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PREPARATION OF SOLUTIONS OF AMMONIUM
POLYPHOSPHATES FOR LIQUID FERTILIZERS

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CONTENTS

I	INTRODUCTION
1a	General remarks on the development and biochemical characteristics of polyphosphatised fertilizers
1b	Present field of research
II	PREPARATION OF AMMONIUM POLYPHOSPHATE
IIa	Operational paramaters
IIb	The T.V.A. process
IIc	Modification of the T.V.A. process
III	PLANT AND OPERATION OF THE MODIFIED PROCESS
IIIa	Layout of plant and operation
IIIb	Operating conditions
IIIc	Product
IIId	Typical operation
IV	LIQUID FERTILIZERS (CLEAR AND IN SUSPENSION)
IVa	Basic solution
IVb	Clear liquid N-P-K formulations
IVc	Liquid compositions in suspension
IVd	Appendix. Granulates
V	BIBLIOGRAPHY

I. INTRODUCTION

I.a General remarks on the development and biochemical characteristics of phosphatised fertilizers.

Liquid fertilizers, either clear or in suspension, are being increasingly used at a rate proportionally much higher than that of the usual solid fertilizers; this trend is particularly noticeable in those countries with an advanced agricultural technology (1).

This progress is all the more significant since liquid fertilizers require some conversion or readaptation of the traditional systems for the handling of solids and involve the introduction of new machines and new techniques (2) (3).

The favourable properties of polyphosphate-based fertilizers compounds as compared with those prepared with orthophosphates are well known. Let us mention the following from the biochemical standpoint:

Their sequestering capacity for the minor elements, such as Mn, Zn, Cu, Fe etc. which are of decisive importance to the satisfactory development of crops. When the polyphosphates are applied to the soil this capacity confers greater mobility on the microelements which are frequently to be found in the ground in such conditions that they cannot be absorbed by the plant; similarly it enables them to be kept in solution, so that when applied by foliar sprinkling, an immediate improvement in the vegetation is noticeable. This is particularly advantageous in those areas where there are deficiency symptoms (4).

Their greater solubility which enables liquid formulations to be obtained even when microelements are present, with gradations that would be prohibitive for compositions based on orthophosphate, logically results in lower transport and application costs per unit of fertilizer.

Among other significant factors which favourably affect vegetable biochemistry, we may mention the gradual degradation of polyphosphates to the ortho level, in which state it is assumed that the phosphorus is preferentially absorbable by the plant, a fact which puts them in the vanguard of controlled-action fertilizers (4); similarly, their lower salinity index (5) as compared with orthophosphates, make their use preferable to that of the latter, particularly as fertilizers for sowing time.

I.b Present field of research

At present, research in the field of polyphosphates,

mostly undertaken as applied research, is directed not so much towards determining the physicochemical parameters by which the transformation reactions are governed, as to obtaining an operational system enabling them to be produced industrially under conditions which can compete with those of conventional (ortho) fertilizers. At the same time research is concentrated on solving the problems of instability during the storage of clear liquid solutions (6) and on the production of solids enabling such liquid solutions to be prepared in situ or near the place of use, to save transport costs.

In research aimed at determining the most favourable "single-stage", preparation conditions, the most important processes are those of Swift (7), (8), Kaltenbach, Gardinier (9)(10) and Ferguson (11); and the work of the T.V.A. (12), whose wealth of background knowledge places it in the forefront of this technology in the field of polyphosphates, is outstanding.

Our process involves a modification of the T.V.A. method in which the raw materials used are wet-process phosphoric acid and anhydrous ammonia, with the well-known T-reactor as core of the arrangement (11)(12).

II. PREPARATION OF AMMONIUM POLYPHOSPHATE

II.a Operational parameters

The determining factors of the method of preparing ammonium polyphosphate (i.e. compositions made up of orthophosphate, pyrophosphate, tripolyphosphate and smaller proportions of other more condensed polyphosphates) depend upon the final product in view, in accordance with the following general considerations:

We know that the chemical process is based upon the condensation of the nitrogenous compounds of phosphorus, produced by dehydration under the thermal conditions maintained during ammonisation. This condensation may possibly be facilitated by the presence of other agents (urea, ammonium nitrate etc.). The final degree of polymerisation obtained, which is more or less suitable for specific uses, depends upon the said thermal conditions, the concentration of the phosphoric acid used, and also upon its degree of technical purity. For example, polymerisation rates of over 50% are suitable for the preparation of clear liquid fertilizers, and polymerisation rates of not more than 30% for the formulation of granulates.

It is also desirable when liquid fertilizers are to be produced that the polymers resulting from the treatment belong fundamentally to the series of pyrophosphates or tripolyphosphates, with a minimum percentage of higher polymers. Various investigations (¹³) have led to the inference that the pyrophosphate type is the most suitable sequestrator of those micro-elements of value to vegetable growth (heavy metals), although long-chain polymers are better as regards Ca and Mg. Moreover, it seems that the solubility of ortho-pyro mixtures for certain degrees of N:P₂O₅ ratio is better than ortho. On the other hand, the balance in the formation of poly chains by rupture or regrouping produces instability which increases with the length of the chain, whose degradation in solution leads to the pyro phase (in formulations of the 10-34-0 type), or tripoly phase (in 11-37-0 formulations), which are more stable at pH approximately 6. As a result of this degrading process, when these solutions become over-saturated with the more insoluble metal components (Ca, Mg, Al, etc.) of their ammonium pyro or tripolyphosphates, they form sediments during storage, particularly at low temperatures.

It is thus necessary to attain suitable reactional equilibrium as stated, by controlling the exothermic conditions producing condensation by regulation of the reactor input temperatures of the wet-process phosphoric acid and the anhydrous ammonia.

