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

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PROGRESS IN THE MAINTENANCE OF SOLUBILISATION OF PHOSPHORIC ACID.

by M. Massenet.

For a long time it has been possible to make phosphate rock available to plants by acidulating the phosphate with mineral acids, principally sulphuric acid. Nowadays, superphosphate is still by far the most widely used of all phosphatic fertilisers.

A mixture of mono-calcium phosphate and calcium sulphate is the main constituent of superphosphate.

Efforts have been made to place at the farmers' disposal other salts of phosphoric acid which, whilst being as readily available to plant as di-calcium phosphate, had a more basic pH-value.

Among the first of these salts to be mentioned is di-calcium phosphate, the plant availability of which has been proved by numerous pot and field experiments and confirmed by several decades of experience. In most agricultural countries the availability of a phosphatic fertiliser is measured empirically by its phosphoric acid solubility in a solution of ammonium citrate, and di-calcium phosphate is completely soluble in this reagent. As far as agriculture and the legal side of the trade are concerned, di-calcium phosphate is an excellent fertiliser.

Theoretically, the manufacture of di-calcium phosphate is very simple. It boils down to the neutralisation of the secondary acidity of mono-calcium phosphate by calcium or by ammonia in the presence of a soluble calcium salt. In actual fact, matters are not at all easy, especially when operating with a concentrated medium.

As a matter of fact, the precipitation of di-calcium phosphate is only complete when pH approaches 7.2 and experience shows that it is not possible to push neutralisation that far; it falls a great deal short of it, without inducing the formation of tricalcium phosphate which is not soluble in ammonium citrate and the plant availability of which is mediocre.

In practice, there has been, up to now, no other way of avoiding this "reversion" of the phosphoric acid than to stop neutralisation at about pH = 4.5 which is tantamount to reverting

to a partial precipitation of the di-calcium phosphate. In the same way, when manufacturing ammoniated superphosphate by the action of ammonia on ordinary super, the quantity of ammonia introduced was limited so as to avoid reversion.

We have discovered that di-calcium can be precipitated in its entirety without reversion, even beyond $\text{pH} = 7$, when operating in the presence of some metallic salts such as magnesium sulphate or ferrous sulphate, for instance.

The attached graphs illustrate this phenomenon (fig. 1 & 2).

To establish these curves, rock phosphate was attacked by nitric acid just in sufficient quantities for the phosphoric acid to pass into solution. Into the slurry obtained, increasing quantities of gaseous ammonia were introduced and, in terms of the ratio $\text{NH}_3/\text{P}_2\text{O}_5$ recorded on the abscissa, the pH and the proportions of phosphoric acid soluble in water, and soluble in water and ammonium citrate and by way of difference the proportion of phosphoric acid soluble only in ammonium citrate have been recorded. All these proportions, given in per cent, have been registered on the ordinate.

The curve in graph No. 1. refers to a trial without the addition of metallic salts, the curve in graph No. 2 to a trial with magnesium sulphate.

On comparing both these curves the effect of the addition of the magnesium sulphate is immediately noticeable (the same result can be obtained with other salts: nickel sulphate, manganese sulphate etc.) pH 9 can be exceeded without formation of a phosphate insoluble in ammonium citrate. It will be noted that the aspect of the pH curve is not the same in both cases.

This discovery enabled us to make an important improvement in the manufacture of ammoniated superphosphate. Instead of fixing only 2 to 2.5% of nitrogen with ordinary superphosphate, as is the practice when reversion is feared, we can take up to 5% of nitrogen by operating in the presence of a metallic salt and this without the consumption of additional sulphuric acid.

Up to now, ammoniated superphosphates containing more than 2 to 2.5% of nitrogen, were obtained by using an excess of sulphuric acid, which in fact was tantamount to adding ammonium sulphate to the ordinary ammoniated superphosphate. In some countries, superphosphate is completely ammoniated without an excess of acid but the product thus obtained is only citric acid soluble similar to basic slag. Citric acid solubility is much less appreciated than ammonium citrate solubility. In France, for instance, one kilogramme of citric acid soluble P_2O_5 is sold at 36 frs. whilst one kilogramme of ammonium citrate soluble P_2O_5 is sold at 75 frs. or at more than double the price.

The field of application of our discovery is still wider in the compound fertiliser manufacture.

When rock phosphate is attacked by nitric acid so as to profit gratuitously by the acidity of this reagent which contributes an indispensable fertiliser element - nitrogen -, calcium nitrate has to be eliminated by filtration or converted into calcium sulphate by adding sulphuric acid, potassium sulphate or phosphoric acid in order to avoid hygroscopicity in the finished fertiliser. For example, when sulphuric acid is used, about 1 kg of sulphuric acid is consumed per kilogramme of P_2O_5 obtained.

