solid chloride is considerably depressed. The amount of water fed to the system plays an important role in the completeness of the reaction. In fact if there is a shortage of water the precipitation of monopotassium phosphate happens too soon physically breaking the hydrochloric acid extraction by the organic phase. On the contrary, if there is too much water the solubility of monopotassium phosphate prevents precipitation.

The next slide shows a plot of the hydrochloric acid extraction by the organic phase versus the percentage of water for a given set of stirring conditions. Obviously, it can be noticed that a minimum percentage of water is required to reach equilibrium. The minimum amount of water in turn depends upon the stirring conditions which determines the droplet size and therefore the size of PK granules. Moreover for a given droplet size distribution, an increase in water concentration increases the hydrochloric acid extraction rate and delays the PK precipitation and the chemical equilibrium will be reached only when the hydrochloric acid extraction takes place before the PK precipitation.

Next slide shows a simplification of the process diagram which has been established only as a basis for preliminary economical evaluation and later on has been induced for pilot plant design. I want to draw your attention to the technique of multiple contact in countercurrent between the solid and the organic phases which is essential for the completeness of the reaction. As a matter of fact there is an equilibrium between the solid and organic phases in such a way that phosphate and chloride concentrations in the organic solution depend upon the composition of the solid phase. Therefore even though there is an intense extraction of chlorides against phosphates, equilibrium concentrations are reached in a single contact. In other words substitution of phosphate by chlorides in the organic phase is not 100 % accomplished in a single stage.

Next slide shows a typical analysis of both phases in a countercurrent system of 3 stages. It can be assumed that product chloride content may become as low as wished depending upon the number of stages and the amine concentration. The regeneration of the spent organic solution obtaining the amine chloride is accomplished by contacting it with slaked lime in a special mixer. After solid/liquid separation, a clear organic liquid is obtained containing more than 95% of free amine which is suitable for recycling and a solid residue constituted mainly by calcium chloride.

Next slide shows that the efficiency of the regeneration depends on the amount of water fed to the reaction system. So before contacting the spent organic with lime an adjustment of the water content of the organic phase up to 4% is required in order to obtain 95% of amine regeneration. Higher percentages of water to improve yields impair the physical conditions of the solid residue. The regeneration must be performed at a temperature above 35°C in order to get good yields using only a slight excess of lime above the stoichiometry, less than 10%. I have little to add to the information given in the text concerning solvent recovery and waste disposal.

Finally some comments about economics. Next slide shows the results of a preliminary cost estimates to produce one metric ton of monopotassium phosphate by this process at Huelva. This evaluation was prepared only to have a feeling about process economics. In this way we were able to learn which points differ for the research work.

Mr. W.H. THOMPSON (Goulding Chemicals Ltd., Ireland)

The advantages of potassium phosphate as a fertiliser material has attracted the interest of the fertiliser industry for a number of years and this interest is shown by the efforts made in recent years in potassium phosphate process development. We have had papers describing methods of production at the past two ISMA Technical Meetings.

Because of the technical and economic difficulties in production of this elusive material, manufacture on a large scale has been rather delayed. There are signs now, however, that potassium phosphates are about to become available as a production material. The Pennzoil Company in California, I understand, are now on the point of production, and my company has a plant at the design stage which we hope will be operational in 1976. The technologies used, however, are very different from that detailed in the paper read here this afternoon, which is novel and elegant and we will be interested to follow its development through the pilot plant and manufacturing stages.

The authors are a little reticent in giving us details of operation of the process. A lot of the information is no doubt proprietary but it would be of interest to know a little about the amine used, its nature, availability and cost, the conditions, temperatures, pressures, materials of construction are all important in helping us to form an opinion on the practicality of the process in large scale operation.