II.b The T.V.A. process

To prepare ammonium polyphosphate in a single stage, T.V.A. uses a T-reactor (in which the thermal shock is produced) fed with gaseous anhydrous ammonia and wet-process phosphoric acid with 50/54% of P₂O₅, which is previously sprinkled in an absorption tower where the unreacted NH₃ from the reactor is recovered. There must be a strict control of the pH in this tower, so as not to exceed the limit value of 1.8 at which crystallisation may occur which would interfere with the efficiency of the plant.

The residence time in the reactor is very short, in order to minimise the formation of insolubles resulting from the impurities in the phosphoric acid (¹²) and the melt produced passes to a degasser, subsequently being converted into granules in a pug-mill in the usual way, or being dissolved (^{12,14,15}) either into clear liquid formulations (10-34-0) or suspensions (11-37-0 to 12-40-0).

II.c Modification of the T.V.A. process

Our modification of the T.V.A. process (¹⁶) involves

the following points:

- The polymerising thermal conversion takes place in the T-reactor fed with preheated wet-process phosphoric acid 50/54% P_2O_5 and anhydrous ammonia, without the partial neutralisation of the phosphoric acid implied by its previous use in the absorption tower to recover the unreacted NH_3 from the reactor. The reaction shock is more exothermic and intramolecular dehydration is favoured.
- The absorption of unreacted NH_3 occurs in a tower sprinkled in countercurrent with the molten material dissolved at the outlet of the reactor. The acidity of the solution recycled to the tower ensures complete recovery of the ammonia used in the process.
- The absorption tower is simultaneously fed at the top with a suitable proportion of water. At the bottom the finished product is extracted, part of which is switched to the degasser where the melt from the reactor dissolves forming the reflux that feeds the said tower in order to absorb the unreacted NH_3 and condense the steam, both from the degasser.

This makes it possible to:

- Prevent the risk of any solidification causing clogging in the absorption tower or associated ducts as a result of an unforeseen rise in the pH, since the composition of the liquid flowing in the said tower maintains its components in solution even at pH 6-7 and over, no strict control of the pH being necessary.
- Complete in the absorption tower the final formulation of the finished product which, because of the total recovery of the materials incorporated in the process, is a function of the easily-controllable supply of NH_3 and PO_4H_3 . The absorption tower thus has the dual function of the recovery already mentioned, and of formation of the finished product, thus obviating the need for additional equipment for the latter.

III. PLANT AND OPERATION OF THE MODIFIED PROCESS

III.a Layout of plant and operation

The plant for this process consists of the devices and installation shown in the diagram of Fig. 1.

It consists essentially of a pre-heater of wet-process phosphoric acid (1) fed at (2) by means of a proportioning pump. A T-reactor, made of AISI 316 L

steel is provided with an input (4) for the preheated phosphoric acid and (5) for the preheated ammonia gas, the latter supplied from a suitable source (6). The melt from the reactor flows via (7) to a degasser (8) where it is dissolved by the liquid coming from the bottom of the absorption tower (12) and conveyed by the pipe (9). The residual gases (unreacted ammonia and steam) are piped through (10) to the said tower (12) where they will be absorbed and condensed. The acid solution from the degasser (8) is pumped from its lower outlet (13) and refluxed to an intermediate point of the tower (12) by means of the pump (14).

Together with the recirculating solution there is introduced through the top (15) of the absorption tower (12) the additional flow of water (16), which is necessary to maintain the formulation of the solution at 10-32-0 to 11-35-0 with a pH of between 6 and 7, without risk of solidification.

The bottom (11) of the absorption tower forms, via the branch line (17) to the outside, the point of extraction of the finished product. In this way, the double connection at the bottom (11) of the tower becomes the nerve centre for the graduation of the recycling of the finished product intended for the dissolution of the melt from the reactor and the absorption thereby of the unreacted NH_3 gas and water vapour. This is easily done by graduating the flow of final product extracted by (17) by means of the valve (18).

At the top (15) of the absorption tower (12) a cooling system (19) with free outlet to the outside is installed, which condenses the steam not absorbed in the tower by its operating temperature, and returns it to the circuit, which enables us to maintain a regular composition of the flowing material at any time.

The device is completed by heat exchangers, such as (20) and (21), which are respectively the liquid-ammonia evaporator and ammonia gas preheater, and (22) the initial preheater of the phosphoric acid supplied by (2) before it reaches its final reactor-input temperature in the preheater (1).

A flowmeter, manometer and temperature gauges make up the control system in the different operating stages of the assembly.

The continuous line in the figure shows the flow of liquid materials, and the dotted lines show the flow of vaporised materials.

III.b Operating conditions

In the device described a study has been made of the operating conditions of the process, determining the degree of polymerisation reached in the final product flowing from the absorption tower as a function of the temperatures of the NH_3 gas and PO_4H_3 fed to the T-reactor, for various initial concentrations of P_2O_5 in the acid.

Figs. 2 and 3 are graphs of the results obtained.

In Fig. 2 curve a corresponds to the values obtained when working with input temperatures of 130°C for the phosphoric acid and 150°C for the ammonia; curve b corresponds to 120°C for the acid and 175°C for the ammonia.

Having aimed at producing in the plant described products with not less than 50% polymer, suitable for the formulation of clear liquid N-P and N-P-K compounds of satisfactory graduation and stability, we find that this can be achieved only when the wet-process phosphoric acid has an initial concentration of the 54% P_2O_5 , under the working conditions described.

On this premise, study was made of the variation in the degree of polymerisation at different input temperatures for the NH_3 and PO_4H_3 with 54% P_2O_5 . The results are given in the diagram of Fig. 3, where curves a, b, c and the point d correspond to the values obtained with input temperatures for the NH_3 gas of 100°C , 150°C , 175°C and 75°C respectively for each of the acid temperatures indicated on the axis of the abscissae.