The possibility of operating at a higher pH than 7 without reversion allows of the conversion of calcium nitrate to calcium carbonate by simultaneous or successive additions of carbonic or ammonia gases. This is an important saving as carbon dioxide is generally a useless by-product of the synthetic ammonia manufacture.

The new process proves to be particularly interesting to the ammonia manufacturer who has at his disposal, on the one hand, the raw material from the nitric acid manufacture, on the other hand, carbonic gas. Thus by means of a continuous method, non-hygroscopic fertilisers having varying formulas can be obtained without filtration or evaporation.

If it be desired to manufacture fertilisers with a P_2O_5/N ratio higher than 1, a portion of the ammonium nitrate solution has to be extracted from the ammoniated sludge. As the pH is high after the addition of ammonia, this solution contains no more phosphoric acid.

Up to now many processes have been planned in order to convert calcium nitrate into calcium carbonate, in the presence of phosphoric acid, but they all came up against phosphoric acid reversion.

To our knowledge, our process is the only one which has been realised on a large scale. The first pilot-plant has been operating with a capacity of 30 tons a day of compound fertilisers having the formula 13 - 11 - 13 and both storage and agricultural properties of this fertiliser have given complete satisfaction.

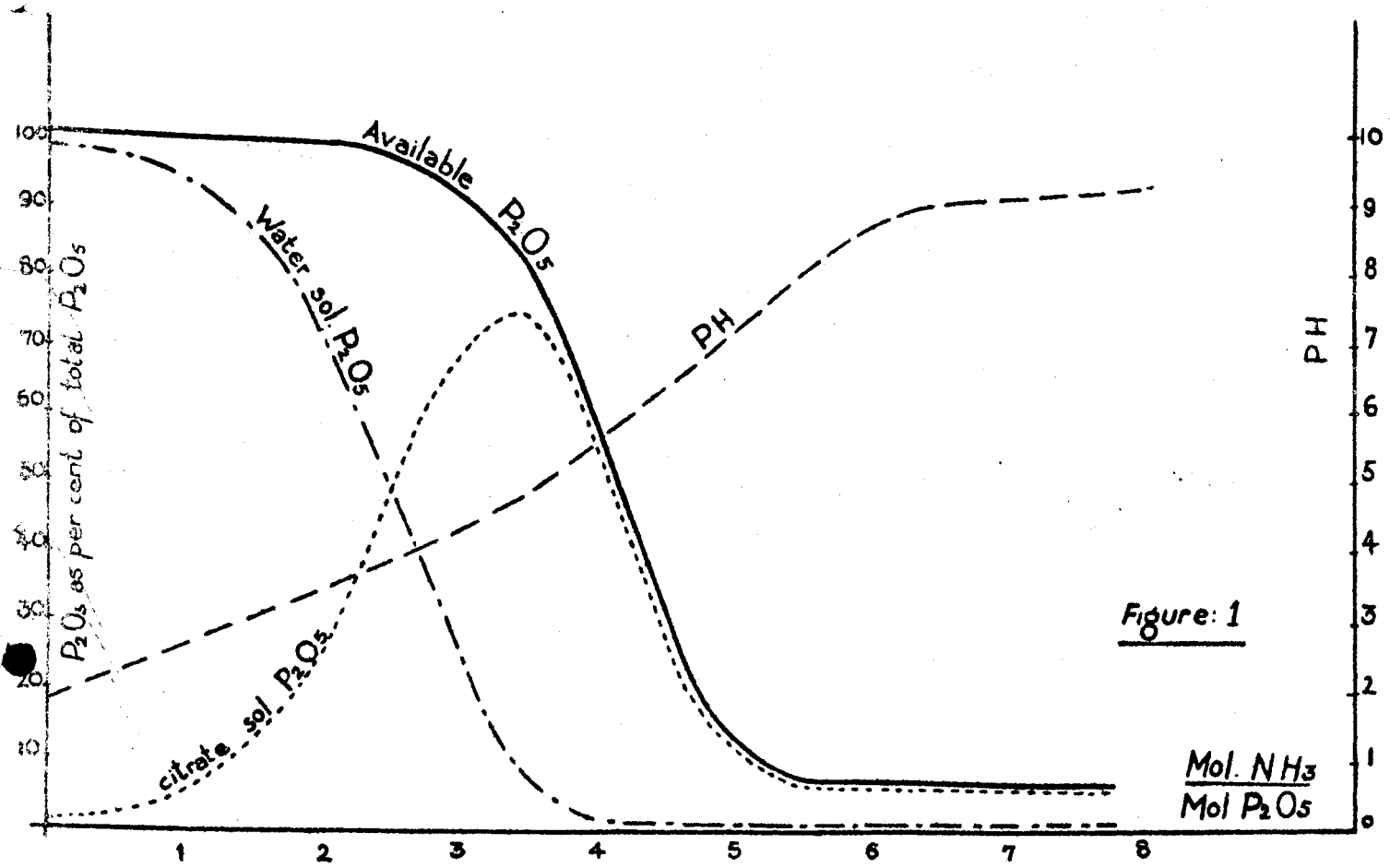


Figure: 1

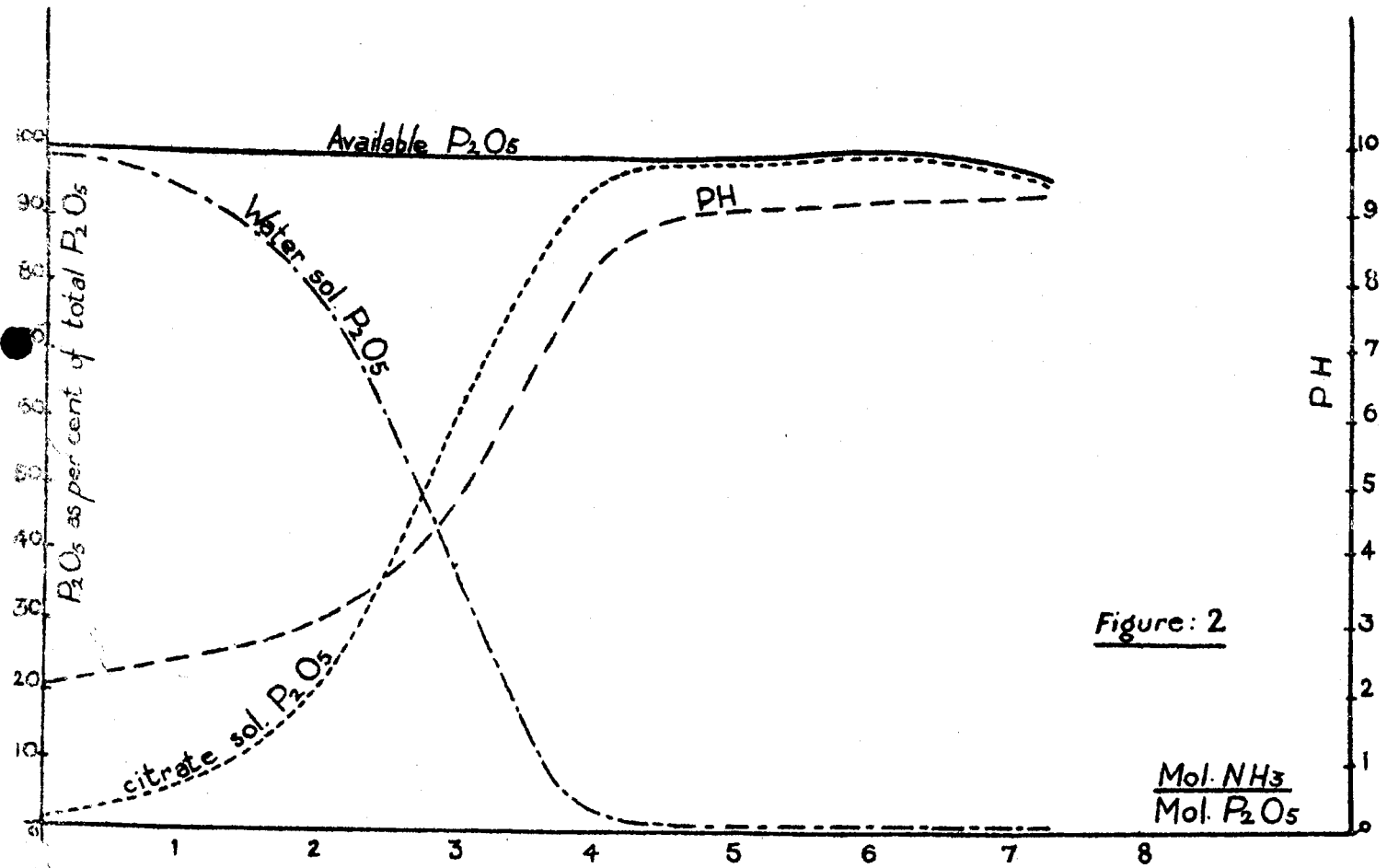


Figure: 2