I would like to draw the authors attention to a patent filed in the U.S.A. in 1971 and published by the British Patent Office B.P. 1361799 in July of this year to the Occidental Petroleum Corporation, in which a similar technology is used for the purification of phosphoric acid. Here the amine used is a water immiscible primary fatty amine, in a hydrocarbon solvent and the modifier used is a water immiscible alcohol. The amine solvent system is contacted with phosphoric acid in a two phase system and surprisingly the amine solvent system extracts all the impurities, organic and inorganic, cationic and anionic from the crude phosphoric acid. The amine is regenerated by contact with an alkali chloride and a base as in the process under discussion here. The amine does not in this case react with the phosphoric acid. The main difference in technique appears to be in the strength of the acid used. In the Occidental process there is an upper strength limit of 30% P_2O_5 whereas the authors seem to use concentrated acid and in a one phase system. That the mechanism should be so different depending on the acid concentration is in itself remarkable.

There are a number of questions I should like to put to the authors but I must limit them to a statutory three.

1. In view of the possibility of absorption of impurities into the organic medium have the authors observed a build up in the recycle system or do all the impurities in the acid and potash finally appear in the product? Where does the water introduced with the acid leave the system?
2. Is there a limitation on the strength of acid used? Is it necessary to use clarified acid and is fertiliser grade potash adequate?
3. How do the costs of a ton of product compare with the costs of an equivalent quantity of triple superphosphate and sulphate of potash?

May I offer my congratulations to the authors and wish them well in the development and exploitation of the process.

Mr. NOGUEIRA

In order to answer Mr. THOMPSON's comments, I will try to extend our information on the process. Regarding process conditions let us say that precipitation reaction is exothermic while regeneration on the contrary is endothermic. The heat balance becomes positive and a steady stage is reached in which a temperature gradient is established ranging for 45 to 50° in the first precipitation stage to 35 to 40° in the regeneration one. The process should then be considered as operating at room temperature. Operating pressure is of course atmospheric since equipment is opening to the atmosphere. Concerning construction materials mild steel can be used in most of the equipment but reinforced plastics are suitable too. As you can realize all these features make the process of a relatively low investment. Although I could not get a copy of the patent mentioned by Mr. THOMPSON just in time for this meeting, I have to disagree with Mr. THOMPSON's statement that extraction mechanism is different depending on the acid concentration; what happens is that the organic to aqueous phase ratio and the amine concentration in

the organic solution might be kept low in order to avoid phosphoric acid extraction. It is not a question of mechanism but of stoichiometry. Adjusting the amine to phosphoric acid molar ratio, one can extract all the impurities more acid than phosphoric acid and of course all the soluble organic impurities; those to my knowledge are the main impurities in crude phosphoric acid. The reason for an upper strength limit of 30% P_2O_5 might be dual: first the action mass law is playing its role and a limitation of acid strength is required to depress phosphoric extraction and consequently P_2O_5 losses. Secondly a two phase system requires acceptable phase disengagement characteristics but can be a hard task with more concentrated phosphoric acid mainly due to its high viscosity. In our process we reduce high concentration of phosphoric acid mainly to prevent the aqueous third phase after contacting.

Regarding the statutory 3 questions they looked to me if they were actually 6. Impurities: we have not observed any build up of impurities in our continuous system at the bench scale facility. The inorganic impurities do appear in the final product. The organic soluble impurities from phosphoric acid become insoluble in the regeneration stage and are removed with the calcium chloride solid residue. Nevertheless this precipitate makes things more difficult in the further treatment of the solid residue. Water with the acid leaves the system about 50% with a PK product and 50% with the spent organic solution, apparently dissolving the amine chloride. We have obtained moisture content of the PK product ranging from 8 to 12% depending upon granulating conditions. As to the strength there will be no acid strength limitation at all since one can always extract phosphoric acid with an amine counter-currently no matter which strength of acid is used. What happens is that in order to obtain simultaneous granulation water content must be kept below certain value. These make us to prefer an acid concentration of about 45% P_2O_5 .

Raw materials: commercial wet phosphoric acid can be used and fertilizer grade potash is quite adequate. Obvious reasons do not allow me to disclose any information concerning a procedure that we are developing to improve the process, namely a preconditioning of the phosphoric acid raw materials.