It can be inferred from the graphs that degrees of polymerisation of 50% or more are obtained when operating at the following NH_3 and PO_4H_3 temperatures:

<u>NH_3</u>	<u>PO_4H_3</u>
150°C	130°C
100°C	140°C
75°C	150°C

Lower rates of polymerisation suitable for the formulation of granulated products are obtained with lower operating temperatures.

In the reactor, values fluctuating between 225°C and 250°C are obtained with the raw-material input temperatures indicated for obtaining a minimum of about 50% polymerisation; whereas for polymer levels of under 50% they vary between 150°C and 225°C.

The content of materials in suspension and impurities of the wet-process phosphoric acid used in the process is of decisive importance in the thermal operating conditions, in the degree of polymerisation obtained and to the characteristics of the final product, having a fundamental influence upon the stability in store of the formulations prepared with the base solution flowing from the plant.

III.c Product

The raw product produced in this plant consists of a liquid of pH varying between 6 and 7, containing in suspension all the solids comprised in the wet-process phosphoric acid and those formed in the process from the impurities dissolved in the raw material.

When the solids are separated the solution remains clear indefinitely, and its formulation contains from 10 to 11% of N and 32 to 35% of P_2O_5 which is polymerised into the pyrophosphate state.

Before dissolving, the molten material flowing from the reactor emits a compound containing between 10 and 12% of N and 54 to 60% of P_2O_5 , which may if desired be conveyed to a granulator of the pug mill or similar type, when operating under the thermal conditions specified for a 30% polymerisation rate, which is favourable to its granulation. In this case, the unreacted HN_3 and steam are recovered in an auxiliary absorption tower by means of water or the acid material considered most suitable.

The crude base solution is used directly for the composition of liquid fertilizers (in suspension or clear) of the N-P or N-P-K type, with or without minor elements, to which we refer in Section IV.b, a single filtration being effected after their composition is completed in the case of clear liquids. Nevertheless, after filtration, and with or without the optional inclusion of microelements, it constitutes a high-grade, clear liquid fertilizer.

III.d Typical operation

The dimensions of the reactor and of the absorption tower are the vital points which determine the maximum production capacity of the plant described.

For this reason, although the figures we give below are expressed in Kg or litres they can be scaled up by a factor dependent upon the flow of phosphoric acid capable of being supplied to the reactor and of the ammonia gas supplied to obtain the desired formulation, in such a manner that a sufficient exothermic level is maintained to obtain the degree of polymerisation considered most suitable.

Conditions of operation and flow of materials

Reactor feed:

Phosphoric acid, wet process, 54% P ₂ O ₅	7.8 Kg/h
Anhydrous ammonia gas (15°C and 50mm Hg overpressure)	2,090 l/h
Input temperature of acid	150°C
Input temperature of ammonia	100°C
Temperature reached in the reactor	230°C

Collector feed:

Molten material leaving reactor	7.5 Kg/h
Reflux of absorption tower (approx.)	180 Kg/h
Constant volume of solution in degasser	1 litre
Temperature of material in degasser	90°-100°C

Absorption tower feed:

Recycling of acid material of degasser (approx.)	193 Kg/h
Gases flowing from outlet of reactor	1.7 Kg/h
Water	2.9 Kg/h

Production extracted at bottom of absorption tower:

Solution pH 6.5 (10.8-35-0)	12 Kg/h
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Composition of flowing material in the reactor feed:

Wet-process phosphoric acid	4.2 Kg/h P ₂ O ₅
	1.3 Kg/h H ₂ O
	0.7 Kg/h impurities
Ammonia gas (1.60 Kg/h NH ₃)	1.32Kg/h N

Composition of flowing materials in the degasser feed:

Molten material from reactor	4.2 Kg/h P ₂ O ₅
	0.9 Kg/h N
	0.1 Kg/h H ₂ O
	0.7 Kg/h impurities

Reflux of absorption tower

	63 Kg/h P ₂ O ₅
	23.7 Kg/h N
	63 Kg/h H ₂ O
	12.6 Kg/h impurities

In the absorption tower feed:	
Recycling of acid material of degasser	67.2 Kg/h P ₂ O ₅ 24.6 Kg/h N 63.1 Kg/h H ₂ O 13.3 Kg/h impurities
Gases flowing from reactor outlet	0.4 Kg/h N 1.2 Kg/h H ₂ O
Liquid water in top of tower	2.9 Kg/h H ₂ O
In the extraction (production) of the bottom of the absorption tower:	
Solution pH 6.5 (10.8-35-0)	4.2 Kg/h P ₂ O ₅ 1.3 Kg/h N 4.2 Kg/h H ₂ O 0.7 Kg/h impurities

IV. LIQUID FERTILIZERS (CLEAR AND IN SUSPENSION)

IV.a The basic solution

As already indicated in Section III.c, the raw product, after filtering, is in itself a high-grade clear liquid fertilizer. The formulation most commonly prepared by this system is 10-32-0 or 10-34-0 with 50% of its P₂O₅ polymerised.

It is satisfactorily stable in store and produces no sedimentation even at -6°C. It is capable of keeping heavy metals in solution in level concentrations of minor elements active in plant growth.

The stability of the above-mentioned clear liquid compounds with minor elements depends to a great extent upon the presence in certain proportions of elements such as Mg, Ca, Fe and Al, which accompany the wet-process phosphoric acid (6). Even though in filtration they are separated for the most part as insoluble pyrophosphates, it is advisable to use as raw material a phosphoric acid with a minimum content of such elements, in order to avoid the depletion of the sequestration capacity of the polyphosphate formed by a rather large dose of such components.

IV.b Clear liquid N-P-K formulations

The preparation of these formulations consists of integrating the supplementary nitrogen and the K₂O, calculated according to the intended composition, with the base solution obtained by the process.

The raw materials used are: CLK (60% K₂O) as a source of potash, and urea or the 32-unit solution (aqueous solution of urea and ammonium nitrate with 32% N) as

an additional source of nitrogen.

It is simple to prepare. The other constituents are incorporated with the raw polyphosphate product produced by the process described, and stirred until they dissolve. The insoluble materials from the raw materials are filtered or centrifuged.

The following table gives those formulations which we have found by experience to exhibit total solubility of their constituents at ambient temperature. In formulations with a higher quantity of macronutrients (on the basis of the raw materials mentioned) it is necessary to turn to suspensions.

The stability to crystallisation is verified by subjecting the clear liquids to substantial cooling and ascertaining the temperature at which turbidity occurs, as indicated in the Table.

The Table also indicates the type of supplementary nitrogenous constituent used in the only variable formulation in the preparations. All the integrant products were of industrial quality.

TABLE: Clear liquid formulations with a basis of 10-34-0 ClK (60% K_2O) and supplementary nitrogenous constituents (urea or 32-unit solution)

Type of formulation	Composition N-P ₂ O ₅ -K ₂ O	Nitrogenous constituent		Crystallisation temperature
		Urea or 32-unit solution		
1:1:1	10-10-10	x	x	9°C
	9-9-9	x	x	-5°C
	7-7-7	x	x	-5°C
1:2:2	5-10-10	x	x	-5°C
2:2:1	14-14-7	x	x	-5°C
	14-14-7	-	x	-15°C
	10-10-5	x	x	-5°C
1:2:1	8-16-8	x	x	-5°C
	7-14-7	x	x	-5°C
Others	7-20-7	x	-	-1°C
	6-20-6	x	-	-3°C

IV.c Liquid fertilizers in suspension

Suspensions with a polyphosphate base, in our case the raw ammonium polyphosphate flowing from the plant described, have the following fundamental characteristics:

- High degree of macronutrients.

- Facility for accepting a suitable dosage of microelement-bearing soluble salts without risk of instability through separating precipitations or crystallisations.
- Ease of preparation, no filtering stage.
- Stability independent of impurities in the raw materials.
- Total utilisation of materials without losses in insoluble residues.

It is well known that all that is required to prepare these products is a container provided with a powerful mixer or "micronising" (jet-mill) system, the raw materials being placed in this device, and the operation being continued as long as is necessary to stabilize viscosity.

Formulations 13-18-9 based on the following materials (by weight) were prepared and tested in experimental fields and applied at cereal sowing time with satisfactory results:

Raw ammonium polysulphate (11-35-0)	560
32-Unit nitrogenous solution	222
Potassium chloride (60% K ₂ O)	150
Attapulгите	30
Water	38

This formulation, given as an example, shows a viscosity/temperature gradient of 8 cP/°C between 5° and 25°C, with a mean viscosity of 340cP at 25°C. The stability is increased if about 4% attapulгите is used instead of the 3% specified in the test formula, whereby its viscosity attains 540cP at 25°C.

To obtain similar degrees of viscosity, using ammonium orthophosphate instead of polyphosphate and the same type of nitrogenous and potassium constituents as described, lower formulations are required, such as 10-14-7 for this type, i.e. nine units of macro-nutrients less than the former.

In accordance with the example cited and when applied in practice on the land, the saving expressed in figures lies in the spreading rate of 600 kg per hectare of the formulation based polyphosphates, as compared with 710 kg per hectare of the formulation based on orthophosphate: in this case a saving of about 18 to 20%.

By way of example of a case in which no additional nitrogen is incorporated, we may mention the type

5-15-15, based on ammonium polyphosphate and potassium chloride; whose viscosity at 25°C is 250 cP and whose stability is satisfactory for sedimentation.

In the same way we can refer to a whole range of formulations, already reported in publications, which have been chosen as suitable for each type of crop and soil, and which open up a wide field of use for this type of fertilizer.

IV.d Appendix. Granulates

We cannot end this chapter without reference to granulated compounds, whose preparation requires a plant of the usual pug mill type, into which the molten substance from the T-reactor is poured, in conditions suitable for obtaining a degree of polymerisation not exceeding 30%.

In return for its production cost, this auxiliary process offers the same advantages cited for suspensions, namely of operating in more favourable thermal conditions and needing more economically obtainable concentrations of the raw material, phosphoric acid; nevertheless the work for this process demands a high rate of recycling of fines in the granulators and an additional plant for the absorption of the excess NH_3 and steam from the reactor.

At the 1970 ISMA Technical Conference, the TVA presented a paper (15) on this subject, covering the granulation system used in addition to their device.

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DISCUSSION

MR. P. J. GORRINDO (Sociedad Anonima Cros.):

In our paper we offer a contribution to the techniques normally used in the developed countries for the preparation of NP or NPK liquid fertiliser compounds. We do not make any reference to liquid nitrogenous fertilisers. The use of liquid fertilisers is the subject of debate and we shall not enter into a discussion of whether they offer advantages or disadvantages as compared with solid fertilisers; there are undoubtedly both advantages and disadvantages and the degree of development of liquid fertilisers will depend on many factors in the economy and agrarian structure of the countries concerned. But liquid fertilisers are certainly here and the world tendency to make increasing use of them cannot be ignored.

The major disadvantage of liquid NPK fertilisers was the low total nutrient content which was a result of the relatively low solubility of orthophosphates. The use of other phosphate materials of higher solubility was then considered and this led to polyphosphates. As we know, this name is used to cover certain mixtures of compounds in which not all the phosphorus is in ortho form, but, as a result of condensation or loss of intramolecular water in the manufacturing process, part of the phosphorus occurs in the form of pyrophosphate, tripolyphosphate and in some cases as higher polymers.