Economics. Finally I must apologize for not being able to give an answer to the last question. However let me say that in my opinion a good comparison only will be made considering that monopotassium phosphate is produced in a complex plant constituted by a conventional wet phosphoric acid plant in the monopotassium phosphate plant as the tail end of the complex, but even though monopotassium phosphate has extra-advantages as an intermediate fertilizer material that are very difficult to translate in those cost figures.

Mr. DAVIS (T.V.A., U.S.A.)

In the USA we are quite interested in potassium phosphates for production of clear liquid fertilizers. I wondered if the authors had done any work in production of clear liquids particularly those that might contain polyphosphates and if so what sources of acid were evaluated and what were the product storage qualities.

Mr. NOGUEIRA

We have not made any work in this respect yet.

Mr. DRECHSEL (Pennzoil Chemical Inc., U.S.A.)

I too wish to concur with the Goulding group my congratulations on this rather unique and elegant process. I did have some questions initially before I read the paper and I think those have been completely resolved. I do want to make one point and perhaps the author could comment on this. I think in many respects this process compares to the so called Knudsen process, the ion exchange process. In many ways this is a liquid/liquid ion exchange process. I think both of the processes have merits and perhaps some disadvantages and one thing that I would like to bring up is in the present world situation where we face a very severe energy crisis, we have also a very severe material shortage, the price of chlorine and caustic soda for example have gone almost out of sight. In this instance we take off half the potassium chloride molecule, the chloride aspect of it. This is the by-product of the system. It is a calcium chloride solution and is simply flushed into the ocean and I am wondering whether under any circumstances we can permit to simply eliminate a valuable by-product like this much chlorine in such a new process.

Mr. NOGUEIRA

With respect to the first question I think that there is some similarity between our process and the process mentioned by you. I think there are 2 main differences. The first one is that process is a cationic exchange process and the second difference in my opinion is that we are using a liquid liquid system or a liquid solid system using liquid exchange resins and they are using solid resins. I think the possibility to make this process operating continuously is easier in this way than in a solid liquid system. Regarding environmental problems of the waste disposal I have some comments to make with respect to some research work we are at present doing and this is regarding regeneration of the organic solution. We know that this is the weak point of the process. Regarding regeneration of the organic solution we are working on an idea that may decrease production cost, a high temperature hydrolysis of the amine chloride. In this treatment the spent organic solution containing the amine chloride is mixed with water and the mixture is held at high temperature for a certain period of time. This causes the hydrolysis of the amine chloride in the organic phase and the migration of the free hydrochloric acid to the aqueous phase. The two phases are separated by heating and the aqueous phase can be concentrated to obtain hydrochloric acid by-product.

Mr. BELPAYRE (Chimie Rupel, Belgium)

I would like to know if any excess of phosphoric acid used is not lost in the form of calcium phosphate during the amine regeneration and what excess phosphoric acid has to be used to reach a 98.5% efficiency.

Mr. NOGUEIRA

I think the question is related to the yield of P_2O_5 and in the text of the paper there is a yield of 98.5% of P_2O_5 and this is of course when the calcium chloride is precipitated. But there is a possibility to recover this P_2O_5 value, that is a liquid/liquid washing of the spent organic solution containing the amine chloride and there is a small amount of monoamine phosphate with a saturated solution of sodium chloride. In this way we get the P_2O_5 losses into the solution and then afterwards we can precipitate the P_2O_5 with lime. If you wish you can separate the precipitation of calcium phosphate from that of calcium chloride but either way losses are only 1.5% P_2O_5 in order to get this nice product.

Mr. KNUDSEN (Superfos, Denmark)

I think the main difference between the process we use and the process presented here is on the economic side because you have to remove first the calcium from the rock in the form of calcium sulphate and afterwards you add calcium hydroxide to remove the chloride. Why not use the calcium from the rock to remove the chloride directly in a cation exchange process. I don't know if this is a question really. It is rather a comment.