An additional advantage is, as is known, the sequestrating capacity of these polyphosphates; as a result of this, it is possible to keep in solution some trace elements such as Zn, Fe, Mn, Cu, Mg etc., which play an important role in agriculture.

Early techniques for the preparation of ammonium polyphosphates used superphosphoric acid, which, having reached an advanced degree of concentration through the provision of external energy, was already partly polymerised. By neutralising this superphosphoric acid with anhydrous ammonia ammonium polyphosphates were formed but a great deal of heat generated by the neutralisation process had to be extracted from the system. The consumption of energy was considerable and the process was uneconomic. Other techniques appeared later (such as those of TVA, Swift, Ferguson, Kaltenbach and Gardinier, and others) in which phosphoric acid

at a concentration in the region of 54% P_2O_5 or more was made to react with ammonia. The considerable heat developed as a result of the exothermic nature of the reaction was used to cause, in situ, not only the complete evaporation of the water of dilution of the phosphoric acid but of part of the intramolecular water, thus achieving considerable levels of polymerised P_2O_5 . The heat balance was thus considerably improved. As can be seen, the chemical theory of the process is not complex, but its application in practice is slightly more so.

On this basis we developed and tested an installation which is described in our paper. We consider that it allows us to produce directly and with relative ease liquid NP fertilisers, the well-known 10-34-0 solution, from wet process phosphoric acid and ammonia.

In applying our process, the key unit of the installation is a T-reactor, as with TVA, Swift and others. Up to this point, we have made no fresh contribution but we have done so on the rest of the installation.

There are processes in which the ammonia escaping from the T-reactor, together with the water vapour formed, is collected in a scrubber which is sprayed with the phosphoric acid entering the system. This requires quite careful control of the pH of the scrubber liquid, since if the pH is in excess of 1.8 the N/P ratio approaches a minimum of solubility of the partially neutralised acid, with a risk of solidification in the scrubber.

In our plant, the phosphoric acid, heated to a certain temperature, but without partial pre-neutralisation, is fed directly to the T-reactor, together with the hot vaporised ammonia. In our system, the unfixed ammonia leaving the T-reactor is also passed to a scrubber which is sprayed with an acid liquid formed by dissolving the molten polyphosphate leaving the reactor with part of the finished 10-34-0 product. In addition, supplementary water required to achieve a suitable concentration of the finished product is added at the top of the scrubber. In this way we obtain from the base of the scrubber on the one hand the liquid which is on its way to the bottom of the collector where it will rapidly

dissolve the molten polyphosphate leaving the reactor, and on the other the 10-34-0 solution. This solution, when working at suitable temperatures, is obtained with a pH of 6.5 and polymerisation in the region of 50%.

The impurities in the finished product depend on the quality of acid used. With some acids it is possible to obtain clear liquids directly, but, at other times, simple filtration is required. With the addition of supplementary nitrogen in the form of urea, ammonium nitrate or nitrogenated solutions, and of potassium salts, liquid NPK fertilisers are obtained, either as clear liquids or in suspension.

MR. W. A. DEKKER (Windmill Holland, N.V. Netherlands): We could have a whole symposium on the subject of liquid fertilisers on which so much work has already been done and, in particular, the T.V.A. has encouraged the use of fluid fertilisers. We may, however, take pleasure in the fact that, in addition to all the work done in the U.S.A., Europeans are also making their contribution in this field. As far as this paper is concerned, the authors of CROS are to be complimented on the development work which formed the basis for this paper. It shows clearly that they have been able to master the difficult ins and outs of the techniques of making liquid fertilisers. In that respect I would like to ask the authors the following questions:

1. In your paper it is stated that the CROS process is a modification of the T.V.A. process. Although I admit that there is a great resemblance between the processes of T.V.A., Swift, Ferguson, Gardinier and others, my conclusion is that the process which you describe is a refinement of the Swift process. Could you give us your comments?
2. In view of question number one, you must have been aware of possible patent infringements. It would be interesting to hear your views on this point.
3. On page 16-10 you mention something about the stability of the liquid and about filtration. I will quote this section:

"The stability of the above-mentioned clear liquid compounds with minor elements depends to a great extent upon the presence in certain proportions of elements such as Mg, Ca, Fe and Al, which accompany the wet-process phosphoric acid (6). Even though in filtration they are separated for the most part as insoluble pyrophosphates, it is advisable to use as raw material a phosphoric acid with a minimum content of such elements, in order to avoid the depletion of the sequestration capacity of the polyphosphate formed by a rather large dose of such components."

This part is not quite clear to me and it would be appreciated if you could clarify this.

4. Since I have the feeling that the design of the T-reactor is the heart of the process, could you tell us a little more about your experiences with scaling, clogging, corrosion and the stream factor of the T-reactor.

May I last but not least compliment the authors on their paper, on behalf of all of us.

MR. P. J. GORRINDO: Mr. Dekker says the CROS process is very similar to and a refinement of the Swift process. This is partially correct. I believe that all contributions by technicians to industrial technology must in fact be improvements of processes already in use, already known and already developed. When we faced the problem of learning about liquid fertilisers based on ammonium polyphosphate, and how to prepare them, we naturally had recourse to those sources of information already available. In some ways, our process is very similar to the T.V.A. process. For instance, our T-reactor is exactly like the TVA T-reactor. I do not know whether the T-reactor used by Swift is very similar to that of the T.V.A. or not. We did not lay stress on investigating and improving the T.V.A. or Swift reactor, because the contribution which we proposed to make to the technology was not in fact directed to producing a reactor or installation which would give better polyphosphates with a higher polymer concentration, leaving less sediment, but rather to devising a flexible and easily handled installation which would produce known ammonium polyphosphate 10-34-0. Specifically, then, we did not set out to study or to improve upon the Swift

or the T.V.A. reactors, but to use a reactor of a type known to us and to improve and modify in accordance with our own ideas the installation and layout of the reactor, collector and scrubber; we feel that a plant established on these lines is in many ways easier to run than previous ones. We differ appreciably from the T.V.A. process, since the latter supplies phosphoric acid through the scrubber, where it undergoes a first pre-neutralisation. In this sense, we are in a way more similar to the Swift process, because this also supplies the T-reactor directly with phosphoric acid. However, unlike the Swift process, we have retained the scrubber because we consider it better to collect the emerging unreacted ammonia at reactor temperature in a scrubber, which will facilitate operation of the plant, rather than to introduce the molten polyphosphate together with the water and the ammonia (in the centre of this reactor) inside a container, as Swift does, in which the molten material dissolves and absorbs the ammonia, giving off a little water. Here we differ from the Swift process. For this reason, I feel that by using known components, such as a T-reactor, a collector, a degasifier for separation of the gases, and a scrubber, we achieve a process, which can be called the Cros process, if you wish, which we feel may be of interest to liquid fertiliser technology.

In our work we do in fact talk of filtration, and also of sequestration at the same time. They indeed appear to be contradictory terms; if heavy metals are sequestered, it seems incorrect to speak of filtration. However, our interest was in testing how our installation works, and not in seeking an acid which would give optimum results from the point of view of polyphosphate proportions, or a fertiliser with improved concentration or polymer characteristics. We tried out in our installation, for testing purposes, various acids from very different sources, of a greater or lesser degree of purity, and in some cases, owing to a higher concentration of iron, aluminium or magnesium in the acid added, the sequestering capacity of the polyphosphates was insufficient to sequester them all, and a light and virtually negligible precipitate of these metals appeared; in order to obtain a clear liquid we preferred to filter it. We consider that if there are black products in suspension, it is necessary to filter in order to achieve the aspect of a clear and acceptable solution.

Another question - have we noted any clogging in our installation? When the plant is operating normally there is usually no clogging; i.e. when the installation has started up and is operating in normal working conditions we have not encountered severe clogging. It would certainly occur with very impure acid but usually with acids of more normal purity we have not had blockages. On the other hand, if anything such as the breakdown of a phosphoric acid transfer pump or a fall in the pressure of the ammonia or any flow defect occurs, then the reactor temperature falls quickly resulting in a disproportionate phosphorus ratio and blockages do occur in the section between the reactor and the collector. However, I would stress that in normal operation, and we have operated for about 2000 hours in all (not continuously) we have not, I repeat, encountered any problems of clogging.

MR. O. H. LIE (Norsk Hydro, Norway). I would like to comment on the paper because I am sure many other companies will have made some study of the T.V.A. process in their own laboratories. There is one point which causes problems in the T.V.A. process and this is corrosion in the absorption section. I would like to ask the author of the paper whether he has solved this problem by using the particular lay-out he has chosen. My second point is that I fail to see that the operation of the T.V.A. absorber is very difficult. To judge by our own experience, it can be run without any trouble for long periods. I think that one of the benefits of the T.V.A. process is that it is self contained.

The end-consumed ammonia from the T-reactor is absorbed in the incoming stream, thus permitting the process to produce liquid fertilisers and solutions. It seems to me that the author's process would have to be modified to produce granules. He must have some other means of absorbing the ammonia from the T-reactor. Thank you.

MR. P. J. GORRINDO: We have not yet had enough experience to make any definite statement about the construction materials of the plant from the point of view of corrosion. We use stainless steel (316) in both the reactor and the absorber; in virtually 2000 hours of operation we have not noted corrosion at any point. There was in fact a corrosion problem, slight or severe depending

on how you look at it, but this was at start-up; we introduced a small sheath into the reactor, for insertion of the element regulating the temperature, and then severe corrosion occurred at the base of the sheath where the thermometer is inserted. But this was after about one hundred hours of operation, and having sent the reactor for repair and recommended the use of a good electrode in welding, we replaced it and for the rest of the thousand odd hours worked since we have not had any further corrosion problems. However, it is a matter we are intending to look at more closely, when we start up a pilot plant which we are installing at one of our factories here in Seville, to produce some 750 kilos/hour of ammonium polyphosphate. This is due to start up in a couple of months or so.

The absorption in the column, being a modification of the technique in which the ammonia is absorbed in the column by a phosphoric acid with its full acid potential, means that the absorbing material in this case is, as I said, a solution of the molten material which leaves the reactor and dissolves in the finished product. We had some doubts about how the absorber would work and whether an unduly large one would be needed for the installation. Our experience, somewhat to our surprise, has been that we have never had problems with the absorber, which is very small, but suited to the size of the plant; it is not unduly large and the result is that the acid potential remaining in this liquid, a mixture of the molten material and the finished product, is sufficient to absorb completely all the ammonia coming from the reactor, which is about one third of that introduced in the process. In early tests, we used a tower filled with Raschig rings which did cause difficulties because when we tried to absorb all the ammonia so as to ensure that there were no losses at the head of the absorber, we had to have a very large quantity of spraying and recirculating liquid. Owing to the size of the column, there was flooding and, as a result, the operation of the absorber was indifferent. However, by removing the filling and using an empty scrubber with full cone sprays, the problem disappeared, and the ammonia is absorbed perfectly in normal operation. Of course if for any reason there is a stoppage of washing liquid then there will be a loss of ammonia from the top, but these cases are minimised since we must remember that at the top

of the absorber we have the addition of supplementary water required to produce the required formula and to adjust the density of the product; and this water also dissolves part of the ammonia and recovers it. The absorber operates normally and does not give us any trouble. We have not thought of any other method of absorbing the ammonia.

Our installation is planned for direct production of liquid fertilisers, as I said. Indeed if solid ammonium polyphosphate is required our installation is not suitable, since the scrubber cannot then be sprayed with a solution which will gather the final product. The ammonia then has to be recovered in another tower, using a different system. This we have not tried.

The following questions and answers were the subject of correspondence.

MR. T. P. HIGNETT (T.V.A., U.S.A.):

1. What phosphate rock do you use for acid manufacture?
2. What are the main compounds present in the precipitate?
3. Does the precipitate form immediately? Is it filtered immediately or after a delay to allow for completion of precipitation?
4. Is the filtration reasonably rapid?
5. What is the percentage of P_2O_5 in the precipitate?

MR. GORRINDO:

1. We have only used Morocco phosphate rock.
2. We have no precise analysis, although we have good reason to believe that fundamentally they consist of ammonium, iron, magnesium and aluminium pyrophosphates.
3. It depends on the phosphoric acid used. Only in a few cases do we get immediate, although very small, precipitation.
4. It is, in the cases when it becomes necessary.
5. After reasonable storage time, we have never found any substantial change in P_2O_5 content, within the limits of conventional fertiliser analytical methods.

MR. M. KOTLAREVSKY (Etablissements Gardinier, France):

1. What is the analysis of the acid used?
2. What type of steel do you use for the acid pump?
3. What polymerisation rates have you obtained?
4. What problems of foaming in the scrubber and mixing tank (No.8) have you had?
5. What is the analysis of "PPA" obtained?
6. What is the capacity of the plant described?

MR. GORRINDO:

1. Differing grades of wet process acid were tested. A typical analysis might be:
54% P_2O_5 ; 3-4% SO_4 ; 1-2% R_2O_3 ; 0.3-0.4% Ca.
2. The material chosen for this pump is "Uranus B-6", but other equivalent alloys may also be used.
3. This depends on the input temperature of the acid and ammonia. The ratio of polymerisation rate/temperatures has already been shown in our paper by means of the curves in Figure 3.
4. We have not experienced any problems of foaming in these units.
5. The analysis of the polyphosphate at pH 6.5 shows the following composition:
10-11%N; 33.3-35.0% P_2O_5 (total), 50-52% poly.
6. The laboratory plant described has a capacity of 55-60 kg/h of 10-34-0 solution. A 750 kg/h semi-pilot plant is to be started up next spring.

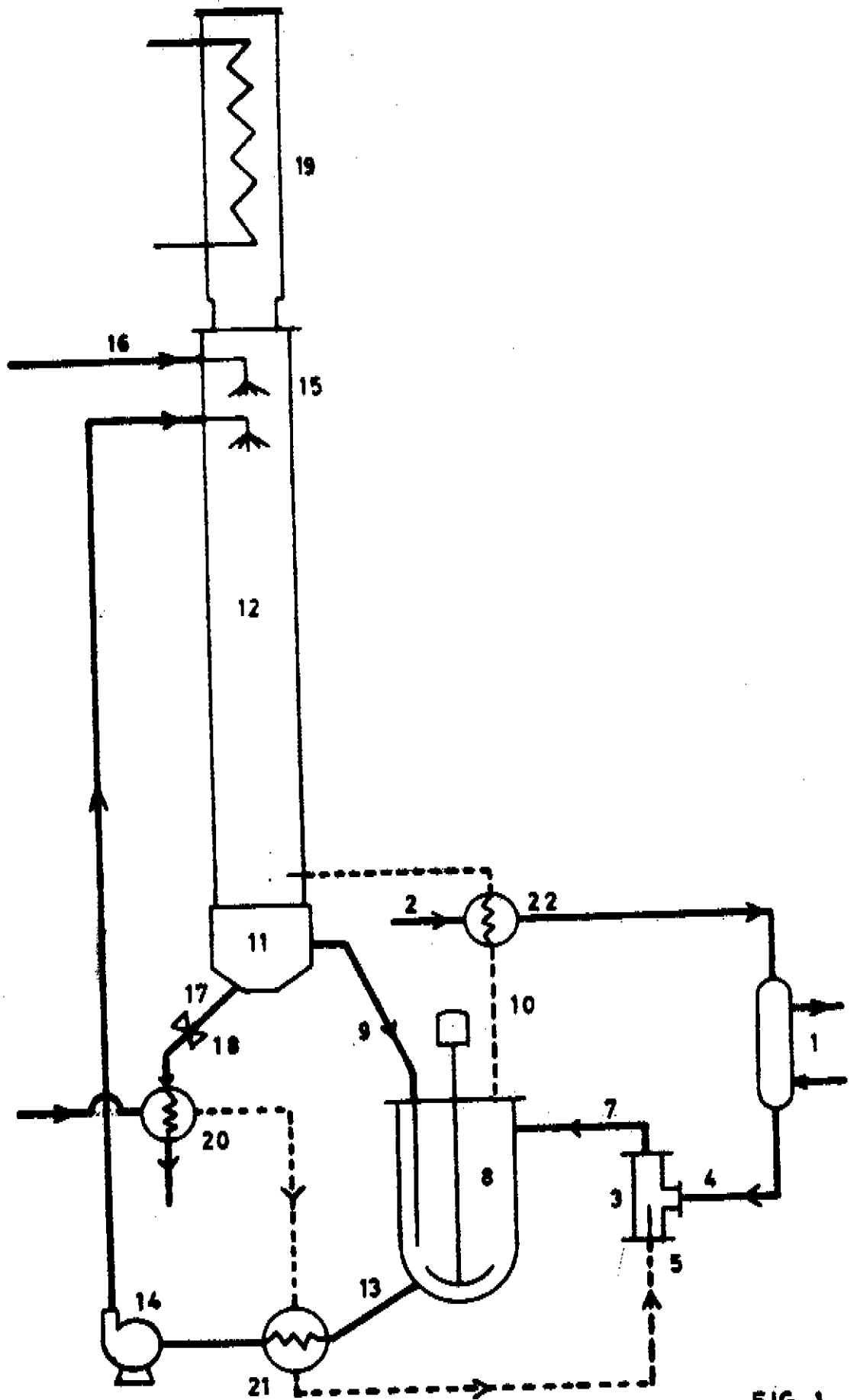
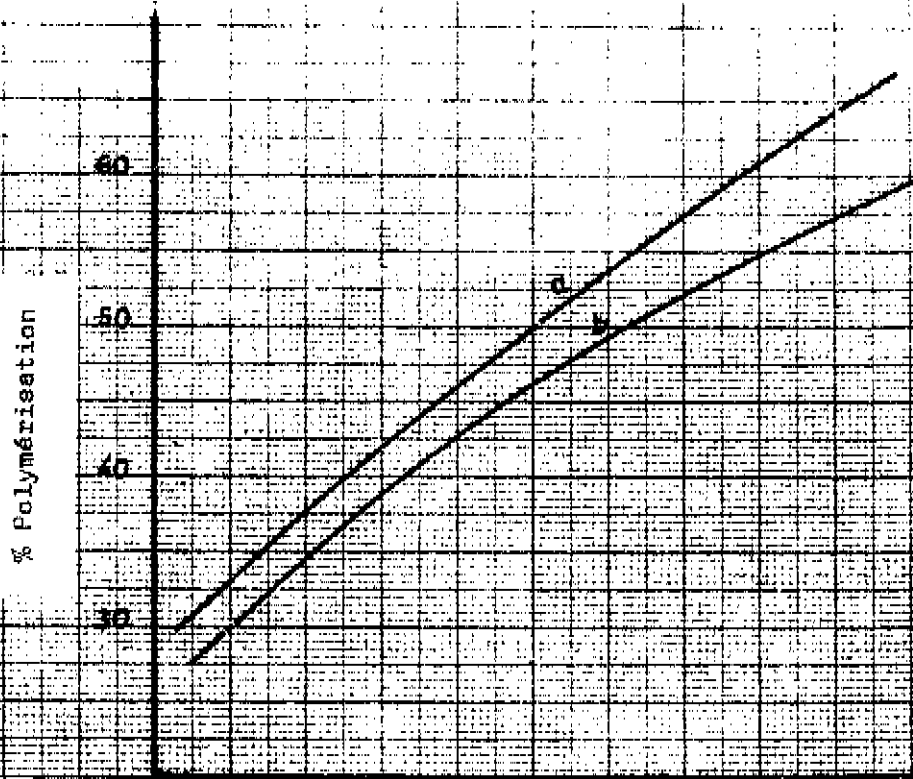
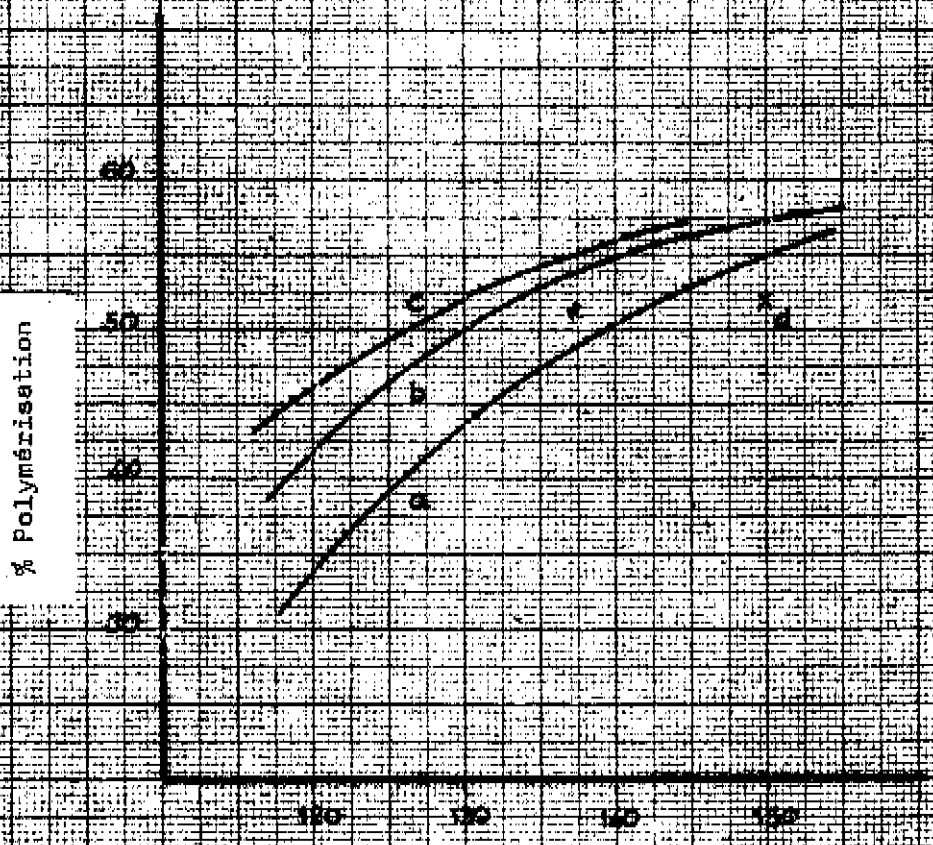


FIG. 1



$25 \text{ P}_2\text{O}_5$

FIG. 2



Température °C

FIG. 3